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Hafnium influence on the microstructure of FeCrAl alloys

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Abstract. Due to their special properties at high temperatures, FeCrAl alloys micro-alloyed with Zr can be regarded as potential materials for use at nuclear power plants, generation 4R. These materials are resistant to oxidation at high temperatures, to corrosion, erosion and to the penetrating radiations in liquid metal environments. Also, these are able to form continuously, by the self-generation process of an oxide coating with high adhesive strength. The protective oxide layers must be textured and regenerable, with a good mechanical strength, so that crack and peeling can not appear. To improve the mechanical and chemical characteristics of the oxide layer, we introduced limited quantities of Zr, Ti, Y, Hf, Ce in the range of 1-3 %wt in the FeCrAl alloy. These elements, with very high affinity to the oxygen, are capable to stabilize the alumina structure and to improve the oxide adherence to the metallic substrate. FeCrAl alloys microalloyed with Hf were prepared using VAR (Vacuum Arc Remelting) unit, under high argon purity atmosphere. Three different experimental alloys have been prepared using the same metallic matrix of Fe-14Cr-5Al, by adding of 0.5%wt Hf, 1.0%wt Hf and respectively 1.5%wt Hf. The microhardness values for the experimental alloys have been in the range 154 ... 157 HV0.2. EDAX analyses have been performed to determine chemical composition on the oxide layer and in the bulk of sample and SEM analyze has been done to determine the microstructural features. The results have shown the capacity of FeCrAl alloy to form oxide layers, with different texture and rich in elements such as Al and Hf.

1. Introduction

FeCrAl alloys along with the ZrCrAl alloys class can be used for realizing the metallic structures of the reactor in nuclear power plant, generation 4R. The components that can be made from these modern alloys are: the outer jacket of the reactor, recirculation pipes for the liquid metal, pumps for distribution of the cooling medium etc. Modern type LFR reactors working in closed cycle with optional fuel flexibility and fast neutron spectrum are cooled with metallic medium like Pb or Pb-Bi alloy. This particularity ensures a much higher level of security at a lower overall volume compared to the previous generation reactors. Such materials must provide excellent mechanical and technological characteristics, among which: plasticity and ductility, mechanical workability, weldability, thermal shock resistance and mechanical strength, creep resistance at high temperature, high chemical stability in specific environmental conditions (temperatures above 400 – 800°C), corrosion and erosion resistance, high thermal conductivity to ensure optimum heat transfer.

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Special FeCrAl alloy is similar to ferritic stainless steels, but contains a higher aluminum percent and some microalloying elements like: Hf, Ta, Ti and Y. This alloy is designed to be used at temperatures up to 1400C and exhibits outstanding electro-thermal characteristics: high resistivity, low temperature coefficient, long life at high temperatures and high resistance to oxidation [1, 2, 3, 4, 5].

Oxidation resistance is given by the presence of a special and adherent layer at the surface level of the alloy, a layer that contains complex oxides of aluminum and chromium, which prevent deep oxidation at high temperatures. The Al₂O₃ layer acts like a ceramic material and a barrier against the effects of corrosive or erosive environment generated by metal coolant and provide optimum protection, if it keeps a high density and if the oxide does not peel over time.

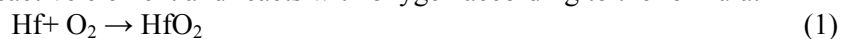
Class of alloys that possess necessary characteristics for the operation in the new 4R nuclear power plant is the alloy FeCrAl, known in the literature as the Fecralloy trade mark. It is known that the addition of chromium can increase the ductility at room temperature, but it does not have a substantial effect on the flow resistance at 600 °C for alloys with up to 25% Al. At high contents of aluminum, the ability to form at the surface level of a textured and uniform aluminum oxide is diminished. Thus, in excess of 8% Al, the aspect of the oxide is not uniform, adherent and compact, the superficial layer containing very thin alumina whiskers. The choice of a correct aluminum content of the FeCrAl alloys must be correlated with the content of chromium, according to the equation: % Al = (40 - % Cr)/6 [6,7]. At the same time, the chromium content below 12% does not offer sufficient resistance to oxidation. The addition of rare earth elements with high affinity for oxygen (yttrium, zirconium, hafnium, titanium and cerium) leads to the formation of highly stable oxides on the surface of alloys FeCrAl [8, 9].

The protective oxide layer, with self-generation effect and with high adhesion to the substrate of alloy FeCrAl, must be textured and must have a good mechanical strength at cracking process or at dissolving effects. There are various known technologies for producing oxide layers on the surface of the alloy, such as the deposition of layers by plasma spraying in a vacuum (PVD), re-melting the surface with a jet of electron irradiation, laser deposition, plasma metalizing [10, 11, 12, 13, 14]. These methods aim to eliminate the porosity of the surface, by remelting of the superficial layer of oxide and obtaining a roughness as low as possible, for avoid the mechanical anchoring effect on the metallic surface of the molten lead. For designing the correct chemical compositions of FeCrAl alloy (micro-additions of rare earth elements), the influences of all alloying elements on the properties of these materials must be taken into account.

Alumina forming alloys exhibit interesting anti-corrosion properties under high temperature oxidizing conditions since aluminum allows the formation of an α -alumina scale. Under thermal cycling conditions, the oxide scale may undergo severe spallation. The addition of reactive elements is known to improve the high temperature oxidation performance of alumina forming alloys. FeCrAl – type alloys are of interest for applications at high temperatures, also in molten lead or in a mixture of lead and bismuth. Small additions of reactive elements, like hafnium, alter the morphology of the oxides, leading to the formation of an adherent alumina scale. Utilizing the rare elements in these alloys has a beneficial effect to increase the chemical bonding between metal and oxide, and/or to the formation of pegs anchoring the oxide scale. Reactive elements like hafnium are also believed to act as vacancy sinks to suppress the formation of voids.

Hafnium is used for nuclear reactor control rods because of its ability to absorb neutrons and its good mechanical and corrosion resistance qualities. Its neutron-capture cross-section is about 600 times that of zirconium. Hafnium resists to corrosion due to the formation of an oxide film on exposed surfaces [15]. In FeCrAl alloys micro-alloyed with hafnium, a complex aluminum oxide that contains both aluminum and hafnium forms on the metallic surface. The physical properties of hafnium metal samples are markedly affected by zirconium impurities, especially the nuclear properties, as these two elements are among the most difficult to separate because of their chemical similarity [16].

Hafnium is a very reactive element and reacts with oxygen according to the formula:



Irradiation by high energy particles (electrons, ions, neutrons) may induce the redistribution of impurities and solutes near sinks, such as point defects, dislocations and boundaries. The enrichment and/or depletion of the elements at grain boundaries will influence the mechanical properties of materials. The enrichment of undersized impurity atoms, e.g. phosphorus in ferritic reactor pressure vessel steels, reduces the grain boundary cohesion, causing the materials to fail through inter-granular embrittlement. Radiation induces undersized atom (P) enrichment and oversized atom (Cr) depletion at grain boundaries in E911 steel. This phenomenon can be suppressed by the addition of an oversized atom like Hf. The addition of Hf suppresses radiation-induced undersized atom enrichment and oversized atom depletion. Hf is added to ferritic steel for induce the redistribution of impurities at grain boundaries with influence of the mechanical properties under irradiated effect [16,17].

2. Obtaining experimental FeCrAl alloys micro-alloyed with Hafnium

The research paper aims to design and manufacture FeCrAl alloys as mini-ingot, using VAR furnace (vacuum remelting arc furnace), documenting the procedure and analyzing the microstructure in order to estimate the effect of hafnium addition on the alloys' characteristics. The samples were designed and manufactured at ERAMET laboratory, at the Politehnica University of Bucharest, Material Science and Engineered Faculty (www.eramet.wix.com/eramet), using a MRF ABJ 900 furnace (55 kVA, min. 650 A @ 60% DS). After obtaining the stable vacuum of 1×10^{-4} mBar, the furnace chamber was filled with argon (Ar 5.3) to insure the electric arc stability. Each mini-ingot was remelted and solidified five times, in order to obtain the microstructural homogeneity. The assimilation coefficient for this particular alloy class was over 99.5%, due to the low vapor losses of the components in the electric arc remelting process. Mini ingots had quasi-constant weight (39,63g – 39,96 g) (Table 1).

Three experimental FeCrAl alloys were obtained, with different contents of hafnium: 0.5%wt Hf, 1.0%wt Hf and respectively 1.5%wt Hf added into the same metallic matrix of the experimental alloy Fe-14Cr-5Al. The base alloy was a high purity “extra soft” steel, mark MK3, having the chemical composition: C = 0.02%wt, Si = 0.04%wt, Mn = 0.21%wt, S = 0.02%wt, P = 0.015%wt, Ni = 0.2%wt, Cr = 0.15%wt, Mo = 0.07%wt, 0.14%wt Cu, Al = 0.12%wt and Fe= bal. For obtaining high alloyed material, high purity alloying elements were introduced into the base material: metallic chromium 99.5 % Cr; electrolytic aluminum 99.4% Al; hafnium 99.5 % Hf.

Table 1. Assimilation efficiency and the weights for each experimental batch and mini-ingots.

Sample code	Initial weight batch, g	Weight of mini-ingot, g	Assimilation efficiency, $(G_{\text{ling}}/G_{\text{ch}}) \times 100, \%$	Global efficiency, %
NUC 8 - Fe-14Cr-5Al-0.5Hf	40.0	39.96	99.90	
NUC 9 - Fe-14Cr-5Al-1.0Hf	40.0	39.91	99.77	99.58
NUC10 - Fe-14Cr-5Al-1.5Hf	40.0	39.63	99.07	

3. Results and discussions

To each sample sectioned from the mini-ingots we applied the metallographic rough polishing procedure using abrasive grit paper (400, 600, 800, 1000, 1500 grit), followed by a final polishing using alumina alpha powder (Topol1, Topol, Topol 2 and 3, the grain size of 3 to 0.1 μm). Metallographic analysis was performed with the aim of highlighting the microstructural characteristics of the experimental alloys, in order to estimate the aluminium and hafnium distribution in the superficial layer of oxide. The analysis was conducted using scanning electron microscope FEI QUANTA INSPECT F provided with the electron gun with field emission - EGF with a resolution of 1.2 nm and X-ray spectrometer energy dispersive (EDS) with resolution of 133 eV at MnK.

3.1. Chemical composition and microstructural analysis

The chemical composition of the samples was determined by EDAX analysis in the successive points, in accordance with figure 1. The values obtained for the three batches named NUC 8 - NUC 10 in the center thereof are shown in table 2. Concentration analysis of chemical elements in center of the samples (point 5) shows a good concordance between projected chemical composition and chemical composition performed for each batch separately. Although different amounts of Hf were introduced into the metallic matrix (0.5%Hf, 1.0%Hf and 1.5%Hf), this element is not detected in the center of the sample, due to its migration to other areas, like the peripheral oxide layer.

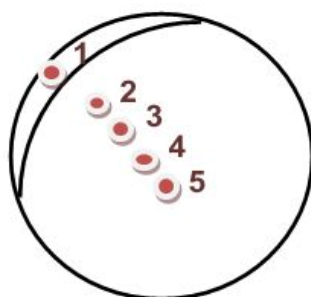


Figure 1. Radial arrangement of the points of analysis of FeCrAlHf alloy.

Table 2. Amounts of alloying elements in the center of the samples (point 5).

Sample	Chemical composition, %wt		
	Al	Cr	Fe
NUC 8	4.17	14.54	81.29
NUC 9	4.68	14.78	80.55
NUC 10	4.51	14.84	80.64

EDAX analysis of these alloys was done in several areas of the surface of the sample in radial points, as shown in figure 1. In table 4, we have shown the chemical compositions of the edge area of the samples analyzed (point 1). The chemical composition of the marginal crust of the samples micro alloyed with hafnium (point 1) indicates that the value of the Hf content is increasing with increasing amount of hafnium in the alloy. This value decreases in the direction of points 1 to 5 due to strong migration of this element to the marginal zone, where it combines with oxygen dissolved in the sample. Due to the simultaneous presence of the two elements with very high affinity for oxygen (aluminium and hafnium), the marginal crust are formed by complex oxides of Al and Hf, whose share is given by the amounts of these elements in the alloy.

Table 4. Chemical compositions on marginal crust.

Chemical composition, %wt					
NUC8 (0.5%wt Hf)		NUC9 (1%wt Hf)		NUC10 (1.5%wt Hf)	
O	22.64	O	15.51	O	13.86
Al	48.58	Al	11.09	Al	0.87
Cr	0.34	Cr	0.96	Cr	0.82
Fe	0.62	Fe	4.07	Fe	3.66
Hf	27.81	Hf	68.37	Hf	80.79

The distribution of elements in peripheral oxide layer for the alloy named NUC 8 is shown in figure 2.

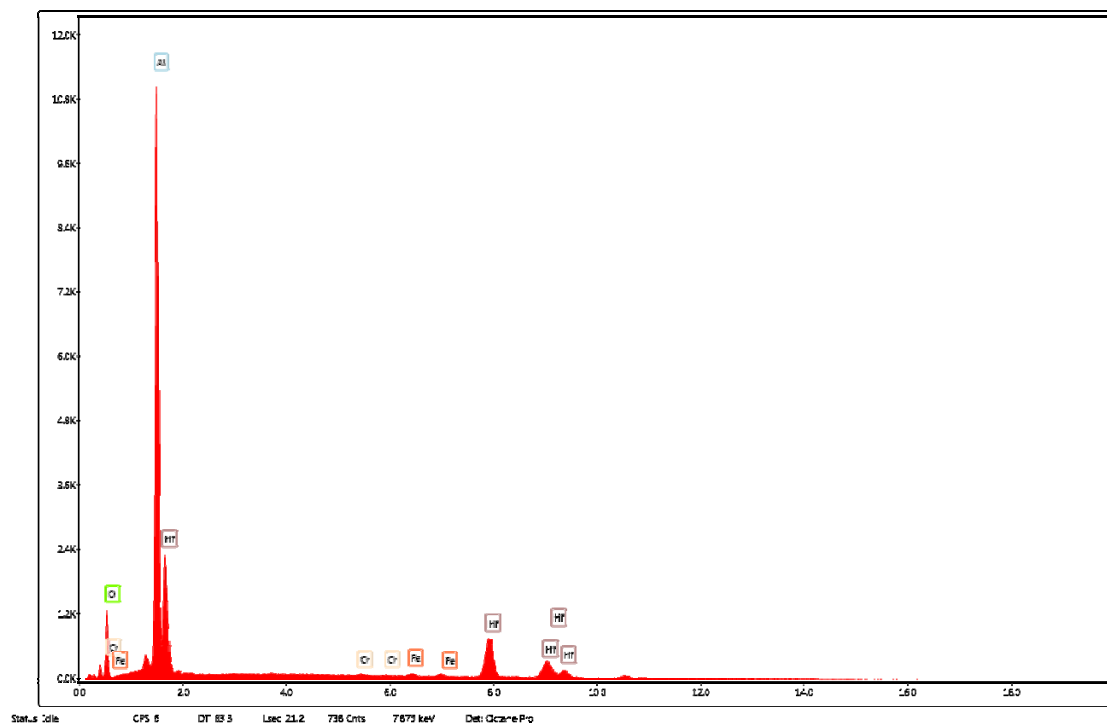


Figure 2. The distribution of elements in peripheral oxide layer for the alloy NUC 8 (0.5 %wt Hf).

The thickness of peripheral oxide, for the 3 samples analyzed, was between 9-13 μm . Their aspect is like elongated and adherent islands, rich in Al, O and hafnium, near other clean areas, as shown in figures 3, 4 and 5. Figure 5 shows the distribution of chemical elements into peripheral oxide layer for alloy NUC 8 from which it appears that, even for small amounts of hafnium in the alloy (0,5%wt Hf) the presence of this element is highlighted in this zone, along with other elements.

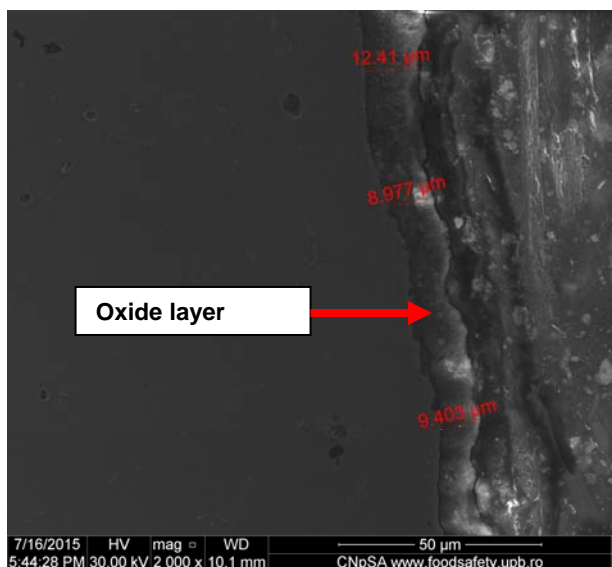


Figure 3. Oxide layers, rich in Al, O and hafnium (sample NUC 8) (2000x).

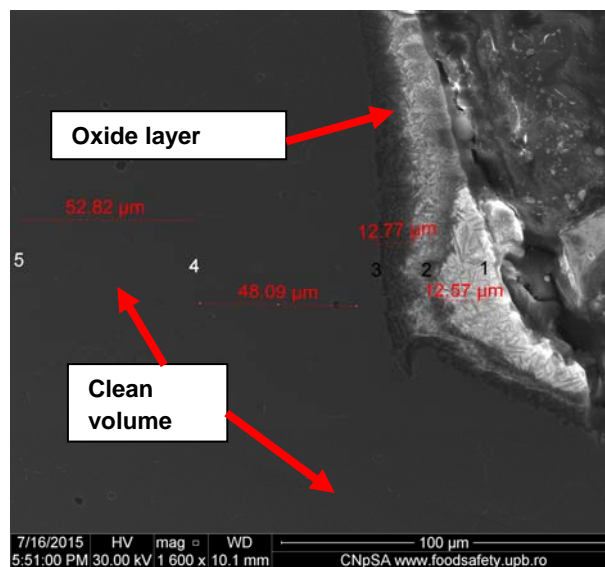


Figure 4. Peripheral oxide layer and clean volume (sample NUC 8) (1600x).

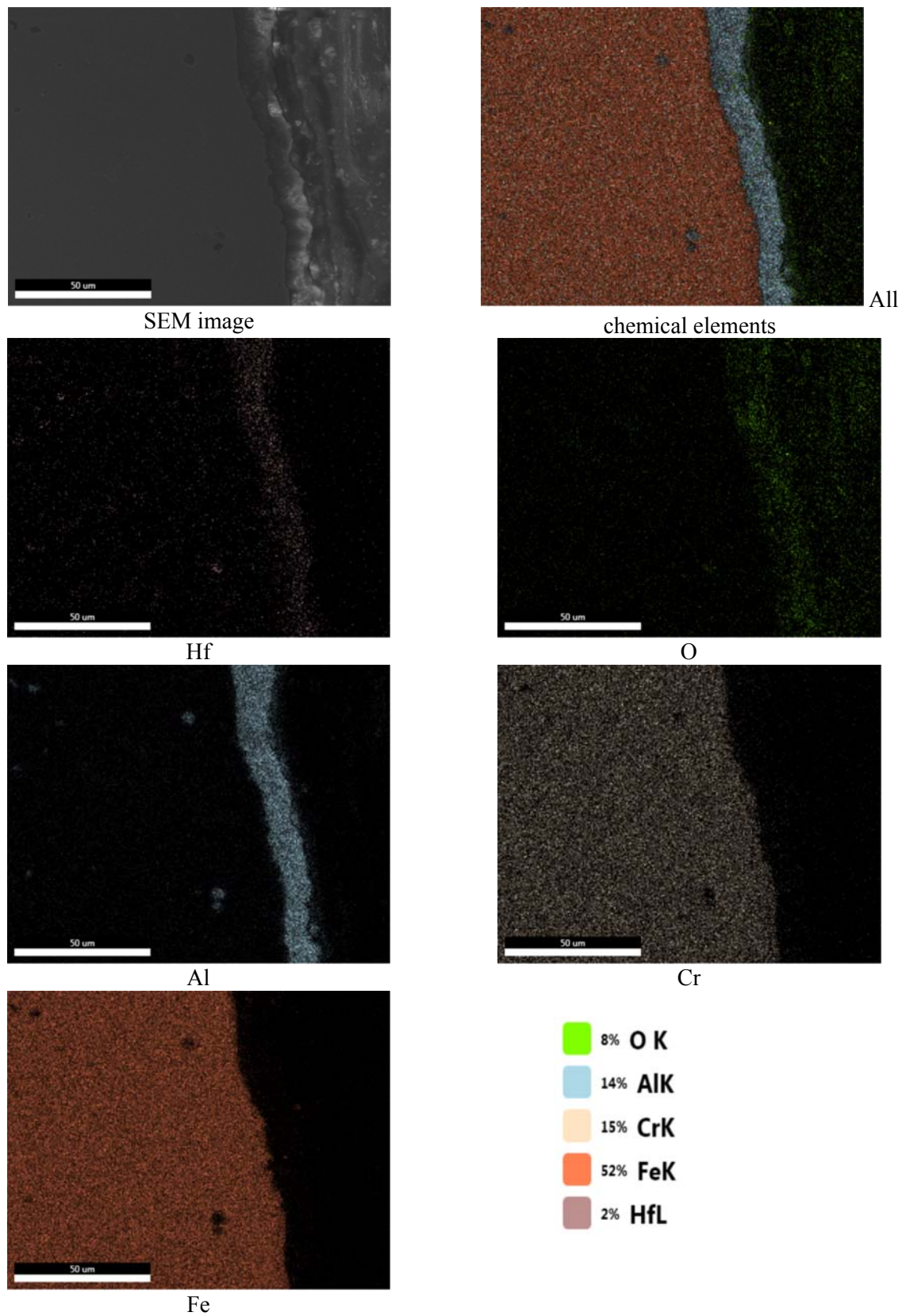


Figure 5. Distribution of chemical elements into peripheral oxide layer for alloy NUC 8.

3.2. Microhardness measurements

Microhardness measurements were made using a Shimadzu HMV 2TE testing machine, with a measuring force of 1.9614 N, a period of 10 seconds and an extended relative uncertainty of 1%. Measurement results of micro-hardness for the three samples analyzed are presented in table 3.

Table 3. Microhardness values ($HV_{0.2}$).

Sample	Individual values*					Average value, $HV_{0.2}$
NUC8	156	162	154	161	151	157
NUC9	157	158	154	148	154	154
NUC10	149	156	154	156	156	154

* The measurements were carried out on the cross sections of mini-ingots, in diagonal line through center zone, with distances between indentations of minimum 1000 microns.

Primary analysis of experimental data shows that there is a quasi-constancy of the micro-hardness values, which reflects an increased homogeneity of all samples obtained in VAR furnace. For all the samples, one can observe that there is a narrow distribution of micro-hardness values, in the range of 154-157 $HV_{0.2}$, which is solely due to the influence of the alloying elements in the metal alloy composition and disposition homogeneous constituents in the metal matrix. These results are similar to other results obtained for the same class of alloys [14].

4. Conclusions

This research is aimed at obtaining and characterizing the alloy FeCrAl, microalloyed with hafnium, potentially usable in nuclear power plant (generation 4R, type LRF).

Compositional analysis performed in the central area of the samples (FeCrAl microalloyed with 0.5%wt Hf, 1%wt Hf and 1.5%wt Hf) shows a relatively similar composition comparative with technological calculations performed. However, despite the different amount of hafnium added in metallic matrix (0.5%, 1.0% and 1.5%), this element is not detected in the volume of the sample. A large amount of hafnium was detected in the peripheral layer, due to its high affinity for oxygen, by quickly migrating during the elaboration of the alloy.

The hardness values are in the range of 154-157 $HV_{0.2}$, normal limits for these materials. This is exclusively due to the influence of alloying elements in the metal alloy composition and due to homogenous arrangement of the metallographic constituents in the metal matrix.

Microstructural analysis of the different areas of the samples shows that the peripheral areas contain complex oxides of elements aluminum and hafnium, whose proportion is given by the concentration of these elements in the alloy composition. Analysis of the chemical composition in the peripheral zone of the samples indicates that the content of hafnium increase with increasing this element content in the alloy. The presence of this element in the center of the sample wasn't detected, due to its migration to the peripheral zone, where the amount of oxygen dissolved in the sample is higher.

For less than 1.5%wt Hf content, this element is present only in superficial layer of oxide. Based on these observations, it can be concluded that alloys of the FeCrAl class can be used at high temperatures in an oxidizing atmosphere, due to their capacity to form a protective and adherent oxide layer, rich in chemical elements such as aluminum and hafnium.

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