MICROSTRUCTURES AND BASE MECHANICAL PROPERTIES OF $Cr_{1-x}Cu_xMnFeNi$ HIGH ENTROPY ALLOYS

OSTROUSHKO Dmytro[1], SAKSL Karel[1], BALGA Dušan[1], SZABO Juraj[1], DURISIN Martin[1]
MILKOVIČ Ondrej[2], ZUBKO Pavol[2]

[1]ÚMV-SAV, Kosice, Slovakia, EU
[2]Technical University of Kosice, Faculty of Metallurgy, Kosice Slovakia, EU

Abstract

A series of high entropy alloys (HEAs), $Cr_{1-x}Cu_xMnFeNi$, was produced by a vacuum arc-melting method. The multi-element systems can crystallize as a single phase, despite containing multiple elements with different crystal structures which often exhibit unusual properties. Their phases, microstructures and base mechanical properties at room temperature were investigated. It has been found that a two face-centered cubic (FCC) crystal structure forms in these alloys with higher Cu addition and a single solid-solution phase with a body-centered cubic (BCC) and two face-centered cubic (FCC) crystal structure forms in these alloys with higher Cr addition. The different hardness between those alloys was observed.

Keywords: High-entropy alloy, crystallize, vacuum arc-melting method, solid-solution phase, hardness

1.   INRODUCTION

Mostly conventional alloys are based on one basic element. Different alloying elements can be added to the basic element to improve its properties of original material and to form new alloy family. For example, steel is based on Fe, and aluminium alloys are based on Al. However, the number of elements in the periodic table is limited, thus the alloy families can be develop to a limited extent. Under consideration of high-entrophy alloys (HEAs), the conventional box and design alloys are not formed from one or two 'base' elements, but from multiple ones together [1]. Due to the distinct design concept, these alloys often show unusual mechanical properties, cryogenic-temperature properties, structural stabilities, and corrosion behaviours. Thus, there has been significant interest in these materials, leading to an emerging yet exciting new field.

It was in 1995 when the marking „a high-entropy alloy (HEA)" was used for the first time [1]. The HEAs are defined as alloys with five or more basic elements. Each of those elements should have a
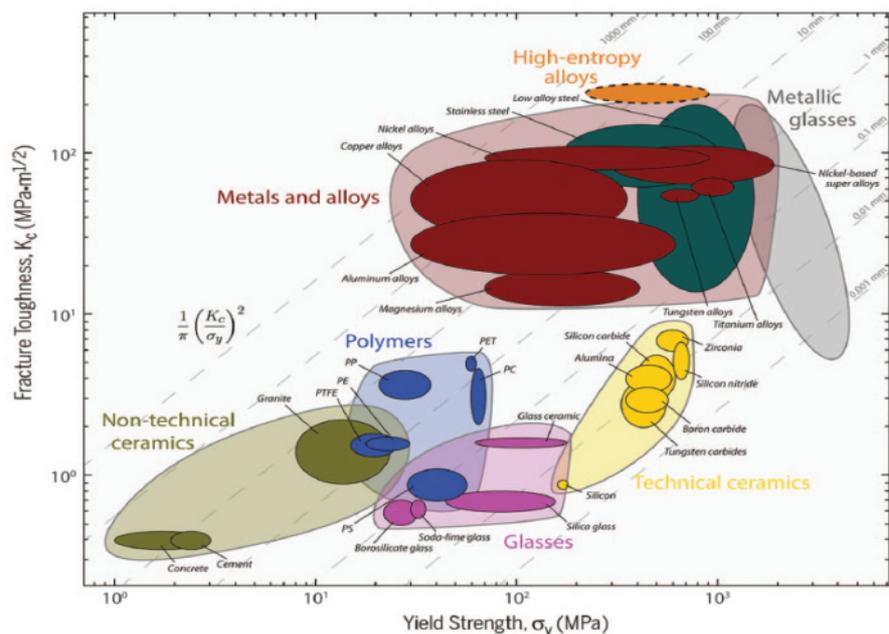
Fig. 1 Ashby map showing fracture toughness as a function of yield strength for high-entropy alloys in relation to a wide range of material systems [5]

concentration between 5 and 35 at. % [2, 3] and can further contain minor elements, each below 5 at. %. The physical (magnetic, electrical, and thermal) properties of HEAs have been reviewed elsewhere [4] and are not discussed in this paper. The HEAs has toughness levels comparable with the best cryogenic steels, specifically certain austenitic stainless steels and high-Ni steels, which also have outstanding combinations of strength and ductility. With respect to the alloy's damage tolerance, a comparison with the other major material classes is shown on the Ashby plot of fracture toughness vs yield strength (in **Fig. 1** [5]). There are clearly stronger materials, which are understandably given that our basic CrCoMnFeNi material type, representing a single-phase material [6]. Toughness of this HEA exceeds that of virtually all pure metals and metallic alloys and has a strength comparable with that of structural ceramics and close to that of some metallic glasses.

The scientific understanding toward the HEAs, however, lags much behind the technical exploration to them. Probably, the most outstanding scientific questions are the mechanism and condition for the solid solution phases (and not intermetallic compounds) to form in these highly concentrated multi-component alloys. The high entropy contribution at elevated temperatures lowering the Gibbs free energy of the solid solution phase [7], and the confusion principle [8] are two mechanisms simultaneously favour the formation of the amorphous phase. In paper Guo et al. [9] model was used, which analysed the mixing enthalpy (Δhmix) and the difference of element atomic radius (δ) of some HEAs and found that simple-solution-type of HEAs falls in opposite corners of the δ-ΔHmix plot (shown in **Fig. 2** [9]). It is further pointed out that as long as the competition from intermetallic phases can be ruled out by composition adjustment, HEAs that locate in the amorphous phase region of the δ-ΔHmix plot indeed solidify into metallic glasses.
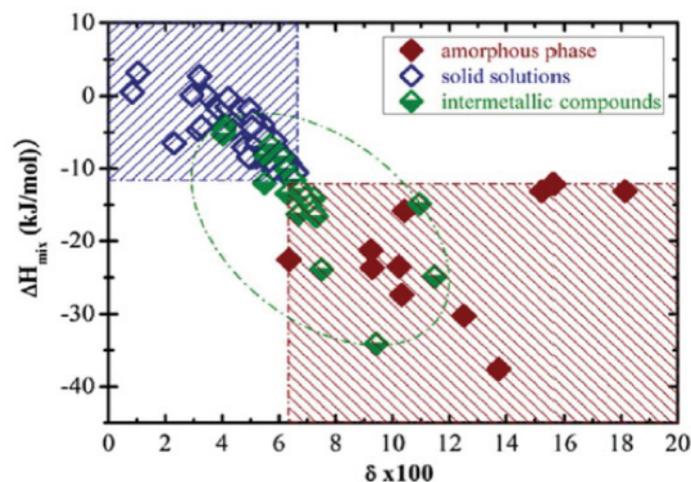
Fig. 2 The δ-ΔHmix plot delineating the phase selection in HEAs. The dash dotted regions highlight the individual region to form solid solutions, intermetallic compounds and the amorphous phase [9]

2. EXPERIMENTS AND SOLUTION TECHNIQUE

We used a Guo et al. model [8] to substitute a cobalt which is a very expensive element so that we replace it with a less expensive copper and we tried to change the ratio of copper and chromium, where we compared the effects of these changes on structural phase and mechanical properties. $Cr_{1-x}Cu_xMnFeNi$, was produced by a vacuum arc-melting method in Compact Arc Melter MAM-1 (**Fig. 3**). Preparation of the ingot is carried out in argon at temperatures up to 3500 °C and vacuum assist cast into an ingot meld diameter 3 mm and length 35 mm. After insertion, it is necessary several times generating a vacuum assisted rotary pump (to values at 5.10^{-2} mbar). For the production of the ingot is not only critical parameter size vacuum but in particular the temperature of the copper meld, in which the melt is cast. Standard weighed is about 2-3 g. Then the ingot was cut into the rolls size 6 x 3 mm (shown in **Fig. 3**).

Fig. 3 Preparation of the ingot by Compact Arc Melter MAM-1

For SEM (EDX) and phase analyses samples were of the same dimensions (6 x 3 mm) as the samples for the pressure test and were cut from the manufactured ingot. Individual pieces were then embedded to poly-fast, then grinded (P300, P600, P800, P1200, P2500), polished in PHOENIX 4000 and grinded by paste of 0.006 mm graininess with distilled water. The XRD measurements (phase analyses) were carried out using the X-ray X´Pert Pro Philips machine and the microstructures and chemical composition analyses were carried out by use of JOEL JSM-7000F equipped with EDX. The studied materials show a fine-grained structure of the grain size in the range of 1 - 20 µm (see **Fig. 4**). For a better distinguishing none etching was applied.

Co-Cr-Fe-Mn-Ni

Cr0.25-Cu1.75-Fe-Mn-Ni

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Cr-Cu-Fe-Mn-Ni

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Cr1.25-Cu0.75-Fe-Mn-Ni
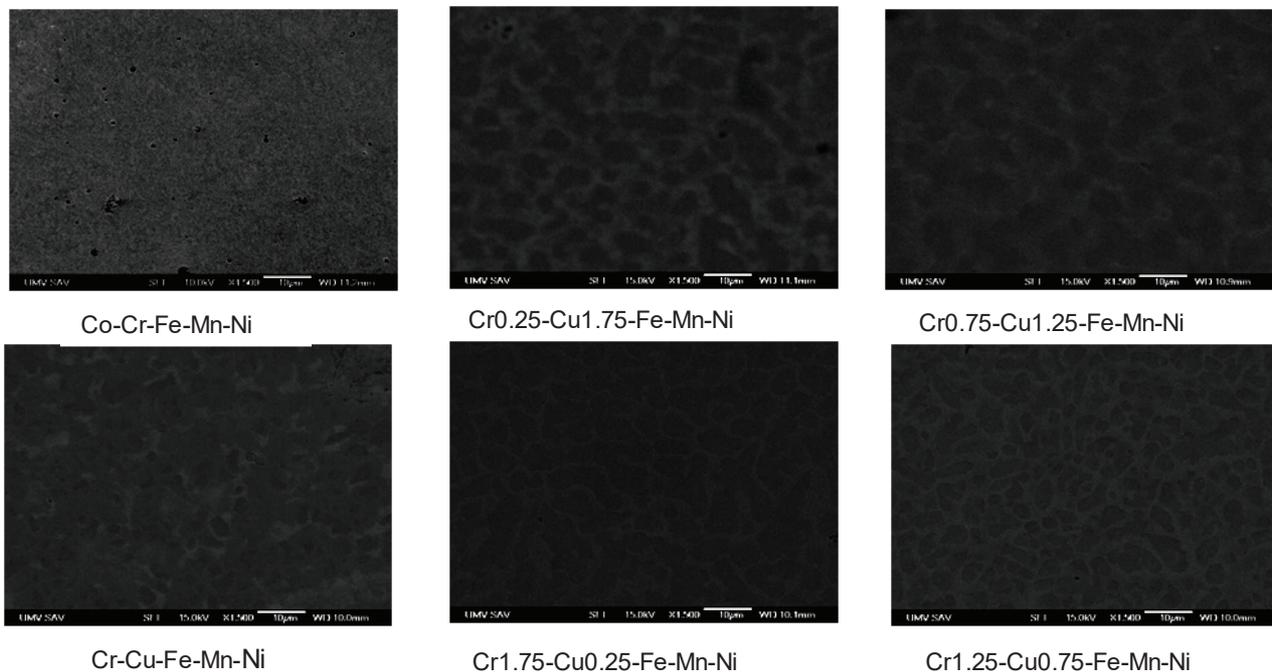
Fig. 4 SEM microstructure of studied materials

3.   RESULTS

Results of EDX, phase analysis (shown in **Fig. 5**), hardness test, yield strengths (*Re)* and strength (*Rm)* for some samples from the pressure test are presented in **Table 1**.

Table 1 Results of the studied materials

name	EDX at.%	phase	hardness	Re (MPa)	Rm (MPa)
1)Co-Cr-Fe-Mn-Ni	Co 20.09Cr 2011Mn 21.52 Fe 20.99Ni 17.45	FCC	169 HV	177	X
2)Cr-Cu-Fe-Mn-Ni	Cr 20.79Mn 20.02 Fe20.99 Ni 19.87 Cu 18.32	FCC+FCC+ BCC	269 HV	720	1780
3)Cr0.25-Cu1.75-Fe-Mn-Ni	Cr 6.25 Mn 21.42 Fe 21.10 Ni 20.35 Cu 30.89	FCC+FCC	185 HV	387	X
4)Cr0.5-Cu1.5-Fe-Mn-Ni	Cr 10.88Mn 19.53 Fe21.32 Ni 19.12 Cu 29.15	FCC+FCC	174 HV	356	X
5)Cr0.75-Cu1.25-Fe-Mn-Ni	Cr 15.7 Mn 19.15Fe 20.26 Ni 19.66 Cu 25.20	FCC+FCC+ BCC	220 HV	312	X
6)Cr1.25-Cu0.75-Fe-Mn-Ni	Cr 27.82Mn 18.33Fe 19.29 Ni 19.08 Cu 15.48	FCC+FCC+ BCC	308 HV	850	1763
7)Cr1.5-Cu0.5-Fe-Mn-Ni	Cr 33.07Mn 20.13Fe 19.74 Ni 18.18 Cu 8.87	FCC+FCC+ BCC	313 HV	994	1887
8)Cr1.75-Cu0.25-Fe-Mn-Ni	Cr 37.66Mn 18.51Fe 22.31 Ni 17.29 Cu 4.22	FCC+FCC+ BCC	360 HV	1070	2022
9) Cr0.1-Cu1.9-Fe-Mn-Ni	Cu 35.58Mn 21.81Fe 20.69 Ni 18.67 Cr 2.26	FCC+FCC	190 HV	371	X
10) Cr2-Fe-Mn-Ni	Cr 38.15 Mn 20.42 Fe 20.93 Ni 20.50	FCC+BCC	341 HV	1530	2072
11) Cu2-Fe-Mn-Ni	Cu 39.36 Mn 20.96 Fe 17.44 Ni 22.24	FCC+FCC	122 HV	400	X
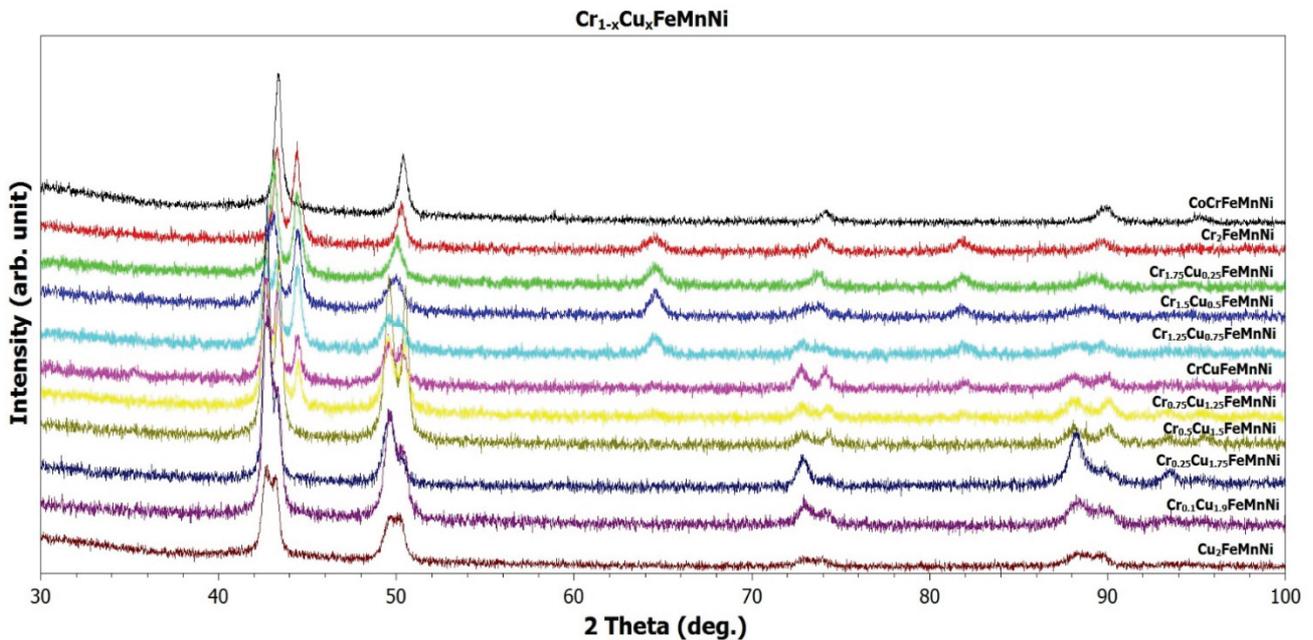
Fig. 5 XRD pattern from the studied materials

The investigation influence of Cu proportion to hardness and strength were carried out on the studied materials. These results are shown on **Fig. 6**. The yellow line represents the yield strengths (*Re)* and red line represents the hardness of the studied materials.
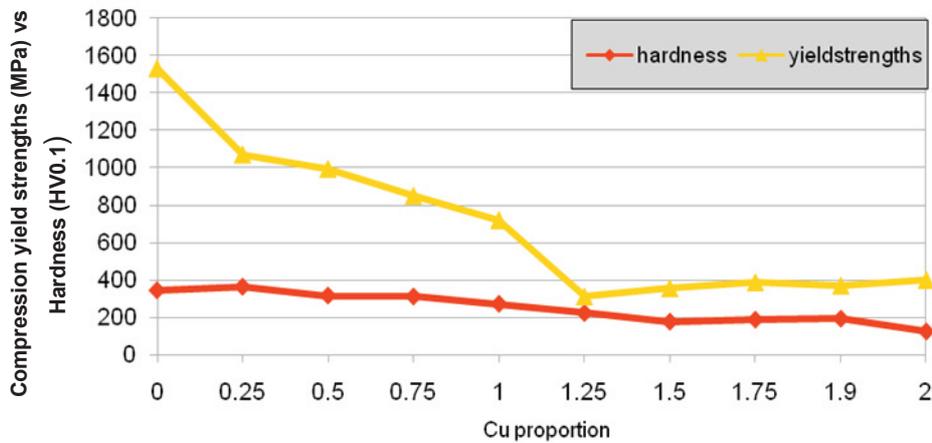
Fig. 6 Influence of Cu proportion to hardness and strength of studied materials

As **Fig. 6** shows, with increasing Cu content the yield strengths (*Re*) decreases as well as the hardness. In relative amounts of Cu from 1.25 and up yield strengths are significantly declined. This corresponds to transformation of three-phase system (FCC+FCC+BCC) to two-phase system (FCC+FCC). When Cr was added, an increase of strengths (*Rm)* and decrease of deformation were registered as it **Fig. 7** demonstrates.
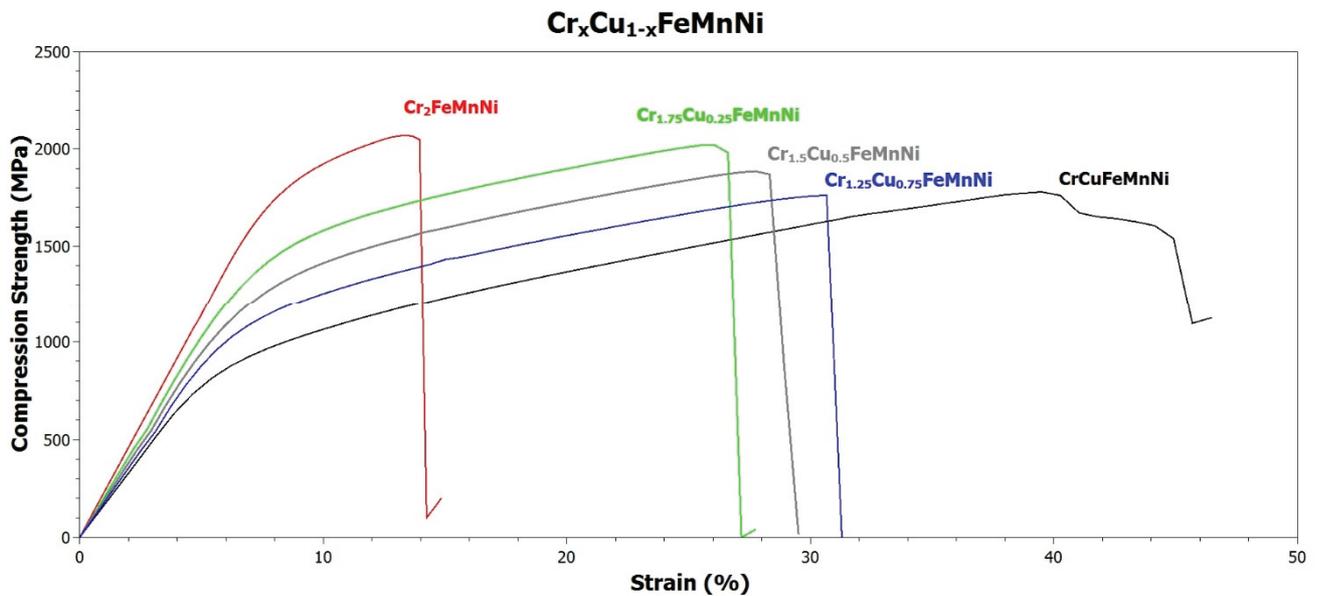
Fig. 7 Graph of pressure test samples which is destroyed

As **Figs. 6 - 7** shows Copper reduces the strength and increases the deformation of the studied materials and Chromium conversely, increases strength and reduces deformation. However, the main role, in a relationship to the mechanical properties is the phase composition of the studied materials.

4.   CONCLUSION

In conclusion, a refractory HEAs system, $Cr_{1-x}Cu_xMnFeNi$, is designed and fabricated by arc melting. Their phases, microstructures and base mechanical properties at room temperature were investigated. It has been found a two face-centered cubic (FCC) crystal structure forms in these alloys with higher Cr chemical content and a single solid-solution phase with a body-centered cubic (BCC) and two face-centered cubic (FCC) crystal

structure forms in these alloys with higher Cu chemical composition. These alloys have high hardness and compression yield strengths.

Further studies need to be done to investigate this kind of material behavior at cryogenic temperature.

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