Sintering Process on Microstructure Evolution of Ni-Co-Al-Fe-Cu-Cr-Ti High-Entropy Alloys

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High-entropy alloys (HEA) contain at least five principal metallic elements in equiatomic ratio or between 5 and 35 at. %. [1,2]. Has been reported that HEA tend to form solid solution (SS) phases with simple FCC and/or BCC structures, resulting in interesting properties like good thermal stability, high strength and ductility [3,4]. The mechanical behavior and microstructural evolution of HEA after sintering process were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), and microhardness.

Elemental powders of Ni, Co, Al, Fe, Cu, Cr and Ti with a purity level higher than 99.5% were used as raw materials for mechanical alloying (MA). The MA systems were quinary NiCoAlFeCu (Q), senary NiCoAlFeCuCr (S) and heptanary NiCoAlFeCuCrTi (H) alloys in equiatomic ratio. The milling process was performed in a high energy ball mill (SPEX-8000M), methanol was used as a process control agent (PCA), and the milling time was 10 h. The ball-to-powder ratio was ~5:1. The as-milled powders were compacted at 375 MPa and sintered at 1200 °C during 3 h in sealed quartz ampoule in vacuum and cooled into the furnace until room temperature.

In figure 1, it is observed the microstructure of the three HEA systems. According to EDS analyses,

in Fig. 1a and 1b, zone A is a homogeneous Al-Ni-Co-rich SS, nevertheless it contains all the elements. In Fig. 1a, the zone B has a Cu-rich grid-liked microstructure, with a dark Co-Fe-rich matrix. In Fig. 1b, the zone B has a microstructure similar to widmanstätten ferrite, and it is composed of one bright Cu-rich phase with no content of Co, and one dark Al-Cr-Ni-rich phase with

no signal of Cu. The addition of Ti makes a more complex microstructure. In figure 1c, Zone A, is a Cr-Fe matrix, with bright Cu-rich regions, and dark regions containing all the elements except Cu,

almost in equiatomic ratio. Zone B, contains a Ti-Co-Ni-Al-rich SS with Cu-rich round-like phase. Zone C has a dark Ti-rich phase inside a Cu-rich matrix. According to phase diagrams, Cu has very limited solid solubility with Fe, Co and Cr, and it is probably the main cause of the complex microstructure formed in this investigation. Moreover, Chen et al. attribute improvement of plasticity in HEA to Cu additions [5]. This assertion is related with microhardness results, which give evidence about Cu-rich phases may be responsible of hardness decreased in alloys (see table 2).

Fig. 2 shows the XRD spectra of the three systems after sintering process. In the Q and S systems are presented phases with both, FCC and BCC structures. Apparently, with the Ti addition appears a HCP phase, related to Co HCP diffraction lines that suffer a very small shift to lower angles. Currently, XRD spectra results are not identified at all, so deep analysis is carrying out.

References.

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- [3] Y.-L. Chen et al., Journal of Alloys and Compounds 477 (2009) 696–705
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(a) A A CIMAN SE SEM COMPO 150KV X300 WD.80mp 1mm

Cu-rich windmanstätten

Cu-rich grid-like microstructure.



Cu-rich round-like microstructure.



FIG 1. SEM microstructure images of (a) NiCoAlFeCu, (b) NiCoAlFeCuCr and (c) NiCoAlFeCuCrTi systems.

TABLE 1. Chemical composition.

System	Composition
(a) NiCoAlFeCu	
Zone A:	Al-Ni-Co-rich SS.
Zone B:	Cu-rich phase.
(b) NiCoAlFeCuCr.	
Zone A:	Al-Ni-Co-rich SS.
Zone B:	Cu-rich phase.
(c) NiCoAlFeCuCrTi	
Zone A:	Ti-Co-Ni-Al-rich SS
Zone B:	Cr-Fe-rich matrix and
	bright Cu-rich phase.
Zone C:	Cu-rich matrix, and Ti-
	rich dark phase.

TABLE 2. Microhardness results.

System	Microhardness
NiCoAlFeCu	202 - 282 HV
NiCoAlFeCuCr.	287 - 354 HV
NiCoAlFeCuCrTi*	$562 - 825 \ \mathrm{HV}$

*The lower microhardness values correspond to Curich phase, while Cr-Fe-rich phase is responsible for the higher values.



FIG 2. XRD spectra of the equiatomic NiCoAlFeCu, NiCoAlFeCuCr and NiCoAlFeCuCrTi systems after sintering process.