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High entropy alloy of $(\text{CrFeTaV})_{1-x}\text{W}_x$ for fusion applications: production via mechanical alloying and irradiation studies

TESI DI LAUREA MAGISTRALE IN
NUCLEAR ENGINEERING - INGEGNERIA NUCLEARE

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Abstract

The need for future sustainable energy sources makes nuclear fusion a promising candidate. In particular, project ITER aims at demonstrating the feasibility of fusion energy through magnetic confinement in a tokamak device. This thesis focuses on the divertor target plates, the components of the tokamak that have the role of extracting heat and helium ash produced during the fusion reaction. As a result, they are exposed to extremely severe thermal and irradiation loads, making the selection of suitable materials a critical aspect of its design. The state-of-the-art configuration for the divertor target monoblock comprises a W armor, a CuCrZr heat sink tube, and a Cu interlayer. However, this design presents some criticalities in terms of stress concentrations at the junction and operational temperature windows of the materials. An alternative configuration for the interlayer is proposed and investigated in this thesis work: a thermal break interlayer made of functionally graded high entropy alloys (HEAs). To this aim, the proposed composition is a low-activation refractory HEA containing Cr-Fe-Ta-V-W. The equimolar composition of this alloy is produced with a planetary ball mill for mechanical alloying. The equipment operational parameters are successfully optimized to obtain a single solid solution of HEA, with a BCC crystal structure. Subsequently, the irradiation resistance of this HEA is investigated by simulating the irradiation environment of a deuterium-tritium plasma. The samples of $(\text{CrFeTaV})_{95}\text{W}_5$, $(\text{CrFeTaV})_{90}\text{W}_{10}$, CrFeTaVW, $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$, consolidated via spark plasma sintering, are irradiated with Ar^+ ions to simulate neutron irradiation damage, and consequently with He^+ and D^+ ions to simulate gas transmutation products. The alloys present a good irradiation resistance, showing no phase transformation and no significant swelling after Ar^+ implantation, with the exception of the CrFeTaVW sample. The samples after Ar^+ , He^+ and D^+ present some variations in surface topography, with the compositions of $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$ showing very little blistering compared to the other compositions.

Keywords: Nuclear fusion, high entropy alloys, mechanical milling, irradiation resistance

Abstract in lingua italiana

La crescente necessità di sviluppare fonti energetiche sostenibili rende la fusione nucleare una tecnologia promettente. Il progetto ITER ha l'obiettivo di dimostrare la possibilità di ottenere la fusione nucleare a confinamento magnetico con un dispositivo di tipo tokamak. Questa tesi si concentra sui target del divertore, un componente del tokamak che estrae il calore e l'elio prodotti durante la reazione di fusione. Questi componenti sono quindi soggette a forti carichi termici e di irraggiamento, rendendo la selezione di materiali un aspetto fondamentale del progetto. Il monoblocco dei target presenta un'armatura in W, un dissipatore di calore in CuCrZr e un interstrato in Cu. Tuttavia, questo design presenta dei problemi relativi alla concentrazione di stress alla giuntura e al mantenimento delle temperature operative ottimali. L'alternativa proposta in questa tesi consiste in una barriera termica realizzata mediante un materiale a gradiente funzionale basato su leghe ad alta entropia (High Entropy Alloys, HEA). A tal fine, viene investigato un HEA di elementi refrattari a bassa attivazione: Cr-Fe-Ta-V-W. La lega equimolare è stata prodotta mediante fresatura meccanica in un mulino planetario, ottimizzandone i parametri di processo per ottenere una singola soluzione solida con struttura cristallina BCC. Successivamente, la resistenza all'irraggiamento di questo HEA è investigata tramite la simulazione di un ambiente di irraggiamento tipico di un plasma a deuterio-trizio. I campioni $(\text{CrFeTaV})_{95}\text{W}_5$, $(\text{CrFeTaV})_{90}\text{W}_{10}$, CrFeTaVW, $(\text{CrFeTaV})_{70}\text{W}_{30}$ e $(\text{CrFeTaV})_{65}\text{W}_{35}$, consolidati tramite sinterizzazione al plasma a scintilla, vengono irradiati con ioni Ar^+ per simulare i danni da irraggiamento neutronico e successivamente con ioni He^+ e D^+ per simulare i prodotti di trasmutazione. Tutte le leghe, ad eccezione di CrFeTaVW, mostrano una buona resistenza all'irraggiamento, non evidenziando trasformazioni di fase né fenomeni significativi di swelling successivi all'irraggiamento con Ar^+ . L'irraggiamento complessivo con Ar^+ , He^+ e D^+ induce modifiche topografiche in tutti i campioni, con un blistering meno marcato nelle composizioni $(\text{CrFeTaV})_{70}\text{W}_{30}$ e $(\text{CrFeTaV})_{65}\text{W}_{35}$.

Parole chiave: Fusione nucleare, leghe ad alta entropia, fresatura meccanica, resistenza all'irraggiamento

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1 | Nuclear Fusion

This thesis work is developed within the context of nuclear fusion and, in particular, of the tokamak, an experimental machine designed to achieve magnetic confinement fusion. This chapter will first introduce fusion energy and magnetic confinement nuclear fusion in Section 1.1. Subsequently, a focus on the divertor of a tokamak is presented in Section 1.2, with the aim of describing the specific component investigated in this thesis work, the interlayer of the divertor monoblock. Finally, Section 1.3 discusses the irradiation damage experienced by the materials of a tokamak as a consequence of the fusion plasma environment. More in detail, the irradiation damage at the interlayer is evaluated.

1.1. Fusion energy

Nuclear fusion is the process through which two light atomic nuclei combine to form a heavier nucleus, releasing a large amount of energy. This process is considered a promising solution in the context of future low-carbon electricity production due to its high energy density.

In order to achieve controlled nuclear fusion on Earth, the reacting nuclei must be confined at extremely high temperatures and densities for a sufficient amount of time to sustain fusion reactions. One of the most promising approaches to accomplish this is magnetic confinement fusion, in which strong magnetic fields are used to confine the plasma and prevent direct contact with the reactor walls. Among the different magnetic confinement concepts, tokamaks represent the most advanced and extensively investigated devices. The two tokamak designs that will be considered in this work are ITER (International Thermonuclear Experimental Reactor), currently under construction in the south of France, and DEMOnstration Power Plant (DEMO), a general term that describes machines which aim, in the future, at demonstrating the feasibility of fusion as a large-scale energy source. In parallel, stellarators are also being explored as an alternative magnetic confinement configuration.

1.1.1. Fusion reactions

To discuss nuclear fusion and its most promising reactions, it is first necessary to introduce the concept of binding energy B of a nucleus. This quantity is defined as the negative of the difference between the nuclear mass and the sum of the masses of the constituents:

$$B(A, Z) = Nm_n c^2 + Zm_p c^2 - m(A, Z)c^2 \quad (1.1)$$

Figure 1.1 shows the behavior of binding energy per nucleon B/A as a function of A . The value of B/A increases with A for light nuclei until a maximum at around $A \approx 55-60$ while going beyond this value it decreases slowly. This suggests that a release of energy is possible with the *fusion* of light nuclei into heavier ones, and with the *fission* of heavy nuclei into lighter ones.

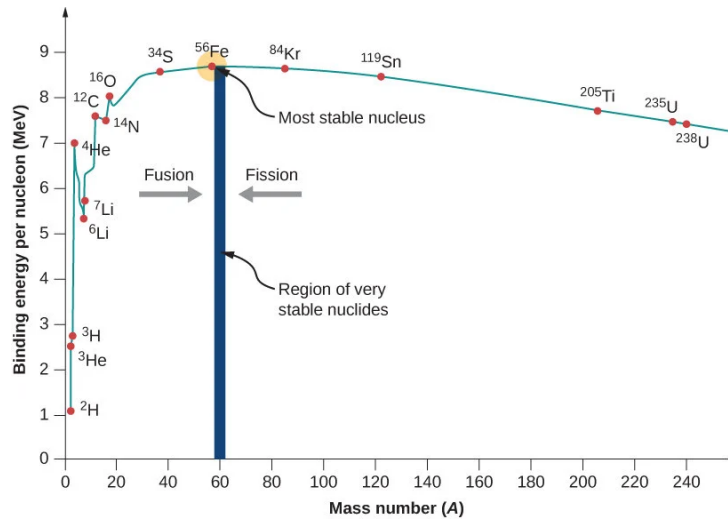


Figure 1.1: Binding energy per nucleon B/A versus atomic mass number A [1].

Fission and fusion reactions can be compared in terms of both the energy released and the probability of occurrence. Fission reactions commonly considered for energy production in thermal reactors exhibit significantly higher cross sections than those of fusion reactions involving light nuclei. This can be better observed in Figure 1.2. In contrast, fusion reactions of low- A nuclei release substantially more energy per nucleon than typical fission processes [2].

From a physical point of view, the main challenge in achieving fusion reactions lies in the fact that the interacting nuclei are charged and therefore experience Coulomb repulsion. This has two main consequences. First, the greater the product of the charges, the stronger the Coulomb repulsion. This explains why fusion reactions of interest for

experimental applications primarily involve light nuclei. Second, increasing the kinetic energy of the nuclei enhances the probability to tunnel through the barrier of Coulomb repulsion. Considering that the kinetic energy of the nuclei is related to their thermal motion, the reaction occurrence is strictly related to the temperature of the medium where they are contained. Additionally, a relation exists between the energy barrier and the cross section of reaction. This allows to understand the threshold behavior of the cross section with respect to the kinetic energy of the center of mass of the system, as displayed in Figure 1.2 [2].

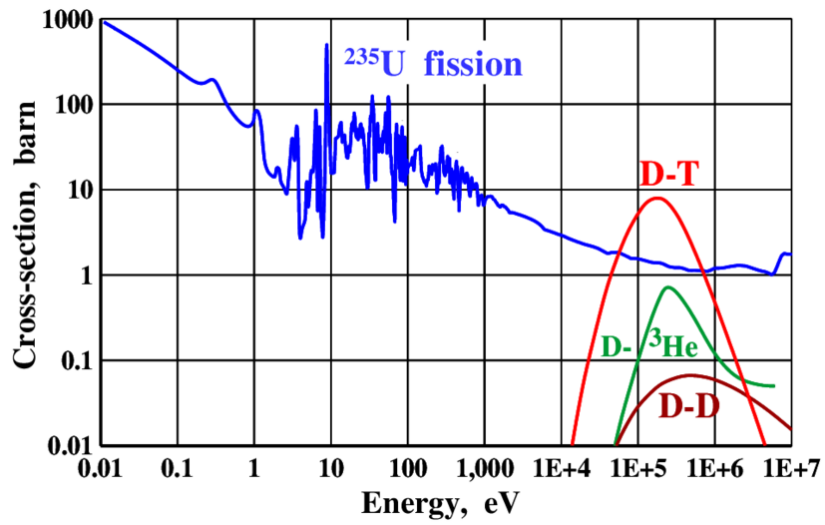
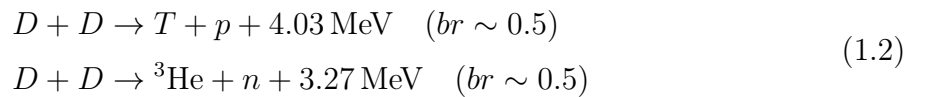


Figure 1.2: Cross section of ^{235}U fission reaction as a function of the incident neutron energy and cross section of three fusion reactions as a function of the center-of-mass kinetic energy of the reacting nuclei [3].

Figure 1.2 presents the cross sections of the three most considered fusion reactions in the framework of experimental applications of nuclear fusion: one occurs between two deuterium nuclei (D-D) and it has two exit channels with a branching ratio (br) of 0.5 each, one between a deuterium and tritium (D-T) nucleus and the last between a deuterium and a helium-3 isotope (D- ^3He). The reactions are:





The D-D reaction (Eq 1.2) has the advantage of using only deuterium, which is abundant and stable but, on the other hand, has the lowest maximum cross section and the lowest released energy among the three reactions. The D-T reaction (Eq 1.4) has the highest maximum cross section but it involves the use of tritium. Tritium is a fast-decaying isotope of hydrogen that occurs only in small quantity in nature. Finally, the D- ${}^3\text{He}$ reaction (Eq 1.3), has a lower cross section but slightly higher production of energy with respect to the D-T reaction. Additionally, exploiting this reaction would lead to producing the least amount of neutrons with respect to the others, which is advantageous considering the damages that energetic neutrons cause to materials. However, the main problem is the extremely low abundance of ${}^3\text{He}$ on earth.

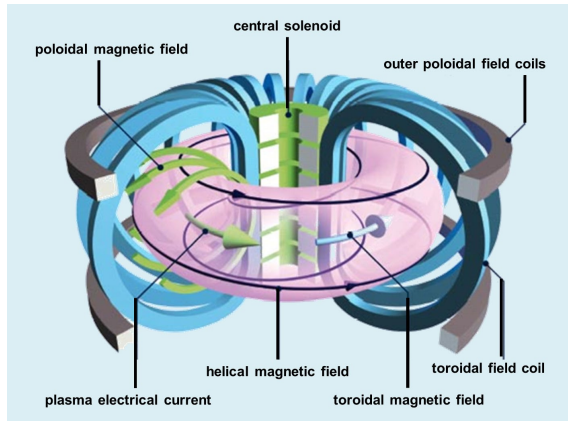
In order to exploit either one of these fusion reactions, a fusion device would need to contain the plasma of ions that are involved in the reaction. Additionally it would have to achieve and maintain the high temperatures needed for the reaction to occur. Finally, it would require an energy recovery mechanism that collects the produced energy. Among the various proposed and developed fusion device designs, this thesis work will focus on a magnetic confinement nuclear fusion machine called Tokamak, which will be described in Section 1.1.2.

Considering the advantages and limitations of the different fusion reactions, the D-T reaction has been identified as the most suitable for fusion energy applications and has therefore been selected for ITER. More in detail, this reaction produces an energy of 17.6 MeV, which is released in the form of kinetic energy of the products of the reaction: the ${}^4\text{He}^{2+}$ ion (also referred to as alpha particle) is released with 3.5 MeV while the neutron is released with 14.1 MeV. To address one of the main challenges associated with this reaction, tritium scarcity, a viable approach is to exploit nuclear reactions between lithium and neutrons that result in tritium production. This strategy, called *tritium breeding*, can be implemented by appropriately incorporating lithium into the components of fusion devices.

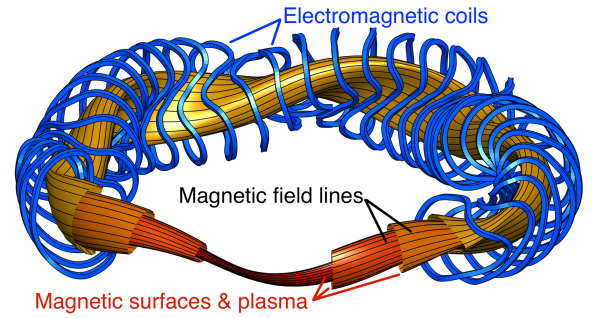
1.1.2. Magnetic confinement nuclear fusion

One of the approaches to achieving and controlling nuclear fusion is based on the magnetic confinement of a plasma composed of the reacting species. This method relies on the use of magnetic fields to confine the charged particles that constitute the plasma. The most common fusion devices for magnetic confinement fusion are tokamaks and stellara-

tors, illustrated on Figure 1.3. They are both toroidal plasma confinement systems but they differ in the way of producing the helical twisting of field lines, needed to prevent the drift of the guiding center of plasma particles towards the walls of the device. Tokamaks present magnetic coils that produce the toroidal component of the magnetic field, while the poloidal component is generated by means of an high intensity current flowing in the plasma. On the other hand, stellarators form the magnetic field cage solely by means of external non-axisymmetric coils [4, 5].



(a) Schematic illustration of a tokamak [6].



(b) Schematic illustration of a stellarator [7].

Figure 1.3: Schematic representation of two devices for magnetic confinement nuclear fusion: (a) tokamak and (b) stellarator.

Both tokamaks and stellarators have innate advantages and disadvantages with respect to technical and physical aspects of a fusion device on the way to burning plasmas. Currently, since stellarator configurations are challenging to build, most fusion experiments are tokamaks. Among these, ITER is the world's largest tokamak to be designed and operated. This thesis is carried out considering the technological challenges identified in the components of ITER and addressing some potential solutions for their implementation in future fusion power plants like DEMO.

1.1.3. Tokamak machine

A tokamak plasma cannot be perfectly confined. Therefore, a system for exhausting heat and particle losses is required to regulate plasma-wall interactions and maintain plasma purity. The most promising solution to achieve this is the divertor. A carefully designed magnetic configuration redirects heat and particles escaping the plasma core towards the divertor, thereby reducing direct interaction with the tokamak walls.

To better understand the role of the divertor it is useful to describe the plasma configuration. Figure 1.4 represents the poloidal cross section of tokamak with a divertor configuration. The magnetic configuration is characterized by an outermost closed magnetic field surface called *separatrix* which is characterized by a zero in the poloidal magnetic field within the vessel known as *X point*. The magnetic field surfaces well inside the separatrix are closed and they determine the region of the plasma core whereas the region right below the separatrix is called *edge region*, which contains significant levels of not fully ionized impurities and neutral particles. The magnetic fields outside of the separatrix are open field lines and they characterize the narrow radial layer where heat flows: the *scrape-off-layer* (SOL) region of the plasma. The power that crosses the separatrix is diverted along the magnetic field line to the divertor where it is exhausted on actively cooled divertor targets. The *strike point* is where the separatrix intersects the divertor target plate [8, 9].

A divertor target has the role of exhausting heating power (mostly coming from fusion alpha particle power), with a peak heat flux assumed to be 10 MW/m^2 for the quasi-stationary operation (2h) and 20 MW/m^2 for slow transient events ($<10\text{s}$). Another important function of the divertor is particle control: provide adequate pumping capability to exhaust the neutralized gas, most notably the He ash, as well as to retain eroded impurities such that they will not enter the main plasma [9].

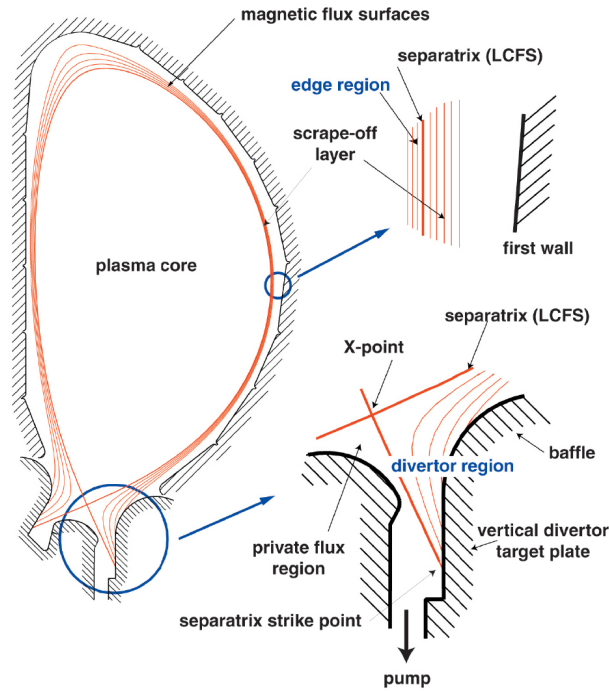


Figure 1.4: Poloidal cross section of a tokamak plasma in divertor configuration [9].

1.2. Design of a tokamak divertor

Having introduced magnetic confinement nuclear fusion and tokamak devices operating in divertor configuration, attention can now be directed toward the component of interest in this thesis: the divertor. The ITER divertor design is presented in order to highlight the critical issues that have emerged regarding the interface between the W armor and the heat sink of the monoblock. Subsequently, possible solutions to these technical problems are investigated, together with the one evaluated within this thesis work.

1.2.1. Divertor components

The divertor is a key in vessel component situated at the bottom of the vacuum vessel and it has the role of extracting heat and helium ash produced during the reaction. The divertor consists in many separate cassette modules arranged in the toroidal direction. The design of the single module of the divertor in ITER, is schematized in Figure 1.5. Contained in a stainless-steel cassette body, the module consists of the following main components:

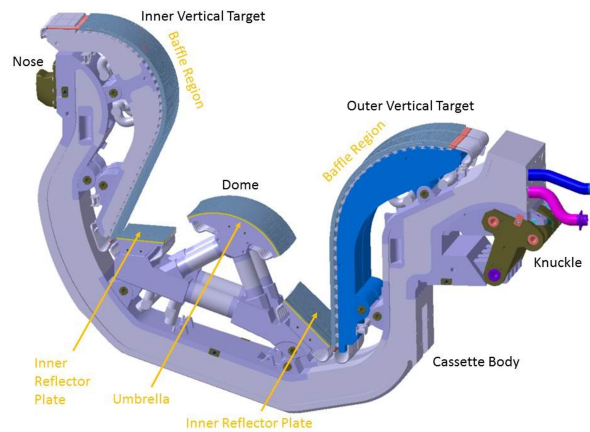


Figure 1.5: Representation of a cassette module of the divertor of ITER.

Target plates. On the sides of the divertor there are two target plates that block the plasma particles flowing in the SOL: the Inner Vertical Target and Outer Vertical Target. The armor material of the targets is tungsten, which has been selected as the preferred plasma-facing material for both the tokamak first wall and the divertor because of its high thermal conductivity, high melting point, low radioactivity and high sputtering resistance [10].

Central part of the module. In ITER, the central part of the module is the dome,

a component whose main function is to achieve high compression of neutrals in the PFR to improve the pumping performance and make helium ash removal more efficient [11]. Additionally, two reflector plates are positioned at the two sides of the dome to protect the cassette body from plasma radiation [12]. These components are W armored.

Pipework of the cooling circuits. There is a significant difference between the power density at the targets (20 MW/m^2) and at the cassette (1 MW/m^2). These distinct differences implicate the necessity of a separate cooling scheme with two cooling circuits each dedicated for the high heat flux components (HHF) or medium heat flux components. The paramount cooling requirement for the HHF components is to ensure a sufficient margin to the critical heat flux (CHF) at the strike point under all off-normal operating conditions. The CHF corresponds to the threshold heat flux at which the transition from nucleate boiling to boiling crisis, or “burnout”, occurs. This phenomenon is characterized by a sudden deterioration of heat transfer, leading to a rapid temperature increase in the heated material [8].

1.2.2. Monoblock of divertor target plates

In ITER, each target consists in a parallel array of many target elements oriented in the toroidal direction. Each element is a rectangular tungsten armor block connected by a cooling pipe in CuCrZr alloy running through the center of the blocks. The schematization of the monoblock is shown in Figure 1.6. The interface between the W armor and the CuCrZr heat sink is one of the critical aspects of the monoblock. The reasons for this criticality are mainly two: the operation temperature window of the copper-alloy and the stress field that generates at the interface. These two points will now be discussed in more detail.

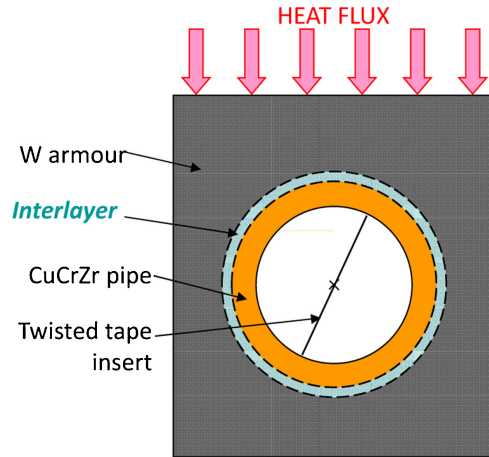


Figure 1.6: Generic representation of a divertor target monoblock [13].

CuCrZr alloy is considered the baseline heat sink material for water-cooled divertor targets because of its ideal properties of thermal conductivity, strength and ductility and its moderate activation. However, it presents a very narrow operating temperature window under irradiation conditions. Specifically, increased operation temperature leads to thermal softening and irradiation creep (above 300–350°C) whereas the lowering of temperature enhances irradiation embrittlement (below 200–250°C) [14]. Hence, meeting this operational window of temperature is a key requirement for CuCrZr. At the same time, W should be kept at temperature well above its ductile-to-brittle transition temperature (DBTT). In fact, if the of W is around 400-500°C, under irradiation scenarios such as in a fusion reactor, the DBTT increases significantly [15, 16].

Regarding the second point, the overall stress field at the interface between the pipe and the W armor is dominated by a mismatch in thermal expansion of the two materials. In fact, the thermal expansion coefficient of CuCrZr is three or four times higher than the one of W at different temperatures [17]. This causes a stress mismatch between the two pipes. Because of this, significant stress concentrations develop at the interface during thermal loading.

To mitigate the challenges associated with this interface, the ITER reference design adopts a thick (1 mm) soft copper interlayer, which serves as a stress-reliever between the two layers [17]. However, even with this design, some problems remain unresolved. The significant difference in thermal expansion coefficient between W and Cu ($\alpha_{Cu} \approx 4 \alpha_W$) causes thermal stresses at the interface and the limitations related to the operating temperature of the CuCrZr pipes are not resolved [18]. To simulate the temperature distribution in the monoblock, a peak local thermal load of 20 MW/m² is considered as the paramount design constraint to which cooling conditions and materials options are subordinated [19]. For 20 MW/m², the entire top region (apex) of the CuCrZr pipe locally exceeds the allowed upper temperature limit, reaching up to 300-450°C [20].

1.2.3. Innovative design concepts for the interlayer of ITER-like divertor monoblock

Considering the experience of ITER divertor, several optimized divertor target concepts have been proposed for the future development of DEMO machines. Among these, ITER-like monoblocks with W-armor have been widely considered, incorporating alternative solutions for the cooling medium (e.g., water-cooled or helium-cooled targets) as well as for the heat sink and interlayer materials [21, 22].

This thesis work focuses of water-cooled ITER-like target monoblock design. In this

context, the ideas of innovation focus on enhancing the heat sink and interlayer materials performance in terms of high-temperature strength, with the goal of overcoming the above mentioned issues already encountered in the ITER [21]. The main design concepts for water-cooled monoblocks are:

- W armor, heat sink made of Cu matrix composite reinforced with W, Cu interlayer [14, 23];
- W armor, CuCrZr heat sink, a functionally graded material of Cu and W for the interlayer [24, 25].
- W armor, CuCrZr heat sink, a thermal break design for the interlayer [13].

Considering the findings reported in the literature, this thesis proposes an innovative approach that integrates the thermal break interlayer concept with functionally graded high-entropy alloys. A comprehensive discussion of high-entropy alloys is deferred to Chapter 2. In the following sections, the concepts of thermal break interlayer and functionally graded materials are introduced.

Thermal break interlayer

The underlying concept of the thermal break design is to reduce heat conduction between the W armor and the CuCrZr pipe using and using an interlayer with a low thermal conductivity, thereby mitigating the interface-related issues discussed in Section 1.2.2. Engineering the thermal break interlayer offers several potential advantages. Firstly, it enables both W and CuCrZr to operate within their respective optimal temperature windows. Furthermore, by limiting heat transfer to the heat sink, the thermal expansion of the CuCrZr pipe is reduced, which in turn decreases the thermal stresses at the interface. In addition, if the interlayer exhibits low elastic stiffness, it can accommodate deformation more effectively and thus act as a stress-relief layer. Finally, since the local peak heat flux at the pipe is reduced, the thermal margin to the CHF is increased [13, 20].

Functionally-graded materials

Functionally-graded materials (FGM) are a class of composite materials that is characterized by variation in composition, microstructure, as well as properties across the dimension of the material [26]. FGMs are particularly attractive for the interlayer application because their composition can be varied in steps, thus reducing stress concentrations at interfaces and mitigating the risk of interfacial failure [27]. In the context of FGM, one proposed solution for the interlayer was based on a graded W/Cu material. However,

this design presented loss of plastic strength at high temperatures due to the softening of the pure Cu matrix. To overcome this limitation, You et al. [28] proposed the use of a precipitation-hardened CuCrZr alloy as the matrix material in place of pure copper. Also this composition presented some non ideal mechanical properties considering their application to the interlayer, such as loss of ductility with respect to the unreinforced alloy and brittle behavior for the layer of higher W content.

A possible direction can be the creation of FGM with HEAs, which present optimal mechanical properties for this application. The combination of the two classes of materials acquire the name of functionally-graded high-entropy alloy (FG-HEA). These materials have been extensively studied for a number of industrial applications [29], but there is no existing literature up to date regarding applications for the interlayer of the divertor monoblock.

1.3. Irradiation damage by D-T fusion plasma

This section focuses on the irradiation environment to which materials are subject to in a D-T plasma, with a particular focus on the interlayer of the monoblock.

1.3.1. Irradiation damage by neutrons, helium and deuterium

As already introduced in Section 1.1.1, the D-T plasma produces a large number of high-energy neutrons which escape from the plasma and irradiate the materials of the reactor vessel. The neutrons entering the material can generate two different effects. Firstly, the collision between the neutron and the atoms of the materials may result in the atom being displaced from its lattice site with considerable kinetic energy. The primary knock-on atom (PKA) possesses sufficient kinetic energy to displace other atoms from their lattice sites, initiating a displacement cascade that produces point defects like vacancies and self-interstitial atoms [30, 31]. The aggregation of these defects can result in the formation of interstitial dislocation loops and vacancy clusters, the latter evolving into voids. Continued growth of voids may eventually lead to irradiation-induced volumetric swelling of the material. Overall, irradiation-induced defects can inhibit dislocation motion, degrading the mechanical behavior of metals, hence promoting hardening, embrittlement, and irradiation creep in the material [31]. Additionally, neutrons also initiate nuclear reactions of transmutation, in some cases leading to the production of gas atoms such as helium and hydrogen isotopes [32].

The D-T reaction also produces 3.4 MeV alpha particles, some of which manage

to escape the magnetic confinement and collide on the walls of the tokamak causing displacement damage on the W first wall. The first wall is also exposed to high fluxes of hydrogen isotopes eventually contributing to damaging the material. Deuterium and tritium retention on plasma facing materials (PFMs) would degrade the fueling efficiency of the burning plasma and, in the sole case of tritium, result in a large radioactive inventory after shutdown of the device [33].

Helium, with its low solubility in the crystal lattice, forms clusters and accumulates at defects, dislocations and grain boundaries of the crystal, leading to swelling or embrittlement [32]. Hydrogen atoms can migrate in the crystal and eventually be trapped by defects and at precipitate sites (voids, bubbles) [34]. The observed differences between the two ions can be explained by the different self-trapping behavior of the two gases. Helium has a stronger self-trapping tendency thanks to the larger binding energy in forming pairs with respect to hydrogen. Consequently, helium tends to spontaneously form larger bubbles close to the projected range whereas hydrogen isotopes tend to be trapped by defects [35].

The creation of new trap sites via energetic neutron bombardment and subsequent creation of displacement cascades will increase the density of trap sites and can thereby impact the formation of helium bubbles and the retention of deuterium in the wall and divertor materials [34]. Additionally, helium bubbles and displacement damage defects generated by helium ions irradiation have an effect on the trapping and diffusion behavior of hydrogen isotopes [36]. Overall, the growth of internal bubbles may lead to the development of blisters, which are bubble-like deformations on the surface of the material. To explain how blistering damage evolves, two mechanisms were proposed: a gas-driven and a stress-driven model. According to the first model, the nucleation and growth of gas bubbles in the layer of maximum concentration of He and D is followed by a cooperative fracture between the bubbles with subsequent crack initiation and propagation. Consequently, the internal gas pressure causes surface deformation and growth of blisters. Alternatively, the stress-driven mechanism attributes blister formation to stress accumulation at the interface between the He and D-rich and pristine material regions [37–39].

1.3.2. Irradiation damage at the monoblock interlayer

Focusing now on the component of interest for this thesis work, the interlayer of the DEMO ITER-like monoblock, it is necessary to define the levels of irradiation damage to which it is subjected. To this end, the effect of the W armor on the penetration depth and energy spectrum of neutrons, helium, and hydrogen isotopes must be considered.

On one hand, helium and deuterium from the plasma impinging on the divertor target stop within a very thin layer of the W armor ($\approx 10^1$ nm) [40]. Neutrons, on the contrary, can penetrate more in the components of the machine. According to Gilbert et al. [32], who consider DEMO tokamak, the neutron flux decreases by more than 95% between the first wall surface and the blanket's outer edge at 57–62 cm depth. This attenuation is accompanied by a progressive change in the neutron energy spectrum as a function of depth. Since many gas-producing nuclear reactions exhibit threshold cross sections, neutron-induced damage is expected to vary significantly throughout the different components of the machine.

As a consequence, at the interlayer, neutrons coming from the plasma should be taken into consideration while helium and deuterium from the plasma do not reach this component. Nevertheless, the production of helium and deuterium from the transmutation reactions of neutrons with the elements contained in the interlayer should be included in the model. In fact, the produced gasses can reach significant concentrations for the introduction of damages in the material [41, 42].

According to You et al. [43], the irradiation damage for an ITER-like water-cooled monoblock in DEMO after 2 fpy (full-power years) reaches values of 3 dpa in the W armor and up to 12.8 dpa in the CuCrZr tube, where dpa is displacement-per-atom, used as a measure of irradiation damage. In fact, the irradiation damage in the copper heat sink is always higher than in the tungsten armor due to the lower energy threshold and higher displacement cross-section of Cu compared to W. Noce et al. [41] have studied the irradiation resistance of the ITER-like DEMO divertor target with a Cu interlayer in different blanket layouts. Even if the study of the blanket impact on the irradiation damage on the monoblock is outside of this thesis's scope, their results indicate that the nuclear damage at the Cu/CuCrZr components can reach up to ≈ 9 dpa/fpy.

The values cited above cannot be considered a direct reference for the neutron damage expected in the HEA investigated as a substitute for the Cu interlayer, but rather as an indicative estimate. In fact, irradiation damage in alloys depends not only on the type and energy of the incident particles, but also on the intrinsic characteristics of the irradiated material, such as atomic mass, bond strength, crystal structure, stacking fault energy, composition, and microstructure [30]. Taking these considerations into account, a reference value of 100 dpa was adopted in this thesis work to represent the neutron damage accumulated at the interlayer after approximately 5 years of DEMO operation. This choice reflects a conservative approach while remaining consistent with literature reference values for neutron irradiation damage in fusion reactor components [30, 44].

2 | High entropy alloys for nuclear applications

In this chapter, a detailed description of high entropy alloys is given, with a consequent focus on their application in nuclear fusion materials. Section 2.1 presents the definition of this class of materials. Section 2.2 describes mechanical alloying, the method used in this thesis work for the production of HEAs. Finally, in Section 2.3 describes how HEAs are a good fit to sustain the harsh environment that characterizes fusion machines.

2.1. Definition of high entropy alloys

High entropy alloys are defined as alloys composed of five or more principal elements in equimolar or near equimolar ratios, with a concentration of each principal element between 5 *at.%* and 35 *at.%* [45]. The name *high entropy alloys* derives from the significantly high values of mixing entropy ΔS_{mix} of such multi-principal element alloys. The total mixing entropy has four contributions such as configurational, vibrational, magnetic dipole, and electronic randomness. However, configurational entropy is dominant over the other three contributions. According to Boltzmann's equation, the configurational entropy change per mole for the formation of a solid solution from n elements with c_i mole fraction is given by:

$$\Delta S_{conf} = -R \sum_{i=1}^n c_i \ln(c_i) \quad (2.1)$$

where R is the gas constant. In equiatomic alloys this equation reduces to:

$$\Delta S_{conf} = -R \ln(n) \quad (2.2)$$

Hence, the entropy increases as the number of elements increases.

The mixing enthalpy for a random solution of elements is given by [46]:

$$\Delta H_{mix} = \sum_{i=1, j \neq i}^n \Omega_{ij} c_i c_j \quad (2.3)$$

where $\Omega_{ij} = 4\Delta_{mix}^{AB}$, with Δ_{mix}^{AB} the mixing enthalpy of binary liquid AB alloys.

Considering Gibbs free energy of mixing in Equation 2.4, the comparison between the enthalpy of mixing ΔH_{mix} and the entropy of mixing ΔS_{mix} is what determines the stability of either a random solid solution of all the elements of the alloy, or a binary, ternary, quaternary ordered compound.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (2.4)$$

Knowing this, depending on the value of the configurational entropy, the following classification is used:

- High entropy alloys (HEA): a mixing entropy $\Delta S_{conf} \geq 1.5R$ is large enough against the strong ordering of such atomic pairs with strong bonding energies at high temperatures.
- Medium entropy alloys (MEA): $1R \leq \Delta S_{conf} \leq 1.5R$.
- Low entropy alloys (LEA): $\Delta S_{conf} \leq 1R$ cannot compete with the strong bonding energies.

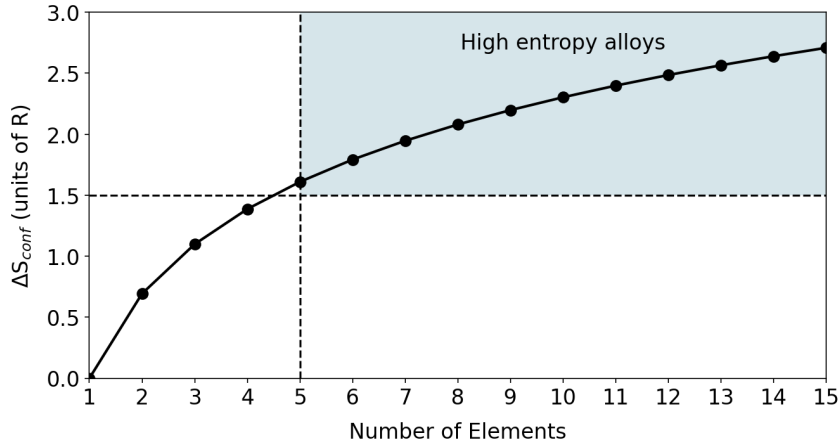


Figure 2.1: Trend of increase of configurational entropy ΔS_{conf} with the number of elements in the alloy.

In Figure 2.1, the trend of increase of configurational entropy with the number of elements is shown for the sole case of equiatomic alloys. It can be calculated that the

increase in entropy from a 13 to a 14 elements alloy is small ($0.07R$), so more principal elements will not get a significant benefit from the high-entropy effect but might increase the complexity in handling raw materials or recycling the alloys. Consequently, a number of principal elements between 5 and 13 is suggested to define HEAs [47].

2.1.1. Four core effects of HEAs

The microstructure and properties of HEAs are affected mainly by four core effects: high entropy effect, which is linked to thermodynamic properties and interferes with phase formation; sluggish diffusion effect, linked to kinetics properties and causes the slow down of phase transformation; severe lattice distortion effect for structure properties; the cocktail effect, which brings excess values to the quantities predicted by the mixture rule due to mutual interactions of unlike atoms and severe lattice distortion [47].

High entropy effect

In HEAs, the high entropy effect is responsible for guaranteeing the greater stability of random solid solution with respect to binary, ternary, quaternary compounds or segregated phases in HEAs. There are three possible categories of competing states: elemental phases, intermetallic compounds and solid solution phases below the lowest melting point of the alloy.

- Elemental phase is the terminal solid solution based on one metal element;
- Intermetallic compound is a stoichiometric compound having specific superlattices;
- Solid solution is the phase with the complete mixing or significant mixing of all elements in the structure of BCC (body-centered cubic), FCC (face-centered cubic), or HCP (hexagonal close-packed).

The equilibrium state of a HEA is the one having the lowest Gibbs free energy of mixing, according to the second law of thermodynamics. Elemental phases based on one major element have small ΔH_{mix} and ΔS_{mix} , compound phases have large ΔH_{mix} but small ΔS_{mix} caused by their ordered structure, finally solid-solution phases containing multiple elements have medium ΔH_{mix} and high ΔS_{mix} . The medium ΔH_{mix} is given by the fact that exists a proportion of unlike atomic pairs in solution phases. Assuming that all heats of mixing for unlike atom pairs are the same, ΔH_{mix} of the random solution state for quinary equiatomic alloy is 4/5 of that of its completely ordered state. Similarly, for septenary equiatomic alloy, the ratio is 6/7 [48]. Hence, a higher number of elements would allow the random state to have the mixing enthalpy closer to that of the completely

ordered state and to become even more competitive with the ordered state under the aid of its high mixing entropy [47].

Severe lattice distortion effect

Solid solution phases in HEAs are multicomponent whole-solute matrices. Hence, every atom is surrounded by different kinds of atom and thus suffers lattice strain and stress mainly due to the atomic size difference, as exemplified in Figure 2.2. It has been suggested that these lattice distortions are caused not only by the atomic size misfit, but also by differences in the crystal structure and bonding preferences of the alloying elements present [49].

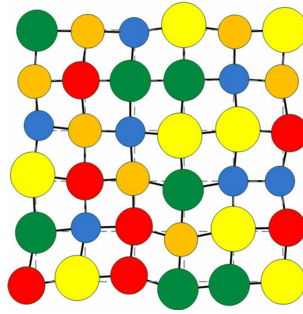


Figure 2.2: Severely distorted lattice in a multicomponent alloy [47].

Severe lattice distortion affects many properties of the material. The localized distortion around the solute atom will interact elastically with dislocations moving through the material, resulting in solid solution hardening. In addition, the electrical and thermal conductivity significantly decrease due to electron and phonon scattering. All these properties become quite insensitive to temperature in HEAs and this can be explained because the lattice distortion caused by thermal vibration of atoms is relatively small compared with severe lattice distortion [47].

Sluggish diffusion effect

The diffusion coefficients of atoms in HEAs are found to be lower than in conventional alloys or pure metals. This phenomenon, called sluggish diffusion effect, supposedly affects phase nucleation, growth and distribution. It also causes slower and finer precipitation and slower grain growth, both of which contribute to the improvement of the material's strength. Finally, it increases creep resistance, prolonging the life of parts used at high temperatures [48].

The first diffusion study was published by Tsai et al. [50] which investigated a CoCrFe-MaNi system. They concluded that the diffusion coefficients of all the considered elements are smaller in the HEA matrix with respect to all the other considered matrices: binary and ternary alloys and pure metals. Additionally, the activation energies of diffusion, normalized in order to take into account the relation with the melting temperature of the matrix, are higher in the studied HEA rather than those in reference metals. This tendency was also observed to be related to the number of constituents in the matrix. These considerations on diffusion coefficients and activation energies are considered to be direct evidence of sluggish diffusion effect in HEAs.

According to Tsai et al., the origin of sluggish diffusion is the variation of the lattice potential energy (LPE) when an atom migrates from one site to the other. In fact, the surrounding atoms of each lattice site in the solid solution phases of HEA have much greater variety than those in conventional ones. Hence, since in HEAs each site is surrounded by different atoms, each site has different bond configuration and thus different LPE. Atoms that experience greater fluctuation in LPE have slower diffusion because sites with lower LPE would increase the energy barrier and activation energy for diffusion, hence becoming atomic traps that hinder diffusion. In conclusion, the large LPE fluctuation leads to higher normalized activation energies and lower diffusion rates, causing the sluggish diffusion effect.

Following studies have, however, showed skepticism about the existence of the sluggish diffusion effect in HEAs [51–53]. Particularly, the study by Tsai et al. has been considered to be based on improper experimental analysis and the conclusions of sluggish behavior to be correlated with a prominent content of Mn in the considered system. Further experiments have also found the effect, when observed, to be independent on the number of elements in the system.

Cocktail effect

Cocktail effect ranges from atomic-scale multicomponent composite effect to microscale multiphase composite effect. At the atomic scale, cocktail effect results from mutual interactions among composing elements, which would bring excess quantities to the average values simply predicted by the mixture rule. In addition to mutual interaction, also severe lattice distortion contributes to bringing excess quantities to those predicted by the mixture rule. At the microscale, the properties are from the overall contribution of the constituent phases. This relates with the phase size, shape, distribution, phase boundaries and properties of each phase [48].

2.1.2. Phase stability in HEAs

The Hume-Rothery rules were created for predicting the solubility and solid solution formation of binary alloys. However, since for HEAs there is no clear distinction between solvent and solute components, the formulation of the original Hume-Rothery rules, and the factors they are based on, require some modifications [49]. For this thesis work, the parameters taken into consideration are:

- the atomic size misfit (δ) between alloying elements affects the formation of a stable solid solution;
- the average valence electron concentration (VEC) which has an effect on the type of crystal structure forming in the alloy.

In the context of HEAs, the parameters are defined as in Eq.2.5, Eq.2.6.

$$\delta = \sqrt{\sum_{i=1}^n c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (2.5)$$

where $\bar{r} = \sum_{i=1}^n c_i r_i$, with c_i and r_i are respectively the atomic percentage and atomic radius of the i-th element and n is the number of alloying elements. If $\delta < 0.0065$, solid solution forms. If not, an amorphous solution is formed [54].

$$VEC = \sum c_i VEC_i \quad (2.6)$$

where VEC_i is the VEC of the i-th element. A $VEC > 8$ favors the formation of FCC-type solid solutions while $VEC < 6.87$ favors the formation of BCC-type ones [46].

Thermodynamic consideration are reflected through the mixing enthalpy ΔH_{mix} and mixing entropy ΔS_{mix} already introduced in Eq. 2.3 and Eq. 2.1. The mixing enthalpy, is used to characterize the chemical compatibility among the many principal components. A solid solution can form when $-11.6 < \Delta H_{mix} < 3.2 \text{ kJ/mol}$ [54]. On the other hand, positive values of ΔH_{mix} promote phase separation whereas large negative values favor the formation of intermetallic compounds and, for even more negative values, the formation of amorphous phases [54, 55].

Finally, the mixing entropy should be $12 < \Delta S_{mix} < 17.5 \text{ J/Kmol}$ in order to achieve a solid solution [56]. In conclusion, it can be observed that the formation of the solid solution is in fact mainly governed by three parameters: δ and ΔH_{mix} and ΔS_{mix} whose range of values are displayed in Figure 2.3.

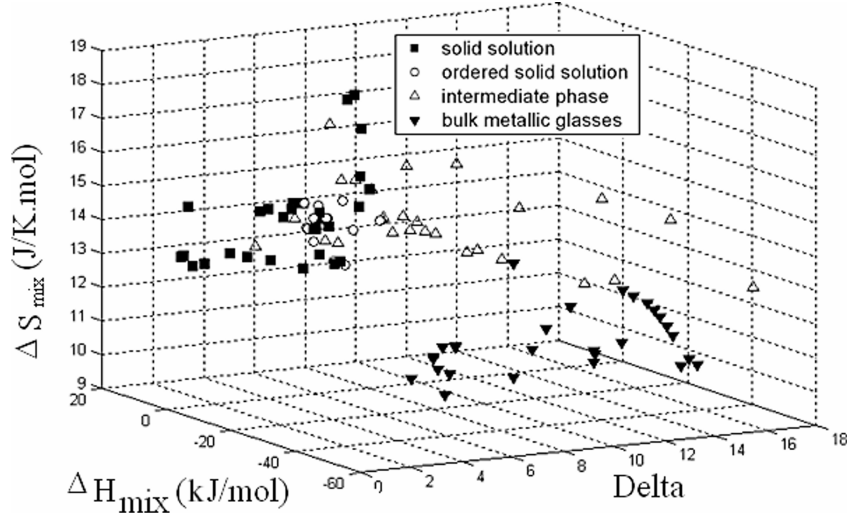


Figure 2.3: δ , ΔH_{mix} , ΔS_{mix} plot to delineate the limits of phase selection [56].

2.2. Mechanical alloying for production of high entropy alloys

Mechanical alloying (MA) is a solid-state powder processing technique capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or prealloyed powders. The non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys [57]. With this technique, the powder particles are subject to intense and prolonged collisions with the milling balls in a high-energy milling machine. The process involves repeated cold welding, fracturing and rewelding of powder particles, leading to atomic diffusion within the particles and resulting in the alloying of the powder.

The process of MA starts with mixing of the powders in the right proportion and loading the powder mix into the mill along with the grinding medium. The raw materials used for MA are pure or pre-alloyed powders that usually have particle sizes in the range of $1 \pm 200 \mu m$ [58]. Milling is continued until a steady state is achieved, characterized by all powder particles exhibiting the same composition as the starting powder mix. Occasionally, metal powders are milled with a liquid medium and this is referred to as wet grinding. If no liquid is involved, the process is referred to as dry grinding. Finally, the milled powder can be consolidated into a bulk shape and heat treated to obtain the desired microstructure and properties.

2.2.1. Process variables for mechanical milling

The process of mechanical alloying involves the optimization of a number of variables with the aim of achieving the desired product phase or microstructure.

Type of milling machine. Ball mills are machines used in various industries for particle size reduction, mixing, homogenization and mechanical alloying. All milling machines include one or more vials containing the sample and the grinding balls. The vials can undergo either a rotational motion, as in attritor mills and planetary ball mills, or a back-and-forth motion, as in shaker mills [58]. In both cases, the vial motion accelerates the milling balls to high velocities, resulting in strong impacts and high-energy collisions.

Milling speed. The faster the mill rotates, the higher the energy input to the powder is. However, above a critical speed, the balls are pinned to the inner walls of the vial and do not collide with them, resulting in no impact force. Therefore, the maximum speed should be just below this critical value so that the balls produce the maximum collision energy [59].

Milling time. The milling time is chosen to achieve a steady state between fracturing and cold welding of the powder particles. The time required to achieve equilibrium, however, depends of the intensity of milling and consequently on the other parameters chosen to perform the milling. However, if the powder is milled for times longer than required, the level of contamination from the wearing of the milling media may increase and some undesired phases may form [58].

Grinding medium. The size and density of the grinding medium has a big influence on the milling efficiency, since a larger weight of the balls will transfer more impact energy to the powder particles. The most common materials used for the milling balls are: hardened steel, tool steel, hardened chromium steel, tempered steel, stainless steel, WC-Co, bearing steel, or other high-density materials [58]. Due to the great impact of the grinding medium on the walls of the container, some material from both the balls and the vial may be dislodged and get incorporated into the powder. Consequently, it is always desirable to have the grinding vessel and medium made of the same material in order to avoid cross contamination.

Ball-to-powder weight ratio. The ratio of the weight of the balls to the powder (BPR) has a significant effect on the time required to achieve a particular phase in the powder being milled. In fact, at higher values of BPR, the number of collisions per unit time increases and consequently more energy is transferred to the powder particles and alloying takes place faster.

Extent of filling the vial. In order to have an efficient energy transfer between the balls and the powder, it is necessary to have enough space for the balls and the powder particles to move around in the milling container. If such amount is large, there is not enough space for the balls to move around and the energy of the impact is lower.

Process control agents. The process control agents (PCA) are used to perform wet milling. The PCA are mostly organic compounds, which act as surface-active agents. The PCA adsorbs on the surface of the powder particles and inhibits agglomeration by minimizing surface tension of the solid material and minimizing cold welding. Hence, wet grinding allows to obtain finer-ground products. On the other hand, PCA normally introduces some impurities in the powder so, to avoid contamination, a dry grinding procedure should be preferred [60].

2.2.2. Planetary ball mill

In this thesis work, mechanical milling was performed with a planetary ball mill. A more detailed discussion of this type of milling machine is necessary for the modeling of the mechanical milling process described in Section 4.2.

The planetary ball mill owes its name to the planet-like movement of its vials, which are arranged on a supporting disk, the sunwheel, that rotates around a common central axis (revolution) and that have a mechanism that causes them to rotate around their own axes (rotation). The rotation direction of the vials is set in counter direction with respect to the revolution of the disk. When rotation and revolution are set in counter direction, the milling is more efficient than when set in normal direction, as a result of higher impact energy and higher number of collisions [61, 62].

The balls in the planetary ball machine show different motion patterns depending on the filling ration and the revolution speed. The three recognized patterns are: cascading, cataracting and centrifugation, shown in Figure 2.4. In the *cascading* regime, the milling balls are taken along by the vial walls and then roll upon each other from the bulk top to its base. During *cataracting* regime, a fraction of the balls detaches from the vial walls and follows a parabola trajectory in flight before impacting into the bulk of balls or to the opposite wall. Finally, in *centrifugation* regime, the balls align to the chamber wall and follows its rotation with almost no relative velocity [63].

Many attempts have been made to correlate the ball patterns to the ratio between the rotation and revolution speed. However, the different results obtained that can be found in literature suggest that this correlation also depends on the geometric characteristic of the planetary ball mill and on the specific milling conditions, such as the angular velocity

of the sunwheel and the bpr [64]. Nonetheless, a general trend can be identified: the specific impact energy of balls increases with an increasing rotation-to-revolution speed ratio, hence moving from cascading to cataracting regime, but it decreases at a critical speed ratio which represents the onset of centrifugation regime [61].

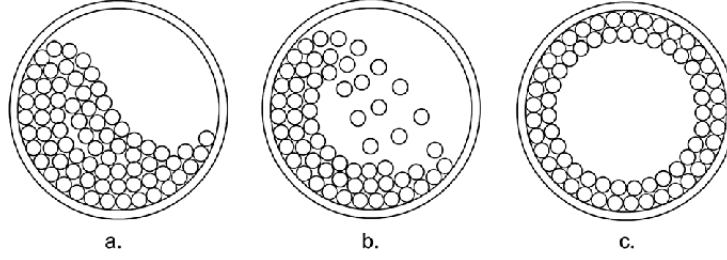


Figure 2.4: Top view of milling ball patterns in a single vial of a planetary ball machine. The regimes are (a) cascading, (b) cataracting, (c) centrifugation [62].

2.2.3. Mechanisms of alloying

During high-energy milling the powder particles are repeatedly flattened, cold welded, fractured and rewelded. The mechanism of MA slightly changes depending the mechanical properties of elements to alloy, i.e. whether the material is brittle or ductile.

In the early stages of milling, the impact with the milling walls and media tends to plastically deform the ductile components, causing the particles to get flattened to a plate-like shape, while brittle particles get fragmented. This phenomenon is illustrated in Figure 2.5.

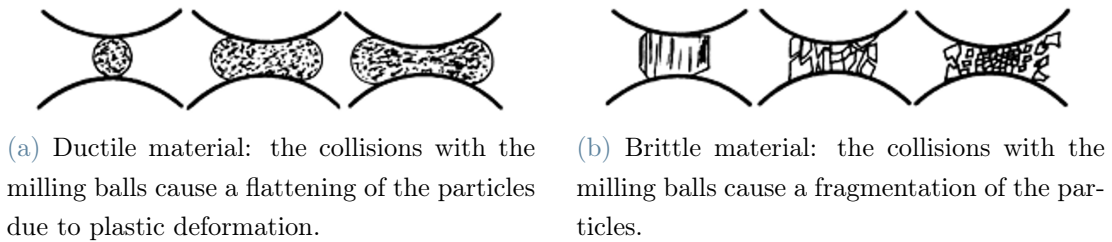


Figure 2.5: Comparison of the effect of milling ball impact on ductile and brittle particles [60].

A system composed of both ductile and brittle components is now considered. As milling proceeds, the flattened ductile particles undergo cold welding, forming composite lamellar structures, while the brittle fragments become embedded within these composites. As a result, a broad range of particle size develops. Meanwhile, alloying begins to

occur due to the combination of decreased diffusion distances, i.e. decrease of interlamellar spacing, increased lattice defect density and any heating occurred in the milling operation. Then, with continued deformation, the composite particles get work hardened and start fracturing by a fatigue failure mechanism. Fragments generated by this mechanism continue to reduce in size [58].

A steady-state equilibrium is achieved when the rate of welding, that tends to increase the particle size, and the rate of fracturing, that decreases it, start balancing. Overall, this mechanism drives both large and fine particles towards an intermediate size and in the end each particle contains substantially all the elements in the proportion in which they were mixed together [58].

It should also be highlighted that, considering the mechanisms of mechanical milling, a lot of defects are introduced in the lattice of the alloyed elements during the process. This causes the crystal structures to eventually reach saturation hardness due to accumulation of strain energy [58]. This is an important aspect to consider, since the harder elements in the considered alloy may reach saturation hardness faster than the other elements, thus hindering the diffusion phenomena that determine the alloying process and that will be discussed in the following paragraph.

2.2.4. Diffusion in mechanical alloying

Diffusion is the mechanism of formation of alloys during mechanical alloying processes. However, diffusion in mechanical alloying differs from the thermally induced diffusion because, rather than being controlled only by thermal energy, it is also and predominantly controlled by mechanical energy.

Diffusion coefficient D can be written as:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (2.7)$$

where D_0 is a material constant, Q is the activation energy, R the universal gas constant, T temperature. Hence, diffusion is proportional to the activation energy and is inversely proportional to the temperature of the material. It appears that in mechanical alloying processes, generally, the temperature reached during collisions is far from reaching the diffusion temperature [65]. Therefore, other factors must significantly contribute to the diffusion process. The answer lies, in fact, in the activation energy.

Activation energy is the increase in free energy needed for an atom to move to an adjacent location. In common metals and alloys, atom movement occurs through interchange

of an atom in a crystal lattice site with a vacant site [66]. Hence, the activation energy of diffusion is given by the sum of the activation energy to form a vacancy Q_f and the activation energy to move the vacancy itself Q_m . During mechanical milling, high energy collisions are imparted to the powder particles and a large amount of defects (vacancies and interstitials) are generated in the material due to plastic deformation. Consequently, the total activation energy required for diffusion is lower because part of the activation energy for the production of vacancies, Q_f , is not required. This mechanically activated diffusion is one of the dominating factors in mechanical alloying and milling. If a large number of vacancies are formed during mechanical milling, it is expected that the temperature for the subsequent diffusion process will be lower [65].

After discussing diffusion from a thermodynamic perspective, the main diffusion mechanisms will now be presented. As already mentioned, in metals and alloys vacancy diffusion is favored. Diffusion in defect-free crystals is called *lattice diffusion* D_l . Other diffusion paths, on the other hand, go through imperfect lattice sites. Among these, the most significant ones are *grain boundary diffusion* D_g and *free surface diffusion* D_s . It has been found that, at low temperatures, surface diffusion dominates over grain boundary diffusion and lattice diffusion: $D_s > D_g > D_l$. As temperature increases, grain boundary diffusion predominates, whereas for higher temperatures, generally for $T > 0.8 T_m$, lattice diffusion becomes the main mechanism of diffusion [67]. The logarithmic variation of the three diffusion coefficients with respect to the inverse of temperature is shown in Figure 2.6. Since mechanical alloying is a process that involves low temperatures, grain boundary and free surface diffusion are always the prevalent modes of diffusion. In both cases, the high energy stored in mechanically milled powder particles drives the structural change in materials to minimize the internal energy level [65].

Free surface diffusion. The continued process of fracturing and welding in mechanical alloying gives rise to three types of free surfaces for diffusion processes to take place. The first type is microcracks, generated either by fracturing or by dislocation motion. To stabilize the particle, atoms would tend to diffuse along the surface of microcracks in order to fill them up, thus lowering the internal energy of the system previously increased by the increase in surface energy. The second type of free surfaces are the cold-welded surfaces between different particles, which are filled by capillarity-driven diffusion, analogous to sintering, until surface energy and stress are reduced. The third type is a pre cold-welding surface, that is a mechanically welded surface in which atoms diffuse in order to form welded boundaries. Overall, the formation of layered surfaces and the repeatedly broken diffused layer leads to better interparticle contact and decreases diffusion distance [65].

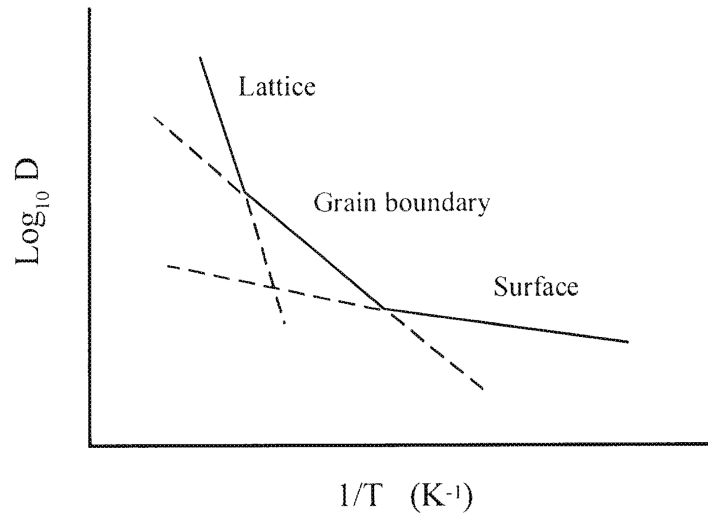


Figure 2.6: Relative importance of surface, grain-boundary, and lattice diffusion as a function of inverse temperature [65].

Grain boundary diffusion. Because of the large plastic deformation and fracturing, the crystallite size and grain size reduce significantly, the former down to nanometer scale [58]. The decrease in grain size leads to an increase in the area of grain boundaries, thus leading to an increase in grain boundary diffusion. The temperature at which the grain boundary diffusion begins to dominate over lattice diffusion decreases with the decrease in crystallite size. This is why, in mechanical alloying, only free surface and grain boundary diffusion are prevalent [65].

2.3. High entropy alloys for nuclear applications

HEAs, thanks their structural characteristics, can exhibit several advantageous properties, including high thermodynamic and phase stability under extreme environments. In particular, these alloys are characterized by high melting temperatures, enhanced mechanical properties at elevated temperatures, and improved resistance to irradiation and corrosion. Owing to their enhanced resilience and performance, HEAs are considered promising candidate materials for applications in the extreme operating conditions of both fission reactors and fusion devices [44].

In particular, HEAs containing refractory elements have attracted significant interest for high-temperature applications due to the elevated melting points of their constituent elements, primarily those belonging to Group IV (Ti, Zr, and Hf), Group V (V, Nb, and Ta), and Group VI (Cr, Mo, and W) [68]. These refractory high entropy alloys (RHEAs) exhibit better high-temperature performance and superior radiation resistance due to

their BCC-type structures which are inherently resistant to irradiation swelling [44].

Finally, for applications in high energy neutron environments, such as in fusion devices, a class of HEAs containing low-activation elements and called low-activation HEAs (LAHEAs), has been proposed to minimize the quantity of radioactive waste. In Figure 2.7, the radioactive decay time limit of all elements when subjected to high-energy fusion neutrons is illustrated.

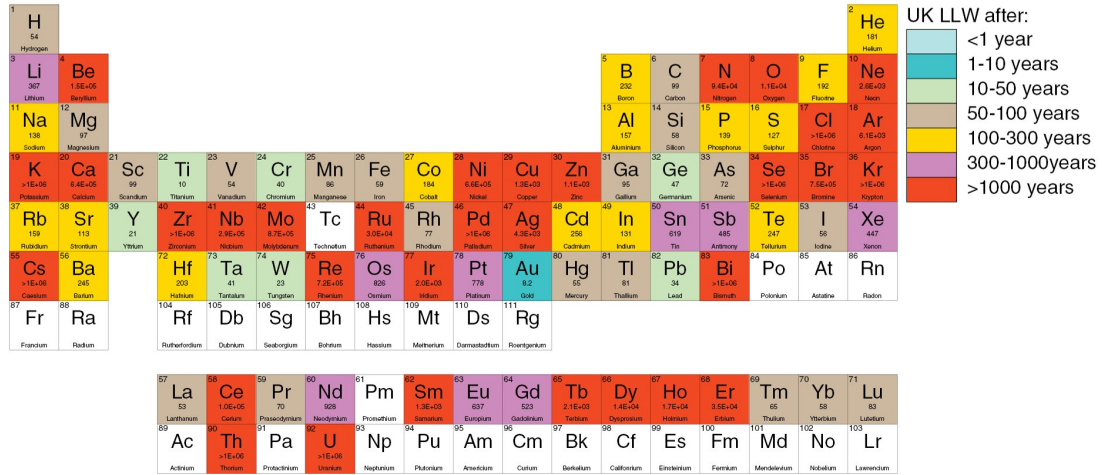


Figure 2.7: Periodic table with each naturally occurring element colored according to the time-interval during which it would satisfy the UK-LLW (low level waste) criteria after irradiation during one full operation cycle (5 years) in the divertor cassette body [69].

2.3.1. Irradiation resistance of high entropy alloys

HEAs have demonstrated enhanced resistance to irradiation-induced degradation. Compared with conventional alloys, they generally exhibit higher resistance to irradiation defect formation, lower void swelling in comparison to conventional alloys, higher microstructural stability (usually phase stability) than conventional alloys under irradiation, and finally limited irradiation hardening [30]. Several mechanisms have been proposed to explain these improved irradiation tolerance characteristics.

Because of the high atomic-level stresses, given by lattice distortion, and the chemical heterogeneity that characterize HEAs, dislocations are difficult to form due to decreased defect mobility [70]. This reduction in defect mobility is particularly pronounced for interstitials. In conventional metals and alloys, interstitials generally diffuse much faster than vacancies. In contrast, the combined effects of severe lattice distortion and sluggish diffusion in HEAs substantially suppress interstitial migration, resulting in more comparable diffusivities for interstitials and vacancies [71]. The reduced mobility of interstitials

increases the probability of recombination with vacancies in the vicinity of the original displacement cascade, thereby suppressing void formation and mitigating irradiation-induced swelling [30].

When considering helium irradiation of HEAs, it has been observed that HEAs have a higher resistance when compared to pure metals and some steels. This is because the lattice distortions in HEAs act as traps for vacancies and irradiation-generated helium atoms, thereby reducing the concentration and diffusion rate of helium and hindering the aggregation of helium bubbles [72].

Considering general alloys under irradiation conditions, local concentration gradients can cause the redistribution of solute atoms and impurities, leading to enrichment or depletion of specific alloying elements. However, in HEAs, the sluggish diffusion effect can mitigate irradiation-induced segregation, thereby contributing to enhanced phase stability [72]. Moreover, this effect becomes more pronounced with an increasing number of constituent elements in the alloy [30].

It has been found that BCC single phase HEA show a better resistance to the irradiation-induced segregation and irradiation-induced phase transformation, if compared to FCC single phase or dual-phase HEA. This is thought to be linked to the more severe lattice distortion, lower vacancy concentration and lower point defect mobility that generates in BCC HEAs [72, 73].

2.3.2. Tungsten-containing high entropy alloys

The study of W-based HEAs has been driven by their interest in nuclear fusion applications, thanks to their combination of the advantages of W-based refractory alloys (i.e. the high melting point) with those of HEAs. A number of studies established that W-based HEAs had excellent mechanical properties at elevated temperatures and irradiation resistance properties.

Regarding the mechanical properties, it has been observed that W-based HEA have a very high yield stress and a stable phase structure even at high temperatures. Additionally, W-based HEAs may be an effective way to suppress the recrystallization and brittleness typical of tungsten-containing materials. In fact, it should be considered that impurities tend to concentrate along grain boundaries, weakening them and leading to embrittlement. Compared with coarse-grained alloys, fine-grained alloys such as HEAs possess a higher grain-boundary density, which allows impurities to distribute more uniformly, thereby reducing local impurity concentrations and improving resistance to embrittlement. [74]. Additionally, it was shown that W-based HEAs have good resistance to

ion irradiation, as evidenced by the inhibition of dislocation loop formation, formation of smaller and more uniformly distributed helium bubbles [52]. In particular, this is the result of two mechanisms. First, the low vacancy migration energy of W-based HEAs leads to a larger overlap between the migration energy of interstitials and vacancies, favoring their recombination. This, in addition to the sluggish migration of He interstitials and clusters, hinders the formation of He-vacancy complexes and the growth of He bubbles into large ones [75].

The first two representative W-based HEAs, WNbMoTa and WNbMoTaV, were proposed by Senkov et al. [76]. in 2010. Subsequently, the need for low-activation elements led to a growing interest in W-Ta-Cr-V-based RHEA, which were first developed by El-Atwani et al. [77]. The high level of chemical disorder of this material, arising from the difference in atomic mass and volume between the period 4 alloying elements (V and Cr) and the period 6 elements (Ta and W), is particularly important from the point of view of its resistance to irradiation damage, microstructural changes, and their impact on the mechanical properties [78]. The presence of Cr reinforces the corrosion resistance of the alloy while V and Ta can improve creep properties, reduce grain size, and enhance the toughness and strength of the alloys [79].

The quaternary W-Ta-Cr-V HEA has shown the formation of Cr- and V-rich phases and precipitates at grain boundaries when irradiated up to 8 dpa with 1 MeV Kr ions. These Cr-V can enhance irradiation stability of the material by promoting defect recombination and suppressing dislocation loop formation [77]. However, such segregation should be carefully considered also in other irradiation scenarios, because they could adversely affect the mechanical properties of the alloy and overall compromise their intended applications [44]. In this regard, increasing the number of constituent elements can significantly improve the thermodynamic stability of this quaternary alloy under irradiation, according to the mechanisms described in the previous section. Following this approach, quinary alloys have been produced with composition WTaTiVCr, where the addition of Ti has resulted in increased plasticity [74].

The composition analyzed in this thesis work is a low-activation refractory W-based HEAs. Starting from the well characterized quaternary W-Ta-Cr-V alloy, the fifth added element is Fe, which, even if it is not a refractory element, it has excellent ductility and has the advantage of being inexpensive if compared to other elements. According to Zhang et al. [79], who studied the microstructure, Vickers hardness, and compressive properties of VCrFeTaxW_x, observed promising high-temperature mechanical properties. Martins et al. [80], focused on the structural and thermal characterization of equiatomic CrFeTaVW, finding a stable microstructure at high temperatures and a thermal diffusivity that remains

far below those of CuCrZr and W, thus making the alloy a promising candidate for thermal break interlayer materials.

2.4. Thesis goals

This thesis is developed within the context of designing a $(\text{CrFeTaV})_{1-x}\text{W}_x$ high-entropy alloy system with five different compositions, proposed as a functionally graded material for the thermal break interlayer of a divertor target monoblock. The focus is directed first on the production via mechanical milling of the powder HEA in the equimolar composition CrFeTaVW, secondly on the characterization, in terms of irradiation resistance, of the previously consolidated samples of compositions $(\text{CrFeTaV})_{95}\text{W}_5$, $(\text{CrFeTaV})_{90}\text{W}_{10}$, CrFeTaVW, $(\text{CrFeTaV})_{70}\text{W}_{30}$, and $(\text{CrFeTaV})_{65}\text{W}_{35}$. In particular, the investigated alloys are assessed under conditions representative of a D–T plasma tokamak environment, with the aim of evaluating their suitability for nuclear fusion applications.

For the production of the HEA via mechanical milling, the objective of this work is to optimize the operating parameters of a newly acquired planetary ball mill at the IPFN laboratories, with the final aim of achieving a single solid solution of the considered HEA. More specifically, the challenges associated with the alloying of W, the hardest constituent of the alloy, will be addressed. Additionally, a theoretical model that estimates the transfer of energy from the milling media to the powder particles is implemented in order to correlate the operating parameters of the planetary ball mill to the mechanisms of alloying emerging from the experimental results. These objectives are addressed in detail in Chapter 4.

The second objective of this thesis work is the investigation of the irradiation resistance of five compositions of $(\text{CrFeTaV})_{1-x}\text{W}_x$ through the analysis of microstructural changes and surface topography. The five samples are $(\text{CrFeTaV})_{95}\text{W}_5$, $(\text{CrFeTaV})_{90}\text{W}_{10}$, CrFeTaVW, $(\text{CrFeTaV})_{70}\text{W}_{30}$, and $(\text{CrFeTaV})_{65}\text{W}_{35}$. These samples were consolidated prior to this thesis work, which instead aims at characterizing their phase composition, morphology and topography prior to irradiation, in the so called *as-sintered* condition. Subsequently, the compositions are characterized after the implantation of Ar^+ , He^+ , and D^+ ions, in order to assess their response to irradiation damage.

In particular, grazing-incidence X-ray diffraction (GIXRD) is employed to evaluate the phase stability of the alloys following irradiation, while scanning electron microscopy (SEM) is used to investigate irradiation-induced surface modifications, such as swelling and blistering, and to correlate these features with the different phases present in the microstructure.

3 | Experimental setup

This chapter aims at presenting the experimental techniques and methods used in this work. Section 3.1 details the materials and methods of the production of powder HEA samples via mechanical alloying. Section 3.2 describes the spark plasma sintering procedure for the consolidation of the powders into bulk samples. Then the irradiation methodology with the ion implanter is introduced. Finally, the characterization techniques of X-ray diffraction and scanning electron microscopy are presented in Section 3.3.

3.1. Production of HEA powders

The HEA powders were produced from elemental powders through mechanical milling using a planetary ball mill. This section presents the specific equipment employed, while the operating principle of the type of mill is described in Section 2.2.2.

3.1.1. Elemental powders

For the production of HEA in the optimization of the planetary ball mill, an equimolar composition of CrFeTaVW was chosen. The starting elemental powders are

- Chromium powder: particle size $<44\mu m$, 99% purity, ThermoScientific;
- Iron powder: particle size $<44\mu m$, 98% purity, AlfaAesar;
- Tantalum powder: average particle size (APS) $\approx 2\mu m$, 99.9 % purity, ThermoScientific; particle size $<44\mu m$, 99% purity, ThermoScientific.
- Vanadium powder: particle size $<44\mu m$, 99.5% purity, AlfaAesar;
- Tungsten powder: particle size $35 - 55nm$, 99.9% purity, Nanografi.

3.1.2. Planetary ball mill

The high-energy ball mill used for this thesis work is the planetary ball mill Powteq BM 40 with vials and milling balls in tungsten carbide (WC). The input parameters will

be discussed in Section 4.3 since they were varied during the optimization process.

The vials containing the alloying powders are prepared and sealed in a glove box under argon atmosphere in order to prevent the oxidation of the powders. After milling, the powders are removed from the vials and stored inside the glove box for subsequent analysis whereas the vial walls and milling balls are cleaned in order to prevent contamination between different alloy compositions. The milling balls are cleaned in an ultrasonic bath using ethanol. The vials are first cleaned with ethanol and then subjected to a short milling procedure with a small amount of water for 10 min at 200 rpm.

3.2. Consolidation and implantation of HEA samples

In this section, the consolidation of the powder samples is presented, followed by the description of the implantation operation.

3.2.1. Spark plasma sintering

Spark plasma sintering (SPS) is an emerging powder consolidating technique. During sintering, external pressure and an electric field are applied simultaneously to enhance the densification of the powder compacts. Material densification by SPS is generally very fast (i.e. within a few minutes) and can be achieved at temperatures 200-500°C lower than those used in conventional sintering.

The physical mechanism describing the SPS process is by most considered to be the micro-spark/plasma formation. According to this theory, the electrical discharge leads to the generation of plasma spark in the gap between the particles of a material, causing a local high temperature state. Hence, differently from other consolidation techniques, SPS does not use an external heating source, but it is the pulsed direct current that passes through the conductive graphite die and through the sample that heats the sample. The sintering process is assisted by the use of pressure, which helps the plastic deformation and allows for a sintered compact of over 99% density [81].

The SPS equipment used in this thesis work is FCT System GmbH and the parameters used to produce the bulk samples are: sintering time of 7 min, temperature of 1400°C, applied force of 9kN. After sintering, the samples were polished to facilitate the observation of possible swelling and blistering induced by the implantation process.

3.2.2. Ion implanter

One of the aims of this work is to study the irradiation resistance of the material in the conditions it would be subjected to in its position as the monoblock interlayer, so severe neutron irradiation and formation of gas transmutation products. To simulate these conditions, the samples were irradiated first with Ar^+ ions and subsequently with He^+ and D^+ .

The implantation with Ar^+ ions is aimed at simulating the neutron damage on the material. High energy heavy ions have been identified as a good proxy to study the effect of neutron irradiation [82]. The microstructure of samples after irradiation with high energy heavy ions and fast neutrons are remarkably similar but irradiation with heavy ions has many advantages over neutron irradiation. With respect to neutron irradiation with fission reactors, ion irradiation allows for a damage rate that is 10^4 times higher. Additionally, ion irradiation can yield these high damage rates with negligible (proton irradiation) or no (heavy ion irradiation) residual radioactivity and at very low cost. Nevertheless, using ions as a surrogate for neutron irradiation presents several challenges such as differences in the PKA spectrum and the shallow penetration depth giving rise to surface effects and a limited analysis volume [83]. In this case particularly, Ar was chosen to perform the irradiation, since it is an inert gas and it is inexpensive.

Concerning the simulation of transmutation gas-products, as already depicted in Section 1.3, the behavior of D retention in the material is strongly affected by a contemporary irradiation with He. For this reason, in this thesis work, the samples were first implanted with He ions and immediately after with D ions.

The fluence and energy of Ar^+ ions were determined with the aim of producing an irradiation damage of 100 dpa, to simulate the neutron irradiation damage that accounts for 5 years of DEMO operation, as detailed in Section 1.3. The energies of He^+ and D^+ were chosen so that their implantation profiles overlap with the damage profile caused by Ar^+ implantation. These calculations are performed with software SRIM and they will be shown in Chapter 5. The fluence of both He^+ and D^+ ions was selected as $5 \cdot 10^{17}$ at/cm², a value commonly found in literature. The irradiation was performed in a Danfysik 1900 implanter (Taastrup, Denmark).

3.3. Characterization techniques

Both powder and bulk samples were characterized with the Scanning electron microscopy (SEM) and X-rays diffraction (XRD). These techniques will now be presented.

3.3.1. Scanning electron microscopy

Scanning electron microscopy (SEM) is a technique that enables the acquisition of high-resolution images (in the order of nm) and detailed surface information. The SEM projects and scans a focused electron beam over the surface of a sample, collecting the different signals produced by the interactions of the electrons with the atoms of the sample to obtain information about the surface topography and composition.

When the electrons enter the sample, they diffuse into the sample, creating a bulb shape volume called *interaction volume*. Then, three phenomena can occur and they can be detected by different detectors to give complementary information [84].

- The electrons that undergo elastic scattering with the atoms of the specimen experience a change in trajectory, causing some of them to be scattered out of the sample surface. These are backscattered electrons (BSE) and they give compositional information about the sample given that elements of higher Z yield more backscattered electrons than the lower Z elements.
- The electrons that interact through inelastic scattering cause the ejection of valence electrons from the atoms of the material. The ejected electrons are called secondary electrons (SE) and they provide information on the surface topography of the sample.
- Finally, characteristic X-rays are emitted when the incident electron beam ejects an inner-shell electron from an atom in the sample, causing the vacancy to be filled by an electron from an outer shell. These X-rays can be detected by an Energy Dispersive Spectroscopy (EDS) detector, that provides elemental information on the sample.

The SEM used for this thesis work is a Thermo Scientific™ Phenom™ ProX G6 Desktop SEM equipped with BSE, SE and EDS detectors.

3.3.2. X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive technique used to determine the crystal structure of materials by measuring how X-rays scatter from periodic atomic planes. Because the wavelength of X-rays ($\approx 0.15\text{--}0.5$ nm) is comparable to interatomic spacings, the scattered waves can interfere constructively or destructively. Constructive interference occurs when the Bragg condition, linking the diffraction angle 2θ to the interplanar spacing d between crystallographic planes, is satisfied: $n\lambda = 2d \sin \theta$.

In this thesis work, two types of measurements were used, depending on the sample that was analyzed.

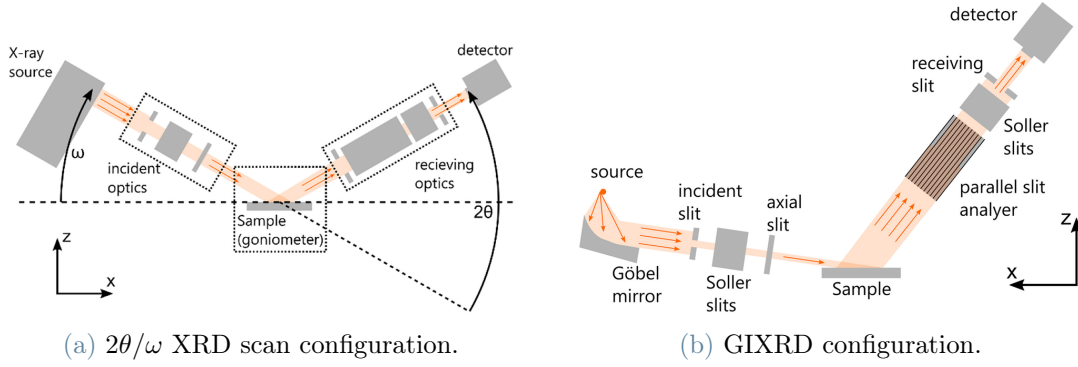


Figure 3.1: Configurations for different types of measurements for XRD [85].

Powder XRD. To evaluate powder samples, the $2\theta/\omega$ scan in Bragg-Brentano geometry is the preferred type of measurement and its geometry is shown in Figure 3.1a. The ω angle is kept to half of 2θ or the scattering angle, and the pattern is plotted as a function of 2θ . During the scan, the Bragg plane is always kept parallel to the surface of the sample and so the Bragg condition is fulfilled only for hkl planes which are parallel to the sample surface. When measuring powder, however, the crystallites are randomly oriented, and all possible reflections will appear in the diffraction pattern. In this work, powder X-ray diffraction was performed at room temperature with monochromatic Cu $K\alpha$ radiation ($\lambda = 0.15408$ nm) using an Inel CPS 120 diffractometer operating at 30 kV and 10 mA. The powders were deposited onto a silicon wafer after dispersion in ethanol. The analysis was performed in the 2θ range from 10° to 80° , with 10-second scan steps of 0.04° width.

Grazing incidence XRD. In GIXRD in a parallel-beam geometry, the incidence angle ω is fixed to a small angle, slightly above the critical angle (below which total reflection will occur), and the detector is moved on the 2θ -circle to collect the pattern. In this way the penetration deeper into the sample is considerably reduced and the sensitivity to the surface of the samples is increased. In fact, the aim is studying the implantation which only occurs within a very thin layer on the surface ($\approx 10^2$ nm). Figure 3.1b shows the configuration to obtain this measurement, illustrating also the additional optics that is required: a Göbel mirror collimates the divergent X-ray beam into a parallel one, while Soller slits limit axial divergence to improve peak definition. For this analysis, in this work a Bruker D8 AXS diffractometer with Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation equipped with a Göbel mirror and a Soller slit with an incident angle of 3° was used.

3.3.3. XRD peak analysis

Theoretically, the intensity diffracted from an infinite crystal should consist in diffraction lines with the shape of Dirac deltas at some discrete diffraction angles. However, a broadening of the diffraction lines is observed in experimental conditions due to the instrument itself and to characteristics of the specimen [86]. Regarding the specimen, there are two primary causes of peak broadening: small crystallite size and lattice strain. In the first case, the smaller crystallite size, hence the smaller coherent diffracting domain, leads to a loss of long-range order and spreads the diffracted intensity over a wide angular range. Lattice strain causes the interplanar distance d to slightly differ from point to point, so that each region of the crystal satisfies Bragg's law at a slightly different angle [87].

Considering the causes of peak broadening, it is possible to obtain information about microstructural properties of materials by performing peak-profile analysis. The functions describing the broadened peaks differ depending on the source of the broadening. It has been found that the small crystallite size produces a Lorentzian-like peak broadening, whereas the lattice strain distribution is more Gauss-like [86]. For this reason, it is common that the experimental peaks are fitted with a pseudo-Voigt function, which is a linear combination of Gaussian and Lorentzian profiles.

The microstructural properties that can be investigated through XRD peak analysis are: the crystallite size D , the lattice strain ϵ , the dislocation density ρ_{disl} and the lattice parameter a .

Regarding the first property, a first correlation between the broadening of the peak and the size of crystallites was proposed by Scherrer [87], which published the following equation:

$$D = \frac{K \lambda}{\beta_D \cos(\theta)} \quad (3.1)$$

where D is the crystallite size, β_D is the crystallite size contribution to the FWHM of the peak in radians, θ is the central position of each peak, divided by two, k is Scherrer constant, usually considered equal to 0.94, λ is the wavelength of the X-ray (Cu $K\alpha$ = 0.15418 nm).

Then, using Stokes and Wilson equation, the lattice strain can be obtained as:

$$\epsilon = \frac{\beta_{strain}}{4 \tan(\theta)} \quad (3.2)$$

where ϵ is the value of lattice strain and β_{strain} is the lattice strain contribution to the FWHM of the peak in radians [86].

To properly evaluate ϵ and D from the above equations, Williamson-Hall method was implemented by considering that the FWHM retrieved by the XRD is given by the sum of β_D and β_{strain} . Hence, by rearranging the equations in this way, the following is obtained:

$$\beta \cos(\theta) = \frac{k\lambda}{D} + 4\epsilon \sin(\theta) \quad (3.3)$$

This method involves plotting the values of $\beta \cos(\theta)$ and $\sin(\theta)$ or the characteristic diffraction peaks of the crystal structure of interest. A linear fit of these points is then performed, from which the slope and intercept are determined. These parameters are subsequently used to calculate the crystallite size D and lattice strain ϵ . It is important to notice that Williamson-Hall model was in fact build considering that both phenomena contribute with a Lorentzian effect rather than differentiating the shape of the two contributions. However, it is still considered a good evaluation of such values.

For what concerns the lattice parameter a , this value can be evaluated using Nelson-Riley extrapolation technique [88], which involves plotting the values of lattice parameter of each diffraction peak of the structure against a correction factor that accounts for instrument systematic errors. This factor is given by:

$$F(\theta) = \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \quad (3.4)$$

and the intercept of the linear interpolation of the plotted points gives the correct value of lattice parameter.

Finally, all the values obtained until now allow for the calculation of dislocation density in the lattice, through the equation:

$$\rho_d = \frac{2\sqrt{3}\epsilon}{D b} \quad (3.5)$$

where b is the Burgers vector of dislocation, that for BCC lattices is $b = a \sqrt{3}/2$ [89].

4 | Production of CrFeTaVW and optimization of planetary ball machine

This chapter presents the experimental procedure adopted to optimize the operating conditions of a Powteq BM 40 planetary ball mill with the objective of producing a single-phase solid solution of the equimolar CrFeTaVW HEA.

Section 4.1.2 presents the thermodynamic calculations and preliminary consideration on the expected lattice parameter for the selected HEA. Section 4.2 presents a theoretical model that correlates the process variables of the mechanical alloying to the characteristics of the resulting milled powders. To this aim, a kinematic model that can quantify the energy and energy rate transferred from the milling media to the alloyed system is presented. This model serves as a tool to support and guide the optimization procedure. Section 4.3 details the experimental optimization procedure, highlighting the correlation between the investigated process parameters and the predictions provided by the theoretical model. Additionally, this Section allows for a further understanding of the microstructural evolution of the milled powders and of the alloying mechanisms both at a microscopic and at an atomic level.

4.1. Prediction of solid solution formation of CrFe-TaVW

Before proceeding with the production of the CrFeTaVW alloy, several preliminary considerations are necessary. First, thermodynamic calculations are required to assess the phase stability of the alloy and predict the crystal structure of the solid solution. Second, an estimate of the lattice parameter is needed to facilitate the interpretation of the XRD patterns obtained from the milled powders. The parameters required to perform these calculations are listed in Table 4.1.

	Cr	Fe	Ta	V	W
Atomic radius [nm]	0.1249	0.1241	0.1430	0.1316	0.1367
Lattice parameter [nm]	0.28996	0.28660	0.33030	0.30300	0.31600
Crystal structure	BCC	BCC	BCC	BCC	BCC
Cohesive energy [kJ/mol]	395	413	782	512	859
Melting temperature [K]	2180	1811	3290	2183	3695
Bulk modulus [GPa]	161.87	166.93	189.72	155.57	310.38
VEC	6	8	5	5	6

Table 4.1: Fundamental properties of elements of CrFeTaVW alloy: atomic radius [90], crystal structure [91], cohesive energy [92], lattice parameter [91], melting temperature [93], and bulk modulus [94].

4.1.1. Thermodynamic calculations for phase formation prediction

In this section, the results of the thermodynamic calculations for phase selection are presented. The parameters used for predicting the solid solution stability and the type of crystal structure have already been introduced in Section 2.1.2.

The values of the VEC and atomic radius of the constituent elements, which are required for the thermodynamic calculations, are reported in Table 4.1. The results obtained for the five $(\text{CrFeTaV})_x\text{W}_{1-x}$ compositions are summarized in Table 4.2. For all compositions, the calculated parameters fall within the ranges associated with solid-solution stability. Furthermore, the VEC values indicate the formation of a stable BCC crystal structure.

	δ	ΔH_{mix}	ΔS_{mix}	VEC
$(\text{CrFeTaV})_{95}\text{W}_5$	0.057	-7.778	12.601	6
$(\text{CrFeTaV})_{90}\text{W}_{10}$	0.056	-7.313	13.077	6
CrFeTaVW	0.054	-6.400	13.382	6
$(\text{CrFeTaV})_{70}\text{W}_{30}$	0.052	-5.513	13.147	6
$(\text{CrFeTaV})_{65}\text{W}_{35}$	0.050	-5.078	12.875	6

Table 4.2: Results of thermodynamic calculations for the five compositions of $(\text{CrFeTaV})_x\text{W}_{1-x}$.

4.1.2. Prediction on lattice parameter of the solid solution

In order to provide an estimate of the lattice parameter of the solid solution of an HEA, the most common approach is to use Vegard's law. This method was originally developed for binary ionic salts [95], but since then it has been applied to solid solution alloys of more than two elements and finally for HEAs. This law is based on a rule of mixture approach: the lattice parameter of the resulting alloy is the composition-weighted average of the lattice parameters of the composition elements. However, deviations from Vegard's law have been extensively observed, especially for metallic systems where the volume of atoms can vary depending on their local chemical environment [96]. Hence, many models have attempted to predict the lattice parameter of solid solutions in terms of the properties of the constituent elements. Most of them have focused on estimating the effective elemental volumes in the solid solution environment and, in addition, consider the elasticity of the constituent elements [96, 97]. These two parameters may be used to estimate the effective bond lengths in solid solutions and then predict the lattice parameter [98].

Considering the composition in this thesis work, Vegard's law is applied with the elemental lattice parameters listed in Table 4.1 and it predicts a lattice parameter for the solid solution of $a = 0.30527$ nm. However, many studies focused on W-based HEA have witnessed the formation of a solid solution with a lattice parameter close to that of W, which is $a = 0.31600$ nm [52, 89, 99–101]. The value predicted by Vegard's law is therefore significantly lower than the experimentally observed values reported in the literature. This discrepancy suggests a deviation from the rule of mixtures, possibly associated with the high elastic stiffness and strong interatomic bonding of W. As a consequence, the influence of W crystal lattice on the lattice parameter of the solid solution is expected to be more pronounced than what predicted by the rule of mixture. In conclusion, the lattice parameter of the solid solution that this work aims to achieve is expected to exhibit a lattice parameter close to that of elemental W, with only minor deviations.

4.2. Theoretical model for transferred energy during milling

The production of HEAs via mechanical alloying is a process that imparts energy to the alloying elements through the milling media. The energy transferred from the milling media to the powder plays a vital role in the interdiffusion of alloying elements and the resultant phase formation [102] and can be related to the milling time and milling conditions [103]. The term *milling conditions* refers to both the intrinsic geometrical and

kinematic parameters of the milling machine in use and the externally imposed input parameters chosen to perform the alloying. The former include the diameter of the vial D_v , the effective diameter of the sunwheel D_s defined as double the distance between the center of the sunwheel and the center of the vial, the angular velocity of rotation of the vial ω_v and the angular velocity of revolution of the sunwheel ω_s . All these parameters are illustrated in the two-dimensional representation of a planetary ball machine in Figure 4.1. The operating parameters, on the other hand, comprise the sunwheel rotational speed in rotations per minute (rpm), the milling time, the size and mass of the milling balls.

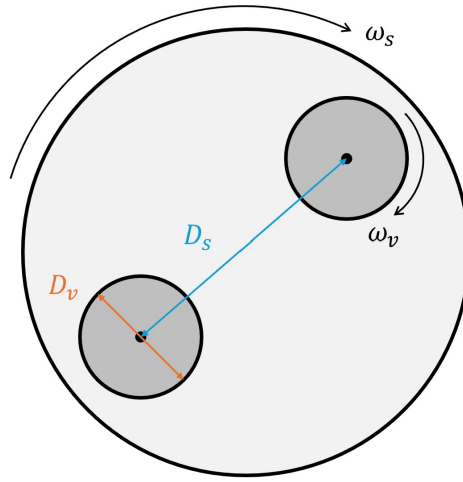


Figure 4.1: Schematic top-view representation of a planetary ball machine with its geometrical parameters.

In this context, the optimization of the processing parameters for the new planetary ball milling machine, BM 40, is guided by the energy transfer conditions established for Retsch PM 400 MA, another planetary ball machine taken as a reference system. This machine has been successfully employed for the production of single solid solution HEAs with compositions comparable to those investigated in this thesis. Because the two milling machines differ in their geometrical and kinematic characteristics, identical input parameters do not result in the same value of energy transferred to the powder. Consequently, the energy transferred from PM 400 MA machine can be considered the optimal energy needed to produce the desired outcome. This, in fact, is the starting point of the optimization procedure for the new machine: knowing such energy value, it is possible to retrieve the input parameters needed to obtain the same result with the new planetary ball machine.

Nevertheless, significant deviations from this value should be considered, as they may arise from different degrees of wear of the milling balls and vials in the two machines. In

fact, the wear of the grinding media has a direct impact on the grinding efficiency [104]. Since the model presented in the following sections does not account for ball wear, the energy transferred by the old machine is likely to be overestimated.

4.2.1. Justification for Model Selection

Many attempts have been made to correlate processing variables to the milling energy. Among them, a common one is a kinematic model presented by Burgio et al. [105], according to which the collisions that occur between the milling balls, milling vials and powder are the main mechanism of energy transfer. Even if this model allows for a good prediction of the experimental results, it presents some strong approximations that have been proven to be faulty over the years. Particularly, this model neglects the role that friction has in the energy transfer which is instead taken into consideration by other models based on Discrete Element Method (DEM) or on direct visualization of the ball motion in the vials [63, 106]. Nevertheless, these models have been discarded for the purpose of this thesis because of their computational complexity, such as the one based on DEM calculations, or because of the presence of empirical factors whose measurement would deflect from the purpose of the optimization.

The operational mode of the planetary ball mill denotes the predominant milling regime, either friction-dominated or collision-dominated operation. In this context, Le Brun et al. calculate the trajectories of balls in the mill in order to predict the operative modes of a planetary ball mill [107]. Depending on the value of the speed ratio i , defined as the ratio between the angular velocity of the vial and that of the sun wheel, the three operational milling modes are determined by the values of i_{lim} and i_{crit} in Eq 4.1. For $i \leq i_{\text{lim}}$ the mode is chaotic or pure impact, for $i_{\text{lim}} \leq i \leq i_{\text{crit}}$ the mode is chaotic + frictional, for $i \geq i_{\text{crit}}$ the mode is frictional.

$$i_{\text{lim}} = 1 - \sqrt{\frac{R_v}{R_s}}; \quad i_{\text{crit}} = 1 + \sqrt{\frac{R_v}{R_s}} \quad (4.1)$$

where R_v is the radius of the vial; R_s is the effective radius of the sunwheel (i.e. the distance between the center of the sunwheel and the center of the vial).

Magini et al. [108] suggest that attrition phenomena also origin from the condition of high filling of the vial, which leads to an increasing reciprocal hindering between the balls. They include the attrition regime in the model by introducing an empirical filling factor.

For the geometrical characteristics listed in Table 4.3, both planetary ball mills work in impact + friction regime, going towards to pure friction regime in the first case. Nevertheless, both machines work in low level of filling of the vial. Overall, the collision model by Burgio et al. has been chosen for the prediction of energy transfer, which has been proven to be in good agreement with experimental results [103], especially for low level of filling of the vial [108].

The parameters chosen to characterize the optimal milling conditions are two. The first one is the energy rate transferred by all the milling balls to the powder, which by some is considered the parameter that governs the end product, particularly through a threshold mechanism associated with the initiation of mechanical alloying [109]. The second parameter is the total energy transferred during the milling process. In fact, it has been reported that a certain amount of energy for a particular duration leads to forming a particular phase [102].

4.2.2. Theoretical aspects of collision model

The collision model is based on writing kinematic equations for a single ball of mass m_b and diameter d_b moving in a vial. It is assumed that the ball moves solidal with the peripheral point of the vial (without rolling or sliding on the inner wall) until it is launched against the opposite wall by a given composition of inertial forces. After a few collisions with the inner wall, the ball becomes solidal again with the wall itself and it is newly accelerated by the vial for the next launch. According to these assumptions, two velocities have been selected to proceed with the energy calculation: the absolute velocity of the ball detaching from the inner wall v_b and the absolute velocity of the ball when it becomes solidal again with the wall after the collisions v_a . Hence, the kinetic energy of the ball during the collision events is given by the difference between the kinetic energy in the two different considered moments, respectively E_b and E_a . The final equation proposed by the article is:

$$\Delta E = E_b - E_a = -m_b \left[\frac{\omega_v^3}{\omega_s} \left(R_v - \frac{d_b}{2} \right) + \omega_s \omega_v R_s \right] \left(R_v - \frac{d_b}{2} \right) \quad (4.2)$$

where R_v is the radius of the vial; R_s is the effective radius of the sunwheel (i.e. the distance between the center of the sunwheel and the center of the vial); ω_v is the angular velocity of the vial; ω_s is the angular velocity of the sunwheel.

According to Magini et al. [108], which have proposed further improvements to Burgio et al. model, a factor K_a should be multiplied to ΔE in order to obtain the energy *released*

by the ball to the system. In fact, factor K_a depends on the elasticity of the collision. For perfectly elastic collisions, $K_a = 0$, for perfectly inelastic ones, $K_a = 1$. If the balls are totally covered with powder, the collisions are almost perfectly inelastic. Additionally, it has been proved that, especially in the early stages of milling, the kinetic energy is totally dissipated. Consequently, for the energy evaluation, a factor $K_a = 1$ has been selected.

Another aspect to take into consideration is the fact that multiple balls in the vial can hinder each other, leading to a reduction in the energy transfer efficiency. This is included in the model by multiplying the released energy by a filling factor φ_b , obtaining that ΔE^* represents the energy released by one ball in a system containing a total of N_b balls.

$$\Delta E^* = \varphi_b \Delta E \quad (4.3)$$

The filling factor is derived from two parameters: n_v and n_s :

$$n_v = \frac{N_b}{N_{b,v}} ; \quad n_s = \frac{N_b}{N_{b,s}} \quad (4.4)$$

where

- N_b is the total number of balls contained in the vial;
- $N_{b,v}$ is the number of balls that can be contained in a simple cubic arrangement inside the vial, given by: $N_{b,v} = \frac{\pi D_v^2 H_v}{4d_b^3}$. D_v and H_v are the vial diameter and height;
- $N_{b,s}$ is the number of balls needed to cover one third of the inner surface wall in a simple cubic arrangement: $N_{b,s} = \frac{\pi(D_v-d_b)H_v}{3d_b^2}$;

To derive a simple analytical form for ϕ_b , we assume: (a) $\phi_b = 1$ for $n_v = 0$ (empty vial), (b) $\phi_b = 0$ for $n_v = 1$ (completely filled vial), (c) $\phi_b \approx 0.95$ for $n_s = 1$ (negligible hindering until one third of the wall is covered). Under these assumptions, the expression for ϕ_b is:

$$\phi_b = 1 - n_v^\epsilon \quad (4.5)$$

where ϵ can be derived by the condition (c) as follows: $0.95 = [1 - (N_{b,s}/N_{b,v})^\epsilon]$.

According to the presented model, the kinetic energy of a single ball is released to i) another ball in the vial, ii) the surrounding region of the hit wall point, iii) the powder trapped between the ball and the wall. These objects constitute the system on which

energy is transferred by the milling medium. However, the energy transfer we are interested in is the one from the balls to the powder trapped during collisions, which is only a fraction of the total energy release considered in the model. An article by Magini et al. [110] address this issue by calculating the quantity of powder material trapped in between a ball and the container wall during a collision. The radius of the circular area at the maximum of compression can be written, in the hertzian collision approximation, as:

$$R_{h,max} \approx 0.8394 (v_b^{0.4} m_b^{0.2} d_b^{0.4}) / E^{0.2} \quad (4.6)$$

where, v_b is the velocity of the ball at impact and E is the Young modulus of the ball milling material. For tungsten carbide $E = 7.2 \cdot 10^{11} \text{ Pa}$ [103].

With the assumption that the powder trapped between colliding bodies is the one adhering to the surfaces, the maximum quantity of trapped material is therefore given by:

$$Q_{max} = 2\sigma_p \pi R_{h,max}^2 \quad (4.7)$$

where σ_p is the surface density of the covering powder and the factor 2 takes into consideration that the surface density is the sum of that covering the ball and vial surface. This quantity can either be determined empirically or, according to Yazdani et al. [111], it can be evaluated under the assumption that the grinding medium is coated by a single layer of powder. With this model, the powder surface density can be estimated as $\sigma_p = \rho_p d_p$ where ρ_p is the powder density and d_p is the mean diameter of powders.

Finally, to account for both the total amount of powder in the vial and the amount of powder trapped in each collision, the transferred energy is multiplied by a factor corresponding to the ratio between the two quantities: Q_{max}/m_p . Hence, the energy transferred by each milling ball to the fraction of total powder mass that is involved in each collision event is given by:

$$\Delta E_{transf} = \Delta E^* \frac{Q_{max}}{m_p} = \varphi_b \Delta E \frac{Q_{max}}{m_p} \quad (4.8)$$

The total energy rate (or power) P_{tot} transferred from the mill to the system during collisions is calculated for all the balls in the vial N_b and considering the collision frequency f_b with which the balls are launched against the opposite wall of the vial. This can be expressed by: $f_b = K(\omega_s - \omega_v)/2\pi$. The value of K depends upon the ball diameter and can be evaluated to be approximately equal to 1.5 for ball diameters of 8 – 10mm [103].

$$P_{tot} = \Delta E_{transf} f_b N_b \quad (4.9)$$

Finally, the total amount of energy transferred during the entire milling process, is obtained multiplying the transferred power P_{tot} for the milling time t_m .

$$E_{tot} = P_{tot} t_m \quad (4.10)$$

4.2.3. Calculations of transferred energy

Equations 4.9 and 4.10 yield the final expression for the transferred energy rate and transferred kinetic energy, both normalized for the powder density, the mean diameter of powders and the mass of powder in the vial. These two relations are applied to obtain the optimized power and energy value for the old machine. Secondly, these values are used as a reference for determining the suitable combinations of input parameters in the new machine.

In Table 4.3 the geometrical parameters of both high energy planetary ball machines are presented. The parameters are: the volume of the vial V_v , the diameter of the vial D_v , the effective diameter of the sunwheel D_s , the speed ratio, which in this case is presented as the ratio between the angular velocity of the sunwheel ω_s and that of the vial ω_v .

	V_v [ml]	D_v [cm]	D_s [cm]	Speed ratio
PM 400 MA	250	7.64	30	1:3
BM 40	250	7.64	36	1:2.2

Table 4.3: Comparison of geometrical parameters of the planetary ball machines: the optimized one, PM 400 MA, and the one to be optimized, BM 40.

A Python code was developed to explore different combinations of input parameters for the new milling machine, with the goal of identifying the most suitable conditions to achieve a target energy within a defined uncertainty range. To establish this target, the optimized input parameters of the Retsch PM 400 MA are: 350 rpm, 2h milling time, 10:1 ball to powder ratio [99]. These parameters have previously enabled successful milling of various elemental compositions, leading to the formation of the desired solid solution HEA.

Since the maximum amount of material involved in each collision depends on the spe-

cific composition of the powders, as shown in Equation 4.7, the normalized transferred energy was calculated for all compositions. Table 4.4 lists such compositions and presents the theoretical powder density of the milled alloy, the powders mean diameter, the normalized transferred energy obtained with the old machine parameters. The average of these normalized energy values is then taken as the target energy for the new machine, while the corresponding standard deviation defines the order of magnitude of the uncertainty range. The results are respectively: $E_{tot}^{avg} = 35.890 \pm 3.063 \text{ J}$ while the transferred energy rate is $P_{tot} = 4.985 \pm 0.425 \text{ mW}$.

	$\rho_p \text{ [g/cm}^3\text{]}$	$d_p \text{ [}\mu\text{m}\text{]}$	$E_{tot} \text{ [J]}$	$P_{tot} \text{ [mW]}$
(CrFeTaV) ₉₅ W ₅	10.647	10	31.714	4.405
(CrFeTaV) ₉₀ W ₁₀	11.158	10	33.235	4.616
CrFeTaVW	12.158	10	36.215	5.030
(CrFeTaV) ₇₀ W ₃₀	13.133	10	39.117	5.433
(CrFeTaV) ₆₅ W ₃₅	13.611	10	40.540	5.631
VFeTiTaW	11.144	10	33.194	4.610
(CrFeTiTa) ₇₀ W ₃₀	12.494	10	37.217	5.169

Table 4.4: Powder compositions used in Retsch PM 400 MA planetary ball machine, with the theoretical powder density of the milled HEA, the mean diameter of the powders, the calculated normalized transferred energy.

4.3. Experimental trials for the optimization procedure

The experimental optimization of the machine is carried out by using different input parameters in order to analyze which combination of the latter are the best to achieve a solid solution. The input parameters to combine are: milling time (t_m), ball-to-powder ratio (bpr), round per minute (rpm), diameter of the milling balls (d_b). For each combination of parameters, the milled powder is characterized with XRD and SEM, in order to verify the complete mixing of the elements and the size of powder particles.

4.3.1. 10g, 10:1 bpr - Variation of the milling time

The first milling experiment was designed to evaluate the temporal evolution of the milled powder. To monitor the progression of the milling process, after every hour of

milling a small amount of powder is removed from the vial for the powder XRD and SEM analysis. Then, the vials are placed again in the planetary ball machine for a new milling cycle. The input parameters chosen for this first experiment are listed in Table 4.5, together with the calculated transferred energy and transferred power. Under these conditions, the model predicts that the target energy is obtained after approximately 5h of milling.

m_p [g]	d_b [mm]	btp	N_b	rpm	t_m [h]	E_{trans} [J]	P_{trans} [mW]
10	10	10:1	13	350	1	7.409	2.058
10	10	10:1	13	350	2	14.817	2.058
10	10	10:1	13	350	3	22.226	2.058
10	10	10:1	13	350	4	29.634	2.058
10	10	10:1	13	350	5	37.043	2.058
10	10	10:1	13	350	6	44.451	2.058

Table 4.5: Input parameters of planetary ball mill BM40 and calculated total transferred energy and transferred power for the set of experiments focused on the variation of milling times.

XRD diffractograms

Since the XRD spectra of the two vials show no significant differences, only the diffraction data from one representative vial are presented in the discussion. Figure 4.2 shows the XRD results for this vial and compares the spectra of the elemental initial mixture and the mixture after 1h, 2h, 3h, 4h, 5h, 6h of milling. Figure 4.2 a) shows the XRD of the hand-mixed sample, in which the peaks correspond to the constituent alloying elements. From Figure 4.2 b) to Figure 4.2 g) the evolution of the powder milled from 1h to 6h can be observed. Overall, the XRD diffractograms show a progressive broadening of all the peaks: the FWHM of the peaks increases and the relative height of all peaks decreases with respect to BCC1. Particularly, in Figure 4.2 g) the following structures can be observed:

- An unidentified phases is located at 35.64° , 62.80° and 75.27° . Its peaks decrease in height with the increasing of milling time.
- The Fe BCC-type and Cr BCC-type peaks persists, broadened and lowered. Alternatively, an intermetallic phase of CrFe could also be forming.
- The BCC1, with lattice parameter equal to that of W, keeps presenting sharp peaks:

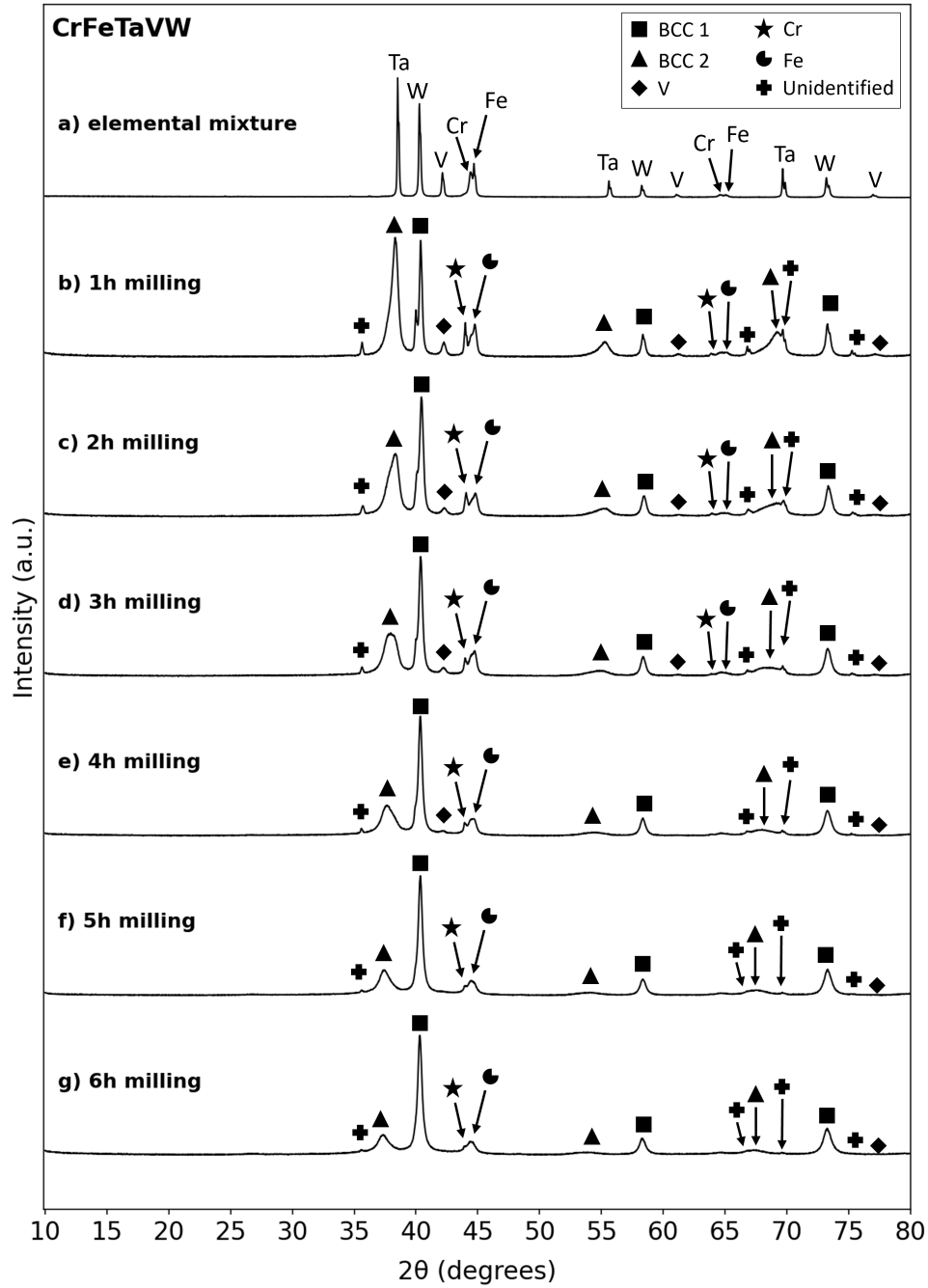


Figure 4.2: Comparison of XRD diffractograms of (a) elemental mixture before milling and mixture after milling for (b) 1h, (c) 2h, (d) 3h, (e) 4h, (f) 5h, (g) 6h at 350 rpm, 10mm of ball diameter and 10:1 ball-to-powder ratio.

no significant broadening is observed with the increase of the milling time.

- The BCC2 peaks start with a lattice parameter close to that of Ta but, progressively with time, they decrease in intensity, they broaden and shift towards lower angles (i.e. towards larger lattice parameters).

This milling experiment allows to uncover the alloying sequence of the considered elements, i.e. the rank of the alloying rates of the elements in getting alloyed in the mixture, and the phase evolution during the mechanical alloying process. It has been found that the alloying sequence of the constituents correlates best, among the mechanical properties of the elements, with their melting temperatures (T_m) on the melting point of the particular elements [112]. It is known, for a pure metal, that the diffusion coefficient is inversely proportional to the melting temperature of the material [65]. For a given crystal structure, a metal with higher melting point has an increased bonding strength and thus a lower self-diffusion coefficient. According to the article by C.-L Chen et al. [112], even if this empirical relation is based on the diffusion of different species in the same matrix with a host element, it has been demonstrated that the above relationship can be extended to the intrinsic diffusion of elements in the matrix with multi-principal elements. Additionally, mechanical disintegration is also found to be consistent with diffusion since an element with lower melting point usually has lower hardness and thus better malleability to aid their spatial dispersion. This means that elements with better malleability can be spread out faster in space and in the latter stage they can diffuse at a faster rate into other elements or solid solution phases.

Considering the composition chosen for this thesis work, the melting temperature of each element is displayed in Table 4.1. According to the melting temperature, the alloying sequence for this composition is: Fe, Cr, V, Ta, W. This can be correlated with what observed in the XRD evolution in Figure 4.2. The elements with lower melting points are Cr, Fe, V, which are in fact the elements whose XRD elemental peaks decrease first, showing that those are the elements that diffuse faster in the matrix. On the other hand, Ta and W have higher melting temperatures hence higher bonding strengths, which causes them to have lower alloying rates [52]. In fact, two main and persistent BCC phases are observed, one with a lattice parameter close to that of W and one with lattice parameter larger than that of Ta. It can be concluded that Cr, Fe, V are diffusing first in the Ta crystal lattice, to form a solid solution alloy with a BCC structure of lattice parameter larger than that of Ta. In contrast, the persistence of sharp W diffraction peaks indicates limited lattice distortion and suggests that W undergoes rapid work hardening during the early stages of milling. This likely prevents further diffusion of the other elements into the W lattice as milling time increases, hindering the formation of a homogeneous

single-phase solid solution.

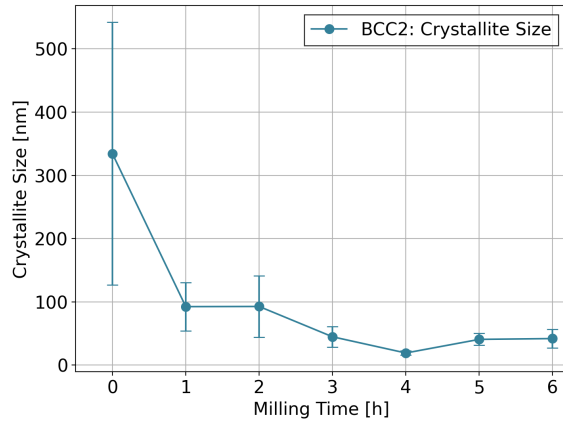
To further discuss the rapid work hardening of W, it should be considered that all elements undergo strain hardening during mechanical milling. As explained in Section 2.2.3, the repeated collisions of mechanical alloying introduce a lot of defects in the crystal lattice of the alloyed elements, until a saturation hardness is achieved due to accumulation of strain energy. Comparing the hardness values of all the elements in the composition listed in Table 4.1, it can be observed that the hardest element is W. Hence, looking at the XRD results, it can be concluded that W is the fastest element to approach strain hardening saturation, even before the other elements manage to diffuse in its lattice.

XRD peak analysis

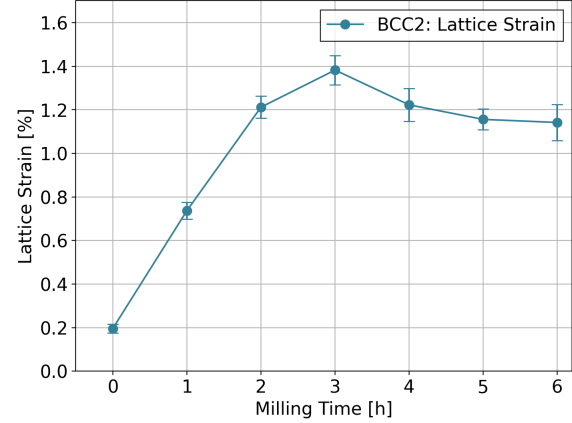
To have a better understanding of the evolution of BCC2, a quantitative analysis can be conducted on the XRD diffractogram. By fitting the peaks with a pseudo-Voigt function, the lattice parameter can be evaluated. Additionally, Williamson-Hall method can be applied to derive the lattice strain and crystallite size. With the above-mentioned parameters, the dislocation density can also be determined. All these calculations are extensively presented in Section 3.3.3. Regarding the Williamson-Hall plots of the XRD of the 4h, 5h and 6h samples, it should be highlighted that the results show poor linear regression, which introduces significant uncertainty in the calculated values. Consequently, no definitive conclusion can be drawn regarding the evolution of crystallite size, lattice strain and dislocation density at longer milling times. The issue with the Williamson-Hall plots for longer milling times may arise from an anisotropic strain that develops specifically in the diffraction plane (200) [113]. Additionally, the smaller the peaks, the more difficult it gets to fit them correctly, thus leading to errors in the W-H method.

The results of the peaks analysis of BCC2, specifically the evolution of crystallite size, lattice strain, lattice parameter and dislocation density with milling time, are shown in Figure 4.3.

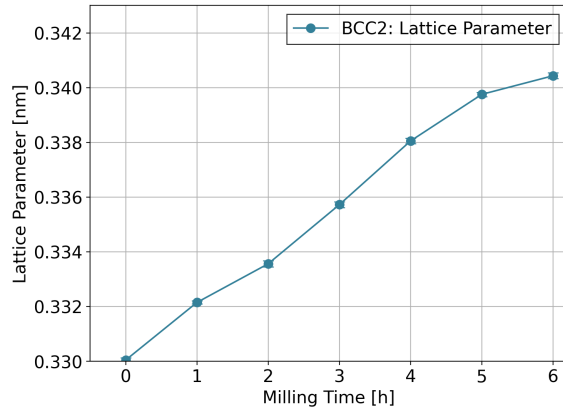
Regarding the crystallite size in Figure 4.3a, the analysis shows a decreasing behavior with milling time, as predicted in Section 2.2.4. From 1h to 4h, the significant decrease of crystallite size can be related to the formation of shear bands, areas of high density of dislocation and elevated atomic-level strain. Within these areas, the crystalline structure undergoes fragmentation resulting in the formation of sub-grains or small crystallites separated by low-angle grain boundaries. After 4h, the crystallite size reaches its minimum value, 19.187 ± 3.546 nm, and further reduction in size is hindered because the stress required for dislocation movement becomes extremely high because of grain boundary strengthening [114]. After this, the crystallite size increases again reaching at 5h the



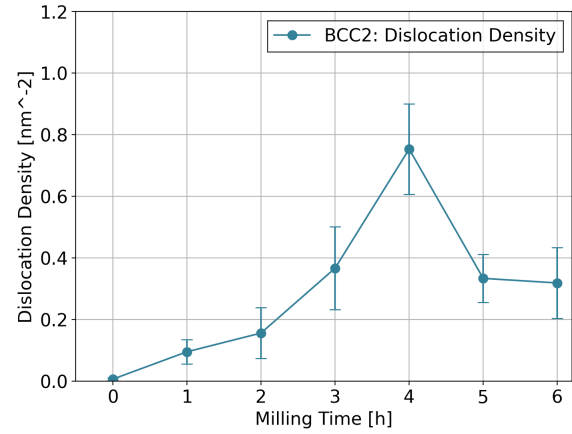
(a) Evolution of crystallite size with milling time.



(b) Evolution of lattice strain with milling time.



(c) Evolution of lattice parameter with milling time.



(d) Evolution of dislocation density with milling time.

Figure 4.3: Evolution of (a) crystallite size, (b) lattice strain, (c) lattice parameter, (d) dislocation density for the BCC2 type-structure.

value of 40.716 ± 9.362 nm and at 6h the value of 42.001 ± 14.879 nm. This minor increase can be attributed to dynamic recovery caused by dislocation rearrangement or by local thermal spikes that could occur during milling [114]. In this case, however, it is not possible to confidently conclude that a real increase in crystallite size is occurring:

In Figure 4.3b the evolution of lattice strain is characterized by a first increase up to 3h of milling, then followed by a decrease. The rise is a consequence of the severe plastic deformation and inclusion of defects in the crystal lattice caused by the collision with the milling balls. The subsequent decrease can be related to a dynamic restoration process of recovery of dislocations. This can be attributed to high stored energies accumulated during the prolonged severe deformation and may be facilitated by the elevated localized temperature spikes that occur during milling [114, 115]. This explanation is consistent

with the behavior of dislocation density in Figure 4.3d. Another explanation for the decrease of lattice strain for long milling times could be related to a strain release in the lattice due to a incipient amorphization of the sample caused by prolonged milling [116].

Figure 4.3c shows an increasing tendency of the lattice parameter of BCC2. Since Ta is the element with the larger atomic radius and its crystal lattice has the highest lattice parameter out of the other elements, as shown in Table 4.1, the observed increase in the lattice parameter of the solid solution cannot be attributed to the inclusion in the BCC structure of atoms with larger atomic radii than Ta. On the other hand, this phenomenon could be related to the accumulation of large amount of structural defects and the increase of strain in the system, that occur due to the severe plastic deformation of the particles during mechanical milling [117, 118].

SEM analysis

SEM was used to obtain the elemental map of the hand mixed powders. Here, the sole samples at 2h of milling and at 5h of milling are displayed. The focus is placed on the distribution of the elements in the powder particles and on the size and shape of powder particles.

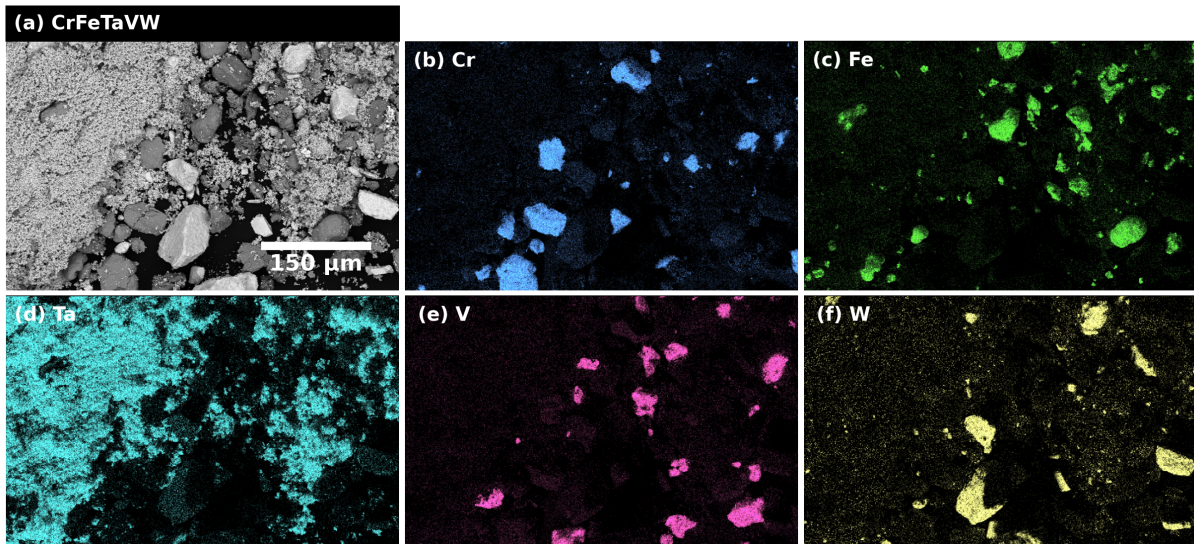


Figure 4.4: (a) SEM image collected with BSE for the hand mixed powder of CrFeTaVW. EDS maps for (b) Cr- $L\alpha$, (c) Fe- $L\alpha$, (d) Ta- $L\alpha$, (e) V- $L\alpha$, (f) W- $L\alpha$ X-ray lines.

Figure 4.4 presents the elemental map of the hand mixed powders, which allows to observe the particle size of the different elemental powders. As already presented in the introduction of Section 4.3, Cr, Fe and V particles have a size that does not overcome the $44\mu m$. Ta presents an APS of $2\mu m$, and in the EDS map figures in fact in the form of

significantly smaller particles in comparison to the other elements. Finally, W particles are nanometric but they tend to agglomerate, forming composite particles of micrometric size.

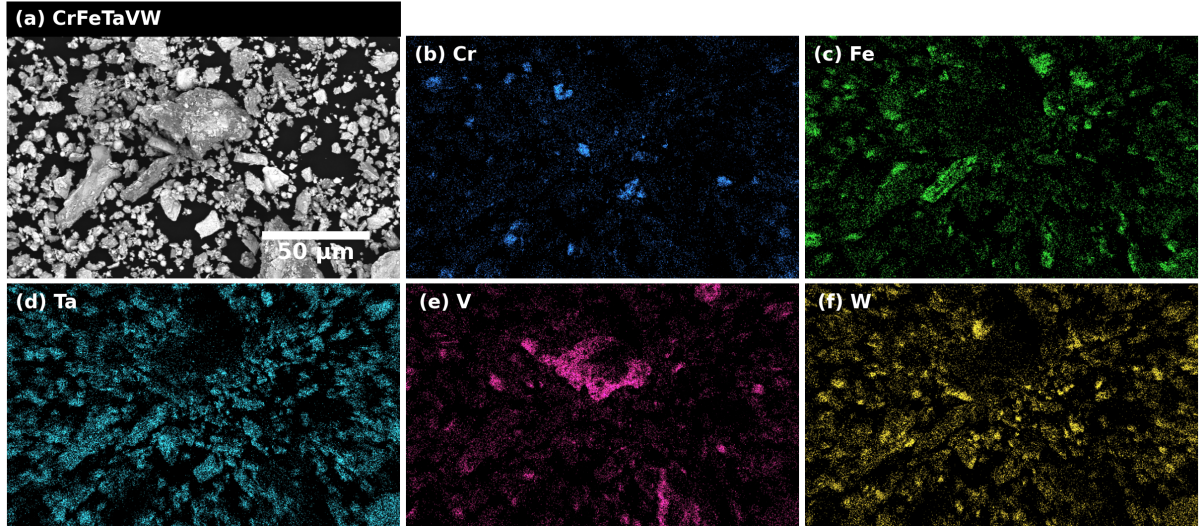


Figure 4.5: (a) SEM image collected with BSE for the CrFeTaVW sample milled for 2 hours with a pause every hour. EDS maps for (b) Cr-L α , (c) Fe-L α , (d) Ta-L α , (e) V-L α , (f) W-L α X-ray lines.

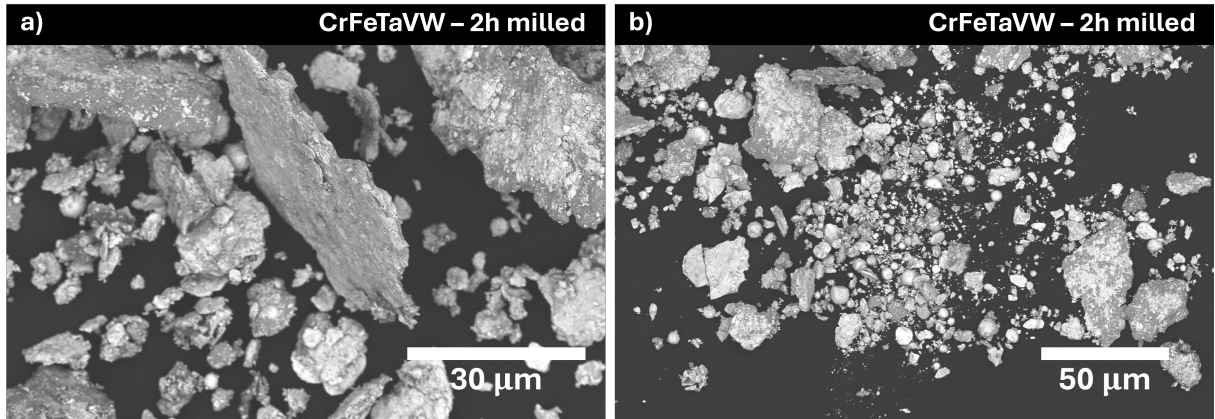


Figure 4.6: Comparison between (a) plate-like composite particles and (b) fragmented or rounded brittle particles in the 2h milled sample. SEM images collected in BSE mode.

The 2h milled powder particles, in Figure 4.5, are very inhomogeneous both in size and shape. Additionally, all the elements are well separated, in agreement with the results of the XRD in Figure 4.2 c). Particularly, Cr and W are localized in smaller fragmented particles, whereas Fe, V and Ta are also present in larger plate-like particles. This is

a confirmation of how collisions affect differently the ductile and brittle particles. This evolution of the particles in the early stages of milling can be further appreciated in Figure 4.6, which compares the plate-like particles of ductile elements with the fragmented or rounded particles composed of the more brittle elements. In particular, Ta exhibits a more homogeneous spatial distribution, which can be attributed to the smaller size of the initial Ta powder with respect to the other elemental powders: a fraction of the Ta particles adheres to larger composite particles during milling, while the remainder undergoes plastic deformation and becomes incorporated into the plate-like structures.

The sample milled for 5h is shown in Figure 4.7. In this case the element distribution appears to be more homogeneous with respect to the previous case. However, the powder dimensions and shape does not appear to be uniform. The images from Cr, Fe, V, W present some brighter spots, which lead to the conclusion that, other than having particles with a homogeneous concentration of elements, some particles still have a higher concentration of a pure elements. This is particularly true for the harder elements like W and Cr, but also for the progressively more ductile elements of Fe and V. This is in agreement with the XRD in Figure 4.2 f) which still shows the presence of elemental peaks, even if broadened and very small.

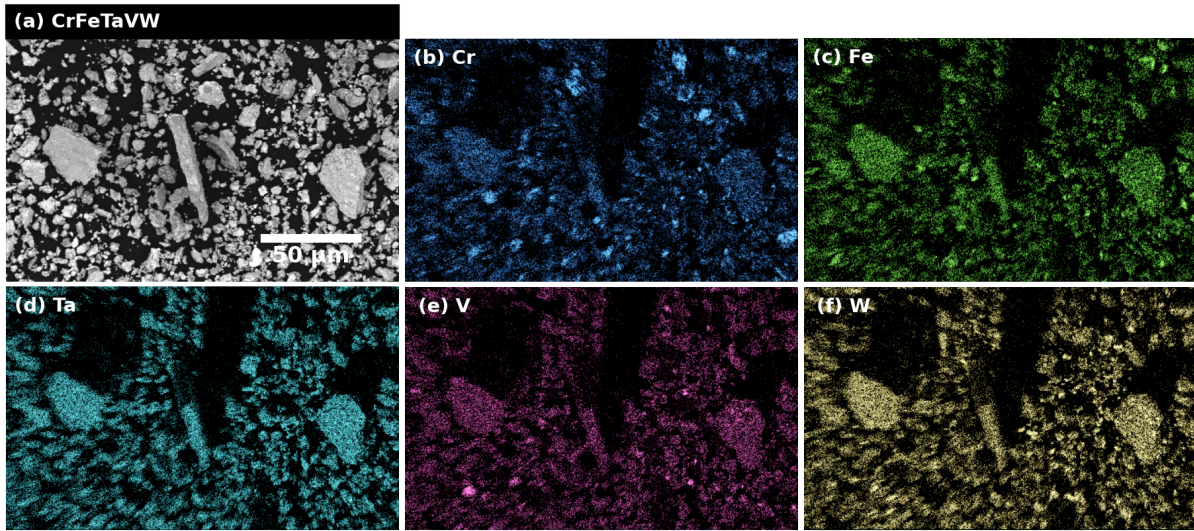


Figure 4.7: Sample milled for 5 hours with a pause every hour. (a) SEM image collected in BSE mode of CrFeTaVW and EDS maps for (b) Cr- $L\alpha$, (c) Fe- $L\alpha$, (d) Ta- $L\alpha$, (e) V- $L\alpha$, (f) W- $L\alpha$ X-ray lines.

Particle size distribution

The images of the powder particles obtained with the SEM in BSE mode allow to

evaluate the particle size distribution in the different milling times. The measure of the particle size is usually performed with laser particle size analyzers [119, 120]. However, in this thesis work, it was instead performed with software ImageJ [121]. This method does not provide a precise evaluation of the particle size distribution, since it is a graphical method that only works with two-dimensional pictures. Additionally, it can be easily observed from previous SEM images, that the particles tend to agglomerate and overlap. Hence, it is difficult with ImageJ to separate the particles for a more accurate measurement of the size. Nevertheless, with an accurate preparation of the SEM sample, (the powder should be well spread on the carbon tape) and with appropriate methods for the separation of connected particles (Watershed algorithm in ImageJ), it is possible to obtain a measurement of the particles dimension. This is expressed in Feret's diameter, which is the longest distance between any two points along the selection boundary. The distribution is presented in terms of the percentiles D10, D50, D90 of each sample of measurements, commonly used in literature to represent the midpoint and range of the particle size [119].

The results of particle size distribution measurements can be observed in Figure 4.8. It is important to notice that this analysis does not report the particle size distribution of the non-alloyed mix of elemental particles. In fact, it is not possible to properly separate the nanometric W particles and the $2\mu m$ Ta particles very close to the other element's larger particles with ImageJ. However, it is considered for the elemental powders the indicative value of average particle diameter, equal to $10\mu m$.

The trend of the particle size evolution can be explained by referring to the different stages of milling, already presented in Section 2.2.3, and it has been observed in other cases in literature [122, 123]. The first significant decrease between 1h and 2h of milling time can be due to the fact that at initial milling stages, the fracture of the brittle particles dominates over the plastic deformation of the ductile one. Then, from 1h to 4h of milling, the increase in particle size is caused by the cold welding of the ductile particles, with the inclusion of the brittle ones in between the layers. Subsequently, due to severe plastic deformation, particles are progressively work hardened, leading the cold welded particles to become brittle and start fracturing, hence reducing the overall particle size, as it happens between the 4h and 5h of milling. Between 5 h and 6 h, the graph exhibits a plateau. This behavior should not be interpreted as the particles reaching a constant size, but rather as a limitation of the measurement technique. In fact, the agglomeration of the fine particles and their adherence to larger ones can affect the measurement accuracy, especially considered that ImageJ cannot separate properly very small particles.

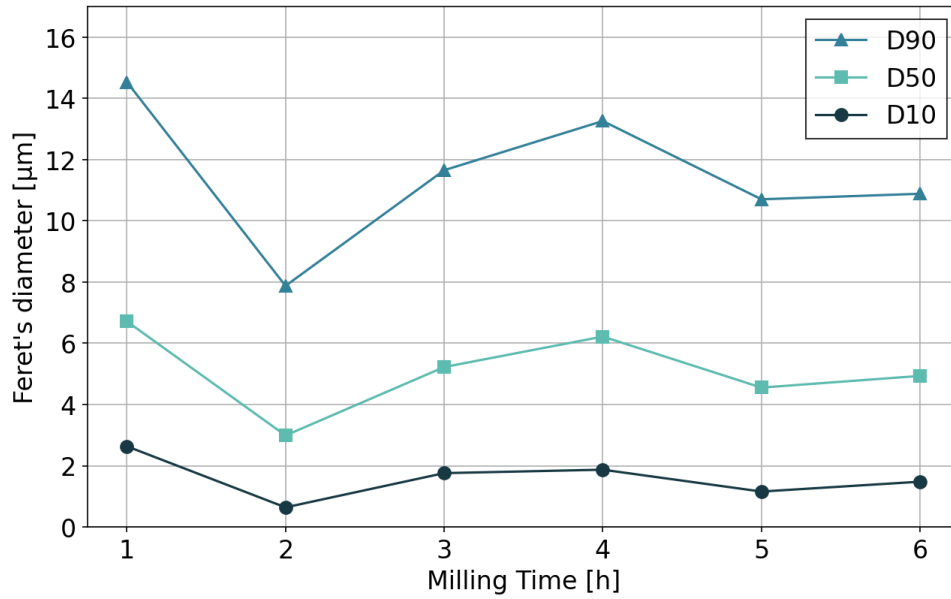


Figure 4.8: Evolution of particle size distribution against milling time for the mechanically alloyed CrFeTaVW powder particles. The evolution is displayed for the 10th percentile (D10), the median (D50) and the 90th percentile (D90).

It can be concluded that, with a total amount of 6h of milling, the powder is not homogeneous in shape and dimension, it shows a partial mixing of the elements but also the persistence of predominantly single-element powder particles. Considering both the XRD and SEM analysis, it can be observed that W has undergone work hardening, that, at an atomic level, prevents the W crystal lattice to modify to host other element's atoms. On the other hand, the progressive broadening Ta BCC-type peak supposedly proves the formation of a BCC solid solution with all the other elements.

4.3.2. 10g, 10:1 bpr - Effect of temperature on work hardening of W

In the previous experiment, intermittent milling was performed for up to 6h and this inevitably led the powder to cool down after every hour of milling. Now, the aim is to investigate the role of temperature in the formation of a single solid solution, specifically observing whether it would prevent the fast work hardening of W. As already presented in Section 2.2.4, in mechanical milling the diffusion mechanisms that lead to the formation of the alloy don't have a strong dependence on temperature. However, maintaining a high temperature for longer (i.e. milling continuously) could improve defect recovery, possibly slowing down the work hardening of W.

For this experiment, the equiatomic composition of CrFeTaVW in an amount of 10g was inserted in each of the two vials. The planetary ball machine was operated with 350 rpm, with 10 mm milling balls, a 1:10 ball-to-powder ratio, and a single cycle of rotation for the sunwheel. In this case the milling time was set to 4h straight.

XRD analysis

The results of the XRD are displayed in Figure 4.9. The diffractogram is comparable to the one obtained with intermittent 4h milling in the previous sets of experiments, with small differences. Two BCC structures are present: BCC1 with lattice parameter close to the one of pure W, BCC2 with lattice parameter of $a = 0.33906 \pm 0.00018$ nm.

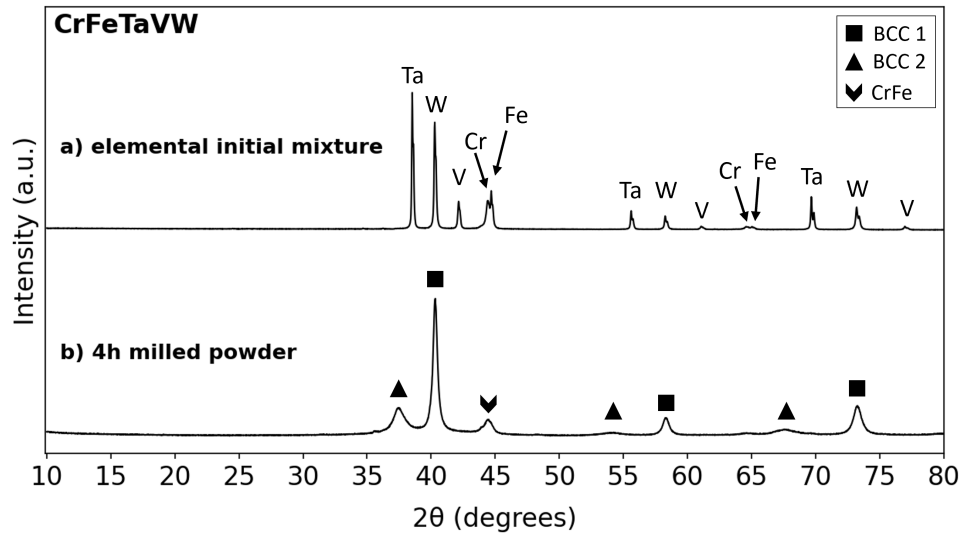


Figure 4.9: XRD diffractograms of (a) elemental mixture before milling and (b) mixture after 4h milling at 350 rpm 10 mm of ball diameter, a 10:1 ball-to-powder ratio.

Similarly to before, the BCC1 sharp peaks suggests that W work hardened and is not including the other elements of the composition into a single BCC solid solution. The lattice parameter of BCC2 in this experiment is similar to the one obtained in the previous experiment after 4h of intermittent milling. Additionally, considering the experience with the evolution of BCC2 obtained in the previous section, it can be concluded that also in this case a solid solution alloy is forming starting from Cr, Fe and V diffusing in the Ta crystal lattice. Finally, a peak at around 44.5° and 64.6° suggests that a CrFe intermetallic with a BCC arrangement has formed. Differently from Figure 4.2 where even at higher milling times the Cr BCC-type peak and Fe BCC-type peak are broadened but distinguishable, here unique peaks have formed.

In conclusion, maintaining a high temperature environment during the whole milling

process is not sufficient to prevent W work hardening and thus for the for the achievement of a single solid solution.

4.3.3. 10g, 10:1 bpr - Effect of pre-alloyed powder on work hardening of W

For this experiment, a pre-alloyed powder of WCr, formed by an atomic percentage of 90% W and 10% Cr was employed. The aim is to investigate whether the pre-alloyed W can help overcoming the fast work hardening of W. Using a pre-alloyed powder can support the inclusion of the other elements into the WCr crystal structure by allowing a faster kinetic of mechanical alloying [124]. The experiment was carried out with a 10:1 bpr and with milling time of 4h straight.

XRD analysis

The result of the XRD is shown in Figure 4.10 and it is comparable to the diffractogram obtained in the previous section. Here, BCC2 has lattice parameter $a = 0.33956 \pm 0.00017$ nm.

Having W in a pre-alloyed condition has not prevented work hardening, leading once again to the formation of a BCC1 with sharp peaks and of a BCC2 solid solution, possibly without the inclusion of W.

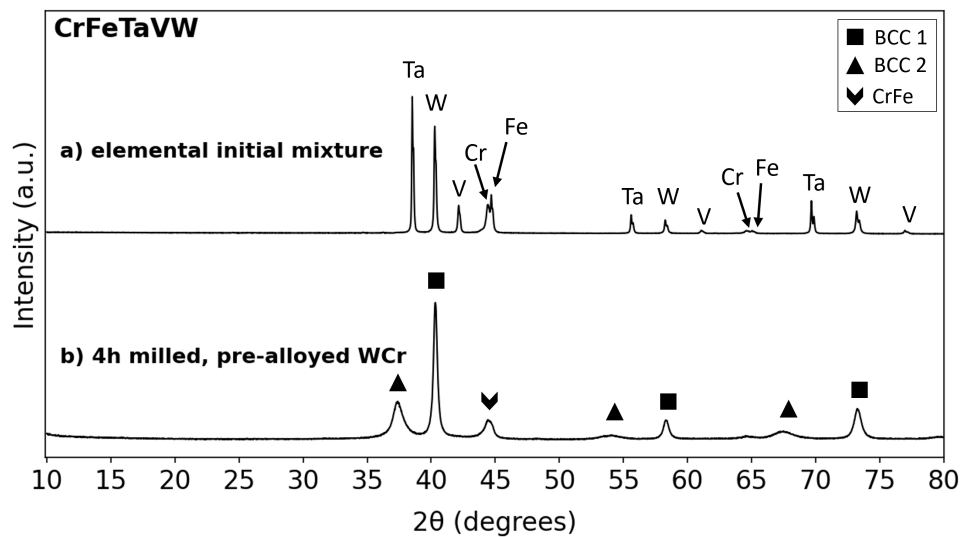


Figure 4.10: XRD diffractograms of (a) elemental mixture before milling and (b) mixture after 4h milling at 350 rpm, 10 mm of ball diameter, a 10:1 ball-to-powder ratio and a pre-alloyed WCr powder.

4.3.4. 10g, 20:1 bpr - Different milling ball diameters

The work hardening of W has been observed in all previous experiments presented. With the aim of preventing this, the transferred energy rate is now increased. To reduce the required milling time while maintaining an equivalent amount of total transferred energy, the ball-to-powder weight ratio is increased to 20:1. Furthermore, milling balls with diameters of 10 mm and 20 mm were employed to investigate the influence of ball size on the alloying efficiency. To optimize the overall machine usage time, two vials were operated simultaneously, one containing the 20 mm balls and the other the 10 mm balls. In order to ensure stable operation, the total weight of both vials had to be approximately equal. Consequently, 24 balls of 10 mm diameter were placed in one vial and 3 balls of 20 mm diameter in the other, resulting in a total mass difference of only a few grams, which was considered to be within an acceptable error range. This choice lead to having respectively a lower and a higher transferred energy compared to the target one.

m_p [g]	d_b [mm]	btp	N_b	rpm	t_m [h]	E_{trans} [J]	P_{trans} [mW]
10	10	20:1	24	350	2	26.939	3.742
10	20	20:1	3	350	2	81.906	11.376

Table 4.6: Input parameters of planetary ball mill BM40 for the set of experiments focused on increased ball-to-powder ratio and different milling ball diameter.

XRD analysis

The XRD diffractograms of the powders produced in this experiment are displayed in Figure 4.11. Figure 4.11 (b) shows the XRD of the vial containing 24 balls of 10 mm diameter. The diffractogram presents the following structures: a BCC1 structure with broad peaks forms with a lattice parameter close to the one of W, a BCC2 with a lattice parameter larger than the one of Ta, a CrFe intermetallic and finally a VTaO₄ oxide. Figure 4.11 (c) shows the XRD of the 3 balls of 20 mm diameter. In this case, the diffractogram presents all elemental peaks slightly broadened with respect to the hand mixed XRD in Figure 4.11 (a).

In Figure 4.11 b) the XRD spectrum of the vial containing the 10 mm balls shows a well alloyed powder. In fact, BCC1 has broadened peaks, supporting the idea that the diffusion of the other alloying elements into the W lattice has now taken place, differently from the previous experiments. In this case the transferred power is much increased with respect to the previous experiments, leading to the conclusion that, in order to obtain a

single solid solution, a certain value of energy rate must be imparted onto the system so that the other elements can diffuse into W before it reaches the saturation point of strain hardening.

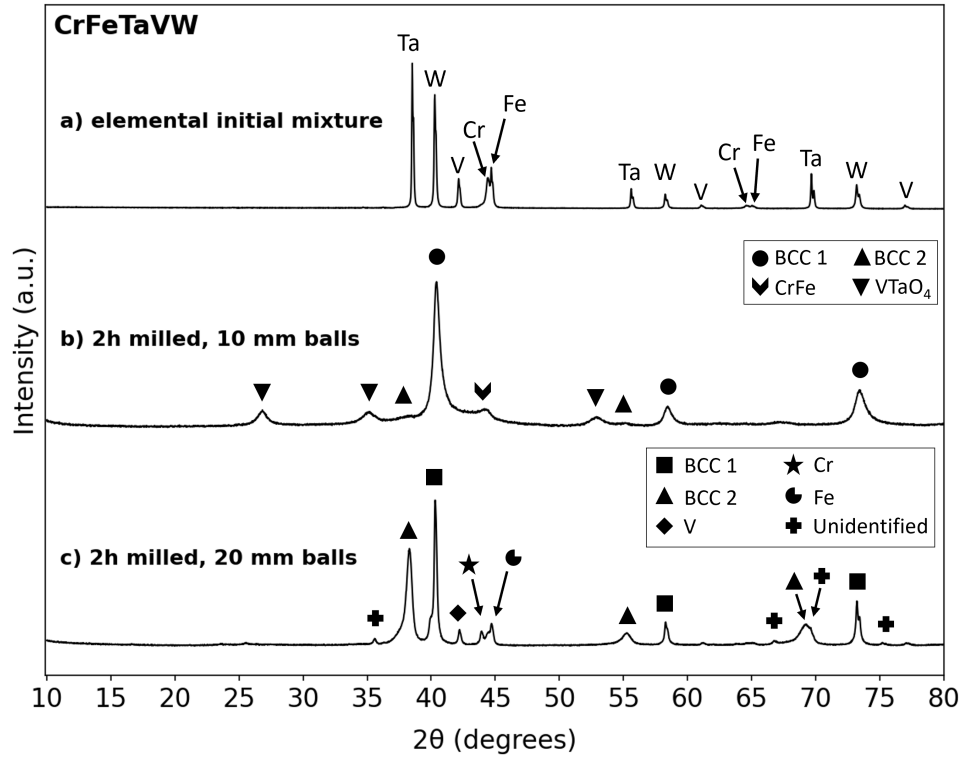


Figure 4.11: XRD diffractograms of elemental mixture before milling (a) and mixture after 2h milling at 350 rpm, 20:1 ball-to-powder ratio and ball diameter of 10 mm (b) and 20 mm (c).

In addition to this, it can be concluded that the solid solution of the HEA forms with a lattice parameter that is smaller than the one of W. This supports the idea presented in Section 4.1.2, according to which the elastic stiffness of W has a strong influence on the lattice parameter of a W-based HEA solid solution, causing strong deviations from Vegard's law. Nevertheless, small deviations from the lattice parameter of pure W were already predicted, and now confirmed with this experimental result.

It should be noted that the low-intensity peaks of BCC2 are present, with the same lattice parameter that was observed in previous experiments and equal to $a = 0.3390$ nm. With the assumption, based on previous results, that BCC2 forms with Cr-Fe-Ta-V and that the diffusion sequence of elements is correlated to their melting temperature, this XRD result suggests that after 2h of milling the diffusion of all elements into W was not completely achieved.

In addition, an oxide VTaO_4 that may have formed starting from an already oxidized V powder present in the laboratory. Many authors have reported the presence of oxide phase formation with high concentration of V and Ta already after the mechanical alloying [52, 125].

Figure 4.11 c) shows that the 20 mm balls were not efficient in producing a solid solution, since all the elemental peaks are still visible even if broadened. The filling ratio of the vials is of significant importance, since it affects the motion pattern of the milling balls but, most importantly, it influences the probability of collisions between the balls, the powder and the vial walls. This highlights the limits of the theoretical model presented in this thesis work, which only takes into account the transferred energy and transferred energy rate as target parameters, without accounting for the influence of the collision frequency on the final outcome.

In the diffractogram, an unidentified phase was detected in the spectrum at the same values of 2θ of the unidentified phase of Figure 4.2. Since the milling balls used in the vials had never been employed previous to this experiment, this observation supports the hypothesis that the phase originates from impurities or surface coatings initially present on the balls and vials and that progressively wear off with continued use.

SEM analysis

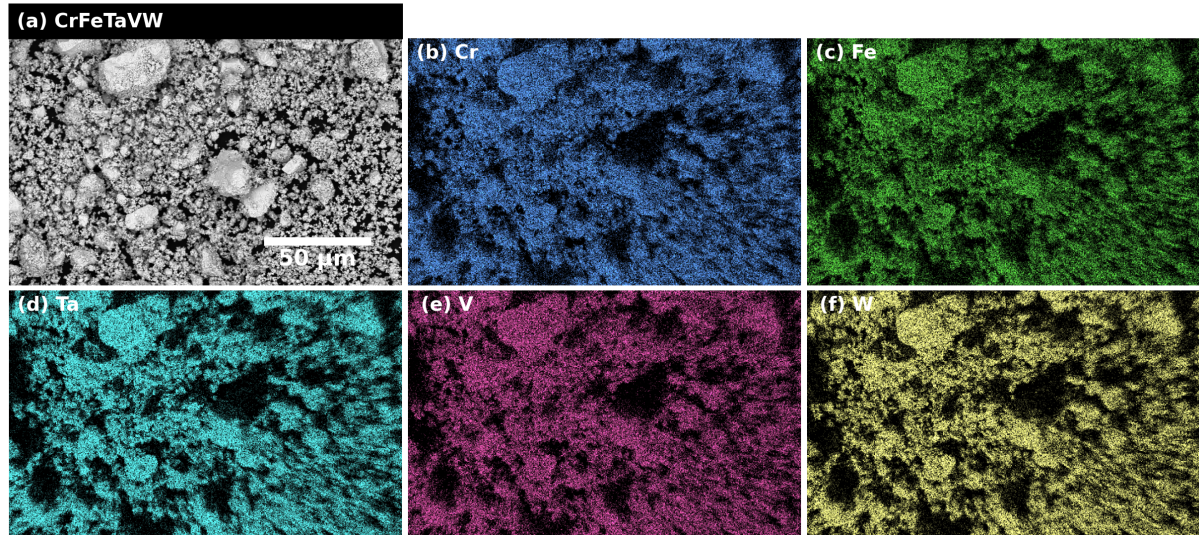


Figure 4.12: Sample milled for 2h milling at 350 rpm with 20:1 ball-to-powder ratio and 24 milling balls. (a) SEM image collected in BSE mode of CrFeTaVW and EDS maps for (b) Cr- $L\alpha$, (c) Fe- $L\alpha$, (d) Ta- $L\alpha$, (e) V- $L\alpha$, (f) W- $L\alpha$ X-ray lines.

The EDS map of the powder produced with 24 milling balls of 10 mm diameter, is

shown in Figure 4.12.

The efficiency of the alloying process can be confirmed by the significant reduction in particle size with respect to what observed up until now in SEM images. The distribution of particle size and the distribution of the elements is in fact more homogeneous. Differently from previous experiments, the brighter spots in the EDS map, that prove the presence of single-element rich phases, cannot be observed in these milling conditions, leading to the conclusion that all particles now have an equal composition of elements.

4.3.5. 10g, 20:1 bpr - Optimization of number of balls

The previous experiment proved that the most promising way to produce a single solid solution of CrFeTaVW is to employ the 10 mm milling balls with a ball-to-powder ratio of 20:1. A new milling experiment was carried out with 26 balls instead of 24, in order to verify that with two additional milling balls the increased transferred energy favors the creation a single BCC structure. The input parameters are summarized in Table 4.7, together with the transferred energy and power.

m_p [g]	d_b [mm]	btp	N_b	rpm	t_m [h]	E_{trans} [J]	P_{trans} [mW]
10	10	20:1	26	350	2	29.086	4.040

Table 4.7: Input parameters of planetary ball mill BM40 for the set of experiments focused on increased ball-to-powder ratio and different milling ball diameter.

XRD analysis

Figure 4.13 shows the result of the XRD, which presents single BCC structure, an intermetallic CrFe and an oxide VTaO₄.

Differently to the case of 24 balls, here the BCC2 is not present after 2h of milling, suggesting that the additional energy has favored the complete diffusion of all the elements into the BCC1, completing the alloying sequence.

SEM analysis

In Figure 4.14 the size of the powder particles appears more homogeneous, suggesting a more efficient grinding process. Additionally, the distribution of the elements appears homogeneous in all of the powder particles, with the exception of a few particles, which are rich in a single element and show a brighter color. Hence, the SEM analysis confirms the idea that a single BCC structure forms and makes up for the majority of the powder

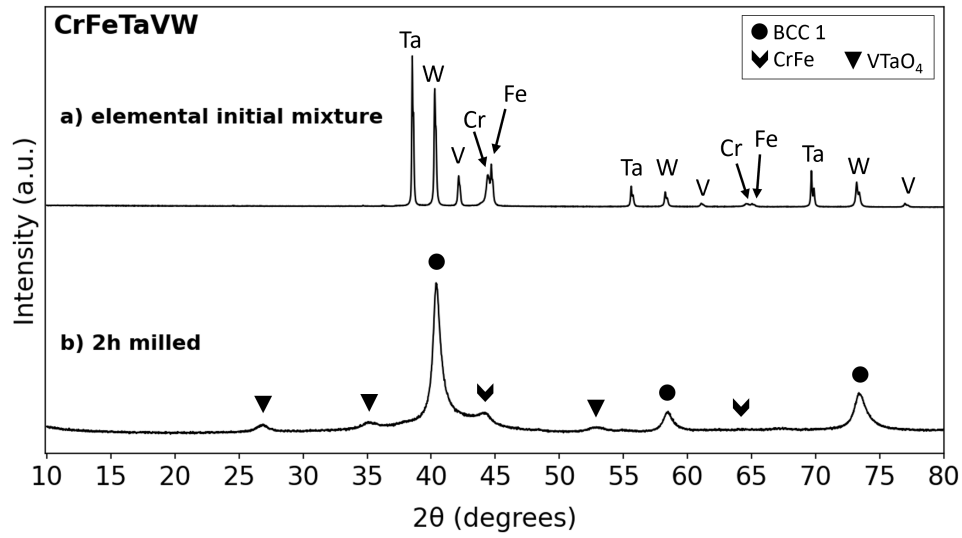


Figure 4.13: XRD diffractograms of (a) elemental mixture before milling and (b) mixture after 2h milling at 350 rpm, 20:1 ball-to-powder ratio and 26 balls of diameter of 10 mm.

analyzed, whereas the particles rich in Cr and Fe may be linked to the intermetallic phase of CrFe also appearing in the XRD.

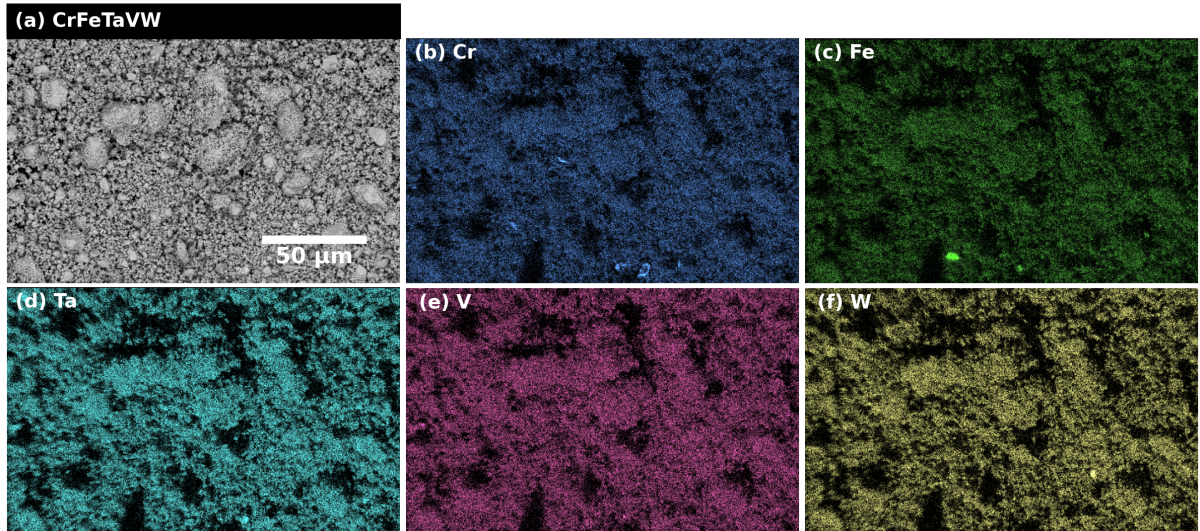


Figure 4.14: Sample milled for 2h milling at 350rpm with 20:1 ball-to-powder ratio and 26 milling balls. (a) SEM image collected in BSE mode of CrFeTaVW and EDS maps for (b) Cr-L α , (c) Fe-L α , (d) Ta-L α , (e) V-L α , (f) W-L α X-ray lines.

4.3.6. 15g, 15:1 bpr - Scaling up of the process

This section deals with the scaling up of the mechanical milling process. Once the optimized parameters for 10g of powder are obtained, it is necessary to move to larger amounts of powder which allow for a more efficient preparation of larger quantities of the sample. Hence, a quantity of 15g of powder was chosen. The experiment was repeated twice: one with $44\ \mu\text{m}$ Ta, one with $2\ \mu\text{m}$ Ta powder particles. Table 4.8 shows the input parameters, the transferred energy and power used for the experiments that were conducted by removing a small amount of powder from the two vials after 2h and 3h for the $44\ \mu\text{m}$ Ta and after 1h, 2h and 3h in the case of $2\ \mu\text{m}$ Ta. It should be highlighted that these calculations do not take into account the different size of Ta particles, considering that they are all performed considering an average particle size of $10\ \mu\text{m}$.

m_p [g]	d_b [mm]	btp	N_b	rpm	t_m [h]	E_{trans} [J]	P_{trans} [mW]
15	10	15:1	28	350	1	10.404	2.890
15	10	15:1	28	350	2	20.809	2.890
15	10	15:1	28	350	3	31.213	2.890

Table 4.8: Input parameters of planetary ball mill BM40 for the set of experiments with 15g of powder.

XRD analysis

The results of the XRD for experiment with $44\ \mu\text{m}$ Ta are shown in Figure 4.15. After 2h of milling, the powder is characterized by two BCC structures and a CrFe intermetallic. After 3h, there is only one BCC left, together with CrFe intermetallic and the VTaO_4 .

Already in Figure 4.15 (b), the peaks of BCC1 are significantly broadened with respect to the elemental W, which suggests that the energy rate supplied by the planetary ball is high enough to favor the accommodation of the other elements into W crystal lattice prior to the onset of work-hardening saturation. BCC 2 presents a lattice parameter larger than that of Ta, suggesting that complete alloying has not occurred yet.

After 3h of milling, a single BCC solid solution is achieved, the BCC2 peaks have disappeared, allowing to conclude that also Ta has also diffused in the W crystal lattice. This may be a further proof of the alloying sequence for this elemental composition, already presented in Section 4.3.1: the elements with lower melting temperature, Cr, Fe, V diffuse first in Ta and then in W, consistent with the trend of increasing melting

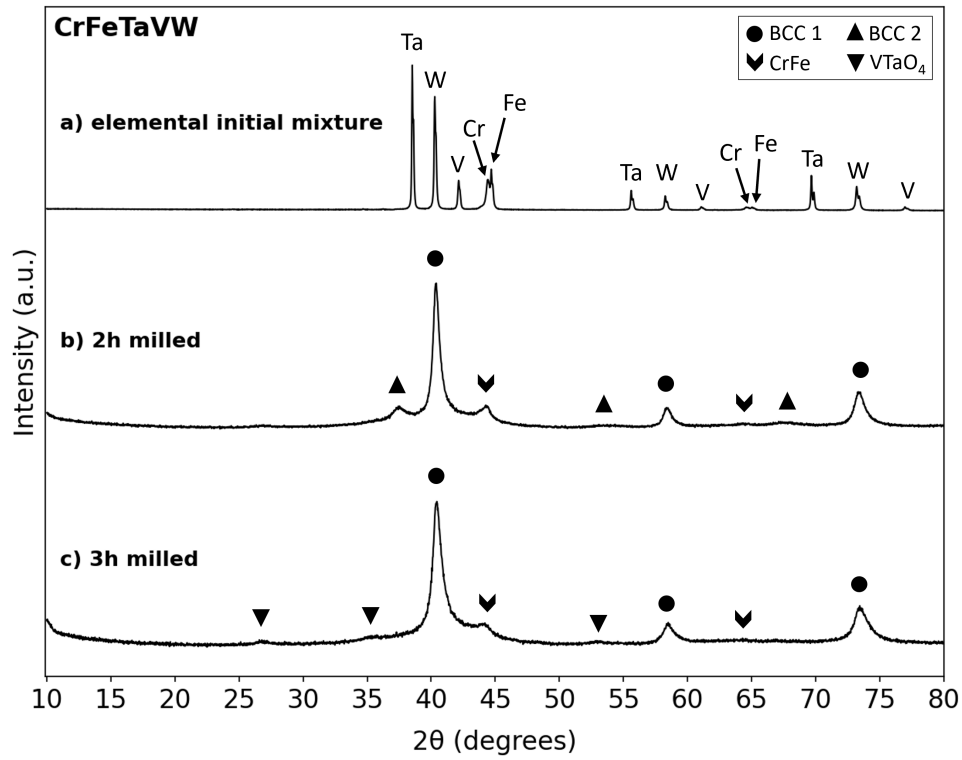


Figure 4.15: XRD diffractograms of (a) elemental mixture before milling and mixture with $44\ \mu\text{m}$ Ta milled at 350 rpm, 15:1 ball-to-powder ratio and ball diameter of 10 mm for a milling time of (b) 2h and (c) 3h.

temperature ($T_m(\text{Ta}) = 3290\text{K}$, $T_m(\text{W}) = 3695\text{K}$). In addition to the CrFe intermetallic, after 3h of milling a small amount of VTaO_4 is formed.

Figure 4.16 presents the evolution of the powder containing $2\ \mu\text{m}$ Ta. In this case, the BCC2 phase already disappears after 2h of milling. This suggests that employing a smaller Ta particle size favors a more rapid evolution of the alloying process. According to the microscopic mechanisms of alloying described in Section 2.2.3, starting from finer brittle particles allows the short diffusion distances required for alloying to be achieved more rapidly, thereby facilitating the formation of a solid solution within a shorter milling time. Additional analysis of the experiment with 15 g of powder will be performed with the powder containing the $2\ \mu\text{m}$ Ta.

XRD peak analysis

To further understand the evolution of BCC1 crystal lattice, the peak analysis has been carried out as described in Section 3.3.3. The results are shown in Figure 4.17.

The lattice parameter of BCC1 evolves in the following way: $a_{1h} = 0.31601 \pm 0.00001$

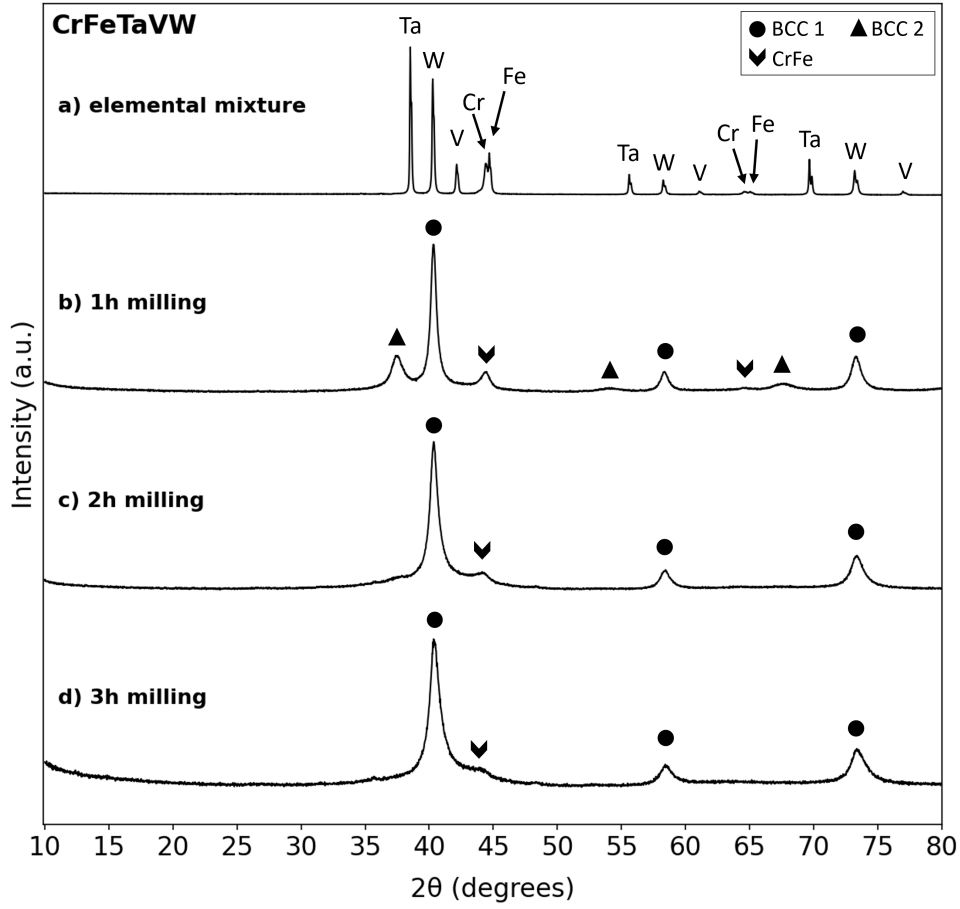


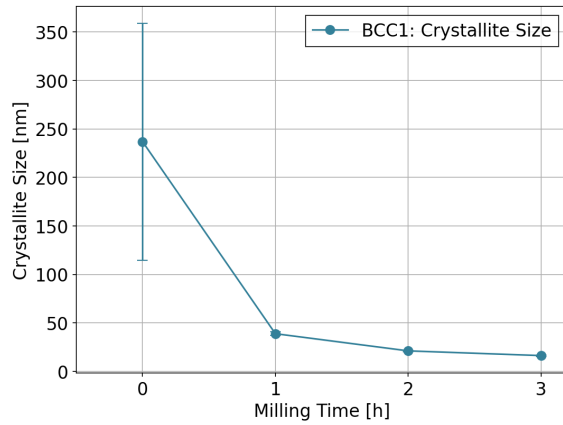
Figure 4.16: XRD diffractograms of (a) elemental mixture before milling and mixture with $2\ \mu\text{m}$ Ta milled at 350 rpm, 15:1 ball-to-powder ratio and ball diameter of 10 mm for a milling time of (b) 1h, (c) 2h, (d) 3h.

nm, $a_{2h} = 0.31576 \pm 0.00002$ nm, $a_{3h} = 0.31547 \pm 0.00003$ nm. The progressive decrease of the lattice parameter of BCC1, also with respect to the lattice parameter of pure W, suggests that the inclusion of the elements with lower atomic radius, Cr, Fe and V lowers the overall lattice parameter of the solid solution, a behavior that is in fact described by Vegard's law.

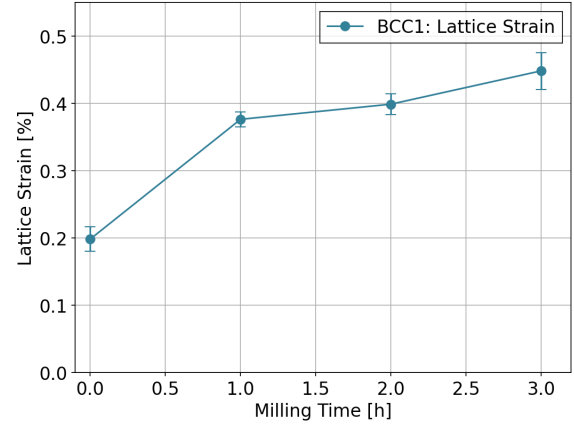
The observed decrease in crystallite size and increase in lattice strain are consistent with the typical evolution of a crystal structure undergoing mechanical milling. Accordingly, the increase in dislocation density is justified.

SEM analysis

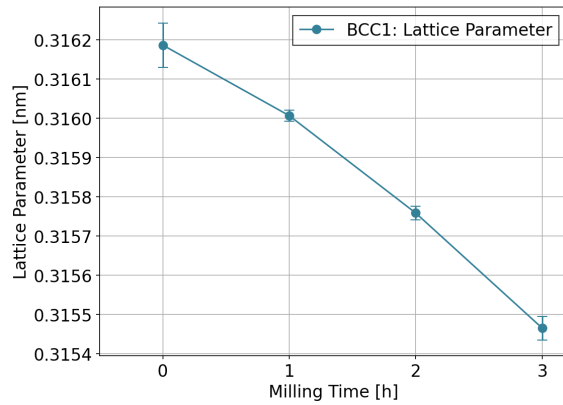
The SEM analysis for the powder containing the $2\ \mu\text{m}$ Ta was carried out after 1h and 3h of milling. The results are shown in Figure 4.18 and Figure 4.19 respectively.



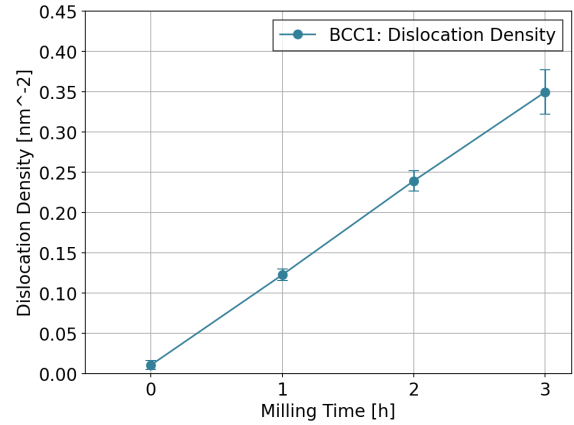
(a) Evolution of crystallite size with milling time.



(b) Evolution of lattice strain with milling time.



(c) Evolution of lattice parameter with milling time.



(d) Evolution of dislocation density with milling time.

Figure 4.17: Evolution of (a) crystallite size, (b) lattice strain, (c) lattice parameter, (d) dislocation density for the BCC1 structure.

What emerges from the comparison between the two SEM EDS maps is that in both cases an homogeneous distribution of the elements in all the powder particles is already achieved. What differs is the particle size distribution. In Figure 4.18 the size of the particle is very inhomogeneous, with the presence some large and some very small particles. In Figure 4.19, on the other hand, the average particles size is significantly smaller.

Overall, this experiment allows to draw some conclusions on the alloying mechanism and microscopic evolution of the powders by putting in relation the XRD and SEM results. It can be observed that after 1h the formation of a single solid solution is already starting to take place, since the transferred energy rate is sufficient to overcome the rapid work hardening of W and promote the diffusion of the other elements into its lattice. This is confirmed by the EDS maps, which reveal a relatively homogeneous distribution of the

elements throughout the powder particles.

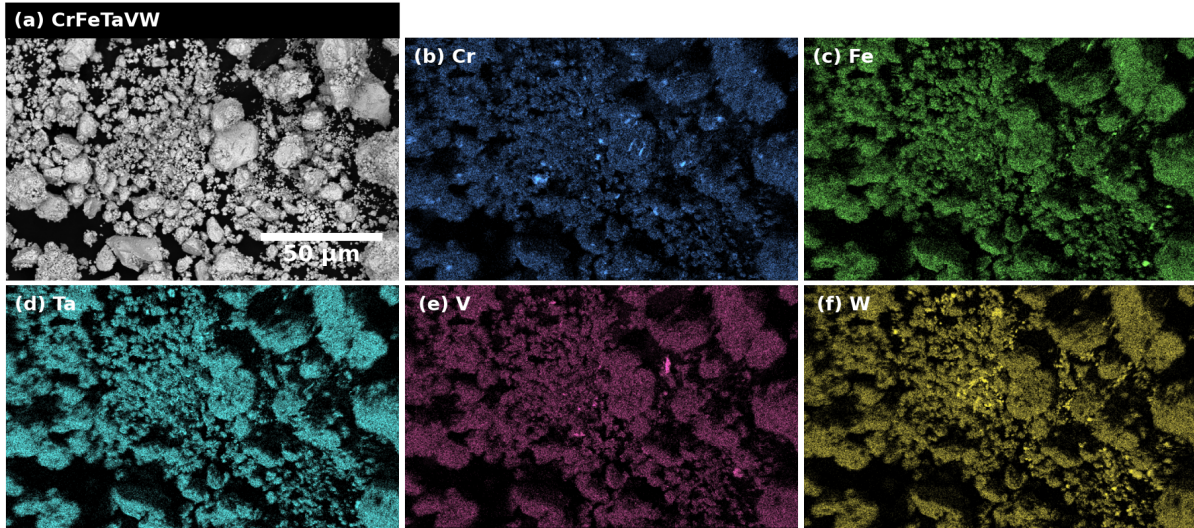


Figure 4.18: Sample milled for 1h milling at 350 rpm with 15:1 ball-to-powder ratio and 2 μm Ta. (a) SEM image collected in BSE mode of CrFeTaVW and EDS maps for (b) Cr-L α , (c) Fe-L α , (d) Ta-L α , (e) V-L α , (f) W-L α X-ray lines.

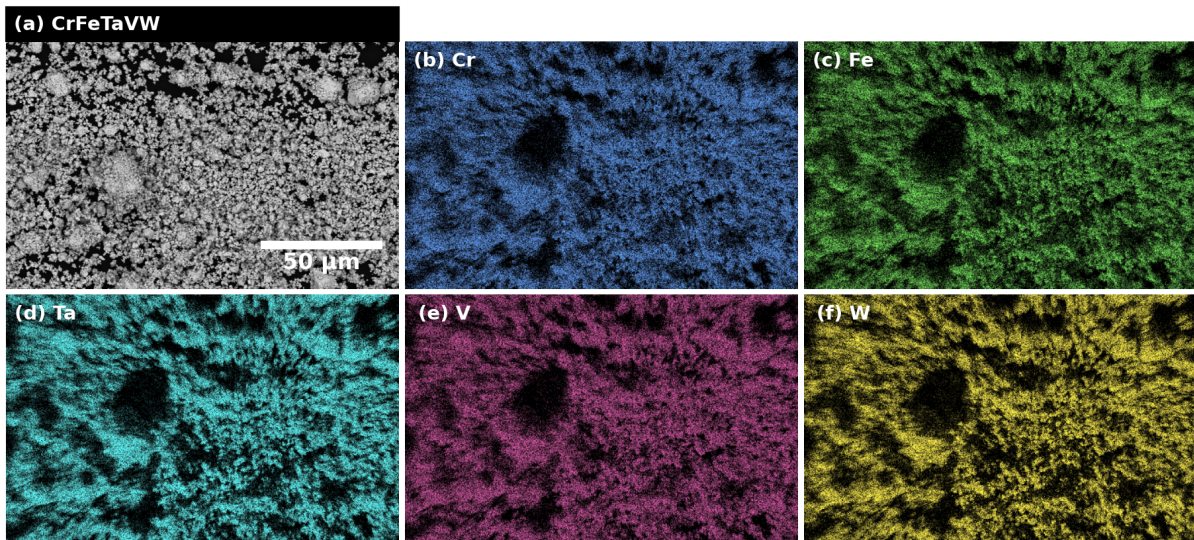


Figure 4.19: Sample milled for 3h milling at 350 rpm with 15:1 ball-to-powder ratio and 2 μm Ta. (a) SEM image collected in BSE mode of CrFeTaVW and EDS maps for (b) Cr-L α , (c) Fe-L α , (d) Ta-L α , (e) V-L α , (f) W-L α X-ray lines.

However, the total transferred energy remains insufficient to complete the alloying process, as evidenced by the persistence of the BCC2 phase, indicating that diffusion

into the W-rich structure is not yet complete. The incomplete formation of a single solid solution may also be related to the broad particle size distribution observed at this stage. As discussed in Section 2.2.3, the alloying process ends when a steady-state balance is established between cold welding and fracturing, resulting in a more homogeneous intermediate particle size. This condition is observed in the powders milled for 3 h, whose EDS maps show a uniform elemental distribution and whose XRD pattern confirms the formation of a single solid solution.

4.4. Summary and discussion of the main results

Summary

A concise summary of the main results of the production CrFeTaVW is now presented, with a correlation to the theoretical model developed to evaluate the transfer of energy and energy rate during mechanical milling.

- For 10 g of powder, using a milling parameter of 10:1 bpr leads to a powder sample with two distinct BCC crystal structures. BCC1 is the work hardened W with lattice parameter equal to the one of pure W. BCC2 is the alloy of Cr-Fe-Ta-V with probably none or very little content of W and with a lattice parameter that increases progressively with milling time. With this value of ball-to-powder ratio, the transferred energy rate is around half of the target value, while the target energy is met after 5h of milling.
- Increasing the ball-to-powder ratio to 20:1, the powder presents only one BCC structure with lattice parameter slightly smaller than the one of W. In this case, the transferred energy rate is close to the target value while the transferred energy is achieved after 2h of milling.
- Increasing the amount of powder to 15 g, the value of transferred energy rate is obtained with a 15:1 bpr, while the transferred energy is met after 3h of milling. Using these parameters, the single BCC structure is achieved.

Discussion

One of the most challenging aspects in the production of W-based HEAs is the rapid work hardening of W. To understand this phenomenon, it should be considered that all elements undergo strain hardening during mechanical milling. This process introduces a lot of defects in the lattice, until the particles reach a saturation hardness due to accumulation of strain energy [58]. Since W is the hardest element of the composition,

it is also the fastest among the other alloying elements to approach strain hardening saturation.

The formation of two BCC structures in the experiments with 10 g of powder and 10:1 bpr, and the achievement of a single BCC solid solution in experiments with 10 g of powder and 20:1 bpr and with 15 g of powder and 15:1 bpr, can be interpreted in light of the alloying sequence proposed by Chen et al. [112]. According to these authors, the elements with lower melting temperatures preferentially diffuse into those with higher melting temperatures during mechanical milling. Applying this model to the alloy analyzed here, Cr, Fe, V diffuse first into Ta and subsequently into W. Hence, in the condition of 10 g of powder and 10:1 bpr, the alloying sequence progresses up to Ta, whose crystal lattice modifies significantly with the inclusion of Cr, Fe, V forming BCC2, and then stops because of the rapid work hardening of W whose crystal lattice is BCC1.

The combined analysis of the experimental results and the theoretical model indicate that, when the transferred energy rate falls below a critical threshold, the lower-melting-point elements are unable to diffuse into the W lattice before significant work hardening occurs. Consequently, achieving a sufficiently high energy rate is essential for successful alloying. Among the processing parameters investigated in this thesis, the ball-to-powder ratio proved to be the most effective for controlling the transferred energy rate.

Once the issue of W work hardening was overcome, the experiments performed at higher values of transferred energy rate and with progressively increasing milling times revealed another important aspect of the alloying process. It should be recalled that the total energy transferred to the powder increases with milling time. Moreover, the degree of alloying depends on the cumulative energy delivered during milling: a minimum amount of energy is required to achieve complete diffusion of the alloying elements and the formation of a single BCC solid solution. Therefore, by varying the milling time, it is possible to identify the total transferred energy necessary for the complete incorporation of all alloying elements into the W lattice.

Finally, the formation of a single-phase BCC solid solution in the considered alloy system was successfully achieved. The measured lattice parameter of the HEA was found to be very close to that of pure W, in agreement with observations commonly reported in the literature and discussed in Section 4.1.2. More specifically, the lattice parameter obtained in this work was slightly lower than that of pure W. This deviation is attributed to the incorporation of three alloying elements with smaller atomic radii than W, resulting in a reduction of the average lattice parameter consistent with the behavior predicted by Vegard's law.

5 | Characterization of bulk samples and irradiation resistance

This chapter presents the procedure of implantation with argon, deuterium and helium of sintered samples of HEA in different compositions: $(\text{CrFeTaV})_{95}\text{W}_5$, $(\text{CrFeTaV})_{90}\text{W}_{10}$, CrFeTaVW , $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$. The implantation allows to simulate the irradiation conditions that a plasma-facing component would be subjected to during its operation. The aim is to investigate the possible change in microstructure and topography of the considered sample.

To begin with, this chapter covers the characterization with XRD and SEM of the as-sintered samples. The aim is to identify the phases that form during the sintering process and characterize the microstructure of the sample. Next, implantation simulations performed with SRIM software are introduced. Finally, the characterization analysis of the Ar^+ , He^+ and D^+ implanted samples, carried out with XRD and SEM, are reported.

5.1. As-sintered samples: analysis of composition and microstructure

In order to evaluate the modifications in microstructure and composition of the samples after the irradiation, a prior detailed analysis of the as-sintered samples is required. This paragraph presents the results of the GIXRD analysis and of the SEM in BSD mode, in order to comment the phases that form in the samples after the spark plasma sintering process. For simplicity, the samples will be often referred to with the sole atomic percentage of W that they contain. Hence, $(\text{CrFeTaV})_{95}\text{W}_5$ is referred to as W-5%, $(\text{CrFeTaV})_{90}\text{W}_{10}$ as W-10%, CrFeTaVW as W-20%, $(\text{CrFeTaV})_{70}\text{W}_{30}$ as W-30% and $(\text{CrFeTaV})_{65}\text{W}_{35}$ as W-35%.

5.1.1. Production of the bulk samples

The production of the powders and the bulk samples was carried out prior to this thesis work. The powder samples were produced with the PM 400 MA planetary ball machine and using the input parameters: 2h of milling, 350 rpm and 10:1 bpr. Subsequently, the powder samples were consolidated with SPS as described in Section 3.2.1.

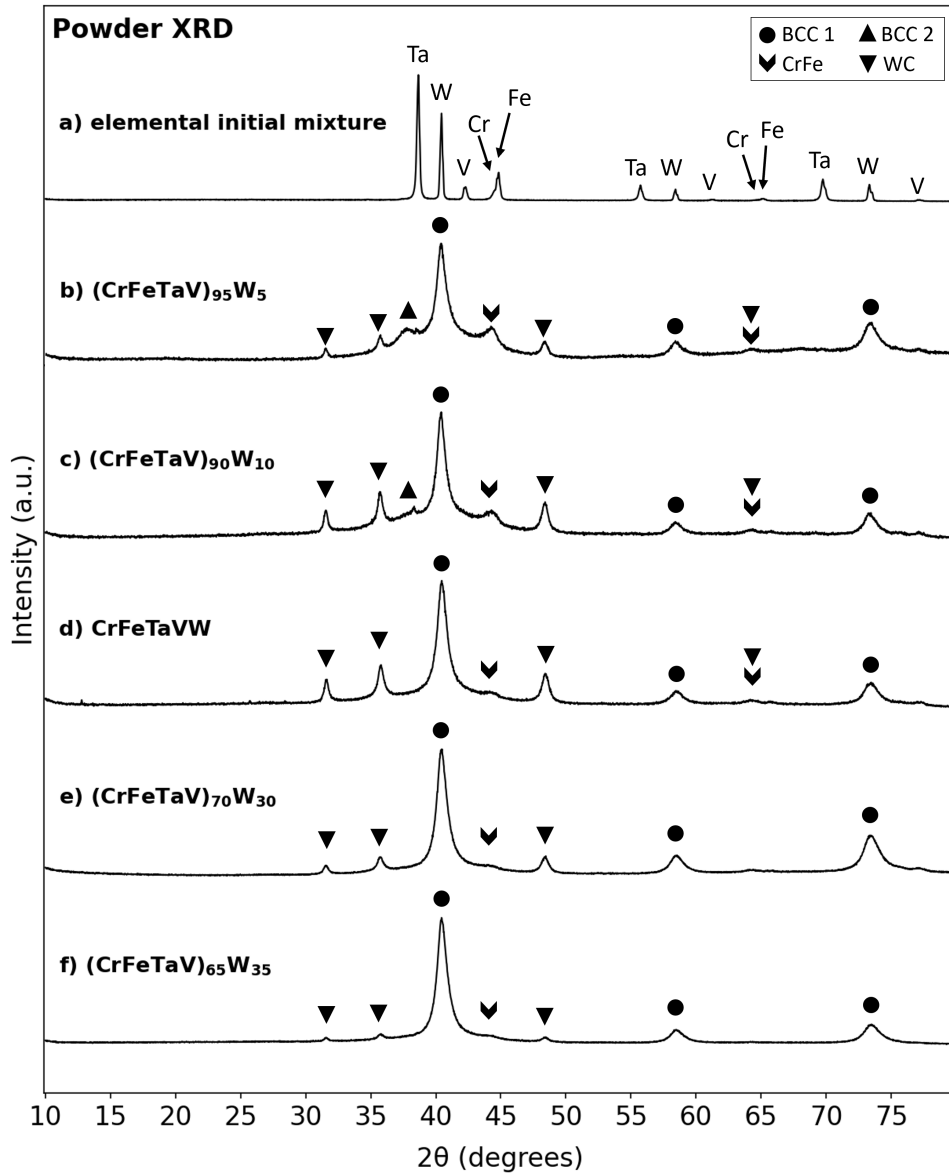


Figure 5.1: XRD diffractograms of (a) elemental mixture before milling and (b)-(f) five compositions of $(\text{CrFeTaV})_{1-x}\text{W}_x$ milled with PM 400 MA planetary ball machine for 2h at 350 rpm with a 10:1 bpr.

The powder XRD of the five studied compositions are reported in Figure 5.1. Figure

5.1 (b) and (c) present the diffractograms of $(\text{CrFeTaV})_{95}\text{W}_5$ and $(\text{CrFeTaV})_{90}\text{W}_{10}$. The powders present a BCC1, BCC2 crystal structures, together with a CrFe intermetallic and WC peaks. Figure 5.1 (d) - (f) display the XRDs of CrFeTaVW, $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$. In these cases, the XRD only witnesses the presence of a BCC1, CrFe intermetallic and WC.

These results can be discussed in light of the concepts and findings presented in Chapter 4. BCC1 is the solid solution comprising all the elements in the composition. BCC2, which has a lattice parameter larger than Ta, is an additional solid solution possibly containing little or no W. The persistence of BCC2 only in the first two compositions may be related to the fact that the amount of W is very low compared to the amount of other elements. BCC2 may be comprised of the excess elements that are not incorporated into the W-containing BCC1 phase. All these diffractograms exhibit the presence of WC, a contamination of the powders caused by the erosion of the milling balls and the container walls.

5.1.2. Characterization with GIXRD of the as-sintered samples

A detailed characterization of the bulk samples is needed, with the final goal of comparing the implanted samples with the initial conditions of the the bulk samples. Following, the GIXRD analysis is presented.

Results

Figure 5.2 presents the XRD of the five compositions, with the identification of the peaks. All compositions present a BCC1, an oxide phase (TaVO_4) and a carbide phase of stoichiometry (M_6C), where M stands for a mix of metallic elements. Additionally, in $(\text{CrFeTaV})_{95}\text{W}_5$ and $(\text{CrFeTaV})_{90}\text{W}_{10}$ the diffractograms present Laves phases, respectively C14 and C15. In compositions $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$ a BCC2 structure appears. For this evaluation, the experimental lattice parameters were obtained with PowderCell software.

The lattice parameter of BCC1 changes depending on the composition of the alloy and it shifts towards lower values while increasing the amount of W. In particular, for the different compositions, the lattice parameters are as follows: $a_{\text{BCC1}, \text{W}-5\%} \approx 0.316 \text{ nm}$, $a_{\text{BCC1}, \text{W}-10\%} \approx 0.316 \text{ nm}$, $a_{\text{BCC1}, \text{W}-20\%} \approx 0.314 \text{ nm}$, $a_{\text{BCC1}, \text{W}-30\%} \approx 0.313 \text{ nm}$ and $a_{\text{BCC1}, \text{W}-35\%} \approx 0.312 \text{ nm}$. Additionally, BCC1 presents slight shifts in the peak positions if compared to the ideal crystallographic planes, suggesting anisotropic lattice distortion.

A BCC2 is also present in the compositions $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$,

with a lattice parameter of $a_{BCC2} \approx 0.31600 \text{ nm}$ in both compositions.

In the case of these analyzed compositions, W-5% presents a C14 Laves phase while W-10% presents a C15. The C14 Laves phase (hexagonal structure) of the W-5% composition has lattice parameters of: $a_{C14} = 4.8800 \text{ nm}$, $b_{C14} = 4.8800 \text{ nm}$, $c_{C14} = 7.8790 \text{ nm}$. The C15 Laves phase (cubic structure) of the W-10% composition has a lattice parameter of: $a_{C15} \approx 7.2000 \text{ nm}$.

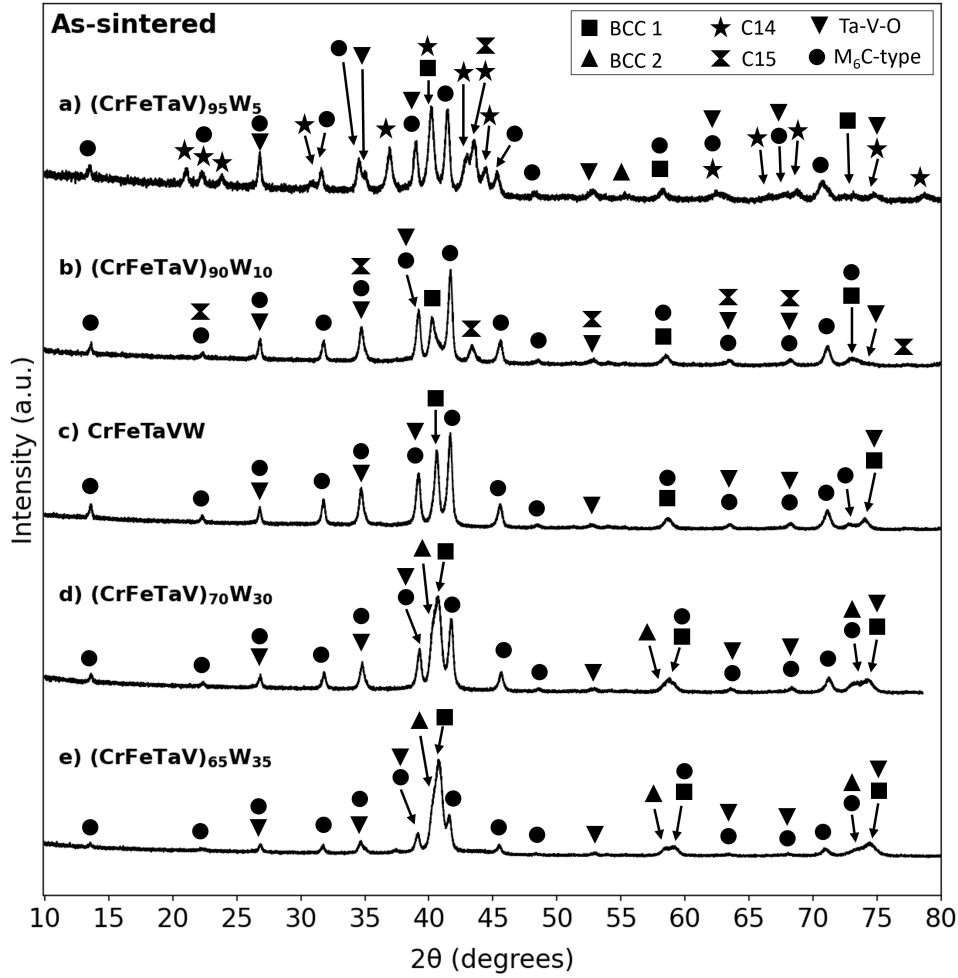


Figure 5.2: XRD of the as-sintered samples for the different compositions of $(\text{CrFeTaV})_x\text{W}_{1-x}$.

Discussion

Looking more in detail at the two BCC structures, it can be reasonably concluded that BCC1 phase is related to the solid solution of HEA, while BCC2 may be attributed to a partition of W in the matrix, so to a W-rich phase, since its lattice parameter is equal to the one of pure W. In fact, if on one hand the BCC2 has a lattice parameter very close

to that of pure W, the lattice parameter of BCC1 progressively decreases with respect to pure W, suggesting a complex crystalline structure that modifies when changing the composition of the elements.

Regarding BCC1, the decrease of lattice parameter may be linked to the partitioning of Ta, which has the largest atomic radius out of all the elements in the composition, into Ta-rich phases [126]. This can only be confirmed with the SEM analysis, given that in the XRD no peak can be uniquely identified as related to a Ta-rich phase.

Focusing on BCC2, it can be evidenced that in the samples with W-5% and W-10%, BCC2 has the same lattice parameter of BCC1, and in the equimolar sample its lattice parameter is very close to that of BCC1. Hence, it is not possible to exclude the presence of BCC2 also in the first three compositions, even if the peaks are not separated in the XRD diffractogram. This may be supported in the SEM analysis by checking if the W-rich phase is present in all compositions or only in the W-30% or W-35%.

To better investigate the Ta-V-O phase, particular attention must be paid to oxide formation during the whole production process. Mechanical milling is conducted in a glove box under Ar atmosphere while SPS is conducted in vacuum. However, residual oxygen may be found during these procedures and it may react with the metals, particularly due to the high temperatures obtained during SPS. At the same time, it should be considered that oxides may also evaporate after formation, so that they do not appear in the final sintered sample. In these compositions, the most stable oxides form with Ta and V, since their evaporation temperatures are very high ($>1800^{\circ}\text{C}$). Also W tends to form oxides but with lower evaporation temperatures, well below the 1400°C used for this sintering process. The only exception is WO_2 with an evaporation temperature $> 1800^{\circ}\text{C}$ [125]. Considering Figure 5.2, no composition presents the characteristic peaks of WO_2 , hence it can be concluded that no W oxide is present after these sintering conditions. On the other hand, Ta-V-O are most probably formed. Literature often witnesses the formation of Ta_2VO_6 [52, 127]. However, in this case, the peaks seem to be coinciding with the ones of TaVO_4 , even if some of them are slightly shifted with respect to their standardized position. This suggests that there is a variation in composition of this phase, possibly presenting different stoichiometry of the elements or substitutional atoms. Consequently, this oxide is referred to as Ta-V-O in Figure 5.2.

Another phase that is common to all compositions is the M_6C . According to Wang et al. [128], SPS operations may lead to the formation of complex transition metal carbides, usually formed at interphase boundaries and usually referred to as η -phases. The carbon could either come from the graphite die used in SPS or from residual carbon in the original

powders, i.e. from the WC contamination. In this case, it is possible that the η – phase forms with a structure of $(\text{Cr, Fe, V})_3\text{W}_3\text{C}$, where Cr, Fe, V may all be included in the structure, thus causing the observed shift in the peaks with respect to the standardized position.

Finally, the first two compositions, with W-5% and W-10%, present Laves phases. Laves phases are a common intermetallic phase which belongs to the group of tetrahedrally close-packed binary structures. They have a stoichiometry of AB_2 where A atoms are larger and B atoms are smaller, with an ideal atomic radius ratio to achieve highest packing density of $r_A/r_B = (3/2)^{1/2} \approx 1.225$. There are three common structure types, C14, C15, C36 which differ for their periodic stacking sequence [129]. In particular, the two structures of interest for this thesis are the C14 and C15, which present respectively an hexagonal and a cubic arrangement.

Only considering the XRD diffractogram, no conclusion can be drawn on the composition and stoichiometry of such phases. However, it has been reported that formation of Laves phases is frequently observed in RHEAs containing Cr, usually associated with the presence of Ta [52]. With respect to the standard TaCr_2 C14 Laves phase, this diffractogram shows slightly shifted peaks of the C14 phase. The difference in lattice constants possibly indicate that atoms with different sizes may have dissolved into the TaCr_2 sublattice [130]: the composition of such phases can only be confirmed with the SEM EDS maps.

Further consideration should be given to the presence of Laves phases exclusively in the W-5% and W-10% compositions. According to Zhang et al. [79], who studied a similar composition of HEA, when the content of Ta exceeds a certain value (in the paper the value of 0.4 is reported), the solid solubility of Ta in the solid solution reaches saturation and, consequently, tends to precipitate in the form of Laves phase. In this work, the saturation value would be at 0.225 of Ta.

5.1.3. Characterization with SEM of the as-sintered samples

The analysis with SEM follows the one with the XRD. In fact, combining these two techniques, it is possible to better define the phase composition of the considered samples. In this case, both BSE mode and EDS maps are used to assess the microstructure and phase composition.

Results

The recognition of the phases that form after the sintering process in the sample is

performed using SEM in BSD mode and with an inclination angle between the beam direction and the normal to the surface of the sample equal to 0° . This configuration is referred to as *normal incidence* configuration. Figure 5.3 shows the results of the five compositions, with the main phases indicated with an arrow and a letter to distinguish them. These phases will then be compared with the ones observed in the XRD in Figure 5.2.

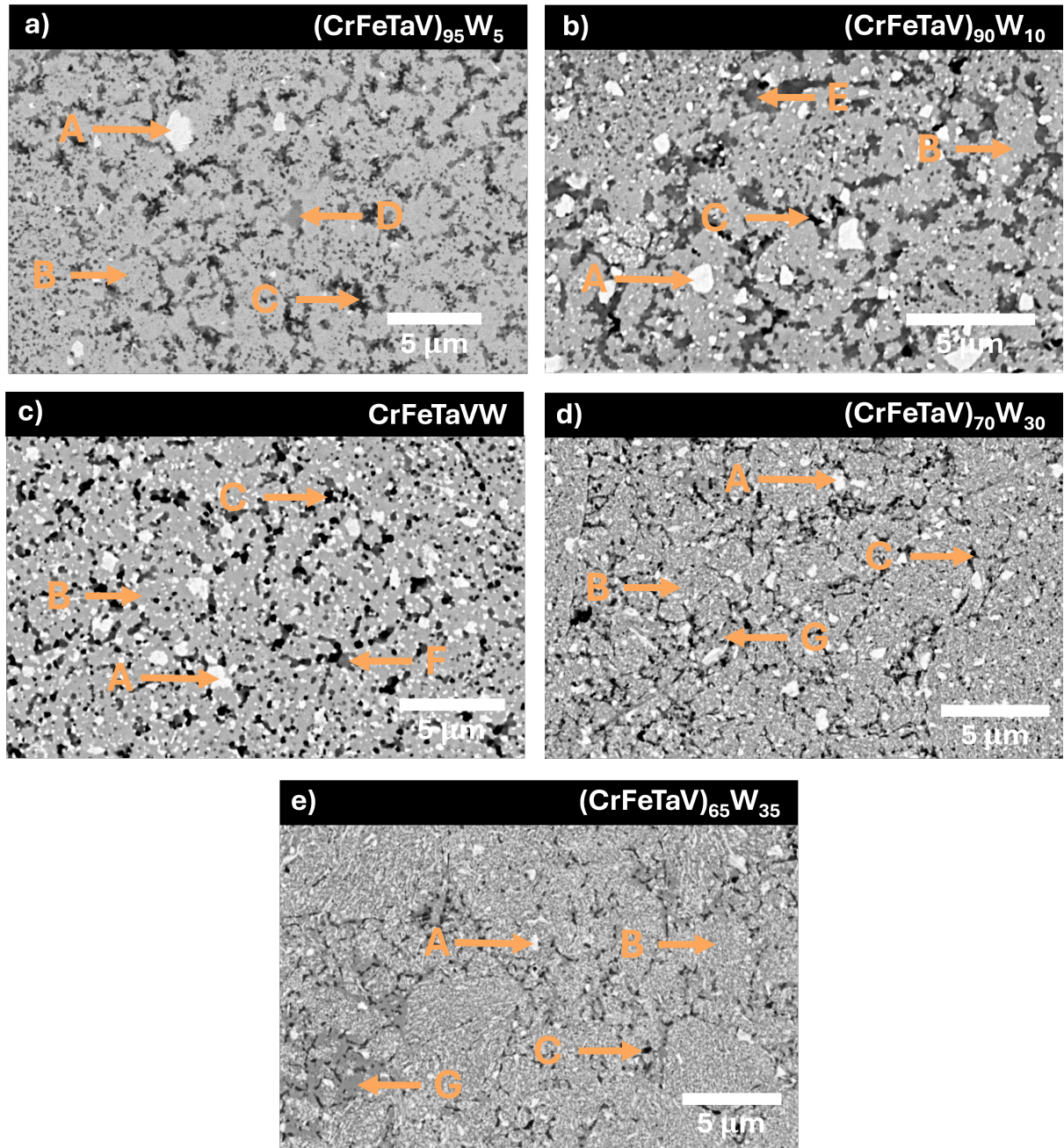


Figure 5.3: SEM analysis in BSD mode with a normal incidence (0°) for the five compositions of the as-sintered samples.

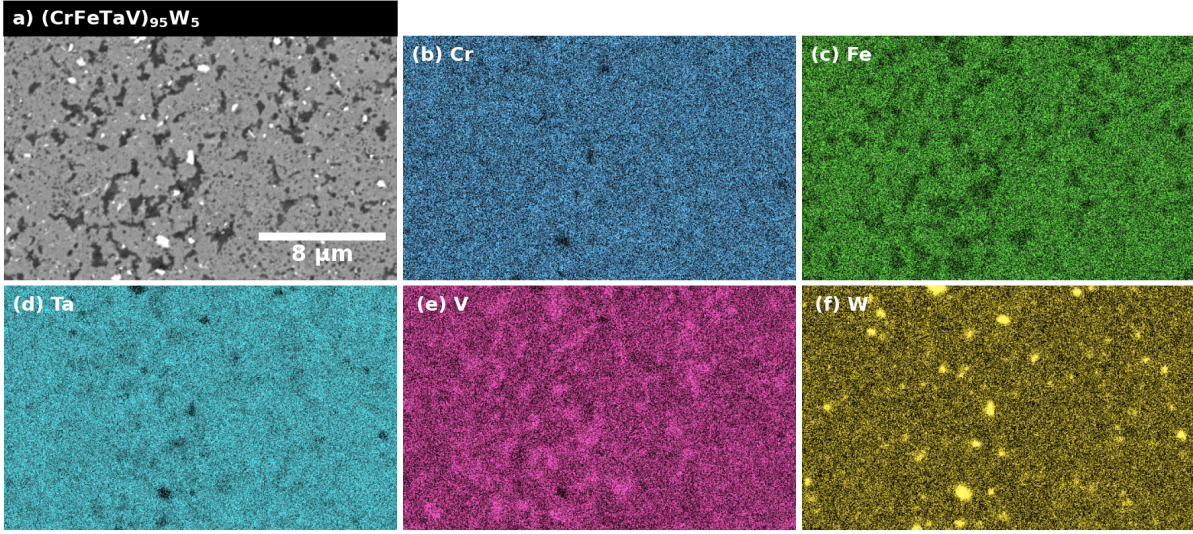


Figure 5.4: As-sintered sample of $(\text{CrFeTaV})_{95}\text{W}_5$. (a) SEM image collected in BSE mode and EDS maps for (b) Cr-L α , (c) Fe-L α , (d) Ta-L α , (e) V-L α , (f) W-L α X-ray lines.

Commenting on the recognized phases, using the EDS maps displayed in Figures 5.4, 5.5, 5.6, 5.7, and 5.8, it is possible to report qualitatively the composition of each phase. Phase-A and Phase-B are present in all compositions and are respectively a W-rich phase and a phase with a uniform composition of all elements. Also Phase-C is present in all samples and it is a V-rich phase. Concerning Phase-C in $(\text{CrFeTaV})_{95}\text{W}_5$ and Phase-E in $(\text{CrFeTaV})_{90}\text{W}_{10}$, both phases are rich in Cr, but it cannot be excluded that they have different stoichiometry, considering that the diffractograms of the two samples present some differences. Phase-F in CrFeTaVW is rich in Ta whereas Phase-G in $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$ is rich in Cr and Fe. Overall, it can be observed that a higher W content favors the development of a more refined microstructure, which complicates the clear identification and separation of the phases.

Discussion

Assessing the phases common to all samples, it can be concluded that Phase-B may correspond to BCC1 of the solid solution whereas Phase-D may correspond to the Ta-V-O, considering that it is rich in V but it also contains Ta. Since Phase A is W-rich, it is expected to produce XRD reflections with a lattice parameter close to that of pure W. This observation therefore reinforces the hypothesis that BCC2 may also be present in $(\text{CrFeTaV})_{95}\text{W}_5$, $(\text{CrFeTaV})_{90}\text{W}_{10}$ and CrFeTaVW, with their diffraction peaks overlapping those of the BCC1 phase.

Phase-D be associated with the C14 Laves phase identified in the XRD analysis. Since this phase is rich in Cr but also presents Ta and V, the Laves phase may form

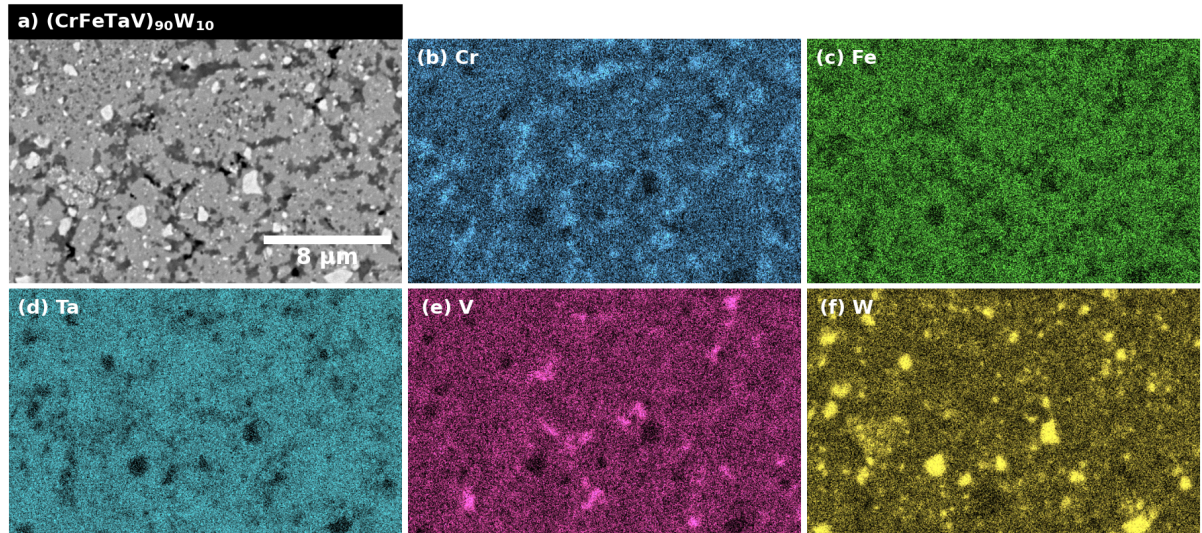


Figure 5.5: As-sintered sample of $(\text{CrFeTaV})_{90}\text{W}_{10}$. (a) SEM image collected in BSE mode and EDS maps for (b) Cr- $L\alpha$, (c) Fe- $L\alpha$, (d) Ta- $L\alpha$, (e) V- $L\alpha$, (f) W- $L\alpha$ X-ray lines.

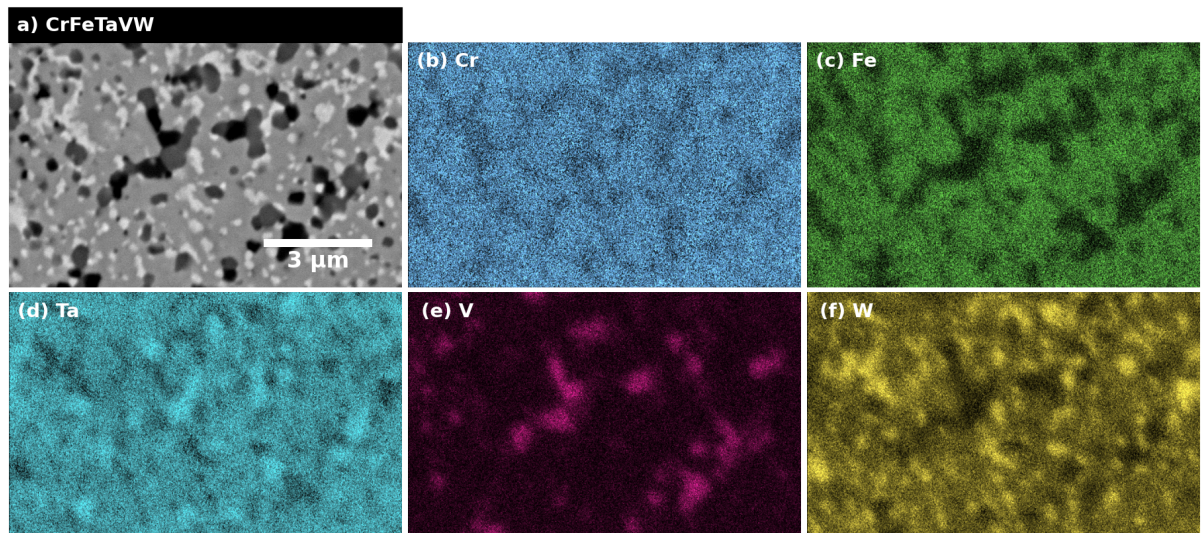


Figure 5.6: As-sintered sample of CrFeTaVW. (a) SEM image collected in BSE mode and EDS maps for (b) Cr- $L\alpha$, (c) Fe- $L\alpha$, (d) Ta- $L\alpha$, (e) V- $L\alpha$, (f) W- $L\alpha$ X-ray lines.

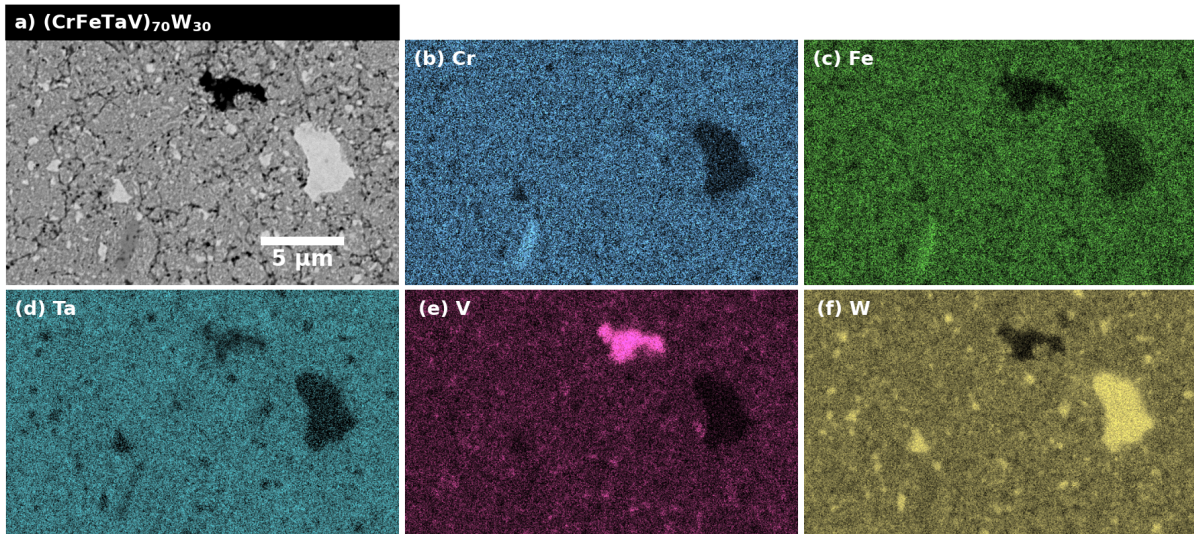


Figure 5.7: As-sintered sample of $(\text{CrFeTaV})_{70}\text{W}_{30}$. (a) SEM image collected in BSE mode and EDS maps for (b) Cr- $L\alpha$, (c) Fe- $L\alpha$, (d) Ta- $L\alpha$, (e) V- $L\alpha$, (f) W- $L\alpha$ X-ray lines.

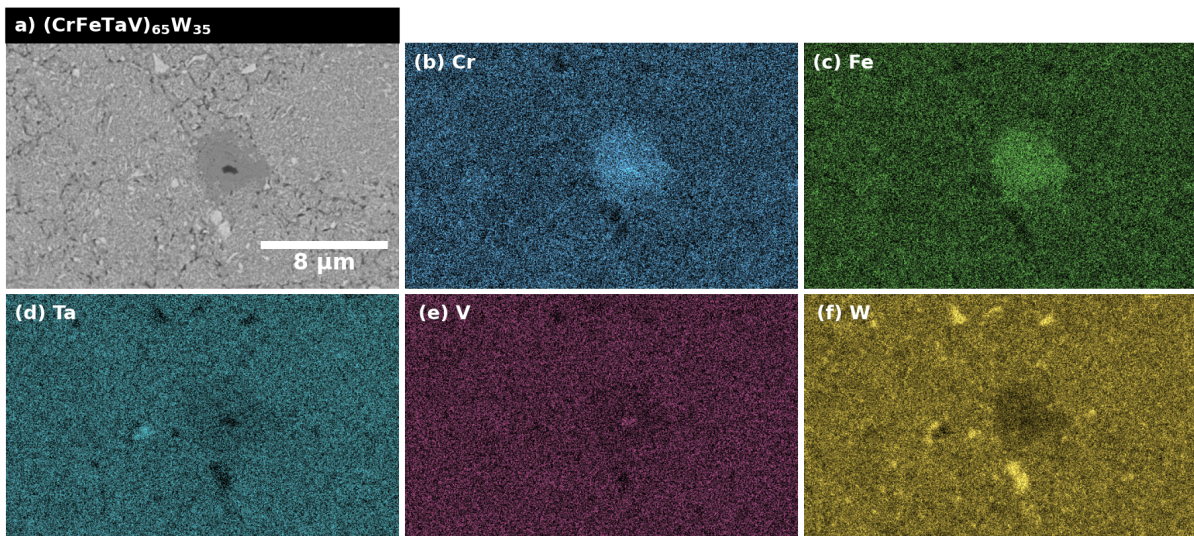


Figure 5.8: As-sintered sample of $(\text{CrFeTaV})_{65}\text{W}_{35}$. (a) SEM image collected in BSE mode and EDS maps for (b) Cr- $L\alpha$, (c) Fe- $L\alpha$, (d) Ta- $L\alpha$, (e) V- $L\alpha$, (f) W- $L\alpha$ X-ray lines.

with a composition of Ta(V,Cr)_2 [52], in which Cr can partially substitute for V as a substitutional element. Phase-E, on the other hand, should be related to the C15 Laves phase. According to the same considerations made for Phase-D, also this C15 structure may have be Ta(V,Cr)_2 .

In Figure 5.3 c), Phase-F is rich in Ta with a strong depletion in all other elements apart from Cr, which remains well distributed along all phases. This phase cannot be linked to any of the phases of the XRD because a possible Ta peak would be superimposed to other structures in the diffractogram. However, the possible partial partition of Ta, which was already predicted from the XRD, would be here confirmed.

In Figure 5.3 d) and Figure 5.3 e), Phase-G is rich in Cr and Fe but also contains all the other elements. It has been reported in literature that these two elements have a strong tendency to associate and segregate as atomic pairs, developing regions enriched in these elements [131]. Other possible phases in these two compositions cannot be distinguished due to the very fine microstructure. As a result, the hypothesis of increasing Ta partition, suggested by the progressive decrease in the lattice parameter of BCC1, cannot be confirmed. Moreover, this decrease in lattice parameter may also be attributed to the formation of regions enriched in Cr and Fe, whose smaller atomic radii would contribute to a contraction of the lattice.

5.2. Simulation for implantation operations with SRIM

The simulation for the irradiation procedure consists in two steps:

1. Regarding the implantation with argon the aim is to generate a 100 dpa of damage considered to simulate the neutron damage after 5 years of operation of the divertor, as presented in Section 1.3. The simulation allows to calculate the fluence needed in order to generate in the samples such value of dpa.
2. Regarding the implantation with deuterium and helium, the simulation is aimed at finding the ion energies that make the implantation profiles overlap with the damage profile generated by the argon implantation .

For each of the composition considered in this part of the thesis, the fluence and energy of implantation of Ar, and the energy of implantation of He and D is calculated using SRIM, a Montecarlo simulation code.

For simulations related to Ar, the aim is to calculate the fluence to set in the ion implanter in order to obtain on the target a damage of 100 dpa. To do so, the chosen

type of SRIM calculation is "Detailed Calculation with Full Damage Cascades", which analyzes all collisional damage in the target by following every recoiling atom until its energy drops below the lowest displacement energy of any target atom. Accordingly, in addition to the final distribution of the incident ion in the target, the distribution of each element of the target is simulated by the software. For what concerns deuterium and helium, the selected SRIM calculation is "Ion Distribution and Quick Calculation of Damage" which focuses on the ion implanted and neglects details about the target damage, allowing for quicker computational calculations. In fact, the aim of this simulation, is to evaluate at which depth from the surface of the sample the majority of the implanted ions distribute. The damage calculated with this option is a quick statistical estimate based on the Kinchin-Pease formalism. Finally, in both cases, the physical HEA samples with different compositions are modeled in SRIM by placing all constituent elements, each in its respective atomic percentage, within a single target layer. This approach is an approximation, as the software does not account for the presence of multiple phases or the spatial distribution of elements in the actual material. The calculation is carried out with a statistics of 50000 simulated ions.

Literature presents many different methods to retrieve the value of dpa in the target from a SRIM simulation. The one chosen for this thesis work is the reference one for the IPFN laboratories, which is used for every ion implantation procedure and that ensures comparison of results. The result for ions and recoiling atoms distribution are delivered in unit of measure of $(\text{at}/\text{cm}^3)/(\text{at}/\text{cm}^2)$. Multiplying this value by the fluence (in at/cm^2) the target density after implantation is obtained. Diving this value by the theoretical target density before the implantation, the value of dpa is obtained. Hence, by selecting the target damage value of 100 dpa, the corresponding desired Ar fluence can be retrieved. In order to be conservative with the calculations, after summing the distribution of every recoiling atom in the target at each position in the depth profile, the maximum value of distribution is taken as the reference value for the calculations.

The SRIM simulations are carried out trying different energies for the incident ions. The final choice for the energies combination of Ar, D, He is taken considering different factors. The main one is that it is demanded to have the peak of distribution of D and He centered on the peak of damage of Ar, thus ensuring that ion implantation occurs in the region of maximum damage within the sample. Secondly, the ion implanter only works in stable conditions within a certain range of energies, which is taken into account in the selection of the different combinations of energies. The final combination of energies is 150keV for Ar, 5keV for D and 10keV for He. The results of the simulations for each composition are shown in Figure 5.9, where the black scatterplot represents the damage

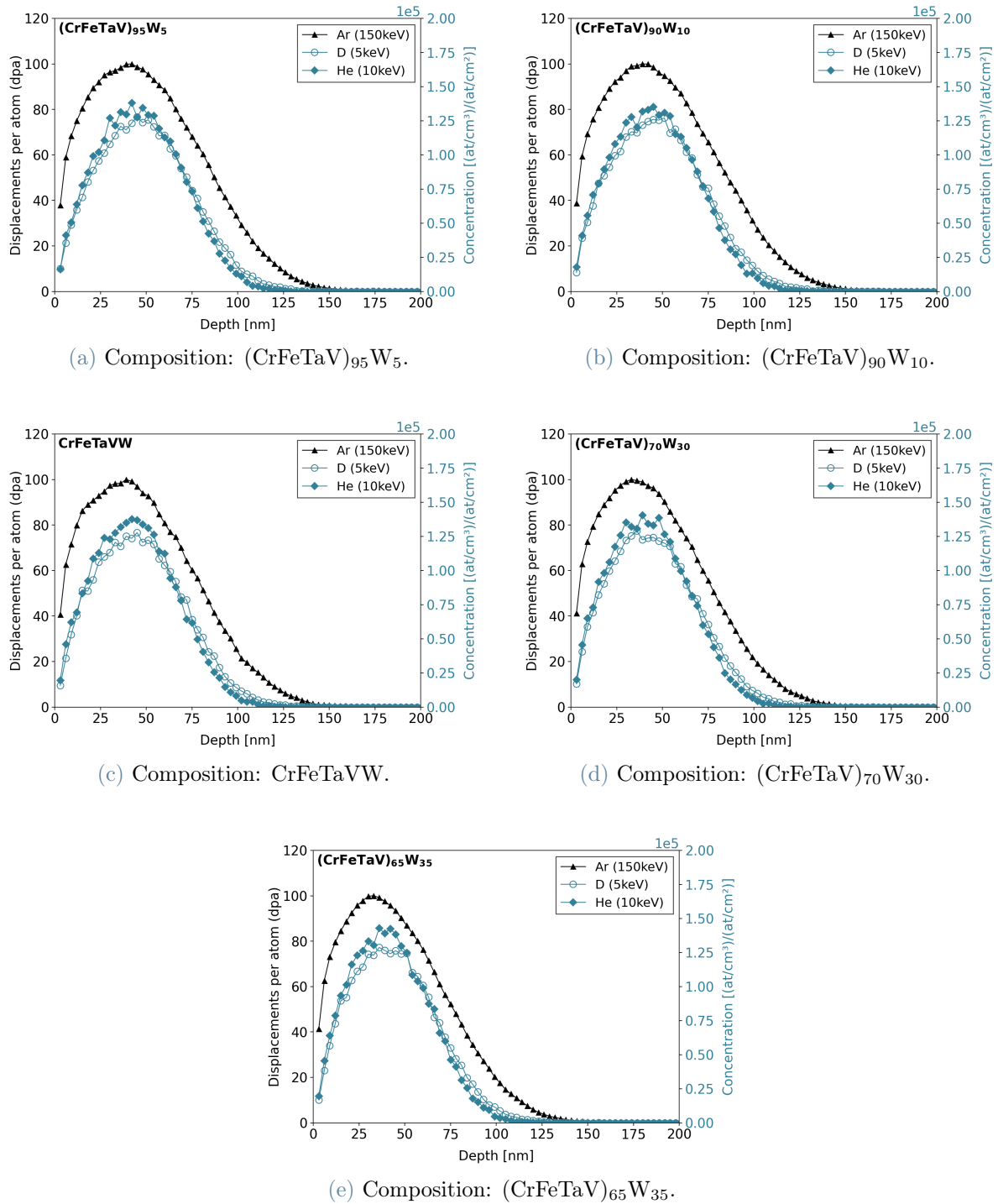


Figure 5.9: SRIM output for simulation of Ar implantation damage and He, D implantation distribution for five compositions of $(\text{CrFeTaV})_{1-x}\text{W}_x$ and at the following energies: 150keV for Ar, 5keV for D, 10keV for He. The black triangles refer to Ar and show the damage in the target calculated, in dpa. The blue circles and the blue squares refer respectively to D and He and show the concentration of the ions in the depth of the target, in $(\text{at}/\text{cm}^3)/(\text{at}/\text{cm}^2)$.

in dpa caused by argon implantation, whereas the two blue scatterplots represent the distribution of deuterium and helium in the depth profile of the target sample. The results of the fluence calculation for the five compositions are shown in Table 5.1, which also displays the theoretical density of the target before the ion implantation, determined by the software.

	Atomic density [at/cm ³]	Ar fluence [at/cm ²]
(CrFeTaV) ₉₅ W ₅	6.635 10 ²²	2.536 10 ¹⁶
(CrFeTaV) ₉₀ W ₁₀	6.605 10 ²²	2.487 10 ¹⁶
CrFeTaVW	6.553 10 ²²	2.363 10 ¹⁶
(CrFeTaV) ₇₀ W ₃₀	6.510 10 ²²	2.238 10 ¹⁶
(CrFeTaV) ₆₅ W ₃₅	6.491 10 ²²	2.146 10 ¹⁶

Table 5.1: Results from SRIM simulation of ion implantation in five compositions of (CrFeTaV)_{1-x}W_x.

5.3. Implanted samples: analysis of composition and microstructure

The ion implantation was carried out in the following sequence:

- the five samples were first irradiated with Ar⁺ ions with a fluence of 2.4 10¹⁶ at/cm² and energy of 150 keV;
- Subsequently, the samples were irradiated with He⁺ ions of 5 10¹⁷ at/cm² fluence and 10 keV energy. Then irradiation continued with D⁺ ions of 5 10¹⁷ at/cm² fluence and 5 keV energy per ion.

Following each implantation operation, characterization with GIXRD and SEM in BSD and SED mode was carried out to evaluate possible changes in phase composition, microstructure and topography with respect to the as-sintered condition.

5.3.1. Results of XRD analysis of irradiated samples

The XRD diffractograms of the Ar⁺, He⁺ and D⁺ implanted samples show that there are no new phases forming in the irradiated samples and all the phases recognized in the previous section persist also after this first implantation. No significant differences in compositions are witnessed with the XRD. For this reason, for each composition, a

comparison between the as-sintered, Ar^+ implanted and Ar^+ , He^+ and D^+ implanted XRD diffractograms will be presented. In particular, the following graphs will highlight the BCC1 (110) reflection, in order to emphasize the different responses of this phase to irradiation across the investigated compositions.

$(\text{CrFeTaV})_{95}\text{W}_5$

The comparison of XRD results in Figure 5.10 shows that no significant variation occurs for this composition after both irradiation procedures. The intensity of the peak of BCC1 slightly lowers with respect to the η -phase peaks.

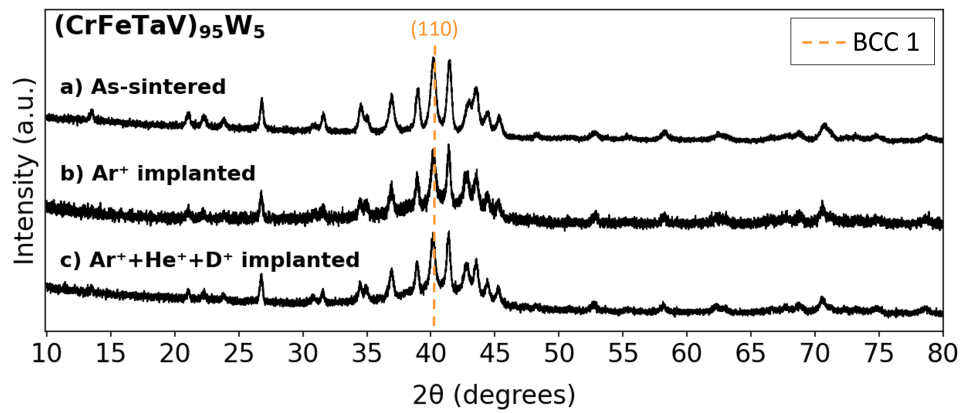


Figure 5.10: Comparison of XRD diffractograms of the $(\text{CrFeTaV})_{95}\text{W}_5$ sample as-sintered, after Ar^+ implantation and after He^+ and D^+ implantation.

$(\text{CrFeTaV})_{90}\text{W}_{10}$

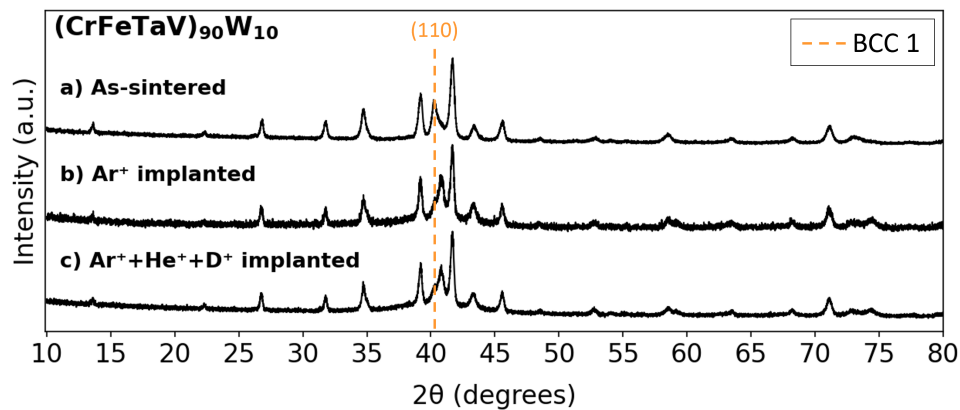


Figure 5.11: Comparison of XRD diffractograms of the $(\text{CrFeTaV})_{90}\text{W}_{10}$ sample as-sintered, after Ar^+ implantation and after He^+ and D^+ implantation.

From Figure 5.11 a shift in the position of the peaks of BCC1 emerges. It should

be noted that the diffraction peaks present a pronounced asymmetry, with the sample in as-sintered condition displaying a shoulder at higher diffraction angles, whereas the sample after both implantation procedures exhibit a shoulder at lower angles.

CrFeTaVW

The equimolar composition shows no shift in the position of the peaks but there is a variation of intensity, as displayed by Figure 5.12.

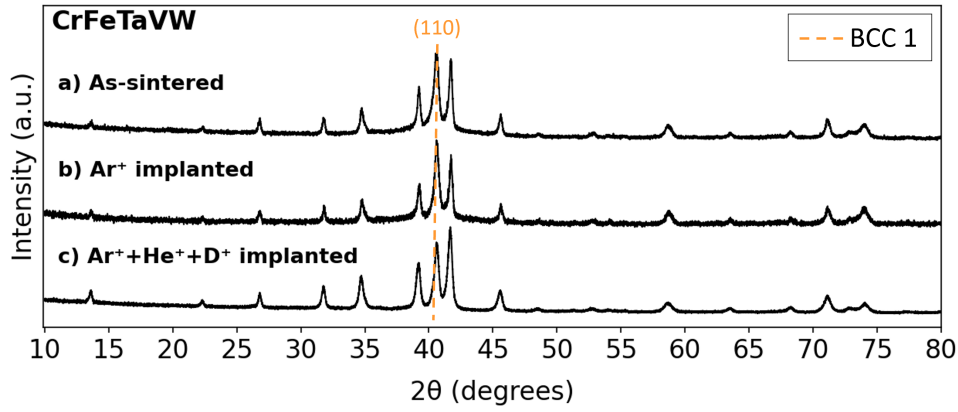


Figure 5.12: Comparison of XRD diffractograms of the CrFeTaVW sample as-sintered, after Ar^+ implantation and after He^+ and D^+ implantation.

$(\text{CrFeTaV})_{70}\text{W}_{30}$

What emerges from Figure 5.13 is that after the implantation with Ar^+ ions and even more so with He^+ and D^+ ions, the peaks of BCC1 increase in intensity with respect to the peaks of the η -phase and of BCC2.

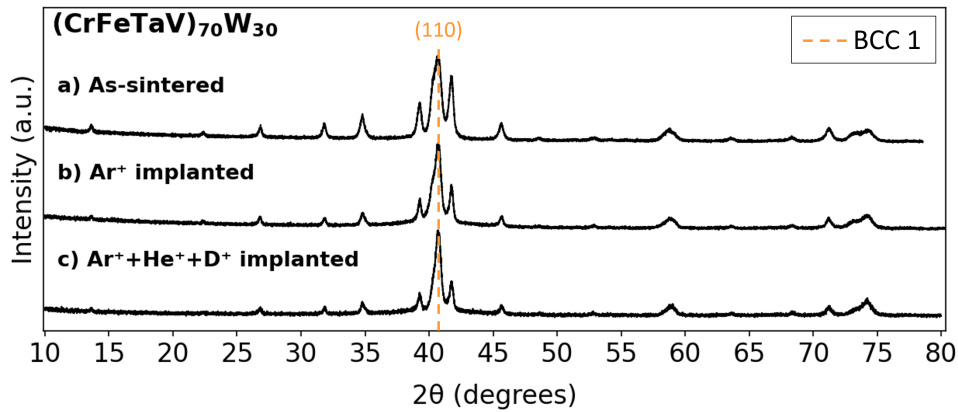


Figure 5.13: Comparison of XRD diffractograms of the $(\text{CrFeTaV})_{70}\text{W}_{30}$ sample as-sintered, after Ar^+ implantation and after He^+ and D^+ implantation.

(CrFeTaV)₆₅W₃₅

This composition exhibits a behavior similar to the previous composition, with an increase in intensity of the peaks of BCC1.

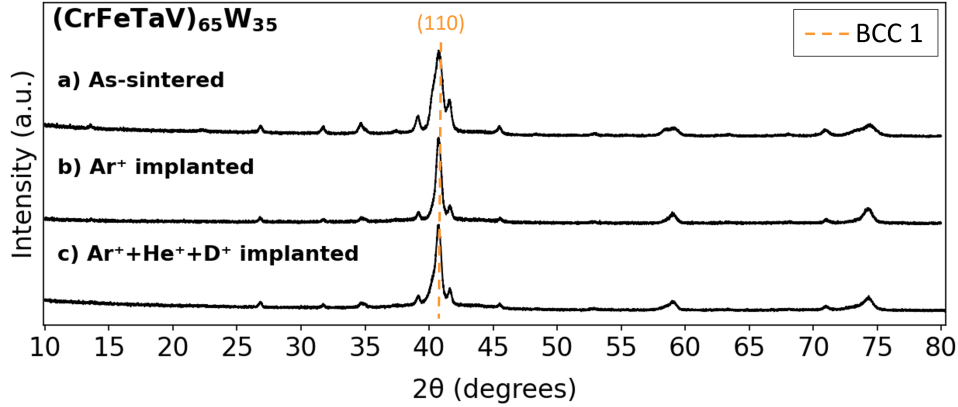


Figure 5.14: Comparison of XRD diffractograms of the (CrFeTaV)₆₅W₃₅ sample as-sintered, after Ar⁺ implantation and after He⁺ and D⁺ implantation.

5.3.2. Results of SEM analysis of samples after implantation

The SEM analysis of the implanted samples was carried out with the objective of investigating the changes in surface topography induced by the irradiation and to assess whether certain phases exhibit a higher or lower susceptibility to ion implantation. For each of the five composition, the analysis was carried out as follows.

To address the first point, the samples were examined with SEM in SE mode and with an inclination angle between the normal to the surface and the beam direction of 70°. This *tilted configuration* is used for the sample prior to irradiation, after the Ar⁺ implantation and in the final Ar⁺, He⁺, D⁺ implantation. The acquired images for the three configurations are compared for each composition, in order to comment the topography evolution before and after each irradiation step. In particular, the tilted configuration, allows for a better evaluation of possible protuberances or cavities on the surface.

For the second objective, the Ar⁺, He⁺, D⁺ implanted samples were examined with an inclination angle of 0° in both BSD and SED mode, in order to link the phases with the corresponding changes in surface topography, and to assess whether certain phases have a stronger reaction to irradiation.

Regarding the as-sintered samples, it should be noted that the surface was polished

prior to observation. The darker regions (valleys) can be attributed to softer phases, which undergo preferential material removal during the polishing process. In contrast, the brighter regions (protrusions) correspond to harder phases that are less affected by polishing and therefore remain slightly elevated. This phenomenon can be observed especially in the compositions $(\text{CrFeTaV})_{95}\text{W}_5$, $(\text{CrFeTaV})_{90}\text{W}_{10}$ and CrFeTaVW , where also from Figure 5.3 it can be noticed that the microstructure is characterized by larger phases. Conversely, in compositions $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$, the surface appears more homogeneous because of the much more refined microstructure.

$(\text{CrFeTaV})_{95}\text{W}_5$

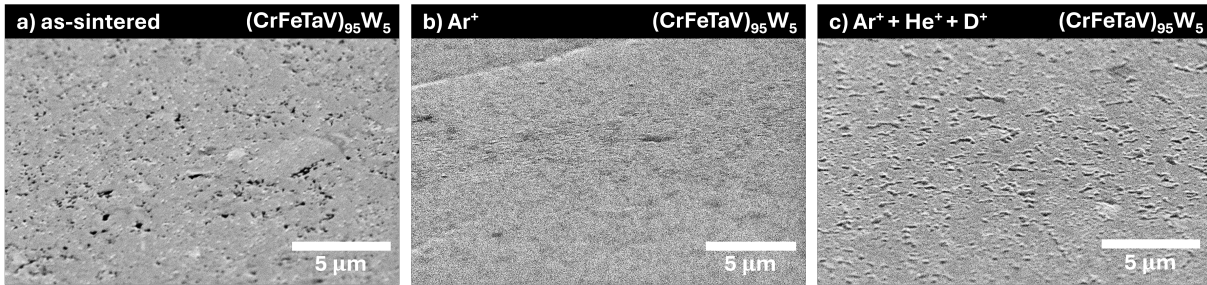


Figure 5.15: Sample $(\text{CrFeTaV})_{95}\text{W}_5$: comparison of surface topography of the as-sintered, Ar^+ implanted, Ar^+ , He^+ , D^+ implanted. SEM in SE mode and tilted configuration (70°).

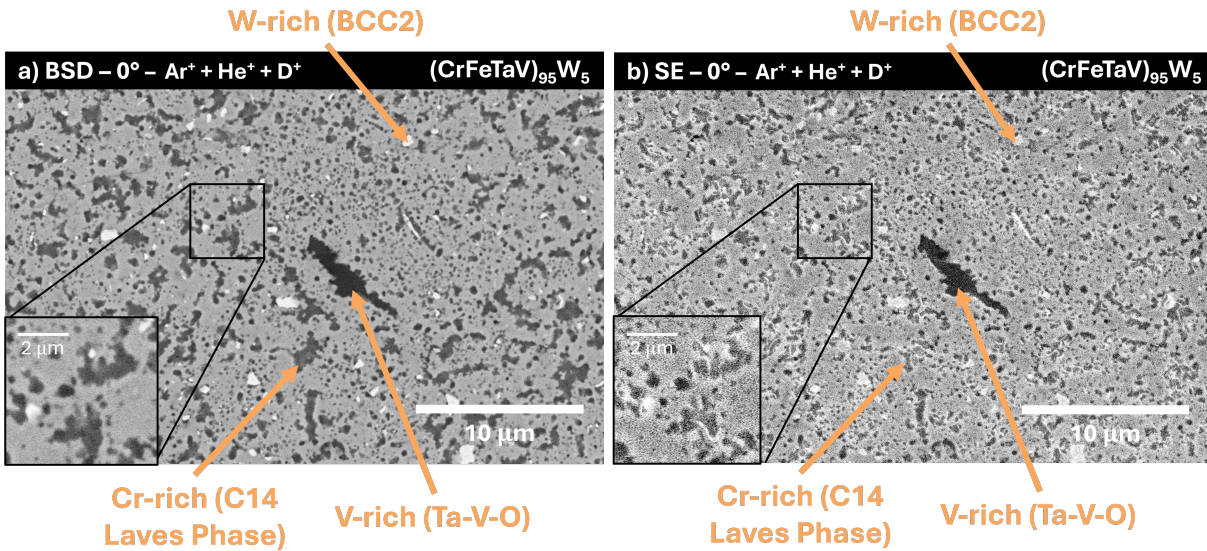


Figure 5.16: Sample $(\text{CrFeTaV})_{95}\text{W}_5$ Ar^+ , He^+ , D^+ implanted: comparison between BSD and SE mode in normal incidence (0°) on the same surface area.

Figure 5.15 shows that after Ar^+ implantation there is no significant effect on the

surface of the sample. In the Ar^+ , He^+ , D^+ implanted some protrusions develop on the surface of the sample suggesting the occurrence of blistering.

Figure 5.16 allows for a better comparison between the phase and the irradiation damage forming on the surface. It can be observed that in the solid solution, in the W-rich phase and in the V-rich phase, there is no evident irradiation damage, whereas in the C14 Laves phase the SE mode shows some edges within the area of the phase, suggesting the formation of blisters localized on that area. The zoom in the bottom left corner shows in more detail the evaluation of irradiation damage in the Laves phase.

$(\text{CrFeTaV})_{90}\text{W}_{10}$

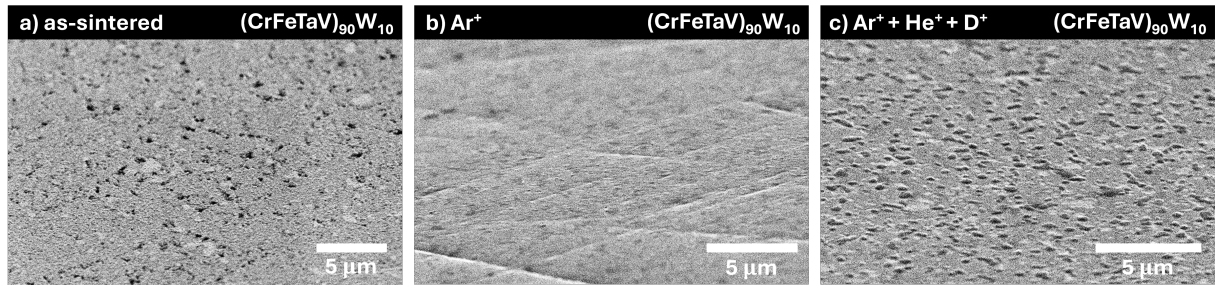


Figure 5.17: Sample $(\text{CrFeTaV})_{90}\text{W}_{10}$: comparison of surface topography of the as-sintered, Ar^+ implanted, Ar^+ , He^+ , D^+ implanted. SEM in SE mode and tilted configuration (70°).

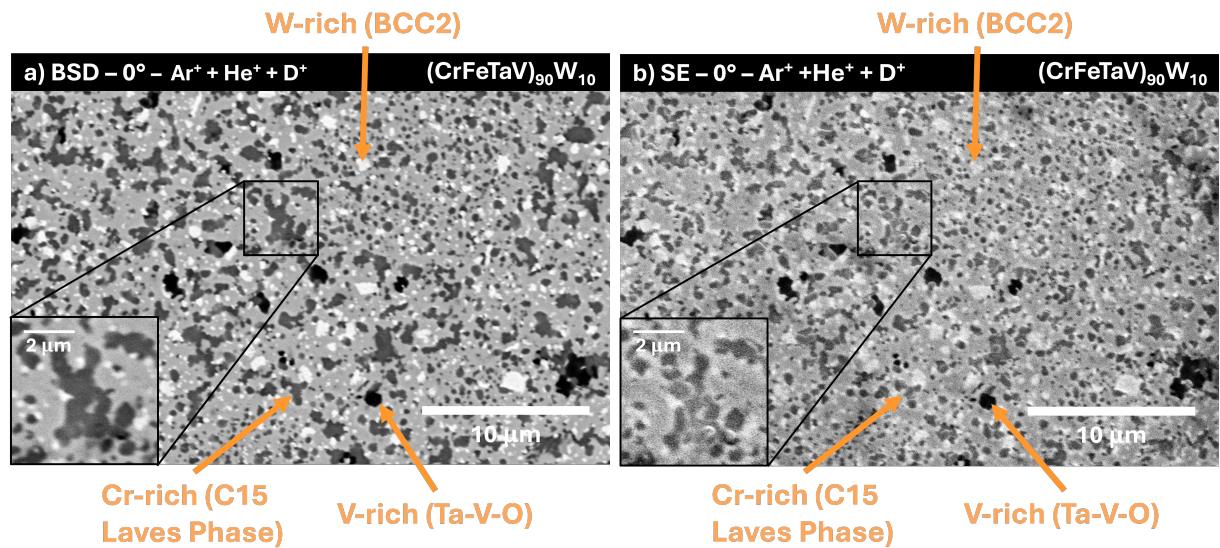


Figure 5.18: Sample $(\text{CrFeTaV})_{90}\text{W}_{10}$ Ar^+ , He^+ , D^+ implanted: comparison between BSD and SE mode in normal incidence (0°) on the same surface area.

Figure 5.17 shows that in the Ar^+ implanted no significant effects occur. In the Ar^+ , He^+ , and D^+ implanted samples, protrusions are observed on the surface, again suggesting the occurrence of blistering. Compared with the previous case, the blistering appears to be more severe.

Also in this case, like in the previous, Figure 5.18 shows that the W-rich phase and the V-rich phase present no evident irradiation damage. On the other hand, the Laves phase, that in this case is a C15, evaluated in SE mode displays some edges, leading to the conclusion that also in this case the blisters form preferentially in this area. If compared to the $(\text{CrFeTaV})_{95}\text{W}_5$ case, here the Laves phase occurs more and with larger structures, possibly explaining the more evident blistering in the SEM images with tilted configuration.

CrFeTaVW

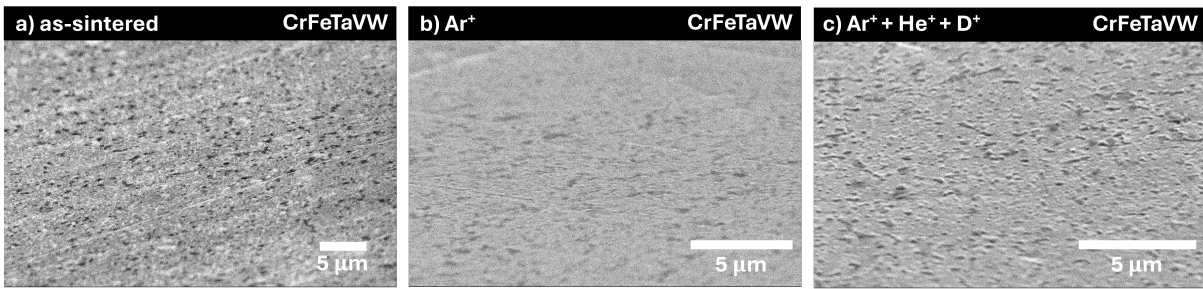


Figure 5.19: Sample CrFeTaVW: comparison of surface topography of the as-sintered, Ar^+ implanted, Ar^+ , He^+ , D^+ implanted. SEM in SE mode and tilted configuration (70°).

In Figure 5.19, the comparison between the as-sintered and Ar^+ implanted SE image suggest that some irradiation-induced void swelling is occurring on the surface of the sample, with the formation of very mild protrusions. In the Ar^+ , He^+ , and D^+ implantation, the sample displays many small protrusions and fewer larger ones.

It should be reminded that in this composition, in addition to the W-rich, the V-rich and the solid solution, also a Ta-rich phase forms. Figure 5.20 in SE mode reveals that the Ta-rich regions are surrounded by bright edges, suggesting that the protrusions are localized within these regions. However, it is now clear whether the protrusions could be explained by the formation of blisters or of volumetric swelling, since the Ta-rich regions are too small to allow the identification of individual blisters within them.

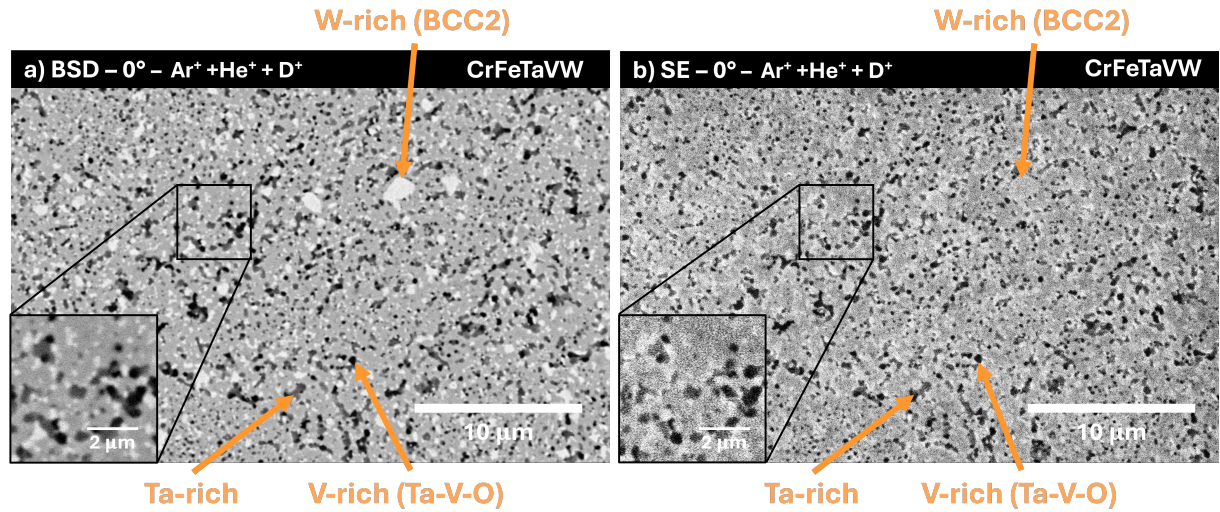


Figure 5.20: Sample CrFeTaVW Ar^+ , He^+ , D^+ implanted: comparison between BSD and SE mode in normal incidence (0°) on the same surface area.

$(\text{CrFeTaV})_{70}\text{W}_{30}$

This sample is characterized by a very refined microstructure. For this reason, the small and evenly distributed protrusions in Figure 5.19 c) may be attributed to the W-rich phase which is uniformly distributed in the sample. However, some large flat areas can be noticed as well, there no irradiation damage seem to have occurred. Looking at Figure 5.22, these areas seem to be associated with the CrFe-rich phase. The fine microstructure of this composition does not allow for further comments regarding localized irradiation damage, leading to rely only on previous consideration to justify the presence of the larger protrusion observed in the tilted configuration. One cannot exclude the presence, also in this composition, of a Ta-rich phase which is preferentially damaged as observed in the equimolar composition.

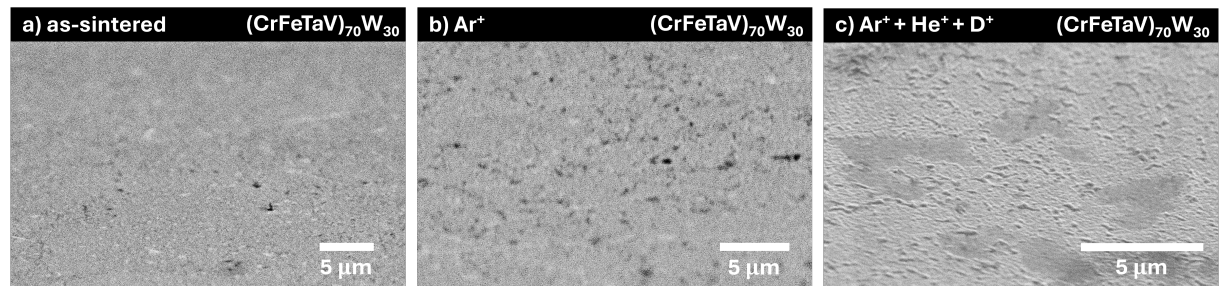


Figure 5.21: Sample $(\text{CrFeTaV})_{70}\text{W}_{30}$: comparison of surface topography of the as-sintered, Ar^+ implanted, Ar^+ , He^+ , D^+ implanted. SEM in SE mode and tilted configuration (70°).

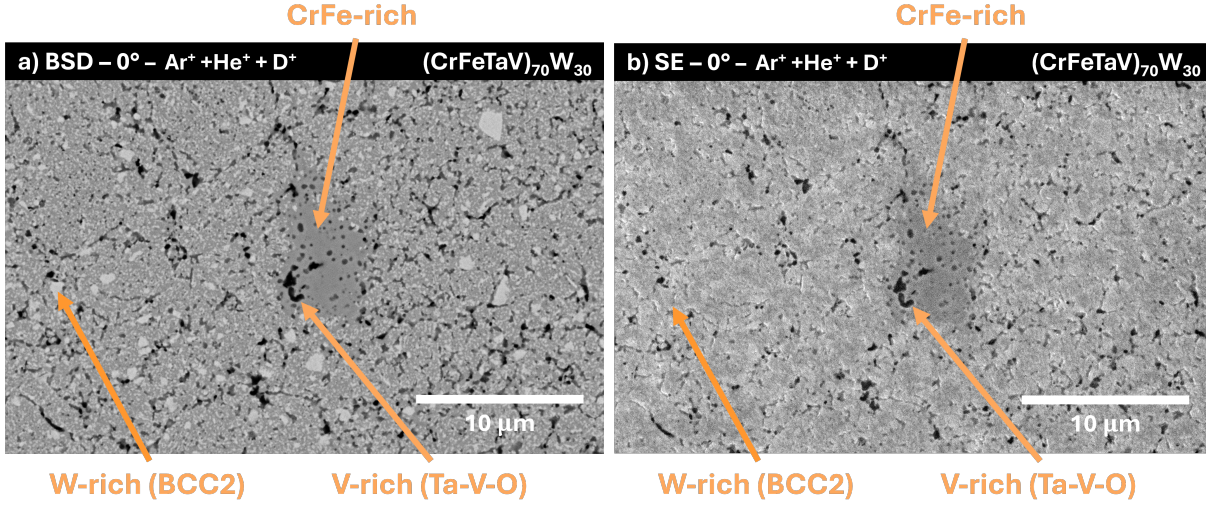


Figure 5.22: Sample $(\text{CrFeTaV})_{70}\text{W}_{30}$ Ar^+ , He^+ , D^+ implanted: comparison between BSD and SE mode in normal incidence (0°) on the same surface area.

$(\text{CrFeTaV})_{65}\text{W}_{35}$

Similarly to the previous case, this sample presents a CrFe-rich phase, which didn't present any irradiation damage. This phenomenon is confirmed also in $(\text{CrFeTaV})_{65}\text{W}_{35}$ composition, as evidenced by Figure 5.24. In this case, an EDS map was performed in order to confirm the composition of the CrFe-rich phase, as displayed in Figure 5.25. It can be observed that the CrFe-rich phase also presents all the other elements, with a slight depletion of W.

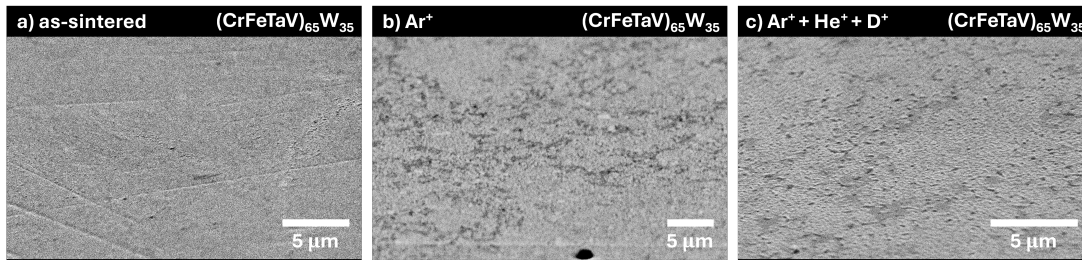


Figure 5.23: Sample $(\text{CrFeTaV})_{65}\text{W}_{35}$: comparison of surface topography of the as-sintered, Ar^+ implanted, Ar^+ , He^+ , D^+ implanted. SEM in SE mode and tilted configuration (70°).

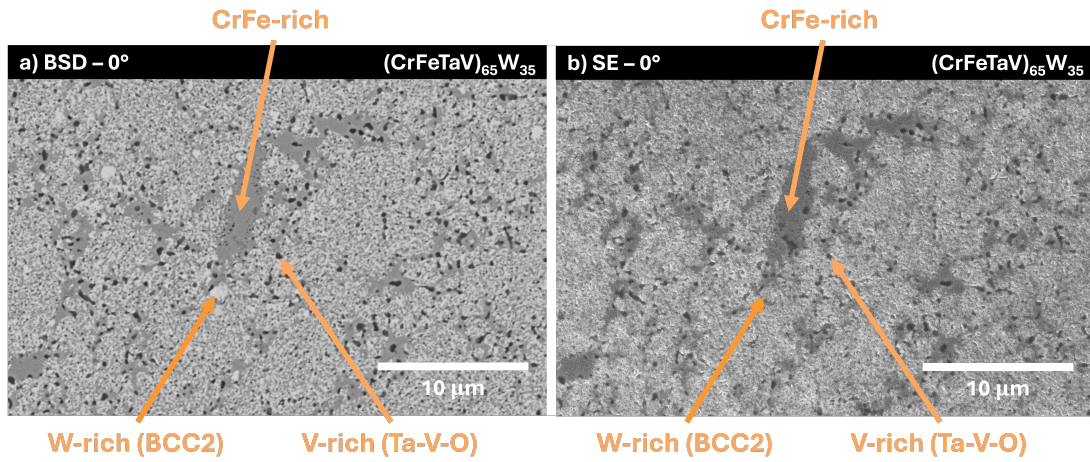


Figure 5.24: Sample $(\text{CrFeTaV})_{65}\text{W}_{35}$ Ar^+ , He^+ , D^+ implanted: comparison between BSD and SE mode in normal incidence (0°) on the same surface area.

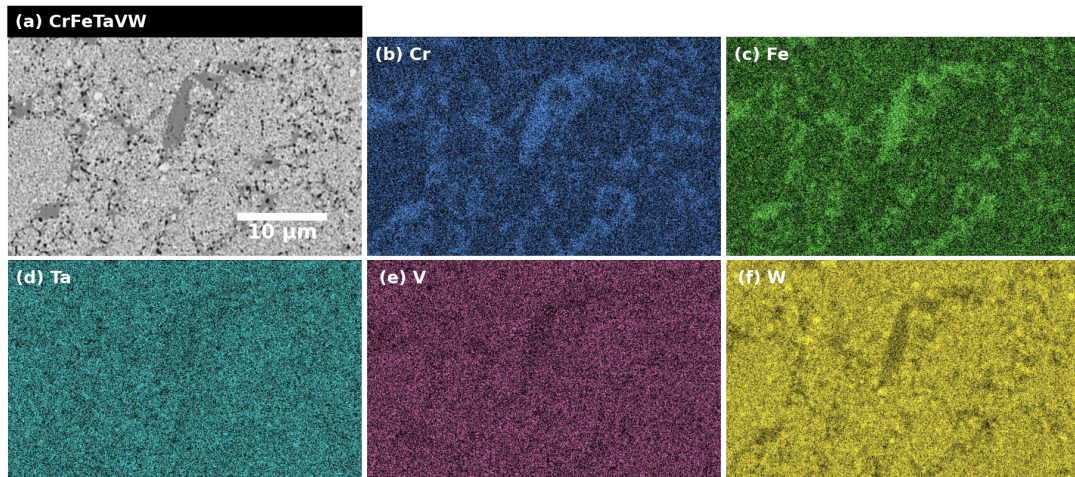


Figure 5.25: Sample of $(\text{CrFeTaV})_{65}\text{W}_{35}$ after Ar^+ , He^+ and D^+ implantation. (a) SEM image collected in BSE mode and EDS maps for (b) Cr-L α , (c) Fe-L α , (d) Ta-L α , (e) V-L α , (f) W-L α X-ray lines.

5.4. Summary and discussion on evolution of microstructure and topography after irradiation

Now, a summary of the results regarding morphology and phase composition prior to irradiation, and variation in phase composition and surface topography after implantation will be reported for each sample, combining the results of the GIXRD, SEM in BSE and SE mode and EDS maps. One observation that is common to all samples is that the carbide

phase only emerges from the GIXRD but it is not identified from the SEM images. This does not allow to evaluate the specific composition of the M_6C , which could possibly be a $W_3(Cr, Fe, V)_3C$. Additionally, all samples show great phase stability throughout the all irradiation steps, with no evidence of irradiation-induced phase transformations or phase segregation.

- **(CrFeTaV)₉₅W₅**: The as-sintered sample presents a Phase-A which is W-rich, Phase-B which corresponds to the HEA BCC1, Phase-C which is the Ta-V-O phase and Phase-D that is the C14 Laves phase of composition $Ta(Cr, V)_2$. After Ar^+ , He^+ and D^+ implantation, BCC1 peaks in the diffractogram show a slight decrease in intensity. With regards to topography, the Laves phase presents large blistering formation localized in its area after He^+ and D^+ implantation. No other significant variation in surface topography is witnessed.
- **(CrFeTaV)₉₀W₁₀**: This composition is similar to the previous one of W-5%. The main differences are that Phase-D is substituted by Phase-E, which is a C15 Laves phase and that also presents blistering after implantation with He^+ and D^+ . Then BCC1, instead of varying in intensity, presents a shift in lattice parameter after the first irradiation step with Ar^+ .
- **CrFeTaVW**: In this case, the as-sintered sample presents a Phase-A which is W-rich, Phase-B which corresponds to the HEA BCC1, Phase-C which is the Ta-V-O phase and Phase-F that is Ta-rich with strong depletion in W and Fe and a minor depletion in V. The GIXRD shows a variation in intensity of the BCC1 peaks, while the SEM results witness some volumetric swelling after the Ar_+ irradiation, which increase significantly after the implantation with He^+ and D^+ . With the BSE pictures in normal configuration it is possible to conclude that the volumetric swelling is localized in the Ta-rich phase.
- **(CrFeTaV)₇₀W₃₀**: Here, the microstructure of the sample is very fine both before and after implantation. Phase-A is W-rich, Phase-B corresponds to the HEA BCC1, Phase-C is the Ta-V-O phase and Phase-F is a CrFe-rich phase with only a minor depletion in W. Possible additional phases cannot be excluded from the SEM images due to the difficult separation of the very small phases. After implantation the BCC1 peaks increase in intensity, while the topography presents some protrusions after He^+ and D^+ implantation. However, because of the fine microstructure, it is difficult to establish a clear correlation between the observed irradiation-induced damage and the corresponding phases.
- **(CrFeTaV)₆₅W₃₅**: For this sample, no significant deviations from the observations

reported for the sample of W-30% are identified.

5.4.1. Discussion on phase composition and phase stability after irradiation

All the phases that form after the consolidation procedure persist after the irradiation steps, showing good phase stability. The observed stability of the HEA phase is consistent with the behavior predicted in Section 2.3.1, where HEAs are described as exhibiting excellent phase stability and resistance to irradiation-induced phase transformations. Regarding the Laves phases, irradiation-induced amorphization is among the most commonly reported irradiation effects [129]. However, no evidence of this phenomenon is observed in this study, as both the C14 and C15 phases remain detectable in the XRD diffractograms after irradiation.

The effects of irradiation on BCC HEA solid solution usually witnessed in literature are mainly a variation in crystallite size and lattice strain. The crystallite size is usually found to decrease because of the introduction of irradiation-induced defects in the lattice [132]. However, literature also reports the opposite behavior, an increase in crystallite size attributed to defect recombination processes promoted by the thermal spike generated by the energy released during a PKA event [37]. On the other hand, lattice strain is usually found to increase because of the lattice distortion introduced by defect clustering [37, 132]. Both lattice strain and crystallite size variation have an effect on the broadening of the peak. Hence, both phenomena could be studied by separating the Lorentian and Gaussian component of the pseudo-Voigt fit, as reported in Section 3.3.3. Nonetheless, in this experiment, the BCC1 peak is, possibly in all compositions, superimposed to the BCC2 peak, so this type of analysis is not carried out in this thesis work. Further considerations on the variation of BCC1 will only be qualitative analyses.

Considering the four compositions of $(\text{CrFeTaV})_{95}\text{W}_5$, CrFeTaVW , $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$, the peaks of BCC1 present a variation in intensity with respect to the other phases after the irradiation steps. Specifically, $(\text{CrFeTaV})_{95}\text{W}_5$, CrFeTaVW present a decrease in intensity while $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$ an increase, also with respect to the peak of BCC2. No strong conclusions can be drawn with regards to this behavior, given the complex superposition of BCC1 and BCC2, possibly in all these samples. It should however kept in mind that the variation in intensity could also be given by the strong dependence of GIXRD on surface texture.

In composition $(\text{CrFeTaV})_{90}\text{W}_{10}$, the (110) reflection of BCC1 shows strong variations in the shape. Particularly, its lattice parameter shifts towards lower values after the first

implantation step. Generally, it is found that lattice parameter increases after irradiation due to the introduction of defects [37]. However, the opposite behavior is found here. Transposing what explained before with regards to the crystallite size, the lattice parameter decrease could be explained by a dominance of the recombination effects favored by PKA induced thermal spikes over the defects accumulation process. It should be highlighted that the shift of BCC1 after implantation reveals the presence of another peak with lattice parameter close to that of W. BCC2 unequivocally shows only in the diffractograms of $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$. However, this result may lead to the conclusion that BCC2 can be in fact present in all composition but it doesn't show because it is superimposed to the BCC1 peaks. Once again, this can only be confirmed with SEM analysis.

5.4.2. Discussion of topography evolution after implantation

Regarding the samples irradiated with Ar^+ ions, CrFeTaVW is the only composition that exhibits a distinguishable difference in irradiation response between phases, with the Ta-rich phase appearing to undergo localized swelling. However, the possibility of volumetric swelling occurring uniformly throughout all phases cannot be excluded.

The most significant variation in surface topography occurs after Ar^+ , He^+ and D^+ implantation, with the formation of blisters in certain regions of the sample. Observing the formation of blisters on the surface of the sample can give information on structural damage in the internal regions of the sample. As described in Section 1.3.1, surface blistering develops due to the gas (He and D) bubbles that form below the surface, in the area of maximum concentration of the gasses. In particular, it is possible to correlate the bubble evolution with the development of blisters on the surface of the material. According to the gas-driven model of blistering formation, the increase in gas buildup leads to inter-bubble fracture and generation of nanocracks, which in turn lead to the formation of cavities that swell progressively with gas accumulation. These cavities are finally responsible for the development of surface blisters [37, 38].

According to Cheng et al. [72], that compared the resistance to He irradiation of W and a W-based HEA of composition CrMoTaWV, the development of smaller and more dispersed bubbles in the HEA leads to the suppression of surface blistering process. In particular, the paper highlights how the combined effect of enhanced He trapping and reduced He mobility given by the properties of HEA lattice, suppresses the development of large He bubbles, leading to the formation of nanometric He bubbles, as witnessed also by other authors in other W-based HEAs [78]. As a consequence, it should be expected

that the presence of small surface blisters is an indicator of the formation of smaller and more uniformly dispersed gas bubbles and consequently superior irradiation resistance, even if the correlation also includes a complex interplay of other factors.

In all compositions, the solid-solution phase (BCC1) does not exhibit blistering in the SEM images acquired during this work. The absence of large (micrometric) blisters is consistent with the behavior discussed above for W-based HEAs. Therefore, the observations made for the composition chosen for this thesis work are in agreement with previous findings reported for other W-based HEAs.

In compositions $(\text{CrFeTaV})_{95}\text{W}_5$ and $(\text{CrFeTaV})_{90}\text{W}_{10}$, the presence of Laves phases determines the formation of large localized blistering. Previous studies on the irradiation resistance of Laves phases have highlighted their susceptibility to irradiation-induced damage. According to Pu et al. [37], Laves phases show lower irradiation resistance if compared to BCC phases, exhibiting the formation of larger He bubbles. Again, considering the relation between bubble size and blistering formation, the micrometric protrusions observed in this thesis work suggest the formation of larger gas bubbles, in agreement with literature results.

In the equimolar composition CrFeTaVW, the SEM analysis of the Ar^+ , He^+ and D^+ implanted sample witnesses the formation of protrusion localized in the Ta-rich regions. Additionally, the fact that the other samples after Ar^+ implantation don't show any localized variation in the surface topography may suggest that the mild protrusions observed in CrFeTaVW after Ar^+ are linked to the Ta-rich phase (Figure 5.19). This would lead to the conclusion that within the Ta-rich region there is a combination of two irradiation-induced damage effects. First, the void swelling caused by the defects generated by the Ar^+ ions. Secondly, the formation of He bubbles with possible intrusion of D that leads to the increase in size of the protrusions. Overall, in BSE images (Figure 5.20) the effect of these two phenomena results in a volumetric swelling localized on the Ta-rich areas. According to Wang et al. [133], that studied the irradiation response of a CoCrFeCuNi HEA, the formation of Cu-rich phases can promote preferential irradiation-induced volume swelling. The justification for this phenomenon lies in the fact that Cu-rich phases may act as local low-stress regions because of the more loosely packed He atoms, causing the migration of He atoms in all the sample toward the Cu-rich phases, resulting in an increased severity of volume swelling in that area. This phenomenology may be applied also in the case of Ta-rich phases, which may be the regions where He bubbles preferentially migrate, especially after the defects introduced by the Ar^+ implantation.

Compositions $(\text{CrFeTaV})_{70}\text{W}_{30}$ and $(\text{CrFeTaV})_{65}\text{W}_{35}$ present large CrFe-rich phases

that show no swelling or blistering phenomena at the micrometric scale. This result should be compared with the equimolar composition, where the Ta-rich phase shows instead a worse irradiation response than the HEA solid solution. The difference may lie in the composition of the two phases. The stoichiometric composition cannot be measured with certainty by the SEM equipment used for this thesis work, because the phases are too small to allow the point analysis to be performed. However, with the aid of EDS maps, it is possible to evaluate the presence of the different elements inside the phase. It was observed in Figure 5.6 that prior to implantation, the composition of the Ta-rich phase in the equimolar sample was strongly depleted in all elements apart from Cr. On the other hand, the CrFe-rich phase is only mildly depleted in W, while presenting a strong contribution of all the other elements. This suggests that it may preserve some of the characteristics responsible for the enhanced irradiation resistance of HEAs and, consequently, exhibit a similar irradiation response. This behavior may be particularly evident in the CrFe-rich phase because its dimensions are considerably larger than those of the other microstructural features present in the samples. Indeed, its large size would facilitate the observation of irradiation-induced effects, whereas in finer microstructures it becomes difficult to distinguish topographical changes caused by irradiation from those resulting from differential material removal during polishing.

In conclusions, the samples with a lower amount of W (W-5% and W-10%) lead to the formation of Laves phases, which exhibit the least favorable irradiation response among the phases identified in these samples. In the equimolar composition, the partition of a Ta-rich phase possibly leads to a localized irradiation-induced volume swelling. The presence of this phase cannot be excluded also from the last two samples of W-30% and W-35%, where the microstructure is so fine that only the large CrFe-rich phases can be analyzed. Overall, the development of void swelling and He bubble formation, witnessed by the formation of surface blisters, could have a negative impact on the mechanical and thermal properties of the material, causing the reduction of thermal conductivity, embrittlement and loss of ductility [72].

6 | Conclusions and future developments

In this chapter, the conclusions of the experimental results and goals of this thesis work will be drawn, together with some considerations of future analysis that could improve the characterization and analysis of the considered samples.

Conclusions

This thesis work aimed to develop a $(\text{CrFeTaV})_{1x}\text{W}_x$ HEA via mechanical milling and to investigate its response to irradiation. These studies were conducted to evaluate this HEA system for its application as a functionally graded material in the thermal break interlayer of a divertor target monoblock.

In the first part of the thesis, the focus lied on the production via mechanical milling of the powder samples CrFeTaVW, the equimolar composition of the HEA chosen for this thesis work. The operating parameters of the planetary ball mill were optimized to achieve the formation of a single-phase solid solution, addressing the main challenge associated with the presence of W. Due to its mechanical properties, W undergoes rapid strain hardening as a consequence of the high density of defects introduced during the milling process, thereby hindering the diffusion of the alloying elements. The theoretical model used to correlate the operating parameters of the planetary ball mill to the mechanisms of alloying proved to be essential in the identification of threshold values of energy and energy rate to impart the system in order to obtain complete alloying of all the elements. In the end, a single solid solution of BCC crystal structure was obtained for the HEA, with the inclusion of an CrFe intermetallic and, depending on the milling conditions, also a TaVO_4 .

The irradiation of these samples was aimed at simulating the conditions of a D-T plasma. After the irradiation with Ar^+ , He^+ and D^+ , the formation of surface blistering allowed for an indicative evaluation of internal irradiation-induced damage, especially of He and D bubble formation. What emerged was an overall good irradiation resistance of the HEA and of the CrFe-rich phase. The Laves phases presented large localized blisters,

suggesting the poor performance of this phase after irradiation while the Ta-rich phase showed some localized volumetric swelling after He^+ and D^+ implantation and possibly also after the sole Ar^+ implantation.

These results suggest an improved irradiation resistance of the selected five-element alloy compared with the quaternary CrTaVW alloy widely reported in the literature, in which a segregation of the smaller-radius elements has been observed under irradiation. Nevertheless, no definitive conclusions can be drawn regarding the evolution of irradiation-induced damage within the bulk of the material, as SEM analysis is limited to the sample surface. Therefore, the assessment of irradiation resistance presented in this thesis should be regarded as partial, providing valuable indications of the material's behavior while highlighting the need for further investigations aimed at characterizing subsurface irradiation effects.

Future developments

Concerning the powder production, it would be interesting to implement the theoretical model by refining the dependence of the transferred energy to the elemental composition considered, and by including the frictional mechanism of energy transfer for more accurate predictions. In this way it would be possible to apply the model for the optimization of other conditions of milling, other compositions of HEAs and to other planetary ball mills.

Regarding the irradiation resistance analysis, Transmission Electron Microscopy (TEM) would be a valuable tool for investigating the formation of dislocation loops, voids, and He and D bubbles beneath the sample surface. This would provide a more comprehensive understanding of the irradiation-induced damage mechanisms and allow the response of the individual phases to be assessed separately.

Annealing experiments should be carried out to assess the thermal stability of the different phases under the high-temperature conditions expected in their intended application. In addition, annealing would likely promote the increase of phase size, thereby facilitating phase separation and improving the quantitative identification of their elemental composition through SEM point analysis. This would also enable a more reliable evaluation of the irradiation-induced damage associated with each phase.

In order to evaluate the feasibility of the proposed HEAs for the application in the monoblock interlayer, mechanical and thermal evaluations should be performed. First of all, mechanical tests of hardness are aimed at evaluating the resistance of the material to the stress concentrations they would be subject to in the interlayer. Secondly, analyses

aimed at measuring the thermal conductivity of the material are useful to assess their performance as a thermal break interlayer.

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