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Executive Summary of the Thesis

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

Laurea Magistrale in Nuclear Engineering - Ingegneria Nucleare

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1. Introduction

In the framework of research on nuclear fusion, tokamak machines confine the plasma with a configuration of magnetic fields. One of the biggest projects for magnetic confinement nuclear fusion is International Thermonuclear Experimental Reactor (ITER), which aims at proving the feasibility of fusion as a new energy source. ITER is designed to operate with a deuterium–tritium (D–T) plasma in a divertor tokamak configuration. The divertor is a component of the tokamak that is situated at the bottom of the vacuum vessel and its role is to extract heat and ash produced by the fusion reaction in order to minimize the contamination of the plasma and to protect the walls of the device. The design of the divertor targets, which are the components subjected to the most severe thermal and irradiation loads, is particularly challenging and relies on the selection of materials capable of withstanding such extreme conditions. Each divertor target is formed by a matrix of monoblocks composed of a tungsten (W) armor and a CuCrZr heat sink tube.

The interface between these materials is a critical aspect of the design due to two main factors: the operation temperature window of the copper-alloy and the stress field that generates at the interface. The first refers to the range of temperatures that the CuCrZr alloys should maintain in order to maintain optimal mechanical properties and that is equal to $\approx 200 \div 350$°C. Regarding the second point, the mismatch in thermal expansion of the two materials generates a concentration of stress at the interface between the pipe and the W armor [1]. To mitigate these issues, the ITER monoblock design incorporates a Cu interlayer. However, this solution has only limited effectiveness in reducing both the stress concentration and the thermal constraints imposed by the CuCrZr alloy. An alternative to the Cu interlayer is proposed and investigated in this thesis. The concept consists of a thermal break interlayer designed to maintain the CuCrZr heat sink within its optimal operating temperature range. The proposed solution is based on functionally graded materials (FGMs), a class of composite materials whose gradual variation in composition and properties would allow to reduce stress concentrations at the interface. Specifically, the material investigated for the FGM is a High Entropy Alloy (HEA) of composition $(CrFeTaV)_{1\text{-}x}W_x$.

This thesis mainly focuses on the irradiation load characteristic of ITER tokamak. The D-T plasma produces a large number of high-energy neutrons (14 MeV) which escape from the plasma and irradiate the materials of the reactor vessel. The neutrons entering the material can generate two different effects. First, the collision between the neutrons and the atoms of the material generates displacement cascades that introduce defects such as vacancies and interstitials. The accumulation of these defects can lead to the formation of dislocation loops and voids. Overall, irradiation-induced defects can inhibit dislocation motion, degrading the mechanical behavior of metals, hence promoting hardening, embrittlement, and irradiation creep in the material. Secondly, neutrons also initiate nuclear reactions of transmutation in the material, in some cases leading to the production of gas atoms such as helium and hydrogen isotopes. Both neutron-induced irradiation damage and transmutation effects are relevant to the performance of the monoblock interlayer investigated in this work.

2. 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.%. The microstructure and properties of HEAs are affected mainly by four core effects. The first is the *high entropy effect*: the significantly high values of mixing entropy given by the large number of elements in the alloy. This promotes the stability of solid solutions over intermetallic compounds and segregated phases. The *severe lattice distortion* effect arises from the different atomic sizes of the constituent elements, which generate local lattice strains and stresses and that consequently hinders dislocation motion and strengthens the alloy through solid-solution hardening. The *sluggish diffusion effect* is related to the value of diffusion coefficients of atoms, which in HEAs is found to be lower than in conventional alloys or pure metals. This reduces atomic mobility, slowing microstructural evolution and enhancing high-temperature performance. Finally, the *cocktail effect* arises from the combined interactions among multiple elements and phases, leading to properties that cannot be predicted by the simple rule of mixtures.

One of the techniques used to produce HEAs is mechanical alloying, a solid-state powder processing technique capable of synthesizing a variety of alloy phases starting from blended elemental powders. 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 mechanical alloying involves the optimization of a number of variables with the aim of achieving the desired product phase or microstructure. The operational variable are, in most types of milling equipments, milling speed, milling time, the choice of grinding medium and the ball-to-powder weight ratio.

For applications in nuclear fusion, the most investigated class of HEAs are refractory HEAs (RHEAs), that contain elements with high melting points and consequently exhibit better high-temperature performance. Additionally, HEAs containing low-activation elements, commonly referred to as low-activation HEAs (LAHEAs), have been proposed to minimize the quantity of radioactive waste. These materials have also demonstrated enhanced irradiation resistance compared with conventional alloys. The mechanisms that may account for this behavior include higher resistance to irradiation defect formation, lower void swelling, higher microstructural and phase stability and finally limited irradiation hardening [2]. Furthermore, the combination of refractory and low-activation elements typically promotes the formation of BCC-structured alloys, which are known to exhibit enhanced irradiation resistance compared with other crystal structures.

One extensively studied composition for fusion applications is a W-Ta-Cr-V-based HEA, first developed by El Atwani et al. [3], which shows good resistance to irradiation damage and good mechanical properties. Nevertheless, this alloy has consistently exhibited phase separation in the form of Cr- and V-rich precipitates. To improve its thermodynamic stability under irradiation, additional alloying elements have been introduced, leading to the development of quinary alloys derived from the original quaternary composition. The alloy considered in this work is a Cr–Fe–Ta–V–W based HEA, in which Fe is incorporated owing to its good ductility and low cost.

3. Thesis goals

The composition investigated in this thesis work is a Cr–Fe–Ta–V–W containing HEA for the application as a FGM in a thermal-break interlayer for the divertor monoblock. The first goal of this work is related to the production of the considered system via mechanical milling carried out with a planetary ball mill equipment. Specifically, the aim is to optimize the operational parameter of the mill in order to obtain a single solid solution of the reference composition of equimolar CrFeTaVW. The additional goal is to experimentally validate the mechanisms governing mechanical milling and possibly correlating them to a theoretical model developed to assess the energy transferred from the milling media to the powder particles.

The second part of the thesis focuses on five samples consolidated via spark plasma sintering (SPS) prior to this thesis work. They are $(CrFeTaV)_{95}W_5$, $(CrFeTaV)_{90}W_{10}$, CrFeTaVW, $(CrFeTaV)_{70}W_{30}$, $(CrFeTaV)_{65}W_{35}$ and they are designed to be part of a five-layer FGM. The investigated alloys are assessed under conditions representative of a D–T plasma tokamak environment, with the aim of evaluating their response to irradiation damage. In particular, the focus lies on the evaluation of the phase stability of the alloys following irradiation and the investigation of irradiation-induced surface modifications, such as swelling and blistering, and the correlation of these features with the different phases present in the microstructure.

4. Experimental methods

For the production of the mechanically alloyed powders of CrFeTaVW, some operational parameters were varied in the different experimental trials in order to evaluate the optimal combination needed to obtain a single solid solution. The parameter of rotations per minutes (rpm) was kept at 350, while milling time (t_m), ball-to-powder ratio (bpr), diameter of milling balls (d_b) were varied. The samples were analyzed with powder X-ray diffraction (XRD) in Bragg-Brentano geometry to evaluate the phase composition in the powder particles and subsequently with Scanning electron microscopy (SEM) in backscattered electrons (BSE) mode and with an Energy Dispersive Spectroscopy (EDS) detector, the combination of which allowed to determine the particle size distribution of the powder and the distribution of the elements in the sample.

The samples consolidated via SPS prior to this work, were here characterized via Grazing incidence XRD (GIXRD) and SEM in BSE and EDS mode, in order to evaluate in detail the phases formed in the material after the SPS process. Then, the samples were implanted in a first step with Ar^+, in order to simulate the irradiation damage caused by neutron escaping the plasma. In fact, high energy heavy ions have been identified as a good proxy to study the effect of neutron irradiation [4] and in this case particularly, Ar was chosen to perform the irradiation, since it is an inert gas and it is inexpensive. In a second moment, sample were irradiated with He^+ and D^+ at the same time, in order to account for the gas transmutation products that form in the material because of neutron irradiation. The implantation was carried out with a Danfysik 1900 implanter (Taastrup, Denmark). The fluence and energy of the ions were evaluated with simulations on software SRIM. The aim was to produce an irradiation damage with the Ar^+ ions of 100 dpa (a conservative value accounting for 5 years of operation in Demonstration Power Plant DEMO) and to overlap the implantation profiles of He^+ and D^+ with the damage profile caused by Ar^+ implantation. The chosen values are reported in Table 1. Subsequently, the samples were characterized after each irradiation step with GIXRD and SEM in BSE and EDS mode, in addition to Secondary electron (SE) mode to assess the topography of the samples.

	Energy [keV]	**Fluence [at/cm^2]**
Ar^+	150	$2.4\ 10^{16}$
He^+	10	$5\ 10^{17}$
D^+	5	$5\ 10^{17}$

Table 1: Fluence and energy values chosen for implantation of Ar^+, He^+ and D^+ ions.

5. Results and discussion

5.1. Production of CrFeTaVW and optimization of planetary ball machine

Prior to the experimental trials for the production of the alloy, a theoretical model based on a collision approach was developed, in order to estimate the transfer of energy from the milling media to the powder particles. At first, the model was applied to evaluate the values of energy and energy rate used to produce W-based HEA with another and already optimized planetary ball mill in use in the IPFN laboratories. This allowed to set an indicative reference value for the operations with the newly acquired mill. The first milling experiment was carried out by keeping a fixed value of 10:1 bpr and increasing progressively the milling time from 1h to 6h with a 1h step. According to the theoretical model, the target transferred energy value would be reached after 5h of milling. Nonetheless, the XRD results showed the following behavior: the peaks of W remained sharp along the whole milling process, while the peaks of Fe, Cr, V, progressively broadened and decreased in height relatively to the W peak, suggesting their diffusion in other crystal structures. Finally, the peaks starting from Ta lattice parameter broadened and shifted towards larger values of lattice parameter progressively with time. According to Chen et al. [5], during the mechanical milling of HEAs, the alloying elements with lower melting temperature diffuse into the ones with higher melting temperature. Applying this hypothesis to the alloy analyzed here, Cr, Fe, V diffuse first into Ta and secondly into W. The XRD results hence suggest that the alloying sequence progresses up to Ta, whose crystal lattice modifies significantly with the inclusion of Cr, Fe, V. However, the sequence stops there, because the rapid work hardening of W prevents the inclusion of all the other elements into its lattice. An example of diffractogram for this set of experiments is reported in Figure 1.

Considering this challenge associated with milling W-based compositions, the subsequent experimental trials were designed to promote the diffusion of all alloying elements into the W lattice. To this end, a pre-alloyed W–Cr powder was employed and the milling time was set to 4 consecutive hours with the objective of maintaining a higher process temperature. Nevertheless, this approach did not lead to the desired result, suggesting that an energy transfer rate below the target value was a determining factor in the alloying behavior of W. Consequently, the bpr was increased to 20:1 in order to raise the energy transfer rate to the target level. What resulted from the experimental results was a powder characterized by a single BCC solid solution including all alloying elements, with the presence of a CrFe intermetallic and, in some cases, a $TaVO_4$. With this fixed value of bpr, the milling time was varied from 1h to 3h with a step of 1h. What emerged was an evolution of the W peaks that progressively broaden and slightly shift towards lower lattice parameters, suggesting the progressive inclusion of the other alloying elements. In addition, for low milling times, the presence of a second BCC structure associated with a distorted crystal structure of Ta, was also witnessed. Thanks to this experiment, it was possible to conclude that, other than having a certain value of transferred energy rate to overcome the challenges associated to the rapid work hardening of W, having a certain value of transferred energy is essential to achieve a complete alloying of all the elements. In fact, for energy values lower than a certain threshold value, the elements that first diffuse in Ta lattice have not fully completed the alloying sequence by diffusing into W lattice. A rep-

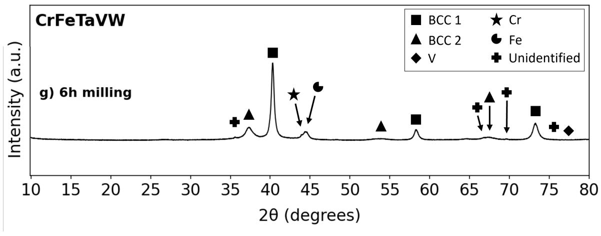

Figure 1: XRD of CrFeTaVW with milling parameters 350 rpm, 10:1 bpr, 6h milling time.

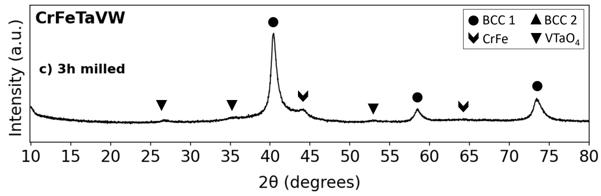

Figure 2: XRD of CrFeTaVW with milling parameters 350 rpm, 20:1 bpr, 3h milling time.

resentative diffractogram is displayed in Figure 2.

5.2. Characterization of bulk samples and irradiation resistance evaluation

The $(CrFeTaV)_{95}W_5$, $(CrFeTaV)_{90}W_{10}$, CrFeTaVW, $(CrFeTaV)_{70}W_{30}$, and $(CrFeTaV)_{65}W_{35}$ samples were consolidated by SPS prior to the start of this thesis. Consequently, the present work focused on the characterization of the microstructure developed during the SPS process. The elevated temperatures and pressures involved in SPS promoted the formation of additional phases compared with those present in the corresponding alloyed powders. GIXRD witnessed the presence in all samples of a carbide phase (M_6C η-phase) and an oxide of composition Ta-V-O, likely the result of carbon contamination from the milling and SPS equipment and residual oxygen exposure during processing, respectively. Only in $(CrFeTaV)_{95}W_5$ and $(CrFeTaV)_{90}W_{10}$, consolidation introduced Laves phases in the material. Laves phases are a common intermetallic phase with stoichiometry AB_2, where A atoms are larger and B atoms are smaller. They are tetrahedrally close-packed binary structures that can present different stacking sequences. In particular, the two structures present in the first two compositions are the C14 with an hexagonal arrangement and a C15 with a cubic one. With SEM analysis in both BSE and EDS mode, it was possible to recognize the phases and correlate them to the GIXRD results. What emerged from SEM analyses was a composition of both Laves phases of $Ta(V, Cr)_2$, the formation in CrFeTaVW of a Ta-rich phase stronlgy depleted in W and Fe, the development of a CrFe-rich phase in $(CrFeTaV)_{70}W_{30}$ and $(CrFeTaV)_{65}W_{35}$.

The samples were irradiated with Ar^+, He^+ and D^+ and subsequently characterized and compared with the samples prior to irradiation, in order to evaluate possible modifications in microstructure and surface topography. With SEM, the analysis of irradiation damage can be carried out by evaluating the surface of the material, which can only present some volumetric swelling and blistering formation. Then, variation in the surface of the sample can give information on structural damage in the internal regions of the sample. In all the samples after the irradiation with Ar^+, a uniform volumetric swelling cannot be excluded. In CrFeTaVW, however, the swelling is possibly localized in the Ta-rich phase. After the irradiation with Ar^+, He^+ and D^+, the samples were analyzed with SEM in two configurations. First, with SEM in SE mode and with an inclination angle of 70° between the normal to the surface and the direction of the electron (*tilted configuration*).By comparing the images acquired in this way before and after each irradiation step, it was possible to evaluate any variation in surface topography and the possible presence of volumetric swelling and blistering. Secondly, an inclination angle of 0° was used 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. What emerged from these analyses was that most samples displayed the formation of blisters on the surface. In particular, large blisters developed in both Laves phases in samples $(CrFeTaV)_{95}W_5$ and $(CrFeTaV)_{90}W_{10}$, suggesting a more severe irradiation damage de-

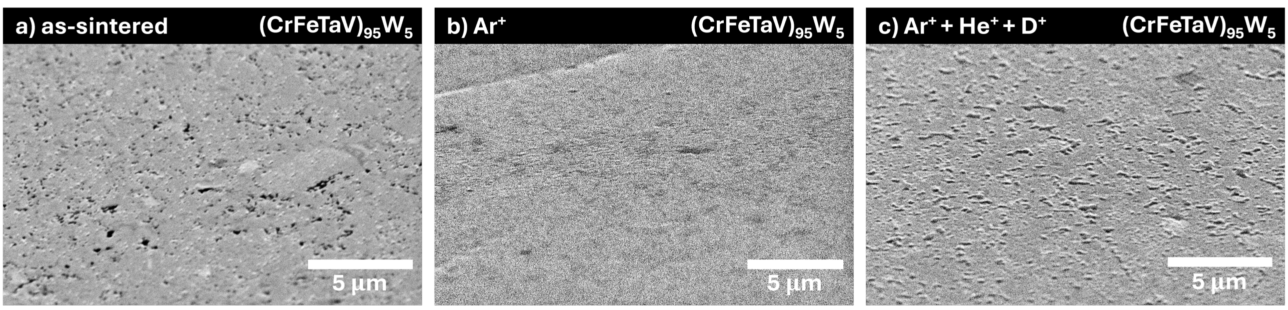

Figure 3: Sample $(CrFeTaV)_{95}W_5$: comparison of surface topography of the as-sintered, Ar^+ implanted, Ar^+, He^+, D^+ implanted. SEM in SE mode and tilted configuration (70°).

velopment in the subsurface of these phases. In CrFeTaVW, the Ta-rich phase presents an even more significant swelling after the implantation with He^+ and D^+. Finally, $(CrFeTaV)_{70}W_{30}$ and $(CrFeTaV)_{65}W_{35}$ samples present a very refined microstructure, that does not allow to separate the different phases. Moreover, it makes it difficult to distinguish between irradiation-induced surface protrusions and topographical features arising from the preferential retention of harder phases during polishing. However, the large size of the CrFe-rich phases allows to verify the absence of blisters localized in those regions. Since the elemental composition of this phase, emerging from the EDS map analysis, comprises all elements with a minor depletion of W, this phase may behave like the HEA solid solution, hence presenting superior irradiation resistance. Figure 3 reports a comparison of the as-sintered sample with the surface after Ar^+ implantation and then He^+ and D^+ implantation. The image for $(CrFeTaV)_{95}W_5$ is taken with SEM in SE mode in a tilted configuration revealing the presence of large blistering formation.

6. Conclusions

The experimental trials allowed to finally find the optimized parameters of the planetary ball mill to achieve a single solid solution of the CrFeTaVW HEA. In addition to the BCC structure, the XRD of the prepared powder also witnessed the presence of a CrFe intermetallic and a $TaVO_4$ inclusion. In addition, the theoretical model that calculates the energy imparted from the milling media to the powder particles allowed to find the optimal value of transferred energy and energy rate to include all the alloying elements in the W crystal lattice before its rapid work hardening.

Regarding the irradiation response of the five investigated compositions, the HEA exhibited good resistance to irradiation-induced segregation and phase transformations, thus improving the quaternary alloy Cr-Ta-V-W performance reported in literature. Consistently with what reported by other authors, the W-based HEA shows no micrometric blistering formations, suggesting that any subsurface irradiation-induced damage is mainly associated with the formation of nanometric He bubbles. However, internal irradiation damage could not be assessed in this work, since the use of a Transmission Electron Microscopy (TEM) device is required. Overall, the phases that showed worse resistance to irradiation are the Laves phases, showing large micrometric surface blisters, and the Ta-rich phase forming in the CrFeTaVW, and whose presence cannot be excluded also in $(CrFeTaV)_{70}W_{30}$ and $(CrFeTaV)_{65}W_{35}$, that is characterized by volumetric swelling, possibly also prior to irradiation with He^+ and D^+.

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