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EFFECT OF HEAT TREATMENT ON HARDNESS AND MICROSTRUCTURE OF MECHANICAL ALLOYED Al-Co-Cr-Cu-Fe-Ni-Mo MULTI-COMPONENT SYSTEMS.

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Abstract.

The structural evolution of equiatomic Ni-Co-Al-Fe-Cu-Mo high entropy alloys during mechanical alloying followed by conventional sintering and annealing at relative high temperatures (1000 and 1100 °C) were studied. It was found that solid solutions with simple fcc or bcc crystal structure were formed in these alloys with multiprincipal elements, in both, mechanical alloyed and sintered condition. The sintered products and annealed bulk samples were examined by hardness test. The mean values of Vickers microhardness indicate that the hardest alloy is NiCoAlFeMoCr (980 ± 83 HV0.2), followed by NiCoAlFeMo (915 ± 71 HV0.2), NiCoAlFeCuCr (269 ± 39 HV0.2) and NiCoAlFeCu (261 ± 31 HV0.2). A higher chemical homogenization was achieved after heat treatments, the standard deviation of microhardness measurements get reduced. The microhardness of alloys with Cu was increased after heat treatments between 61 and 79%. In the other hand, the HV microhardness of alloys with Mo only increased in a range between 3 and 7%, except for the NiCoAlFeMoCr alloy whose hardness decreased 22% after heat treatment at 1100 °C.

1. Introduction.

Traditional alloys are composed of one or two principal elements with minor additions of other elements to modify their properties. The multi-component systems or high entropy alloys (HE) are defined as alloys that are composed of at least five elements in equal or near equal molar ratios. These alloys have the characteristic that rather than forming the expected intermetallics compounds, they usually tend to form simple solid solutions with BCC and/or FCC structures. The HE alloys have attractive properties like high strength, high thermal stability, and high wear resistance [1]. The high entropy alloys can exhibit high hardness and excellent resistance to softening, even above 800 °C [2].

Several systems of high entropy alloys have been explored in the past decade; most of them have been synthesized by conventional metallurgy. Research on high-entropy alloys started mainly with systems containing Cu. Copper improves the plasticity of HE alloys [3]. However, it has been reported that hardness of this type of alloys is increased by the addition of elements such as Al, Cr, Ti, V [4]. These elements with higher atomic radii and/or high melting points promote the hardening of HE alloys. The effect of the addition or substitution of other elements such as Ti, Mn and V has been also explored [5].

Mechanical alloying (AM) is a powder metallurgy technique which enables production of homogeneous material, from mixtures of elemental powders. Materials in nanoscale can be synthesized. In most of the investigations the high entropy alloys have been processed by the liquid route. The production of HE alloys by mechanical alloying can result in microcrystalline or nanocrystalline materials, which mechanical properties may be increased [6, 7, 8].

Knowledge of the microstructure is essential to understand and predict the mechanical properties at the macroscopic level. In HE alloys, the number of phases formed and their structure depend of the alloying elements. It was decided to synthesize multicomponent systems by mechanical alloying, consisting of Ni-Co-Al-Fe-Cu-Cr-Mo, from a NiCoAlFe quaternary base, obtaining two groups: Mo-Cr and Cu-Cr. It was studied the effect of added elements and thermal treatment at high temperature (1000 and 1100 °C) on the mechanical and microstructural evolution of alloys, with an aim to understanding their potential for the requirements of high temperature alloys.

2. Experimental.

Four multi-component systems, NiCoAlFeCu, NiCoAlFeCuCr, NiCoAlFeMo and NiCoAlFeMoCr were synthesized by mechanical alloying. Elemental Ni, Co, Al, Fe, Cu and Mo powders of 99.5% purity were used as starting materials. Equiatomic mixtures of pure elemental powders were milled during 10 h in a high energy ball mill (SPEX 8000M). To minimize oxidation of the powder mixtures, the steel vial was first evacuated with a vacuum pump, and then, filled with argon. Methanol was used as a process control agent to avoid excessive agglomeration. The ball to powder weight ratio was 5:1. Milling products were cold pressed at 1.5 GPa followed by sintering at 1200 °C for 3 h in sealed quartz ampoule in vacuum. The solid products were heat treated at 1000 and 1100 °C in air during 30 minutes. The structural evolution of samples was characterized by X-ray diffraction using a Panalytical X'Pert PRO diffractometer with Cu Kα radiation (λ=0.15406 nm), the step and acquisition time were 0.01º and 260 s, respectively; and scanning electron microscopy (JEOL JSM-7401F). Compositional information of the formed phases was obtained by energy-dispersive X-ray spectroscopy (EDS) technique. The microhardness test was carried out in a Vickers hardness tester CLEMEX MMTX-7. The Vickers microhardness (HV) measurements were made on the polished sample cross-sections using an indentation load of 200 g for a dwell time of 10 seconds.

3. Results and discussion.

3.1 Microstructural features of sintered samples.

Figure 1 shows SEM images of the representative microstructure of the consolidated samples after the cold compaction and sintering process. In previous investigations have been reported the Cu segregation in grain boundaries of alloys produced by melting and casting [5]. The Cu alloys of this study have similitude in microstructure with the reported alloys. NiCoAlFeCu and NiCoAlFeCuCr exhibit the presence of a Cu-rich phase.

During EDS mapping it was observed that Co and Fe are homogeneously distributed. Figure 1a shows the microstructure observed in NiCoAlFeCu alloy. There are two main phases a dark phase (zone A) with high Ni, Co and Al content and low Fe and Cu concentrations. The second one is a bright phase identified as zone B, in which low concentration of Al, medium concentration of Co and Ni and a high content of Cu were detected.

Cu has a high positive enthalpy with Co, Cr, Fe. While Ni and Al have lower positive enthalpy Cu, so they are more attracted to regions where this element [9].

In Figure 1b is a representative SEM image of the microstructure of alloy containing Cu-Cr, that is formed by three phases. A phase with high content of Ni and Al (zone A), which is a dark area with bright rounded Cu-rich precipitates is observed. A bright phase identified as zone B, is a Cr-Fe-rich matrix with plated-like Cu-rich precipitates. The effect of Cr additions is noticed by the appearance of a new dark phase without precipitates, identified as zone C.

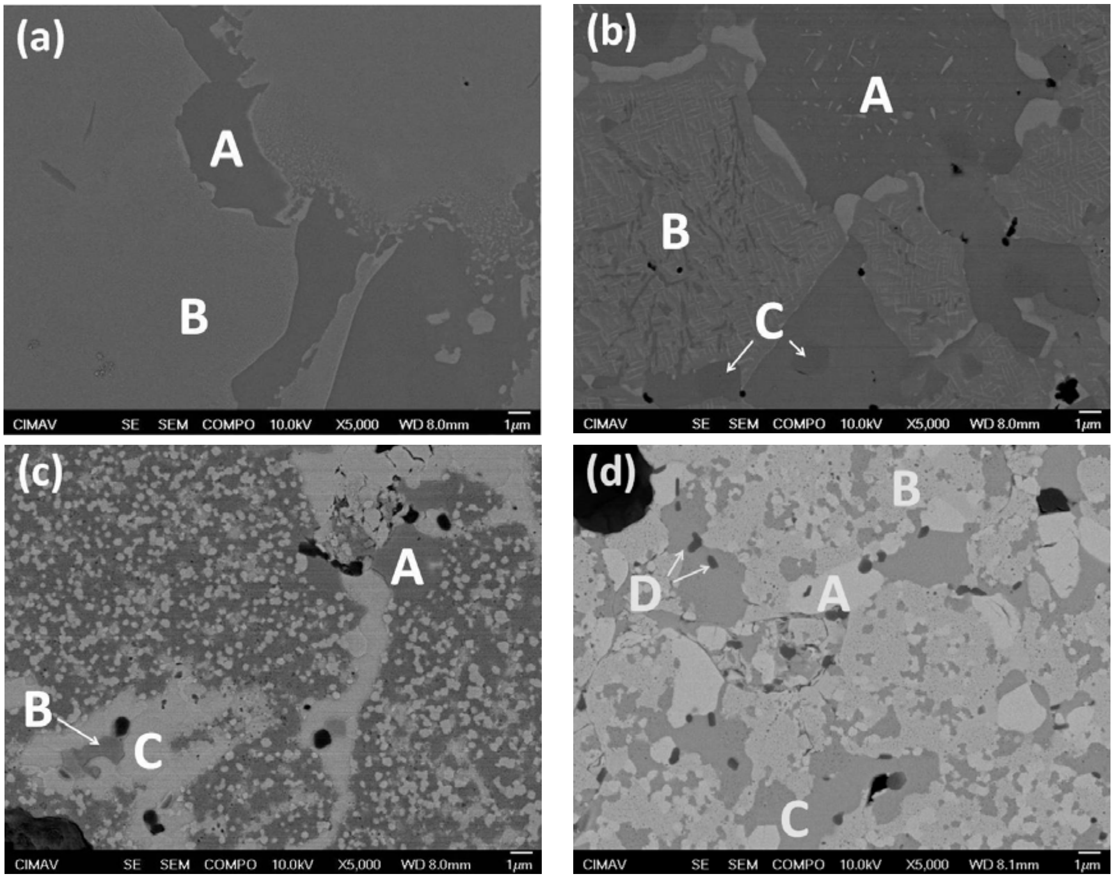


Figure 1. SEM images of sintered alloys: a) NiCoAlFeCu and b) NiCoAlFeCuCr. The effect of Cr addition in microstructure can be observed.

The microstructure of NiCoAlFeMo alloy (Fig. 1c) is composed of three phases. The darkest one, identified as zone A, has a high Ni-Al content, while the content of Mo is very small. Zone B is preferably formed by Fe and Co, with medium Ni content and small percentage of Al and Mo. The brightest zone (C) has the highest content of Mo.

The addition of Cr promotes the formation of one more phase in the alloy containing Mo. The bright zone A has the greatest Mo content, and low Ni and Al content. The bright phase identified as zone B has a high Mo concentration, medium content of Cr, Fe and Co, and low Ni and Al levels. The zone C is a Fe-Co-Ni-rich phase. While the smallest and darkest phase denominated as zone D is mainly formed by Ni and Al, with very low content of Cr and Mo.

All alloys of this study exhibited in their microstructure formation of precipitates in the nanoscale. In NiCoAlFeCu and NiCoAlFeCuCr alloys are Cu-rich precipitates; while those formed in Mo alloys are aluminum oxides.

The HE alloys have a tendency to form solid solutions instead of intermetallics or complex phases, but also is expected to form some compounds with high enthalpy of formation such as oxides, carbides and nitrides [11]. It can explain the presence of precipitates in the microstructure of the alloys.

3.2 Microstructural evolution after heat treatments.

After heat treatments, the microstructure of alloys with Cu has a evident changed, even since the lowest temperature (1000 °C), the representative microstructure of NiCoAlFeCu and NiCoAlFeCuCr alloys is shown in the images of Fig. 2. In the other hand, the microstructure of Mo alloys thermal treated at 1000 °C remains similar to the as-sintered condition. This is evidence about the alloys containing Mo are more stable to high temperatures than Cu alloys.

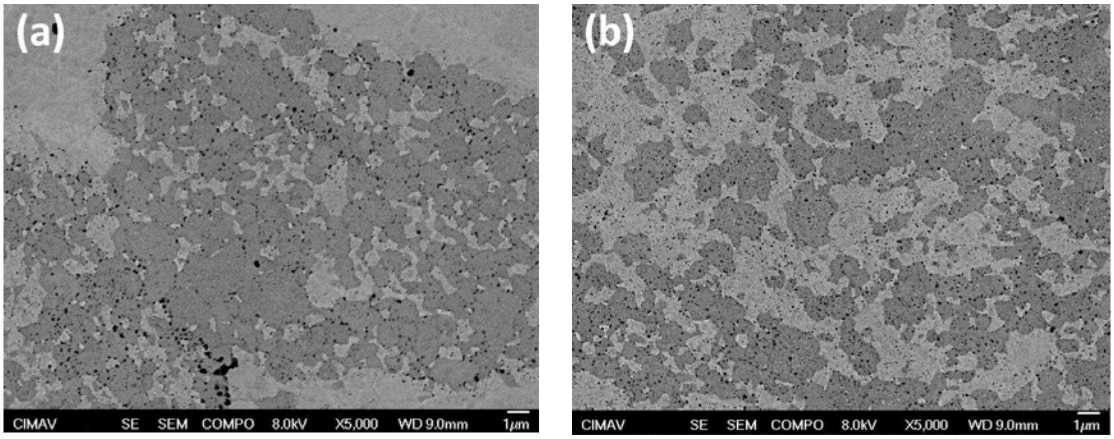


Figure 2. SEM images of (a) NiCoAlFeCu and (b) NiCoAlFeCuCr alloys after heat treatment at 1000 °C during 0.5 h.

EDS-SEM mapping was carried out to identified the chemical distribution of the different alloying elements in the formed microstructure. In Fig. 3 are presented SEM images of the NiCoAlFeMo with their corresponding elemental maps, to show the microstructural evolution trought the heat treatments, that is similar to the case of NiCoAlFeMoCr alloy.

The microstructure of this alloy treated at 1000 °C has not significant changes compared with the sintered condition. However, increasing the temperature to 1100 °C, the chemical distribution becomes more homogenous, instead of three phases (in sintered and 1000 °C conditions), only two phases are observed. A dark Ni-Co-Al- rich phase and a bright Mo-rich phase. This thermal stability to 1000 °C may explain the relative poor increment in hardness of Mo heat treated alloys in comparison with the Cu alloys.

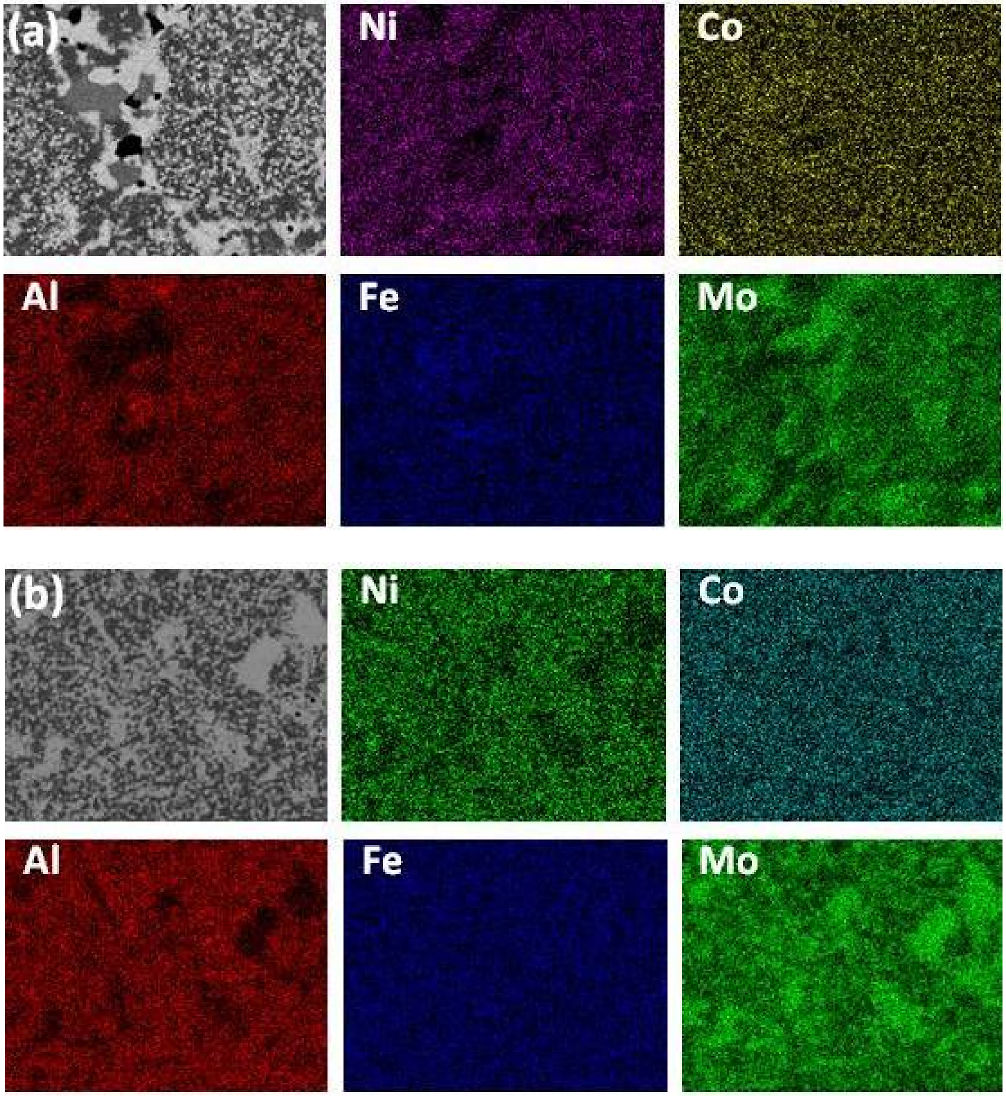


Figure 3. SEM images and EDS elemental maps of thermal treated NiCoAlFeMo alloy at: (a) 1000 ℃ and (b) 1100 ℃, during 0.5 h.

3.3 Structural evolution.

The sintered and heat treated samples at different temperature, subsequently were analyzed by XRD. Fig. 4 shows the XRD patterns of the NiCoAlFeCu and NiCoAlFeCuCr alloys. Obvious phase transformation in NiCoAlFeCu alloy occurs during heat treatments. The same effect is presented in alloy containing Cr (not showed in the figure).

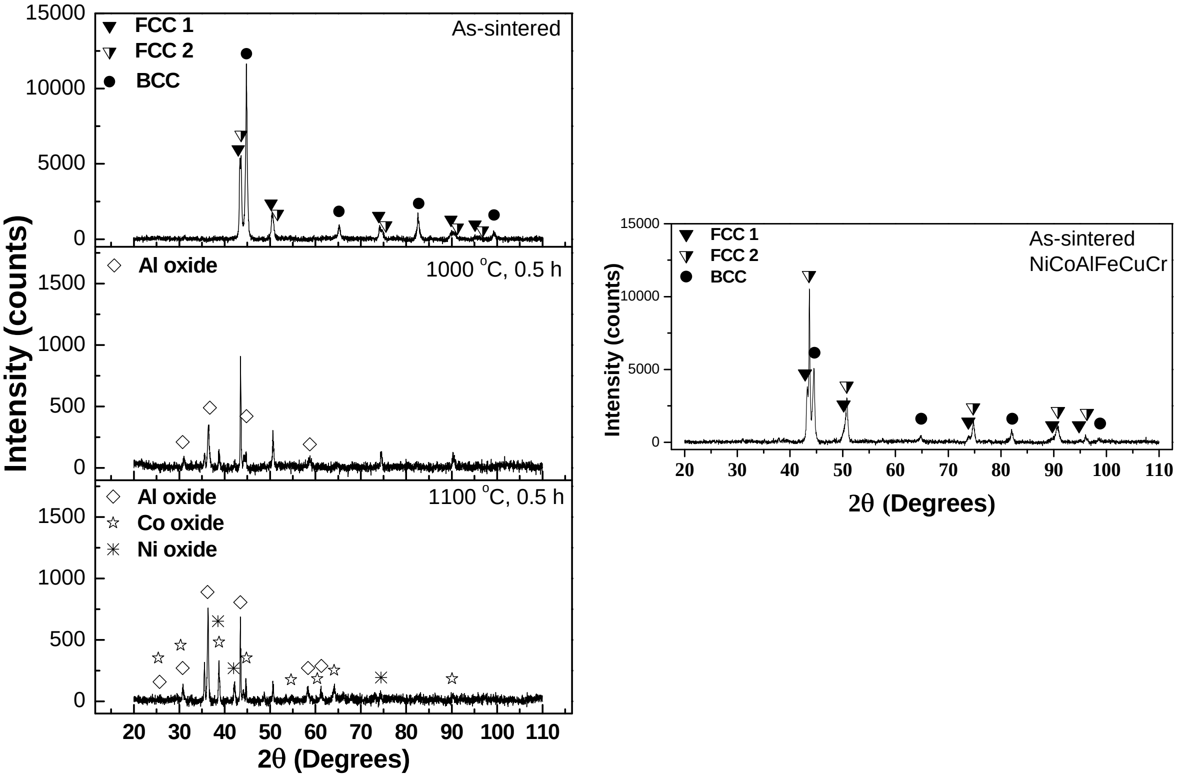
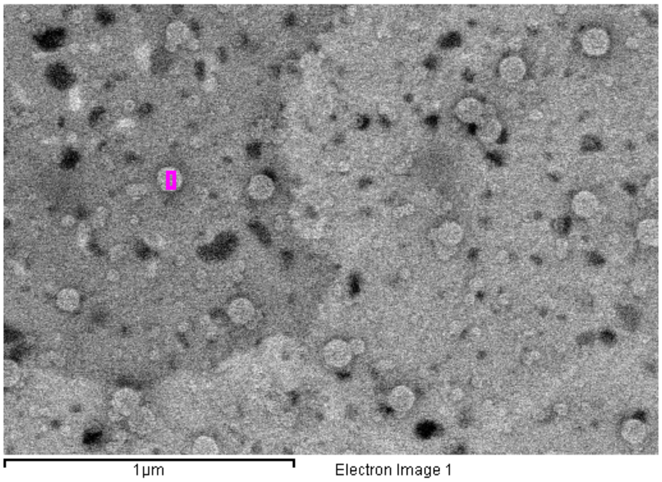


Figure 4. XRD patterns of NiCoAlFeCu alloy at sintering and heat treatment conditions (left) and NiCoAlFeCuCr alloy after sintering (right).

The alloys containing Cu, NiCoAlFeCu and NiCoAlFeCuCr, both present a similar mixture of phases after sintering process. The XRD patterns exhibit the presence of two FCC phases and a BCC phase. The Cr addition favors the formation of FCC phase. After heat treatment at 1000 °C, the characteristic peaks of FCC and BCC phases remain and peaks relating to the formation of aluminum oxide appeared. When the temperature rises to 1100 °C, the formation of oxides increased. The intensity peaks of FCC and BCC phases decreased. Besides aluminum oxide formation, evidence of Co and Ni oxides formation is presented.

In order to verify the presence of oxides of Co and Ni, in Figure 5 is shown a SEM image of the NiCoAlFeCuCr alloy at higher magnification. It is observed the presence of small spheres which according to elemental analysis EDS-SEM results are Co and Ni oxides.



Element	Atomic %
O K	13.46
Al K	15.59
Cr L	2.23
Fe L	14.12
Co L	22.09
Ni L	22.04
Cu L	10.06

Figure 5. SEM image of NiCoAlFeCuCr alloy after heat treatment at 1000 ℃, during 0.5 h. To the righ, a table with EDS results to give evidence about the formation of Ni and Co oxides, and corroborate the XRD patterns.

The addition of Cr in the Mo alloy has a significant effect on the formation of phases. The presence of FCC phase gets reduced, while increases the content of a phase containing Cr (see Figure 6). It is possible that this structural change is responsible for the increase in hardness by adding Cr, a FCC phase due to its crystalline nature, has a lower slip resistance.

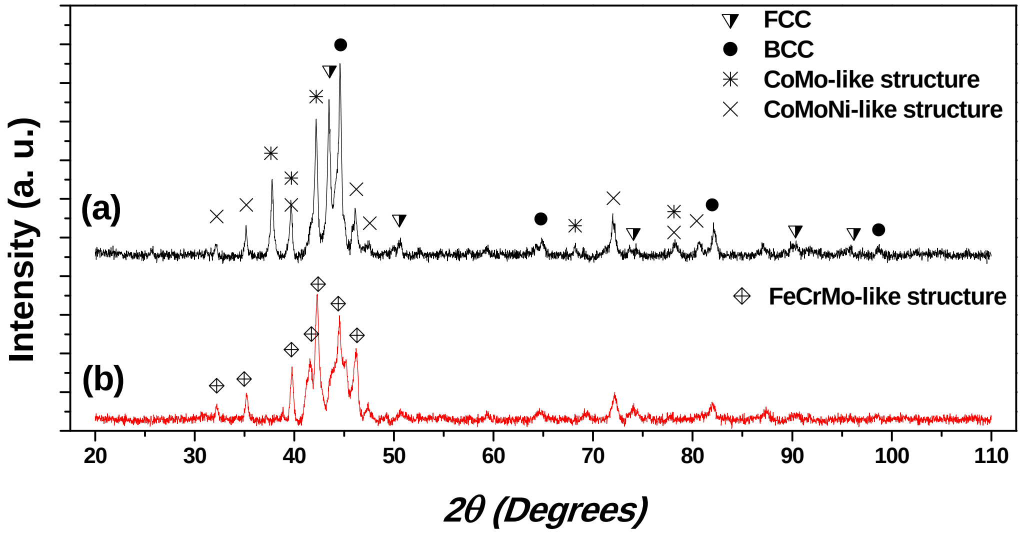


Figure 6. XRD patterns of (a) NiCoAlFeMo and (b) NiCoAlFeMoCr alloys at sintering condition.

the EDS-SEM mapping results reveal the presence of Ni oxides in the heat treated Mo alloys, in regard to the diffraction patterns, aluminum oxide after has the dominant presence. The nanoscale aluminum oxide distributed along the microstructure of Mo alloys promotes the enhancement of hardness by precipitation strengthening mechanism, above the hardening caused by Cu-rich precipitates.

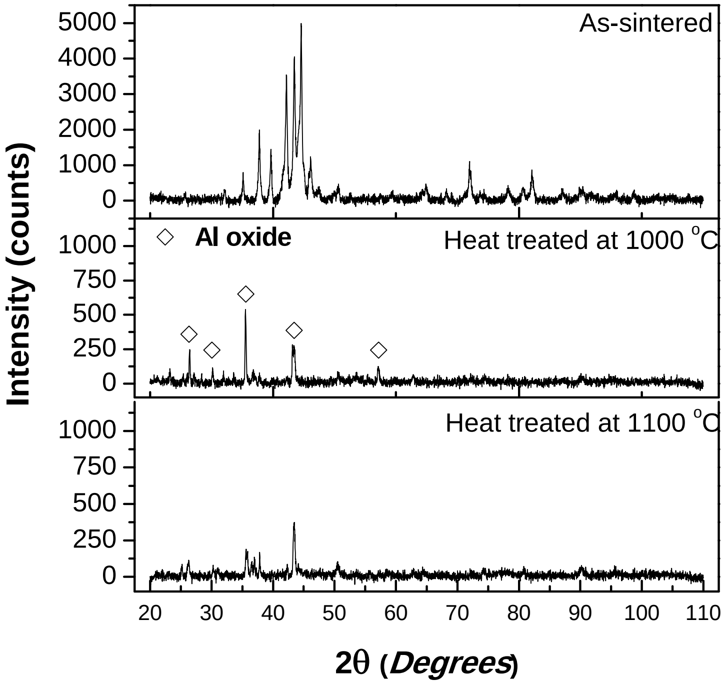


Figure 7. XRD patterns of NiCoAlFeMo alloy at different thermal conditions.

3.3 Microhardness.

The HE alloys exhibit high hardness that varies widely according to the alloying elements. Some of these alloys retain their high levels of hardness after annealing at 800 °C, making them potentially applicable for wear resistance and high temperature resistance [10]. With a proper design of chemical composition promising properties such as hardness can be obtained. The results of microhardness test are presented in table 1.

Table 1. Microhardness results.

High entropy alloy	**Microhardness (HV)**		
	As-sintered	**Heat treated at 1000 °C**	**Heat treated at 1100 °C**
NiCoAlFeCu	261	466	461
NiCoAlFeCuCr	269	447	432
NiCoAlFeMo	915	977	966
NiCoAlFeMoCr	980	1014	766

In bulk samples containing Cu, there is no significant difference in hardness. In Mo alloys, the hardest alloy contains Cr. The effect of Cr is obvious in the hardness results. The addition of Cr promotes a slightly hardening of alloys.

Before heat treatments, the alloys with Mo have the highest hardness value. The NiCoAlFeCrMo has the highest hardness value, while the NiCoAlFeCu alloy has the smallest. The hardness of the alloys exhibited a strong correlation with the chemical composition. Mo has a larger atomic radius (1.39 Å) than Cu (1.28 Å), and has a higher melting point. This difficult the diffusion and enhanced the slip resistance.

After heat treatment, the addition of Cr has the opposite effect in the two groups of alloys. In the alloy containing Cu, Cr not promotes hardening of the alloy after subjecting to high temperature, while improving the hardness of the alloy containing Mo (see Fig. x).

Dispersion of nanocrystalline precipitates in both, Cu and Mo alloys, after sintering process might provide a precipitation strengthening. After heat treatments, the formation of oxides is apparently more substantial. A improvement in hardness is observed after 1000 °C, but as the temperature increases to 1100 °C, the appearance of more quantity of strong but brittle oxides affect the performance of the alloys decreasing slightly their hardness.

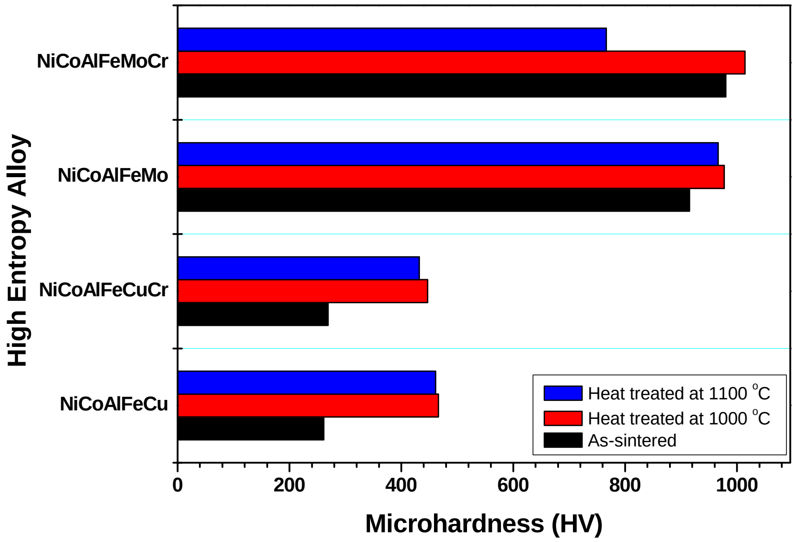


Figure 8. Vickers microhardness results of alloys before and after heat treatments.

4. Conclusions.

The mechanically alloyed and subsequent sintered high entropy alloys exhibited FCC and BCC phases. The heat treatments at high temperatures promote the presence of this type of phases besides the formation of different oxides.

In general, the alloys containing Mo reached greater hardness values than alloys containing Cu. After heat treatments, the hardness increased, at both temperatures 1000 °C and 1100 °C, except the NiCoAlFeMoCr alloy, which exhibited softening at 1100 °C.

The temperature of thermal treatments that were carried out in this investigation has significant effect on the hardness of the studied alloys. The improvement of hardness is greater at the temperature of 1000 °C. A 1100 °C, the greater formation of oxides promotes the embrittlement of the alloys.

The combination of appropriate compositional design and high temperature treatments makes these alloys good candidates for high-temperature applications, even until 1000 °C.

5. References.

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