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The Effect of Zr addition on melting temperature, microstructure, recrystallization and mechanical properties of a Cantor high entropy alloy

E.G. Campari 1,*, A. Casagrande², E. Colombini³, M. Lassinantti Gualtieri³, P.Veronesi³

- ¹ Department of Physics and Astronomy, Alma Mater Studiorum-University of Bologna, Viale Berti Pichat 6/2, 40127 Bologna, Italy; enrico.campari@unibo.it
- ² Department of Industrial Engineering, Alma Mater Studiorum-University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy; angelo.casagrande@unibo.it
- ³ Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Via Pietro Vivarelli 10, 41125 Modena, Italy; elena.colombini@unimore.it, magdalena.gualtieri@unimore.it, paolo.veronesi@unimore.it
- * Correspondence: enrico.campari@unibo.it; Tel.: +39 051 2095148

Abstract: The effect of Zr addition on the melting temperature of the CoCrFeMnNi High Entropy Alloy (HEA), known as the "Cantor's Alloy", is investigated, together with its microstructure, mechanical properties and thermo-mechanical recrystallization process. The base and Zr-modified alloys are obtained by vacuum induction melting of mechanically pre-alloyed powders followed by recrystallization. The alloys were characterized by X-ray diffraction, scanning and transmission electron microscopy, thermal analyses, mechanical spectroscopy and indentation measures. The main advantages of Zr addition are: 1) a fast vacuum induction melting (VIM) process; 2) the lower melting temperature, due to Zr eutectics formation with all the Cantor's alloy elements; 3) the good chemical alloy homogeneity; 4) the mechanical properties improvement of recrystallized grains with a coherent structure. The crystallographic lattice of both alloys resulted to be FCC. Results demonstrate that the Zr-modified HEA presents a higher recrystallization temperature and smaller grain size after recrystallization with respect to the Cantor's alloy, with precipitation of a coherent second phase which enhance the alloy hardness and strength, while maintaining a good tensile ductility.

Keywords: high entropy alloy, microstructure, vacuum induction melting, heat treatment, mechanical spectroscopy, Zirconium.

1. Introduction

The first scientific papers on High Entropy Alloys (HEAs) were published in 2004 [1]. Since then, the unique properties of these materials have attracted attention from research groups all over the world. In the pioneering studies by Cantor et al., it was shown that a single-phase solid solution could be obtained using equimolar contents of Cr, Mn, Fe, Co and Ni [1]. This rather unexpected result paved the way for the development of the new class of alloys [3].

HEAs may contain main elements, each with a concentration in the 5-35 at. % range [2]. The alloys present a high mixing entropy in their liquid state [3] and thus give raise to a solid solution (mostly with FCC or BCC lattice) instead of intermetallic phases. Some promising technological features of HEAs are high hardness [4], good wear resistance [5], excellent strength at both high and low temperatures [6], and a good resistance to oxidation and corrosion [9]. The unique properties of the HEAs are ascribed to the inherent properties of a multicomponent solid solution, such as a distorted lattice structure [10], cocktail effect [11], sluggish diffusion [4] and nanoscale twinning [8].

There are four main approaches to prepare HEAs: (1) from the liquid state (arc or induction melting), (2) from the solid state (mechanical alloying, powder metallurgy), (3) from the gas state (sputtering techniques, mainly for coatings) and (4) from electrochemical processes (again mainly for coatings) [13]. Taking into consideration synthesis from the liquid state, induction melting offers several advantages over arc melting such as faster chemical homogenization and preservation of low-melting point elements. Moreover, arc melting requires several re-melting steps to obtain a good homogeneity. As a result, elements with high vapour tension, such as Mn, tend to evaporate during the process [15]. Instead, the induction melting process results in good homogenization, thanks to the magnetic stirring, as well as providing a limited evaporation of low-melting point elements [16].

A major research area, aimed to widen the potential applications of HEAs, concerns their response to thermo-mechanical processing [17]. The processing routes involve heavy deformation and annealing with microstructural modifications and development of textures [18-26]. In recent works, the deformation and annealing behaviour of the classical equimolar Cantor's alloy was thoroughly investigated, showing that proper thermomechanical treatments could enhance its mechanical properties [20]. Indeed, research showed that the microhardness, grain size and twin density depend on cold working and annealing temperature [21]. Studies on recrystallization behaviour of the CoCrFeMnNi alloy have demonstrated that a single FCC structure is retained after rapid annealing at low temperature [28] and that a successive cold rolling and recrystallization annealing can restore both ductility and workability, rendering the material interesting for structural applications [31]. According to literature data, the improved toughness of CoCrFeMnNi HEAs is explained by a strong distortion of the FCC lattice due to overshooting solution as well as a reinforcement effect caused by precipitation [32]. This approach has already been applied in the past to Carbon containing CoCrFeMnNi HEAs, where thermomechanical treatments promoted the recrystallization of a starting dendritic structure into an equiaxed polycrystalline one [33].

In recent years, much work has been focused on the development of new HEA compositions with good mechanical performances [34]. A promising route is, for instance, to add Zr [35]. Its inclusion in the crystalline structure has been used indeed as a strengthening mechanism both in light alloys [36] and steels [37]. Expected strengthening mechanisms related to Zr-modifications of HEAs are dislocation pinning due to severe lattice-distortion and solid solution reinforcement [38]. Based on previous studies on Mn-free CoCrFeNiZr_x ($0.1 \le x \ge 0.5$) [35], Zr is expected to promote recrystallization after cold deformation and to originate a fine-grained microstructure which increase the alloy strength.

Owing due to these considerations, in this work an equimolar Cantor's alloy was produced with an alternative melting process, starting from pre-alloyed equimolar powders of CrNiFeCoMn prepared by mechanical alloying. Zr metallic powders addition lead to eutectics formation during high temperature annealing, resulting in a reduced melting temperature for the HEAs production with respect to the standard procedure, also producing a simple FCC crystalline structure. The main advantages of this approach with respect to the traditional techniques were the reduced time for the vacuum induction melting (VIM) process due to the eutectic formation between Zr and all elements used in the Cantor's alloy and the satisfactory chemical homogeneity obtained in a shorter time thanks to the use of pre-alloyed powders. A 5 at. % Zr was added, resulting in a liquid phase formation at about 1470 K [41], to be compared with the 2500 K of a traditional arc melting process. As reported for other Iron alloys, like AISI 304 stainless steels, the Fe phase below 15 wt % Zr, is a mixture of α -Fe and γ -Fe, and becomes α -Fe (BCC) at or above 15 wt% Zr [42]. As far as the base Cantor's alloy is FCC, lowering the Zr content with respect to 15 wt % is therefore expected to avoid the appearance of other crystalline structures.

The alloy we succeeded in obtaining after solidification consists of a dual phase HEAs alloy made of a majority equimolar FCC Cantor alloy phase and a minority phase with a different chemical composition but the same crystallographic structure. This minority phase, which is located between the dendrites of the matrix, significantly increased the yield strength and hardness of the Zr-added alloy compared with the base alloy. It is interesting to observe that dual phase high entropy alloys differ from the original concept in that they are flexible in the number of components and also in that they do not necessarily have equimolar composition.

The ability of a mixture to form a solid solution is calculated from the mixing enthalpy (H_{mix}) and the atomic size mismatch (δ) according to the Hume-Rothery rules [13]. In order to apply these concepts to the prediction of solid solution formation in the HEAs of this study, composition-weighted terms for differences in atom radii (δ_r), electronegativity (χ), and average valence electron concentration (VEC) have been computed [43]. The balance between entropic and enthalpic contributions to the formation of a solid solution is expressed by the parameter Ω [43]:

$$\Omega = \frac{T_{\rm m}\Delta S_{\rm mix}}{\Delta H_{\rm mix}} \tag{1}$$

where ΔS_{mix} is the entropy of mixing and T_m the melting temperature. The most critical factor which determines whether an alloy crystallizes into a BCC or FCC structure is the valence electron concentration (VEC), which is calculated according to Eq. 2 [46]:

$$VEC = \sum_{i=1}^{N} x_i VEC_i$$
⁽²⁾

where xi is the concentration of the i-th element.

A VEC value larger than 8 promotes the formation of an FCC phase. A value smaller than 6.87 a BCC phase. Co-existence of FCC and BCC phase is observed for VEC values between 6.87 and 8 [46]. An up to 5 at % Zr addition to the base Cantor's alloy does not significantly alter the expected values of the parameters in eq. 1 and 2. Consequently, this modifying percentage was used in this work.

The limited solubility of Zr in each of the HEAs elements (minimum 0.2 at. % in α Co and maximum 2.7 at. % in α Ni) [44] and generally in FCC solid solutions, e.g. AISI 304 or 316L steels [45], promotes both precipitation phenomena and strong lattice distortions in the dendritic HEAs. If the precipitated phase is an FCC, isostructural with the primary phase, then the mechanical behavior of the Zr added alloy will be similar to that of the standard Cantor's alloy because coherent phase boundaries have negligible influence on dislocation glide. Conversely, incoherent phase boundaries yield significant impediment to dislocation glide, providing strength at the expense of ductility.

In this work we show how an even stronger, with respect to the standard alloy, and yet very ductile HEAs dual phase alloy con be obtained. Moreover, the final microstructure and recrystallization process of the Co₂₀Cr₂₀Fe₂₀Mn₂₀Ni₂₀ together with evaluations of mechanical properties, are described.

2. Materials and Methods

Table 1 lists purity, particle size and unit cell structure of the elemental powders, provided by Sigma Aldrich, used as reactants for the HEAs preparation.

Element	Purity (%)	Particle Size (µm)	Cell
Fe	97.00	<44	BCC
Со	99.80	<2	НСР
Ni	99.70	<5	FCC
Cr	99.00	<44	BCC
Mn	99.00	<75	BCC
Zr	99.80	150	НСР

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

Powder mixtures for the preparation of HEAs were subjected to pre-alloying by 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. Treatment cycles of 15 min followed by 5 min break time (to avoid overheating) were performed for a total milling time of 45 h [13]. The alloyed powders, with composition Co₂₀Cr₂₀Fe₂₀Mn₂₀Ni₂₀ and Co₁₉Cr₁₉Fe₁₉Mn₁₉Ni₁₉Zr₅, were placed in alumina crucibles and thermally treated in a vacuum induction furnace at temperatures exceeding 1720 K for 30 min, during which complete melting was achieved. Induction melting of mechanically pre-alloyed powders was used as a synthesis approach in order to reduce element segregations and loss of Mn.

The as-cast alloys were cold rolled using a laboratory rolling equipment to achieve a 96% thickness reduction (from 3 mm to 0.3 mm). The specimens were subsequently recrystallized by a 30 min annealing in a Kanthal Super HT rapid high temperature furnace. The recrystallization temperatures were previously determined by differential scanning calorimetry (DSC) performed in purified Helium atmosphere using a NETZSCH STA 429 CD instrument. All specimens were annealed at the recrystallization temperature of the Zr-modified alloy, 1143 K, which is higher than the recrystallization temperature of the base alloy (T=1043 K) [41].

The specimens were scanned in alumina crucibles from room temperature to 1700 K, at a heating rate of 10 K/min.

As cast, cold worked and recrystallized specimens, were analysed as follows:

- X-ray Diffraction (XRD), used to determine the crystal structure. A Θ/2Θ scan was performed in the 2Θ range from 35° to 100° using a Panalytical X'Pert PRO diffractometer equipped with a gas proportional detector. A parallel beam configuration was applied, including an X-ray mirror (incident beam optics) coupled with a long soller slit and a flat monochromator (diffracted beam optics). Hence, sample displacement errors were avoided and a correct determination of the unit cell from peak positions could be performed.
- Microstructural investigations were performed by optical microscopy (OM) and scanning electron microscopy in conjunction with energy dispersive spectroscopy (SEM-EDS, ZEISS EVO 50 VP). Specimens used for these analyses were polished and chemically etched (gliceregia solution composed of 1 HNO₃+ 3 HCl + 3 Glycerol – OM Olympus GX71). A Nova NanoSEM 45 equipped with an electron backscatter diffraction (EBSD) detector (Bruker e- Flash1000) was used to obtain grain maps and inverse polar figures. Transmission electron microscopy analyses (TEM, JEOL JEM-2100 apparatus at accelerating voltage of 200 kV) were performed on selected samples prepared by conventional twin-jet electro-polishing of mechanically pre-thinned (100μm) foils. The electro-polishing procedure was performed in a mixture of 95%

C₂H₅OH and 5% HClO₄ at a potential of 27 V. Selected area electron diffraction patterns (SAED) were collected and indexed using a known camera length calibrated using an Aluminium standard. Data were elaborated using a Gatan Digital Micrograph software.

- Micro-hardness was measured by instrumented indentation (CSM Instruments). To
 perform depth-sensing nano-indentation tests, two different loads were applied: 300
 mN force with a linear loading/unloading rate of 450 mN/min and 50 mN force with
 linear loading/unloading rate of 150 mN/min, applied for 15 seconds. The indentations
 were performed using a Berkovich tip and the equivalent Vickers hardness were
 calculated according to the Oliver and Pharr method [47]. The hardness tests were
 performed on both dendritic and interdendritic phases.
- Mechanical measurements were performed in a vacuum by means of the mechanical analyzer VRA 1604 [48,49]. In the VRA apparatus, specimens are mounted in free-clamped mode and excited by flexural vibrations. Specimens are kept into resonance while temperature is changing at the selected rate. The resonance frequency of all specimens is in the 400 to 900 Hz range; the strain amplitude is about 10⁻⁵. Specimens are heated from room temperature up to a maximum temperature of 700 K at 1.5 K/min rate. The internal friction (usually referred to as IF or Q⁻¹) and the dynamic modulus are determined from the envelope of the decreasing oscillation amplitude of the specimen when excitation is turned off and from the specimen resonance frequency.

3. Results and discussion

3.1. Microstructure characterization

The as cast microstructures, shown in figure 1 and figure 2, are representative of what is usually found in the induction melted and rapidly solidified HEAs in the dendritic and homogenized states.



Figure 1. Micrograph of as-cast C019Cr19Ni19Fe19Mn19Zr5



Figure 2. Micrograph of as-cast Cantor's alloy Co20Cr20Ni20Fe20Mn20

The as-cast Zr-modified alloy is made of large grains while finer dendritic grains are found in the base Cantor's alloy, extending from the edge to the center of sample molds, in agreement with the heat flow direction during solidification.

Table 2 reports the results from semiquantitative EDS analyses of the two alloys. Specifically, data refers to: i) an extended area containing both dendritic and interdendritic areas and thus representative of the overall alloy chemical composition; ii) the dendritic structure; iii) the interdendritic second phase.

 Table 2. Semiquantitive analysis of average area, dendritic and interdendritc phase

 of as cast specimens (each reported atomic composition is a 5 point averaged analyses)

	C019Cr19Ni19Fe19Mn19Zr5			Co20Cr20Ni20Fe20Mn20			
	Average Area	Dendritic	Interdendritic	Average Area	Dendritic	Interdendritic	
0	2.33	2.17	2.14	2.88	1.63	3.24	
Со	21.22	22.63	17.27	19.67	20.75	16.80	
Cr	21.18	22.91	4.39	19.98	20.80	19.33	
Mn	10.53	10.08	11.87	17.96	16.34	23.66	
Fe	20.99	22.79	7.88	19.83	20.92	17.21	
Ni	21.52	19.36	38.47	19.68	19.55	19.76	
Zr	2.22	0.07	17.98	/	/	/	

The presence of Oxygen is both due to pre-alloying and to the chemical attack, needed to highlight the alloys microstructure. This second phase is typical of cast samples and can be clearly observed in the maps of figure 3.



Figure 3. EDS mapping of as-cast C019Cr19Ni19Fe19Mn19Zr5. The maps report, from left to right and top to bottom, the electron image of a portion of the specimen and the corresponding elemental distribution of Cr, Fe, Co, Ni, Zr, Mn.

According to EDS analyses and mapping, Co is uniformly distributed over both the dendritic and the interdendritic regions in the Zr modified alloy. Dendrites are made of an equimolar solid solution of Fe, Cr, Ni and Co, the absolute amount of each constituent being slightly higher than the nominal one. Zr is mainly concentrated in the interdendritic regions. These areas are also Ni enriched and Fe, Cr and Mn depleted. The interdendritic phase of the Zr-free alloy includes small spherical grains (8-10 μ m diameter) composed of Mn and Cr oxides. The formation of such inclusions has previously been reported by several authors and they seem difficult to be avoided in the mechanical alloying plus induction melting processing route [50]. Responsible for their presence is the pre-alloying procedure, which leads to partial powder oxidation, as demonstrated by the data reported in Table 3 and by XRD (MnO PDF card number 00-004-0326; MnCrO4 with PDF card number 00-033-0893, not shown here). The as-cast alloys also present deviations from the nominal composition (Table 2). Unfortunately, even though Mn volatility and the early presence of a liquid phase, due to eutectics formation [53], is reduced by induction technology compared with arc melting, nonetheless they are still present.

	Co20Cr20Ni20Fe20Mn20				
	wt%	at%			
0	2.14	7.11			
Со	19.59	17.66			
Cr	20.36	19.68			
Mn	19.65	18.69			
Fe	19.29	19.71			
Ni	18.96	17.15			

 Table 3. Semiquantitive analysis of Co20Cr20Ni20Fe20Mn20 (at%) powder after ball milling.

Table 4 reports the computed values for the Ω and δ parameters for the two alloys, together with those calculated from the compositions of the dendritic and interdendritic phases. In Table 5 the parameters values needed to achieve solid solutions are reported [46]. For comparative purposes, data presented in table 4 are also plotted in figure 4, together with values reported from the literature for other HEAs [55].

Table 4.	Calculated	parameters of	f the studied	HEAs
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		δ%	Ω	ΔH _{mix} [kJ/mol]	ΔS _{mix} [J/molK]	VEC	ΔX%
Co20Cr20Ni20Fe20Mn20	NOMINAL	1.73	5.7	-4.16	13.38	8	1.47
	Real Dendrite	1.77	5.84	-4.14	13.37	8.0	1.48
	Real – Interdendritic	1.77	5.50	-4.36	13.35	8.0	1.47
C019Cr19Ni19Fe19Mn19Zr5	NOMINAL	3.2	3.8	-6.91	14.36	7.8	1.45
	Real Dendrite	2.18	5.82	-4.19	13.23	8.0	1.49
	Real Interdendritic	11.17	1.23	-19.37	13.20	7.98	1.46

Table 5. Suitable range to form solid solution

	ΔS_{mix}	ΔH_{mix}	δ
Solid Solution Phase	$10 < \Delta S_{mix} < 19.5$	-22<\(\Delta H_mix)<7	0<8<8.5
BMGs	$7 < \Delta S_{mix} < 14$	-35<\(\Delta H_mix\)<-8.5	δ<9



Figure 4. Phase formation according to Ω and δ parameters.

The parameters values obtained for $Co_{20}Cr_{20}Fe_{20}Mn_{20}Ni_{20}$ are in agreement with those found into literature [43]. From the VEC value, an FCC structure was predicted for both systems (VEC>7.5).

XRD patterns of the as-cast alloys are shown in figure 5. An FCC phase is indeed observed. It must be pointed out that the relative peaks intensities are different for the two alloys, and different from those expected for a randomly oriented FCC metal, where the most intense peak is (111) **Error! Reference source not found.** On the other hand, the most intense peak for the alloys here investigated corresponds to the (200) plane in the base alloy and to the (311) plane in the Zr-modified HEA. These results suggest the existence of a preferred orientation along the <200> and the <311> direction.



Figure 5. XRPD data of as cast HEAs, with and without Zr modifier, showing an FCC structure. The Miller indices of the lattice planes are indicated.

The calculated lattice parameter for the Zr-free HEA is (0.360±0.002) nm, in agreement with literature [60]. The Zr added alloy has a slightly shorter unit cell edge, i.e. (0.357±0.002) nm. XRD patterns of the HEAs after annealing are reported in figure 6. Both

alloys still exhibit an FCC structure with lattice parameter (0.359 ± 0.002) nm and (0.358 ± 0.002) nm for the base and the Zr-modified alloy, respectively.

The Zr-containing alloy also exhibits low intensity peaks associated with oxide phases (ZrO₂, MnCrO₄ with PDF card number 00-033-0893 and Mn₂O₃ with PDF card number 01-089-4836). The relative intensities of the peaks in the patterns differ from those expected from randomly oriented crystallites **Error! Reference source not found.**, like it has been found on as cast specimens. However, both annealed alloys display an intense (220) peak which possibly indicates a <220> preferred orientation in a direction perpendicular to the recrystallization direction.



Figure 6. XRPD data of of Zr-CoCrFeNiMn (top) and CoCrFeNiMn (bottom) after recrystallization, showing an FCC structure. The Miller indices of the lattice planes are indicated.

Figure 7 shows optical microscopy images of two HEAs after cold rolling and after recrystallization. The cold-rolled base alloy shows a deformed elongated dendritic microstructure, without cracks, figure 7(a). After annealing, figure 7(b), twinned grains with average size (15±2) μ m appear (ASTM E112 – 13 [63]). In the Zr-added alloy, despite the presence of a Zr-rich phase in the cold rolled specimens, cracks are still absent, figure 7(c). The fully recrystallized microstructure of this alloy, figure 7(d), presents finer equiaxed geminated grains with an average grain size of (6.0±1.5) μ m (ASTM E112 – 13 [63]) in the dendritic regions and of (1.5±0.5) μ m into the interdendritic regions, figure 7(e).



(a)



(c)





(d)



(e)

Figure 7. Optical microscope images of the Zr-free (top) and Zr-modified (bottom) HEA. (a) Zr-free after cold rolling; (b) Zr-free after recrystallization; (c) Zr-modified after cold rolling and (d) Zr-modified after recrystallization; (e) Detail of Zr-modified after recrystallization: twin boundaries in the interdendritic phase are visible.

The different recrystallization size between dendritic and interdendritic phase, appears to be related to the nature and quantity of Zr. The usual influence of solutes on recovery, recrystallization and grain growth behavior can help understanding the observed grain size differences. Solute atoms can influence the stacking fault energy and/or impede the movement and the rate of dislocation climb and cross slip, which are the mechanisms that control recovery rate [62].

Table 6 reports results from EDS analyses performed in the two distinct areas of the recrystallized Zr-added alloy. When compared with as-cast data (Table 2), it is observed that the chemical composition of the dendritic area is unchanged and that Zr is still concentrated in the interdentritic phase. Despite Mn depletion, the Co, Cr, Fe and Ni content in the interdentritic phase is now close to the equiatomic composition.

Region	Со	Cr	Mn	Fe	Ni	Zr	0
Dendritic	22.52	21.63	9.91	21.31	20.1	0.08	1.97
Interdendritic	16.02	15.51	8.24	16.59	15.48	21.82	6.34

Table 6. Semic	uantitive anal	lysis of the	Zr-added all	lov	(atomic %)
		1			· /

The images and the corresponding SAED patterns collected from the out of plain section of cold worked and recrystallized Zr-modified HEA are shown in figure 8 and figure 9, respectively. The images were recorded from the interdendritic region. The SAED patterns reveal that the interdentritic phase has an FCC structure (Fm3m), as expected from XRD data. The calculated lattice parameters for both the cold-worked and the recrystallized phase are (0.36±0.02) nm, in agreement with those obtained from XRD.



(a)





Figure 8. (a) CoCrFeMnNiZr after cold working, (b) SAED pattern of CoCrFeMnNiZr after cold working



Figure 9. (a) CoCrFeMnNiZr after recrystallization, (b) SAED pattern of CoCrFeMnNiZr after recrystallization

Available literature data indicate that only a single FCC phase exists in the CoCrFeMnNi HEA [66] so that all grains can be considered as belonging to the same phase. Grain maps and inverse pole figures obtained by EBSD of the as-cast and recrystallized alloy are shown in figure 10 and figure 11, respectively. The colour code assignment in the grain maps is based on size. Instead, grains with the same crystal orientation (with respect to the selected viewing direction) are given the same colour in the pole figures. The image of the as-cast alloy shows very coarse grains (average grain size: 11.1 μ m), whereas the recrystallized sample exhibits a finer grain structure (average grain size 5.2 μ m, in agreement with the (6.0±1.5) μ m value determined by optical microscopy).



Figure 10. EBDS map of the as-cast alloy, consisting of coarse fcc-single-phase grains



Figure 11. EBDS map of the recrystallized alloy, consisting of fine fcc-single-phase grains

3.2. Mechanical properties

The microhardness of the as-cast, cold-worked and recrystallized samples of the two HEAs compositions was measured in randomly selected locations as described in section 2 and the results are visible in figure 12. A higher hardness is observed for CoCrFeNiMnZr (grey bars) with respect to CoCrFeMnNi (black bars) in the as-cast and the recrystallized samples. This increase is reasonably due to the precipitation of a second phase coherent

with the matrix. As reported in the optical micrographs of figure 7, no cracks are visible for both compositions. This is a further demonstration that the Zr-added alloy has toughness and ductility comparable to the traditional Cantor's alloy.

No statistically significant difference in microhardness is observed between the coldworked alloys. They both harden with the typical behavior of FCC structures with low staking-fault. As expected as a result of the usual solute effect on hardness, the smaller hardness values were observed in the CrCoFeMnNi Cantor's alloy in the as cast and recrystallized state. Noteworthy the cold-rolled base alloy exhibits a better work hardening capability compared to the Zr-modified one.

The result of microhardness tests of the dendritic and the interdendritic phase in the CoCrFeNiMnZr alloy are reported in figure 13. The values obtained for the Zr-rich interdendritic phase are higher compared to those measured in the dendritic region, in the as cast and in the cold rolled states, supporting the assumption of a strengthening effect for Zirconium. The two phases, after recrystallization, have very similar microhardness values and comparable with those of the as-cast alloy. A state of easy deformation is restored.

The dynamic Young's modulus E and damping were measured for the two alloys as explained in section 2. Cold-rolled specimens were heated a first time in vacuum up to 700 K in order to relax, at least partially, the stress induced by the deformation process. Then a second thermal run was performed up to 700 K. In figure 14 are reported the data acquired during heating at 1.5 K/min. The results closely resemble those obtained on the same Cantor's alloy by other experimental groups and therefore prove how the induction technique used in this work is able to produce good quality material. The dynamic modulus decreases monotonically while the damping increases with the typical trend due to dislocation bending. A damping value of about $4 \cdot 10^{-4}$ is measured at room temperature, which increases to 18.10-4 at 700 K. E= (140±10) GPa at 300 K. The Zr-added alloy exhibits the same overall behaviour, except for a higher damping at room temperature: Q-1=6-10-4 and a lower modulus value at 300 K: $E = (130 \pm 10)$ GPa. In both cases the uncertainty on E is mainly due to the uneven thickness of the cold rolled specimens. These modulus values are lower than those usually obtained by computer calculations (E ~200 GPa at 300 K) [68] but in agreement with other experimental results [57,69]. Density was measured to be (7.3±0.4) g/cm³ and (7.6±0.4) g/cm³ for the base and Zr added alloy, respectively.

From a mechanical point of view, the two HEAs alloys differ little by presenting very similar mechanical properties. The presence of a second isostructural phase in Zr-added alloy does not lead to the emergence of structural problems in industrial use. Both alloys are largely deformable and tough even at low temperatures and can be reinforced by microtwinning and grain size reduction.



 $\label{eq:Fig.12} Fig. 12. \qquad Microhardness \ of \ Co_{20}Cr_{20}Ni_{20}Fe_{20}Mn_{20} \ and \ Co_{19}Cr_{19}Ni_{19}Fe_{19}Mn_{19}Zr_5 \ alloys.$



Figure 13. CoCrFeNiMnZr alloy: Microhardness value in the dendritic (black bar) and interdendritic (grey bar) zones.



Figure 14. Internal friction (black) and dynamic elastic modulus (green) for cold worked specimens with (a) Co₂₀Cr₂₀Ni₂₀Fe₂₀Mn₂₀ and (b) with Co₁₉Cr₁₉Ni₁₉Fe₁₉Mn₁₉Zr₅ nominal composition. Heating rate 1.5 K/min. Resonance frequency at room temperature 540 Hz (a) and 514 Hz (b). Modulus values are normalized to their value at 300 K.

4. Conclusions

In this work, for the first time, CoCrFeMnNi and 5 % at Zr-modified CoCrFeMnNiZr HEAs were synthesized using vacuum induction melting of mechanically pre-alloyed elemental powders. The conventional strategy to obtain recrystallization of the original structure by cold deformation followed by annealing was used for both compositions. It resulted effective in achieving an equiaxed structure, suitable for structural employ. The 5 at. % Zr addition does not modify the crystalline phase of the alloy but considerably lowers the melting temperature for production and speeds up the process. The melting temperature of the CoCrFeMnNiZr alloy was found to be lower than the Zr-free counterpart, due to the formation of eutectics between each single element and Zr, yielding a good elemental homogenization in short times. The as-cast alloys showed a dendritic solidification microstructure with a clear distinction between the dendritic and the interdendritic phases in the case of the Zr-modified alloy. The crystallographic structure of both phases resulted FCC, in agreement with the VEC calculations. DSC analyses confirmed that Zr is effective in increasing the recrystallization temperature compared to the unmodified alloy. In addition, the Zr-modified HEA exhibits a significant size reduction of austenitic grains compared to the Zr-free HEA, leading to a finer microstructure.

The preliminary tests confirm the good mechanical quality of both the base and Zradded alloys.

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