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Al, Cu and Zr addition to High Entropy Alloys: The Effect on Recrystallization Temperature

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Abstract. The equimolar Cr, Mn, Fe, Co and Ni alloy, first produced in 2004, was unexpectedly found to be single-phase. Consequently, a new concept of materials was developed: high entropy alloys (HEA) forming a single solid-solution with a near equiatomic composition of the constituting elements. In this study, an equimolar CoCrFeMnNi HEA was modified by the addition of 5 at% of either Al, Cu or Zr. The cold-rolled alloys were annealed for 30 minutes at high temperature to investigate the recrystallization kinetics. The evolution of the grain boundary and the grain size were investigated, from the as-cast to the recrystallized state. Results show that the recrystallized single phase FCC structures exhibits different twin grains density, grain size and recrystallization temperatures as a function of the at.% of modifier alloying elements added. In comparison to the equimolar CoCrFeMnNi, the addition of modifier elements increases significantly the recrystallization temperature after cold deformation. The sluggish diffusion (typical of HEA alloys), the presence of a solute in solid solution as well as the low twin boundary energy are responsible for the lower driving force for recrystallization.

Introduction

High entropy alloys (HEAs) are characterized by the concentration of each element in the range of 5-35 at.% and high mixing entropy in their liquid state. These materials exhibit promising technological characteristics such as high hardness [1][2], good wear resistance [3], excellent strength at both high and low temperatures [4][5], and generally good resistance to oxidation and corrosion [6].

The unique properties of HEAs are attributed to the inherent properties of multicomponent solid solution formation [7], such as distorted lattice structures [8], the cocktail effect [9], sluggish diffusion [4] and formation of nanoscale deformation twins [6][10]. It is well-known that HEAs can exhibit sluggish diffusion and severe lattice distortion effects [11] which might hide the grain boundary migration in the re-crystallization process [12] and dislocation movements [13], respectively. These are the reasons for which annealing of the cold rolled alloys necessarily needs to be performed at high temperature for prolonged duration.

According to the literature [6][11], the most employed process routes to synthesize structural HEAs, are from the liquid state (e.g melting and casting) [6][12], and from the solid state (powder metallurgy) [14]. In a previous study, the present authors synthesized a CoCrFeNiMn HEA modified with 5% at. Zr by means of a new production route which include vacuum induction melting followed by thermos-mechanical recrystallization[15]. This novel processing scheme, considered as a valid alternative to traditional arc melting, could be exploited thanks to the low temperature involved. The authors demonstrated that good chemical homogeneity could be achieved more efficiently compared to the traditional approach. Eventually mechanical and thermal treatments were performed. Considering the successful outcome of our previous work [16], additional elements were explored as modifiers of the common CoCrFeNiMn alloy, namely Al and Cu. The influence of these alloying elements, Al and Cu (5% at.) alloying elements, as well as Zr on the mechanical properties were evaluated and the results were evaluated. Preliminary results on chemical resistance in industrial and urban atmospheres were exhibited.

Materials and Methods

The following elemental powders (Table 1), supplied by Sigma Aldrich, were exploited as reactants to prepare equiatomic $Co_{20}Cr_{20}Ni_{20}Fe_{20}Mn_{20}$, $Co_{19}Cr_{19}Ni_{19}Fe_{19}Mn_{19}Zr_5$, $Co_{19}Cr_{19}Ni_{19}Fe_{19}Mn_{19}Al_5$ and $Co_{19}Cr_{19}Ni_{19}Fe_{19}Mn_{19}Cu_5$.

Table 1: Composition of the metal powders used (BCC = body centered cubic; FCC = face centered cubic; HCP = Hexagonal close-packed arrangement).

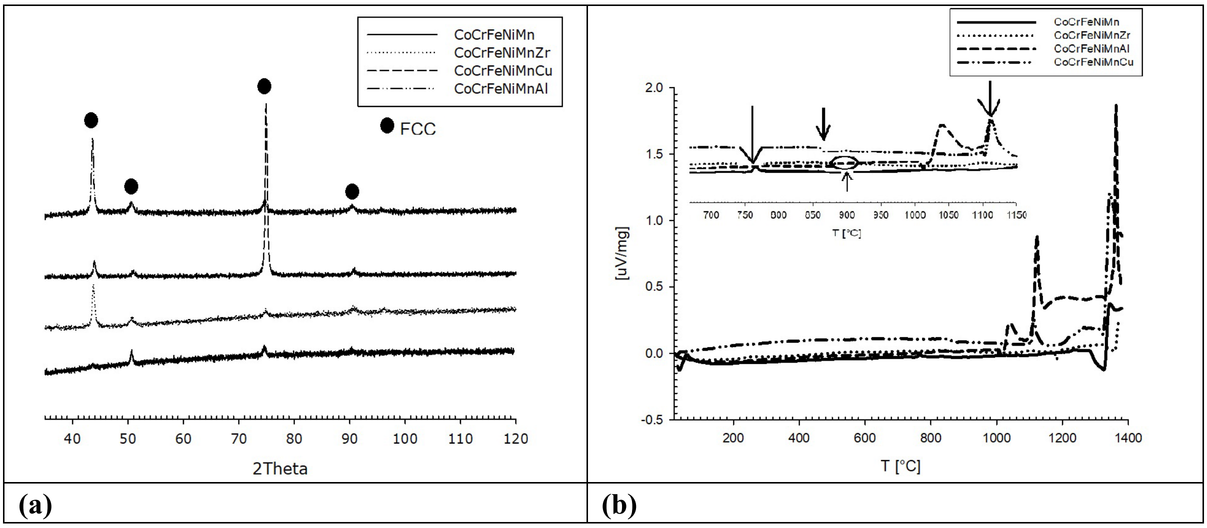
Element	Purity (%)	Particle Size (µm)	Cell
Fe	97.00	<44	BCC
Co	99.80	<2	HCP
Ni	99.70	<5	FCC
Cr	99.00	<44	BCC
Mn	99.00	<75	BCC
Zr	99.80	150	HCP
Cu	99.00	<10	FCC
Al	99.00	<75	FCC

The powder mixtures were subjected to mechanical milling in Argon atmosphere using a Planetary Ball Mill (PM 100 by Retsch GmbH, steel balls with BPR 15:1) working at 400 rpm for a total milling time of 45 h (more than 15 h is required to achieve mechanical alloying [17][2]). The pre-alloyed powder mixtures were melted in alumina crucibles using a vacuum induction furnace at 1600° C for 3 min. Exploiting a laboratory scale rolling equipment, the as-cast structures were cold rolled to about 96% reduction in thickness.

By thermal analyses (DSC) in purified helium atmosphere (NETZSCH STA 429 CD instrument) the thermomechanical treatment temperature was defined. X-ray Powder Diffraction (XRPD) was used to identify the crystal structure. The microstructures were studied by optical microscopy (OM) and scanning electron microscopy in conjunction with energy dispersive spectroscopy (SEM-EDS, ZEISS EVO 50 VP). Samples for these analyses were polished and chemically etched. Mechanical properties by instrumented indentation (CSM Instruments) were evaluated, to perform depth-sensing nano-indentation tests 300 mN. The indentations were performed using a Berkovich tip and the elastic modulus and equivalent Vickers hardness were calculated according to the Oliver and Pharr method [18].

Results

The formation of single FCC-structured HEAs following the induction process was confirmed by XRPD, as shown in Fig. 1(a). Recrystallization at 780 °C, 850 °C, 900 °C and 1125 °C for 30 min were carried out for the base alloy and the alloy modified with Zr, Al, and Cu, respectively. The DSC curves (as depicted in Fig. 1(b)) exhibit the presence of several exothermic peaks more or less pronounced, indicating that some elements reach different recrystallization temperatures.

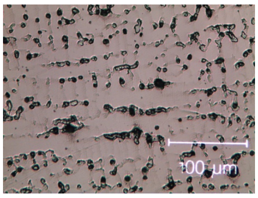
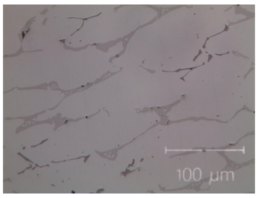
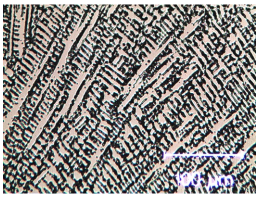
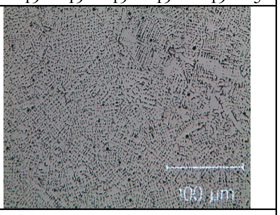


(a) **(b)**

Fig. 1: (a) XRD pattern of as cast modified-HEAs, (b) DSC of cold rolled modified-HEAs

The optical images of HEAs and the related EDS analyses (Table 2) exhibits the typical dendritic structure and their semiquantitive composition, where Cu and Al modified alloy show a finer microstructure (Table 2) than the Zr-HEA. The different microstructure between Zr-HEA and the others is both due to the different solidification process performed and the formation of a double FCC phase structure. Indeed, the former was carried out slowly in the furnace to promote the Zr solubility into the HEA matrix, the latter was quickly cooled down at room temperature. Therefore, only the Zr-modified alloys show a significant interdendritic phase at different chemical composition, due to the low Zr solubility. The microstructures after recrystallization treatment were exhibited in Fig. 3.

Table 2: Semiquantitative chemical analyses of modified HEA in as cast condition

	$Co_{20}Cr_{20}Ni_{20}Fe_{20}Mn_{20}$	$Co_{19}Cr_{19}Ni_{19}Fe_{19}Mn_{19}Zr_5$		$Co_{19}Cr_{19}Ni_{19}Fe_{19}Mn_{19}Cu_5$		$Co_{19}Cr_{19}Ni_{19}Fe_{19}Mn_{19}Al_5$
						
		Dendritic	**Interdendritic**	**Dendritic**	**Interdendritic**	
Co	20,18	22,12	18,62	19,77	11,26	20,57
Cr	20,70	23,59	4,54	19,46	11,18	21,69
Mn	18,53	10,60	11,48	12,66	19,96	14,87
Fe	20,42	22,81	8,03	19,81	10,71	20,69
Ni	20,17	20,57	38,27	18,56	18,69	20,15
Zr	/	0,3	19,06			
Cu				9,76	28,22	/
Al				/	/	2,02

The driving force for recrystallization of the dendritic microstructure arises from the elimination of dislocations introduced during the cold rolling. The promotion of grain boundary migration and the twinned microstructure, characterized by different grain size lead to a FCC structure (Fig. 3) as confirmed by XRD diffraction pattern (Fig. 2). Unfortunately, the enlargement of equiaxic grain sizes, limits the mechanical reinforcement of these alloys. A high temperature for recrystallization is essential for the Cu-HEA, but renders the microstructure instable as the smaller recrystallized grains are consumed by excessive growing of a few grains, i.e. secondary recrystallization [18]. The speed of the atomistic process at high temperature and the particular thermodynamic conditions, which are far from the equilibrium of HEA, define the boundary migration. The low driving force observed is justified by the solute effect which is strong even at low concentrations, indeed the solubility in dendritic phase of Zr-HEA reaches only 0.2-0.3 at.% [19]. As already known, the addition of Zr in equiatomic HEAs promotes recrystallization following cold deformation and gives a microstructure composed of a large number of fine grains which increases the strength of the alloy [24]. Due to the sluggish diffusion behaviour of HEAs and the low mobility of the grains boundaries, the high concentration of Al and Cu slows down recovery and recrystallization. Consequently, an elevated annealing temperature is needed to recrystallize the microstructure that at the same time results in increased grain size.

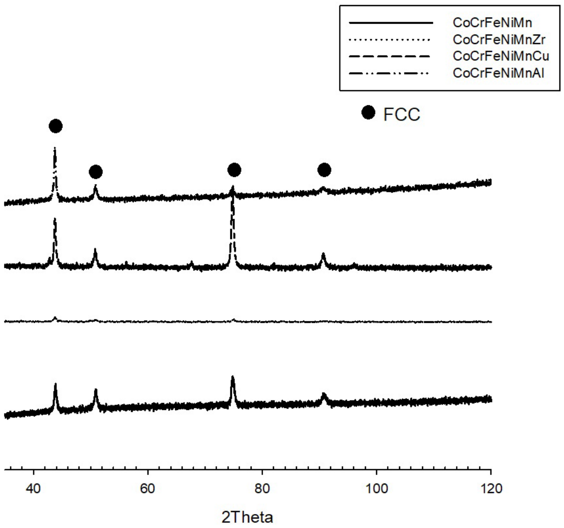


Fig. 2: XRD patter of modified-HEAs after recrystallization

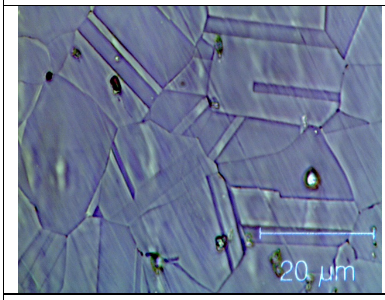
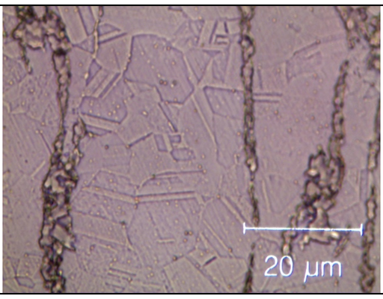
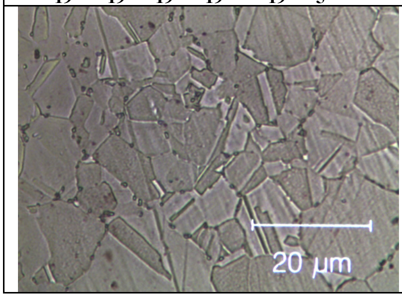
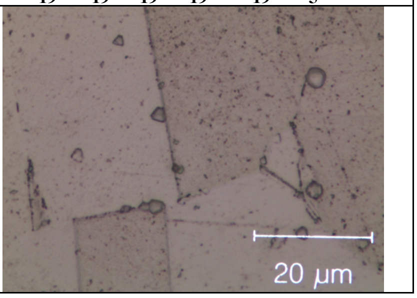
CoCrFeNiMn	CoCrFeNiMnZr
	
$Co_{19}Cr_{19}Ni_{19}Fe_{19}Mn_{19}Al_5$	$Co_{19}Cr_{19}Ni_{19}Fe_{19}Mn_{19}Cu_5$
	

Fig. 3: SEM images after recrystallization

Preliminary mechanical test results, i.e. hardness and Young modules, of both as cast and recrystallized alloys are shown in Fig. 4. Recrystallization results in higher values.

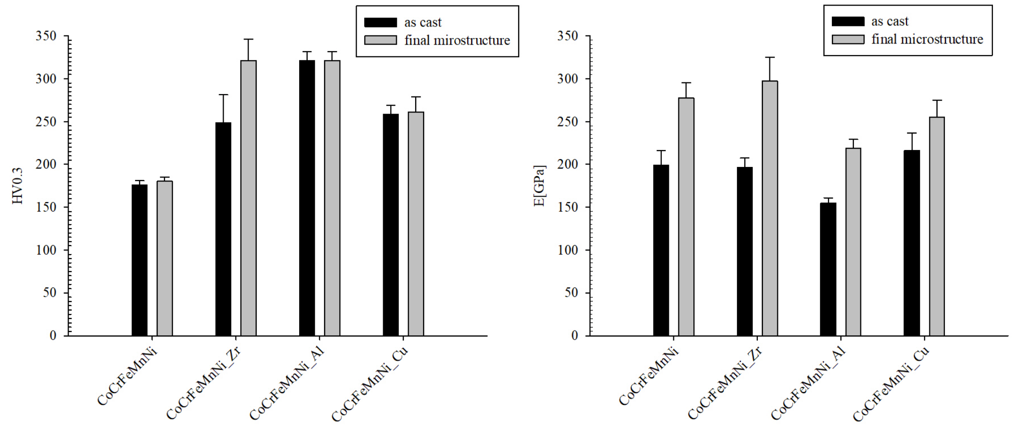


Fig. 4: HV and E

Preliminary corrosion tests were carried out in two environments, i.e. 3.5 %NaCl and 0.5M H2SO4, and the results are shown in Fig. 5. The behavior of all HEAs is better than AISI 420 but worse than AISI 304, in particular in term of pitting potential in NaCl environment

The presence of MnS in CoCrFeNiMn alloy decreases the corrosion resistance in a NaCl solution, but the unmodified and the Al-modified HEAs show similar behavior in a H2SO4. The Cu-modified HEA shows the worst characteristic in both the environments, as expected. These data will be discussed more exhaustively in a future work.

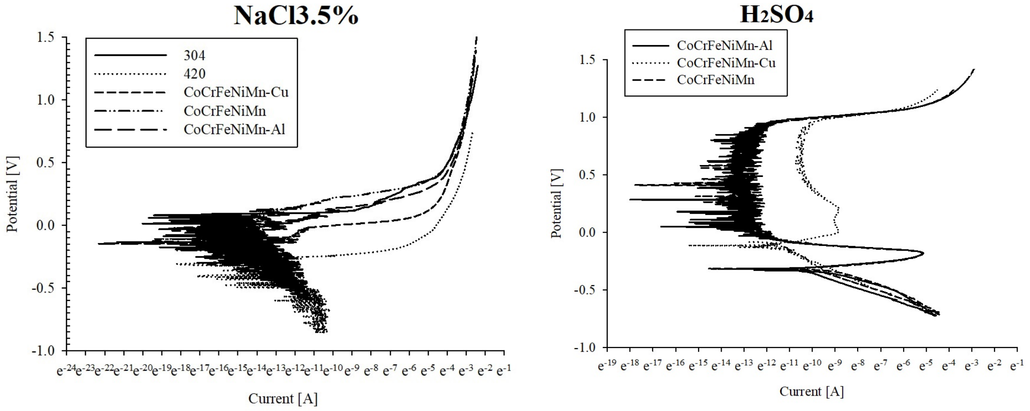


Fig. 5: Corrosion Test

Conclusions

In the present work, CoCrFeMnNi HEAs were modified adding the 5% of Al, Cu and Zr. The alloys demonstrated the capability to form a single-phase solid solution (FCC), which is suitable to be used at cryogenic temperatures. Moreover, the solid solution strengthening should be more effective in these HEAs compared to conventional ones. Microstructure morphology after annealing could be tracked back to a cold deformation structure with the presence of twins, thus in agreement with XRD analysis that confirms the FCC structure. The application of conventional strategies to promote the recrystallization of dendritic structure by cold deformation followed by recovery and recrystallization, transforms the dendritic structure into a polycrystalline microstructure, suitable for structural applications. In comparison to HEAs without alloying element added, the alloys with Zr and Al show a significant reduction of austenitic grain sizes with an higher density of geminates. Unfortunately, the high recrystallization temperatures of the alloy containing Cu caused a significant enlargement of the austenitic grains which inhibits the mechanical reinforcement.

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