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Enhanced mechanical properties and microstructural modifications in electrodeposited Fe-W alloys through controlled heat treatments

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ABSTRACT

Among W alloys, Fe-W has seen much attention recently, due to the need of moving toward the design of environmentally friendly materials. Coatings with 4, 16 and 24 at.% of W were electrodeposited from an environmental friendly Fe(III)-based glycolate-citrate bath. The samples were annealed in vacuum at different temperatures up to 800 °C. Different crystalline phases are formed upon annealing: α-Fe, Fe_2W, Fe_3W_3C, Fe_6W_6C, and $FeWO_4$. Their grain size and distribution within the coating was studied by means of Electron Backscattered Diffraction (EBSD) technique. The effect of annealing on the mechanical properties of the coatings was analyzed performing nanoindentation measurements. The results show a considerable increase of the hardness followed by a rapid decrease at higher temperatures. The highest hardness value, i.e. 16.5 GPa, is measured for the sample with 24 at.% of W after annealing at 600 °C owing to the precipitation of α-Fe crystallites. This study indicates the possibility to substantially increase the hardness of electrodeposited Fe-W coatings by optimization of the annealing treatment. In addition, the critical influence of the carbide and oxide phases on the mechanical properties of alloys is discussed. Hence, Fe-W coatings rich in W can be applied as a possible candidate for protective coating applications at elevated temperatures.

1. Introduction

In recent years, the attention toward electrodeposited W alloys has grown thanks to the remarkable properties of the alloys and their potential applications. W alloys exhibit good oxidation, mechanical and tribological resistance as well as good thermal stability [1–5]. Among W alloys, Fe-W has especially seen much attention recently, due to the need of moving toward the production of environmentally friendly materials. The Fe-W coatings have the prospect to be used as a replacement for coatings manufactured with environmentally hazardous processes such as the hard chromium coatings [3,6–9]. Typically, asdeposited Fe-W alloys with high W content (up to 30 at.%) show relatively high hardness, i.e. about 10–13 GPa, which is comparable to that of electrodeposited chromium [10,11]. Nevertheless, W-rich are alloys usually brittle due to higher internal stresses [12]. Thermal treatment can reduce the internal stress of the coatings and further improve their mechanical properties. However, most of the studies concerning the effect of heat treatments on hardness of electrodeposited W alloys have been performed on Ni-W [8,13–18] and Ni-Fe-W [9,12] systems. Only a few studies have assessed the thermal stability and the phase transformations occurring upon annealing of Fe-W alloys [4,5,19]. However, the effects of the heat treatment on the mechanical properties of such alloys have been overlooked.

It is well known that the functional properties of an alloy are mainly determined by its composition and structure. In our previous study, Fe-W alloys with various W contents were electrodeposited from an environmentally friendly glycolate-citrate electrolyte and the structure development of the coatings at various annealing temperatures has been studied, as shown in Fig. 1 [20]. The crystallographic structure of the as-deposited samples changes with increasing the W content: a nanocrystalline structure was found for the sample with 4 at.% W, a mixed nanocrystalline-amorphous structure for the sample with 16 at. %W, and a fully amorphous structure for the sample with 24 at.% W. The amorphous structure of the sample with 24 at.%W was confirmed by the diffuse rings of the Selected Area Diffraction pattern (SAD) obtained by TEM analysis, see inset of Fig. 1c. The crystallographic evolution upon annealing differs for the Fe-W alloys, in correlation with their composition (i.e. W content and co-deposited impurities) and asdeposited crystal structure. The Fe-W alloy rich in W shows higher thermal stability. As a matter of fact, the as-deposited amorphous structure of the coating is partially retained after 1 h annealing at 800 °C. The formation of stable phases is also observed as expected from the Fe-W binary phase diagram [21,22], i.e. α-Fe and the intermetallic Fe_2W phase. The formation of W intermetallic phases during annealing is rather typical for this type of electrodeposits and it has been observed also for Ni-W and Co-W alloys [15,23]. In addition, different non-metallic elements (i.e. carbon, oxygen and hydrogen) co-deposited within the coating affect the microstructure development upon annealing leading to the formation of iron tungsten oxide $FeWO_4$ and iron tungsten carbide Fe_3W_3C, Fe_6W_6C phases, as observable in Fig. 1. The formation of tungsten carbides and tungsten oxides upon annealing has important consequences both for the thermal stability and the mechanical properties of the coating [24,25]. In particular, as shown by previous studies, Fe_3W_3C and Fe_6W_6C phases are characterized with high hardness and high elastic modulus [26–28].

The presence of co-deposited non-metallic elements in the Fe-W coatings was revealed by Glow Discharge Optical Emission Spectroscopy analysis and thoroughly discussed in a previous study [20]. The results showed that Fe-W electrodeposits normally contain up to 80 at.% of O, 10 at.% of C and few at.% of H in the subsurface, i.e. within 1 μm from the surface. In fact, the strongly bonded chemisorbed oxygen-containing layer is formed on the top of the tungsten alloys with almost no activation and the activation energy for oxygen desorption

from the surface is high (269–480 kJ/mol) [23]. Moreover, water can act as an oxidizing agent to W [29]. Therefore, it is hard to avoid the surface oxidation of the Fe-W coatings in practice. The quantity of the light elements is strongly reduced in the bulk of the coatings and thus they can be considered as adsorbed surface impurities. Only for the alloy with 4 at.% of W it was found ~7 at.% of O distributed along the entire film thickness. In the bulk of the three analyzed coatings, the carbon content is lower than at the surface: i.e. ~1–2 at.% for the samples with 4 at.% and 16 at.% of W, and ~0.3 at.% for the sample with 24 at.% of W. The reduction of O, H and C is also depending on the W content of the deposits. Lower amounts of impurities were found for the coating richer in W, which is probably related to the decrease in cathodic polarization and redistribution of the partial currents [20].
The aim of this study is to investigate the effect of annealing temperature on the mechanical properties, i.e. hardness and reduced elastic modulus, of Fe-W alloys electrodeposited with various W contents. The formation, distribution and orientation of sub-micro/nano sized oxides and carbides is evidenced by means of Electron Backscattered Diffraction (EBSD) technique. Furthermore, nanoindentation measurements are performed in order to correlate the differences in the microstructure to differences in the mechanical properties.

2. Experimental

2.1. Electrodeposition of Fe-W coatings

The electrodeposition of the Fe-W coatings was carried out from a bath with the following composition: 1M glycolic acid, 0.3M citric acid, 0.1M $Fe_2(SO_4)_3$ and 0.3M Na_2WO_4. The bath pH was adjusted by addition of either NaOH or H_2SO_4. The design of electrodeposition conditions leading to various tungsten content in Fe-W alloys was discussed elsewhere [3,20]. In order to study the heat treatment influence, Fe-W coatings with 4, 16 and 24 at.% of W were deposited applying a constant cathodic current density of 15 mA cm^{-2} [20]. The coating with 4 at.% of W was deposited at 20 °C, the coatings with 16 and 24 at.% were deposited at 65 °C. The electrodeposition was performed in a typical three-electrode cell and the electrolyte volume was kept at 250 mL. A pure copper sheet was used as the working electrode, platinized titanium was used as a counter electrode, and saturated Ag/AgCl/KCl$_{sat}$ was used as reference electrode. The thickness of electrodeposited coatings was ~10 μm. The values were calculated based on gravimetric and elemental analyses of the electrodeposited alloys and confirmed by measuring the thickness on the cross-section.

2.2. Coating characterization

Secondary Electrons (SE) and Back Scattered Electrons (BSE) were used for imaging of the as-plated and annealed samples in a Leo 1550

Gemini Scanning Electron Microscope (SEM) with field emission gun. The instrument is equipped with Energy Dispersive X-ray Spectroscopy (EDS) and Electron Backscatter Diffraction (EBSD) technique. The EBSD measurements were performed using an HKL Channel 5 system and a Nordlys II detector. Transmission Electron Microscopy (TEM) investigations were performed with a Zeiss EM 912 OMEGA microscope operating at an accelerating voltage of 120 kV. The crystallographic structure and phase composition of the obtained coatings were identified by means of a Rigaku MiniFlex II diffractometer with Cu Kα radiation (λ=1.54183 Å) operated at 30 kV and 30 mA. Vacuum annealing of the samples was performed in a controlled vacuum chamber (1×10^{-8} Pa) keeping the samples for 1 h at 200 °C, 400 °C, 600 °C and 800 °C. Afterwards, the samples were cooled down to room temperature inside the furnace. Moreover, the deposits with 16 at.% and 24 at.% of W were also annealed for 6 and 12 h at 800 °C.

The Fe-W cross-sections were investigated in the ordinary EBSD setup (70° tilt of sample toward the EBSD detector). For each crosssection three phase and band contrast maps of 4×3 μm were obtained applying an accelerating voltage of 20 kV and a step size of 20 nm. The maps were afterwards stitched together by using Map Sticher software. All the maps acquired were processed, i.e. wild spikes were removed and minor noise reduction (4 nearest neighbors required) was performed. In the phase maps, high angle grain boundaries are shown by black lines and are defined by a misorientation larger than 10°.

Metallographic preparation of the samples was performed by mechanical polishing with a 50 nm finishing using OP-S silica suspension as the last step. The mechanical tests on the as-plated and annealed coatings were performed on cross-section area using a NHT^2 Nanoindentation Tester from Anton-Paar equipped with a Berkovich pyramidal-shaped diamond tip under load control mode. A load of 10 mN was applied with a loading segment of 30 s followed by a load holding segment of 10 s and by an unloading segment of 30 s. The hardness and elastic modulus are reported as an average value of fifteen indentations, performed in the middle of the cross-section of each sample in order to avoid the influence from the resin. For the nanoindentation measurements the cross-sections were polished down to a 1μm surface finishing.

3. Results and discussion

3.1. Structural characterization of Fe-W coatings: as-deposited and Annealed

In our previous research, the structure development of the electrodeposited Fe-W coatings upon annealing at various temperatures was studied by means of XRD analysis [20] and it is here shown in Fig. 1. The evolution of the crystallization of the annealed samples was also studied by SEM imaging of the cross-sections of the samples. Metallographic preparation of the cross-sections was performed after the heat treatment at each investigated temperature. The corresponding images are shown in Fig. 2. The cross-section of the sample with 4 at.% of W reveals the presence of internal cracks. The cracks are probably caused by abundant hydrogen evolution during electrodeposition, which results in an increased internal stress of the coating obtained at room temperature. EDS point analysis revealed that the cracks occur in an O and W-rich area and the brighter contrast in the surrounding indicates a chemical composition variation which is probably due to W segregation. The EDS results are presented elsewhere [20]. Upon annealing up to 600 °C, oxygen-rich areas grow in extension, and at 800 °C they appear to be replaced by the formation of bright grains. From EDS point analyses, these grains are identified as the $FeWO_4$ phase. The crosssection of the samples with 16 at.% and 24 at.% of W appear to be crack-free.

In both samples, a contrast variation in form of horizontally aligned lines is visible. The contrast can be inferred to small local variations of the chemical composition along the thickness of the samples which is however not revealed by the EDS line scan analyses performed along both samples. Small composition fluctuations were found in the GDOES measurements of the as-deposited samples [20]. Such fluctuations would resemble the composition variations aligned horizontally with respect to the substrate observed in the cross-section of the two samples with higher W content. Such composition variation appears more evident for the sample with 16 at.% of W, and it is still present after annealing at 800 °C and when the sample is fully crystalline. After annealing at 800 °C, the crystallization of the sample with 16 at.% of W is clearly visible in Fig. 2. Small bright grains appear distributed throughout the whole sample thickness and they are aligned horizontally with respect to the substrate similarly to the bright lines observed in the cross-sections annealed at lower temperatures. The bright contrast of these grains denotes that these are W-rich phases. Bigger round grains, with a diameter of ~2 μm, are also found and identified with EDS point analysis as $FeWO_4$. In the sample with 16 at.% of W the $FeWO_4$ grains appear to be located mostly in proximity of the surface of the coating. Formation of $FeWO_4$ phase in both the samples with 4 and 16 at.% of W due to eventual oxygen contamination during the annealing can be excluded. The formation of the oxides is thought to be related to the co-deposited oxygen within the coatings. As a matter of fact, the distribution of the oxide phases in the samples with 4 and 16 at.% of W is in well agreement with the co-deposited oxygen distribution, as observed from GD-OES analysis on the as-deposited samples [20]. As shown in Fig. 2, in the sample with 4 at.%W the $FeWO_4$ grains are visible throughout the whole thickness, whereas in the sample with 16 at.%W they are mostly located in proximity of the sample surface. GD-OES results show co-deposited oxygen distributed along the entire film thickness of the sample with 4 at.% W. For the sample with 16 at.% of W the oxygen is mostly co-deposited in the proximity of the surface of the coating.

The partial crystallization of the sample with 24 at.% of W is also clearly visible from the imaging of the cross-section after annealing at 800 °C. Here, islands of grains are present which are distributed mostly along the substrate-coating interface and in proximity of the surface of the coating. The brighter appearance together with EDS point analysis confirmed an enrichment of W within these grains. This finding suggests that these grains are the Fe_6W_6C carbides as observed by XRD analysis (Fig. 1). As reported in previous studies, the precipitation of carbides upon annealing of electrodeposited Fe-W coatings is caused by co-deposited carbon within the coatings [4,19,20]. The co-deposition of carbon is often related to the use of organic complexing agents and additives in the electrolyte [30]. However, the surface of the substrate might also serve as a source of carbon contamination, as suggested by the carbides formation along the substrate-coating interface.

The sample with 24 at.% of W was kept at 800 °C also for longer times, i.e. 6 and 12 h, in order to drive further its crystallization. However, for the alloy with 24 at.% of W after 12 h at 800 °C the amorphous peak appears unchanged, as can be seen in Fig. 3b. What appears clearly from the XRD spectra acquired after 6 and 12 h at 800 °C is a strong decrease of the presence of the carbide phase Fe_6W_6C. Already after 6 h heat treatment, most of the XRD peaks of the phase are absent or strongly reduced. On the other hand, an increase of the peaks intensity belonging to the Fe_2W phase is observed. The same trend is found for the sample with 16 at.% of W (Fig. 3a). Here the disappearance of the carbides is more gradual. As a matter of fact, after 6 h annealing at 800 °C the Fe_6W_6C phase is still stable and its peaks are present in the XRD spectra. Only after annealing for 12 h both carbides phases are strongly reduced, while the Fe_2W phase becomes more prominent.

The gradual disappearance of the carbides in both samples is also observed by BSE imaging of the surface of the samples after the annealing treatments at 800 °C (Fig. 4a–f). After annealing for 1 h at 800 °C, the carbide formation at the surface of both the samples with 16 at.% and 24 at.%W is evident and can be seen in form of the round clusters in Fig. 4a and d. As revealed by point EDS analysis, the tungsten content reach up to 45 at.% in these clusters, which fits with the W concentration present in the carbide phases. These round clusters are still found in the sample with 16 at.% of W after annealing for 6 h (Fig. 4b) and when the Fe_6W_6C phase is still present in the XRD spectra. As anticipated by the XRD results, the carbides are not observed in the case of the sample with 16 at.%W after annealing for 12 h, and in the sample with 24 at.%W after annealing for 6 and 12 h, see Fig. 4c and e–f respectively.

3.2. EBSD analysis of annealed Fe-W coatings

To confirm the XRD findings and to further analyse the distribution of the crystalline phases, EBSD analysis was performed on some selected areas of the cross-sections of the samples annealed at 800 °C.

Fig. 5a shows the BSE image of the sample with 4 at.% of W and the red dashed box defines the area where the EBSD phase map and band contrast map were acquired. Both maps are shown next to the BSE image (Fig. 5a). The cross-section image, the phase map and band contrast map of the samples with 16 at.% and 24 at.% of W are shown in Fig. 5b and c, respectively. A band contrast map is providing information about the quality of the EBSD patterns acquired from the analyzed area. This map shows the material's microstructure in a grey scale image where areas providing poor quality patterns, e.g. grain boundaries, amorphous phase or deformed grains, will be shown as dark, while undeformed, crystalline regions which are easy to identify will appear bright [31]. The generated diffraction patterns are characteristic of the crystal structure of the sample and thus they can be used to discriminate between crystallographically different phases. The phases present in the sample need to be specified as a priori information in order for an EBSD software to index the acquired diffraction patterns [31]. The phases used as reference phase for the EBSD indexing were the phases acquired through XRD analysis: α-Fe, Fe_2W, Fe_3W_3C, Fe_6W_6C, and $FeWO_4$. However, when acquiring the diffraction patterns for the samples with 16 at.% and 24 at.% W, the fraction of indexed Fe_2W and Fe_3W_3C phase was very low, i.e. below 1%. For this reason both phases were excluded from the analysis and are not presented in the maps. For the three phase maps shown in Fig. 5 the same color code is used: the blue grains belongs to α-Fe phase, the red grains to the $FeWO_4$ phase, and the green grains to the Fe_6W_6C phase.

In the phase map of Fig. 5a, it is shown that the annealed 4 at.%W sample contains large α-Fe grains of a few micrometres in size and $FeWO_4$ grains which are distributed throughout the sample thickness. The fraction of zero solutions (appearing in the image as white pixels) is low, i.e. 2.2%, and it is due to retained porosity in the sample, concentrated mostly nearby $FeWO_4$ grains. Three phases are present in the phase map acquired from the 16 at.%W sample: α-Fe, Fe_6W_6C and $FeWO_4$. The bright grains horizontally aligned in the cross-section are indexed as the carbide phase Fe_6W_6C. This appears clearly by looking at the line of carbides situated approximately 2 μm from the substrate. This area is highlighted in the BSE image and in the corresponding phase map. Sub-micron oxide $FeWO_4$ grains (~200 nm in size) appear to be present across the entire coating thickness, while a bigger $FeWO_4$ particle (~3 μm) is present in the centre of the coating. Similar oxide grains are also visible in the SEM image in the proximity of the surface of the sample (Fig. 5b) but are not included within the phase map. Different from the case of the 4 at.%W sample here the α-Fe grains are much smaller, as shown by the grain size histogram in Fig. 6a. Most of the grains are smaller than 250 nm, and the average α-Fe grain is 200 nm in size. The indexed α-Fe grains of the annealed sample with 24 at.% of W are also of submicrometer diameters, Figs. 5c and 6b. Here, the average grain size is 140 nm. The Fe_6W_6C carbide phase present in the vicinity of the substrate is also correctly indexed, see Fig. 5c. What appears clearly also from the maps acquired from the

24 at.% of W is the large fraction, i.e. 61%, of zero solutions (presented in white in the phase map and in black in the band contrast map). The reason for such high fraction of zero solutions can be inferred to the nanocrystalline/amorphous nature of the sample which is preserved after the heat treatment and thus not possible to be indexed by EBSD technique. The broad amorphous peak still visible in the XRD spectrum acquired after annealing at 800 °C, see in Fig. 1, already indicated the presence of this retained nanocrystalline/amorphous structure in the sample.

EBSD analysis was also conducted for the 16 at.% and 24 at.% of W samples annealed at 800 °C for 12 h. The results are shown in Fig. 7. In the 16 at.%W sample, in Fig. 7a, bright grains are visible and distributed throughout the whole sample thickness. They are larger in size with respect to those observed in the same sample after annealing for 1 h. Furthermore, they are distributed more homogenously within the coating and are not aligned horizontally with respect to the substrate anymore, as in the case of the sample annealed for 1 h. As a matter of fact, the phase map acquired from the selected area shows that these bright grains are not the Fe_6W_6C carbides, as previously observed, but instead Fe_2W grains. $FeWO_4$ grains appear to be still present within the cross-section, also the average size of α-Fe grains has increased with respect of the sample annealed 1 h (Fig. 6c). After 12 h annealing, the α-Fe average grains is 0.5 µm. As revealed by the SEM image in Fig. 7b, the microstructure of the 24 at.%W sample is similar to what was seen after 1 h annealing (Fig. 5c). Also in this case, larger grains are visible at the substrate-coating interface, where the Fe_6W_6C carbides were previously located. However, after 12 h annealing the grains are indexed as Fe_2W, as shown from the phase map. These findings indicate that longer annealing times result in the crystallization of stable phases as expected from the Fe-W binary phase diagram [21,22]. This is observed with the gradual dissolution of the carbides phases and the crystallization of the Fe_2W phase. It is expected that the carbon coming from carbide phase dissolution segregates along the grain boundaries, as suggested by previous studies [32]. It is worth mentioning that according to the Fe-W-C phase diagram, both Fe_6W_6C and Fe_3W_3C carbides are expected to be stable at 800 °C [20,26]. The observed dissolution of the carbides is likely caused by the annealing perfomed in vacuum (1×10^{-8} Pa). Annealing treatments performed in other atmospheres (e.g. Ar atmosphere) will be performed to explain the observed mechanism. The average size of α-Fe grains is instead almost unchanged after the 12 h annealing treatment, see Fig. 6d.

3.3. Mechanical characterization of Fe-W coatings: nanoindentation

To study the effect of the thermal treatment on the mechanical properties of the Fe-W coatings, nanoindentation tests were performed on the as-deposited and annealed samples. The obtained values of the hardness and of the reduced elastic modulus (E_r), extracted from the load-displacement curves according to the method of Oliver and Pharr [33], are shown in Fig. 8. When working with electrodeposited W alloys with various W contents, an increase in the hardness of the material with increasing its W content is commonly found in literature [3,12,13]. Different mechanisms play an important role with respect to the observed hardness increase, i.e. grain boundary strengthening, amorphization of the coating induced by W addition, and solid solution strengthening. In electrodeposited W alloys the first two mechanisms are thought to be more influent on determining the hardness increase, while a lower contribution is expected from the solid solution effect [34]. Both mechanisms are strongly correlated with the concentration of W deposited within the coatings. As a matter of fact, the addition of W content in the coatings is often associated with a continuous decrease in the crystallite size. The refinement of the microstructure is followed by an increase of the volume fraction of grain boundaries that are responsible for the hindering of dislocations motion and thus resulting in an higher mechanical strength of the material (Hall-Petch relationship) [14,34]. When reaching a certain co-deposited W content in the alloy, the crystallite size is so small that the long-range order is virtually lost and the material becomes amorphous [35]. Due to the lack of longrange order, conventional deformation mechanisms of crystalline materials (e.g., dislocation motion, creation of vacancies, planar defects like stacking faults, etc.) are not operative in amorphous alloys and, therefore, their hardness is larger.

The measured hardness of the as-deposited coatings shows that the sample deposited with 24 at.% of W is characterized with the highest hardness (Fig. 8a), confirming that the W-induced amorphization of the structure leads to a substantial increase of the hardness value. However, the hardness increase is not linear with the increase of the W content of the coatings. As a matter of fact, the sample with 4 at.% of W shows surprisingly high hardness, ~10 GPa. Namely, it is higher than the one measured for the sample with 16 at.%W which is ~7 GPa. The higher hardness value of the sample with 4 at.% of W could be explained by the presence of the oxygen rich areas observed in its cross-section, see Fig. 2, and as measured by GD-OES analysis [20]. The co-deposited oxygen could lead to the formation of nanoscale oxides distributed along the sample grain boundaries which are reported to increase the measured hardness [25]. Also, internal stresses in the coating due to the co-deposited oxygen can result in an increase in hardness. However, the strengthening mechanism caused by the oxide precipitation is thought to be the main factor influencing the increase in hardness [36]. As seen Fig. 8b, the reduced elastic modulus of the as-deposited samples shows a similar trend. The formation of these oxides can explain why the elastic modulus of the sample with 4 at.%W is higher than that with 16 at.% W.

Upon annealing, the samples with 16 and 24 at.% of W show the same hardness trend: an increase of the hardness up to 600 °C, where the maximum value is measured which is 16.5 GPa for 24 at.%W sample, followed by a strong decrease after annealing at 800 °C. The increase of hardness upon annealing can be explained by different mechanisms: grain boundary relaxation for the lower annealing temperatures [37], and the precipitation of fine crystallites [9,13]. For the sample with 16 at.% of W the phases responsible of the precipitation strengthening are both Fe(W) solid solution and $FeWO_4$, and α-Fe for the sample with 24 at.% of W. The hardness drop observed at 800 °C is related to the grain size increase of the mentioned phases, as observed both from the SEM images and EBSD analyses.

Thus, the hardness of the samples with 16 and 24 at.% of W appears to not be influenced by the presence of the hard Fe_6W_6C phase, whose hardness and the elastic modulus is reported to be ~15,6 GPa [26] and ~327 GPa [28], respectively. For the sample with 24 at.% of W, Fe_6W_6C phase is not expected to influence the hardness. As a matter of fact, the carbides are located at the substrate-coating interface and at the surface (Figs. 2 and 5c), and thus far from the area where the indents were performed. The SEM images of indent imprints are shown in Fig. 9. In the sample with 16 at.% of W, the Fe_6W_6C carbides are instead distributed throughout the whole sample thickness. However, as shown in Fig. 9e and h, the carbides seem to follow the deformation of the softer α-Fe phase without hindering the penetration of the indenter. Hence, at 800 °C the detrimental effect of the α-Fe grain growth is the main factor influencing the hardness of the coatings. The average α-Fe grain size after annealing at 800 °C for 1 h is very similar in both coatings, see Fig. 6a and b, which is reflected in similar hardness values as seen in Fig. 8a.

The effects of the annealing treatments are less pronounced for the sample with 4 at.% of W. Only a slight increase in the hardness is revealed up to 400 °C, which is followed by a constant decrease at 600 °C and 800 °C. The decrease in hardness for the sample with 4 at.%W is due to grain growth that sets in at lower temperatures due the lower thermal stability of this sample.

The variation of the E_r value of the three coatings upon annealing is shown in Fig. 8b. Here, the variation of E_r with temperature differs for each sample. The trends can be related to the microstructural transformations occurring upon annealing of the three samples. For the sample with 4 at.% of W, E_r remains almost constant with increasing temperature. The elastic modulus is an intrinsic property of the material which mainly depends on the bonding energy between the atoms. Hence, the elastic modulus is mostly not depending on grain size since variations typically occur when the grain size approaches the amorphous regime [38]. Upon annealing, the main microstructural change which occurs for the sample with 4 at.% of W is the grain growth of the as-deposited nanocrystalline Fe(W) solid solution, therefore E_r remains almost constant with increasing temperature. The slight decrease in E_r observed between 200 °C and 400 °C might be ascribed to the growth of internal cracks that occur before the crystallization of the $FeWO_4$, see Fig. 2. For the samples with 16 and 24 at.% of W, E_r increases up to 600 °C. Here, the increase of E_r is related to the structural relaxation and the density increase of the material, observed when annealing amorphous alloys [39,40]. Above 600 °C, the different crystalline phases found within the cross-section of the samples lead to the observed different trends for E_r. In particular, the precipitation of a secondary phase, i.e. F_6W_6C, contributed to the increase in the E_r observed for the sample with 16 at.% of W. A precipitation strengthening effect on the elastic modulus of electrodeposited coatings was also observed on annealed NiW coatings [17]. In the sample with 16 at.% of W, the F_6W_6C phase is distributed throughout the whole sample thickness (see Figs. 5b and 9h). Hence, the stiff bonds of the F_6W_6C phase (caused by its high elastic modulus of ~327 GPa [28]) contribute to the measured E_r and lead to the sharp increase of E_r observed in Fig. 8b. For the sample with 24 at.% of W, the carbide phase is located at the substrate-coating interface and in proximity of the surface of the coatings, thus it is not expected in the indent imprint (see Figs. 5b and 9i). Hence, the E_r value at 800 °C is related to the presence of the α-Fe crystalline phase. This is the same phase as found in the sample with 4 at.% of W annealed at 800 °C. Therefore, the measured E_r decreases (Fig. 8b) and approaches the value measured for the sample with 4 at.% of W.

The results here presented show that the microstructure of the Fe-W coatings influenced their mechanical properties both in the as-deposited condition and after heat treatments. In the as-deposited condition, the W-induced amorphization was found to be the main strengthening mechanism. The amorphous structure of the sample with 24 at.% of W substantially increased the hardness of the coating. Upon annealing, the observed increase in hardness is related to grain boundary relaxation and precipitation strengthening mechanism. In particular, the precipitation of α-Fe at 600 °C for the sample with 24 at.% of W leads to the maximum hardness value, i.e. 16.5 GPa. The precipitation of Fe_6W_6C phase contributed to a sharp increase in the E_r of the sample with 16 at.% of W after annealing at 800 °C. Finally, the grain growth mechanism of the α-Fe phase had detrimental effects on the hardness of the studied coatings.

4. Summary and conclusions

The influence of heat treatment on the microstructure and mechanical properties of electrodeposited Fe-W alloys at various W contents has been studied. The structural changes occurring upon annealing have been observed through XRD and EBSD analysis.

Nanohardness measurements on the cross-section of the Fe-W coatings have been performed to estimate the effect of annealing on the mechanical properties of the material. Based on the results presented in this study the following conclusions can be drawn:

- The crystallization of sub-micron/nano sized $FeWO_4$ phase occurs along the entire coating thickness upon annealing above 600 °C for the samples with 4 at.% and 16 at.% of W, respectively.
- Longer vacuum annealing treatments of 6 and 12 h of the samples with 16 and 24 at.% of W led to the formation of stable phases as expected from the Fe-W binary phase diagram. This occurs through gradual dissolution of the carbide phases and the crystallization of the Fe_2W phase.

- The results from EBSD and XRD analyses on the sample with 24 at.% of W highlight the outstanding thermal stability of that material. As a matter of fact, A partial broad amorphous shoulder is still observed in the XRD diffractogram acquired after the 6 and 12 h annealing, and the α-Fe average grain size also remained unchanged at both conditions. Furthermore, EBSD phase maps acquired from the sample with 16 at.% and 24 at.% of W after annealing for 12 h at 800 °C confirm the XRD findings regarding the process of a gradual dissolution of the carbides phases followed by Fe_2W crystallization. In fact, Fe_2W grains are found in the areas where the Fe_6W_6C were located after 1 h annealing at 800 °C.

- The annealing treatments enable to improve considerably the hardness of the as-deposited Fe-W samples. A maximum hardness of 16.5 GPa was measured for the sample with 24 at.% of W after annealing for 1 h at 600 °C and was related to the precipitation of fine α-Fe crystallites. Upon annealing at 800 °C, the hardness decreased for all the samples due to grain growth.

- The hardness of the coatings appears to not be influenced by the presence of carbide phase. In fact, the α-Fe grain growth is the main factor influencing the hardness of the Fe-W coatings. However, the influence of the Fe_6W_6C phase is observed in the reduced elastic modulus of the sample with 16 at.% of W, i.e. at 800 °C the Fe_6W_6C phase formation leads to a sharp increase of the measured E_r.

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