SELECTED PROPERTIES OF TWO HIGH ENTROPY ALLOYS

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Abstract

The work deals with two types of high entropy alloys (HEAs) of $Fe_4CrCuMnNi$ and $Fe_4CrCuMnNi$ type, which were laboratory synthesized by vacuum arc-melting method. Much cheaper Fe of higher portion replaced cobalt in high entropy alloy of CoCuCrMnNi type. Tensile tests and micro-hardness for both HEAs and a susceptibility to hydrogen induced cracking for $Fe_4CrCuMnNi$ were carried. Reached results in as cast state of both HEAs were compared each other. Mechanical properties were more favourable in case of $Fe_4CrCuMnNi$. On average, yield stress was by 29 % higher, strength insignificantly lover by 14 MPa, while ductility by 2 % higher. Micro-hardness HV0.5 showed higher level in case of alloy with higher Fe content. Regarding hydrogen induced cracking of $Fe_4CrCuMnNi$ alloy under conditions in accord with NACE Standard TM0284-2013, Item No. 21215 the exposed samples were without any defects, even when length of sample was approx. 15 mm and diameter 3 mm only. Using Ni and Cr equivalents FCC+ BCC and/or BCC solid solution structures were found out. Microstructure, segregation and micro-fracture investigations were part of solution.

Keywords: High entropy alloy, tensile test, hardness, hydrogen induced cracking, microstructure

1. INTRODUCTION

High entropy alloys (HEAs) are minimally formed by 5 metallic elements [1]. High entropy alloys show unique properties and their applicability is possible both in oxidative mediums and in ones of chlorides, at cryogenic as well as at creep temperatures [2]. Those properties can be reached thanks four effects: a) high entropy effect, b) sluggish diffusion, c) possibility of crystallographic lattice torsion and d) HEAs position in Ashby´s diagram [1-4]. Only solid solutions are in question. In some works attention was payed to HEAs with different combination of Al, Co, Cr, Ni, Fe, Mn, Ti, Mo. Sometimes, beside single phase intermetallic phases were also observed, responsible for extremely high strength to the exclusion of toughness. In those cases all conditions were not complied with above mentioned ones. Tsai [5] demonstrated effect of increased Al content (BCC stabilizer) on hardness increase with stronger BCC formation. Otto [6], Gludovatz [3], showed positive properties of CrCoMnFeNi HEA, while Lin [7] studied $Cu_{0.5}CoCrFeNi$ alloy showing entropy effect with FCC phase only. Chou [8] investigated behaviour of HEAs $Co_{1.5}CrFeNi_{1.5}$ with $Ti_{0.5}$ and Mo_x addition which supported resistance against pitting corrosion. As can be seen from **Figure 1**, mentioned elements have similar atomic radius and atomic number as well. This fact predestines alloy, representing single-phase material, to favourable high entropy effect [9]. For example paper [3] deals with alloy of FeCrMnCoNi type, which showed tensile stress increase from 759 MPa at 20 °C on 1280 MPa at -196 °C with increase of ductility by 25 % at stable coefficient of deformation strengthening (0.4). Otto [6], Gludovatz [4], showed positive properties of CrCoMnFeNi HEA. Crystallographic structure corresponded to FCC. Replacement of Co by cheaper Cu resulted only in double FFC structure and/or with BCC formation. In case of higher Cu-content (up to 25 at. %, FCC stabilizer) to the exclusion of Cr (supporting BCC), only double FFC were detected.

The work is target on HEAs on Fe basis with Cu ($Fe_{2.5}CrCuMnNi$ and $Fe_4CrCuMnNi$), which replaces expensive Co and orientates on selected properties of these new alloy types that has not been published by now.

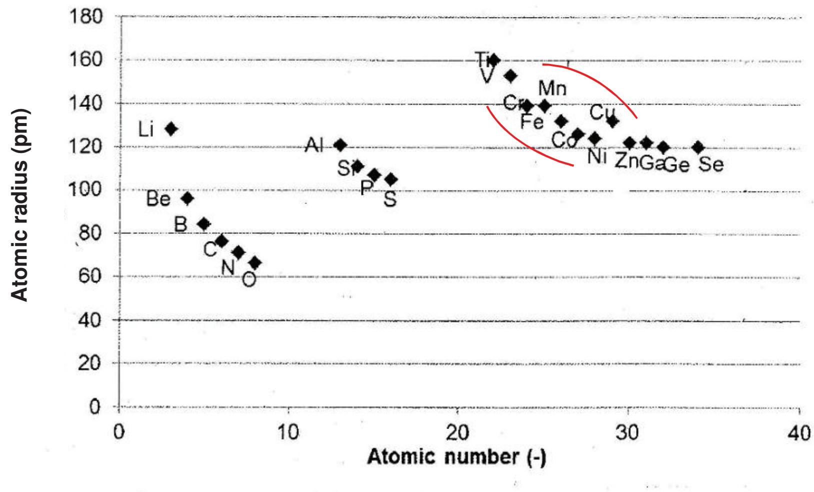

Figure 1 Plotting of atomic radius of elements vs atomic number. Red framed area shows position of Cr, Cu, Mn, Fe, Co and Ni

2. EXPERIMENTAL PROCEDURE

Two high entropy alloys ($Fe_{2.5}CrCuMnNi$ and $Fe_4CrCuMnNi$) were synthesized by a vacuum arc-melting method in Compact Arc Melter MAM-1 (**Figure 2**). Preparation of the ingots was carried out in argon at temperature up to 3 500 °C and vacuum assisted casting into ingots with a 3 mm diameter and 35 mm in length. During all process, vacuum assisted rotary pump (at $5 \cdot 10^{-2}$ mbar) was necessary to generate several times. For the production of any ingot, not only critical parameter of vacuum level is important, but in particular the temperature of the melting, at which the melt is cast. Standard weight was approx. 2-3 g. Further, the ingot was cut into rolls with dimensions of 6 x 3 mm (**Figure 2** right). Manufactured samples were put to the tensile test, used for hardness determination and for hydrogen induced cracking (HIC) in accord with NACE Standard TM0284-2013, Item No. 21215 (with exception of samples dimensions, those corresponded to 15 mm in length and to 3 mm in diameter only). Tensile tests for two samples (200 kN Zwick-Extensometer) at ambient temperature (in the beginning testing rate corresponded to 0.083 mm / s, from R(v) 0.017 mm / s), micro-hardness HV0.5 (LECO 2000) and hydrogen induced cracking (HIC) in corrosive solution A at temperature 25 ± 3 °C and pH_{start} was 2.8, while pH_{finish} 3.0. After tensile test fractures of samples were studied as well as maximal enrichment of inter-dendritic and/or dendritic (DR) areas vs basic material in as cast state and also microstructure after exposition in H_2S using light microscope Olympus IX 70 and SEM JEOL JSM-6490 LV. For micro-hardness LECO 2000 was used.

Figure 2 Preparation of studied alloys using Compact Arc Melter MAM-1 and ingots

3. RESULTS AND ANALYSIS

Results of tensile test are summarized in **Figure 3**. From results follows that average yield strees was in case of alloy $Fe_{2.5}CrCuMnNi$ by 22.8 % lower in comparison with alloy $Fe_4CrCuMnNi$, while tensile strength was slightly higher (by 4 %) in the second mentioned alloy. Tensile strength values of each pair differ each from other by 22 MPa (alloy with 50 wt. % of iron) and/or by 25 MPa. Elongation corresponded to 16-17 % for $Fe_{2.5}CrCuMnNi$, in case of $Fe_4CrCuMnNi$ alloy it was approx. 20 % on average, however between the both tested cases was important difference - see curve 3 and 4 in **Figure 3**. This could be ascribed to porosity, how it was revealed by microstructure analysis. It is necessary to emphasize, a cast material is in question.

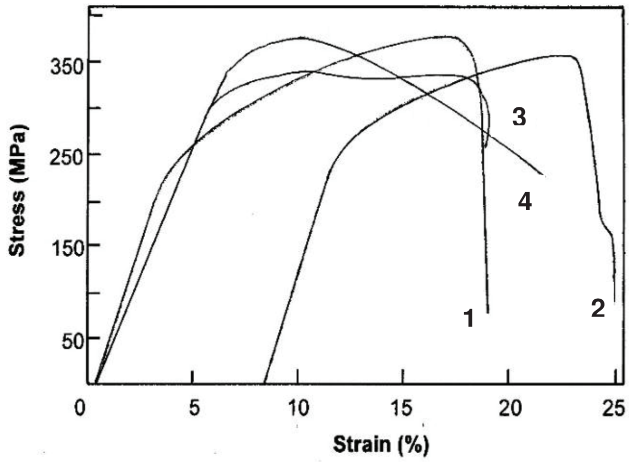

Figure 3 Stress-strain dependence for two pairs of HEAs a) $Fe_{2.5}CrCuMnNi$ (No. 1 and 2), b) $Fe_4CrCuMnNi$ (No. 3 and 4)

Micro-hardness HV0.5 of alloy $Fe_{2.5}CrCuMnNi$ ranged from 168 to 224 and on average was 197, while for steel $Fe_4CrCuMnNi$ average value corresponded to 272 and the range was lying between 152-311 HV0.5. Those values traces differences detected after tensile test in the alloy of $Fe_4CrCuMnNi$. Mechanical properties are depended on elements forming the HEA. Through the cocktail effect those form either FCC or BCC structures and/or in mixture. Alloys with single FCC phases are always related with Cu, Mn, Ni, while such Cr is BCC stabilizer [2, 9]. It can be supposed, presence of higher Fe content without carbon presence could support more BCC structure in view of the fact that material of HEA was heated up to extreme high temperature of 3 500 °C followed fast cooling. To predict microstructure type Ni equivalent and Cr equivalent (Ni_{eq} and Cr_{eq}) were calculated according principles presented in [2, 11].

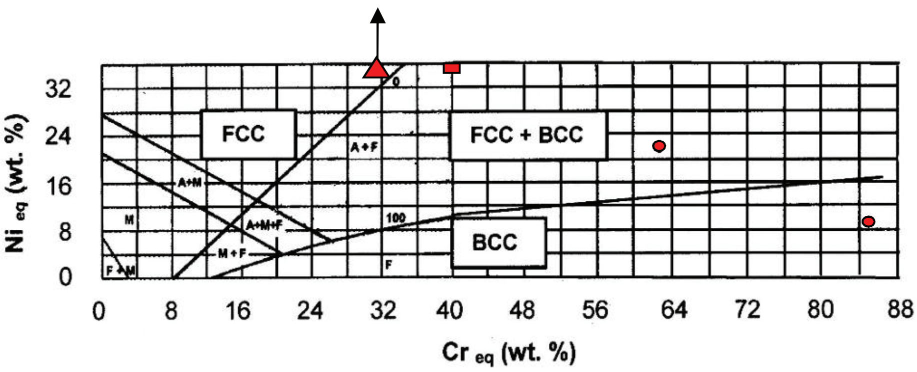

Figure 4 Calculated values of Ni_{eq} and Cr_{eq} - red point in FCC + BCC area corresponds to $Fe_{2.5}CrCuMnNi$, the one in BCC to $Fe_4CrCuMnNi$, while rectangle represents FeCrCuMnNi and triangle $FeCrCuMnNi_2$

From Schaeffler´s diagram (**Figure 4**) follows, that the HEA with 50 wt. % of Fe is mixture of FCC + BCC phases, while the second HEA should be fully BCC structure. Ren [11] reported that $CuCrFeNi_xMn$ system with twice Ni portion consisted of simple FCC (red triangle in **Figure 4**) while the single Ni portion contributed to FCC+ BCC solid solution structure (little rectangle in **Figure 4**). In both cases Ni content was minimal 20 wt. % unlike presented 12.5 or 5 wt. % in $Fe_{2.5}CrCuMnNi$ or $Fe_4CrCuMnNi$. With exception of curve 4 (**Figure 3**) practically all materials showed similar tensile strength. On average, sample 4 showed micro-hardness approximately by 68 HV0.5 higher. Generally, on average, higher iron content resulted to slightly higher micro-hardness in case of HEA with 80 wt. % of Fe in comparison to HEA with 50 wt. % of Fe.

Hydrogen induced cracking of the alloy with 80 % of Fe proved an excellent resistance against hydrogen embrittlement. In section none cracks were observed as well as on the surface. It is necessary to state, conditions for test were quite in agree with above mentioned standard, with exception of sample dimensions. Those were much smaller (see **Figure 5**) than minimal regular sample that should be 20 x 6 x 100 mm. Consequently, much more hydrogen had to diffuse into exposed small sample resp. hydrogen concentration was much higher there than it would be in regular sample. Hydrogen embrittlement is not only depended on own microstructures, however also on regular hydrogen redistribution in traps [10]. The more fine traps are in microstructure with regular redistribution, the better hydrogen resistance can be awaited. It can be admitted, some pores being typical behaviour of cast materials represent favourable potential hydrogen traps, too. Porosity was detected in fine form, especially in central area of each sample, even when in sample for HIC testing ($Fe_4CrCuMnNi$) it was less, than in alloy with 50 % of Fe, as it also **Figure 6** demonstrates. Generally microstructures of investigated HEAs differed one from other and $Fe_{2.5}CrCuMnNi$ alloy showed finer and noticeable dendritic structure than the alloy $Fe_4CrCuMnNi$.

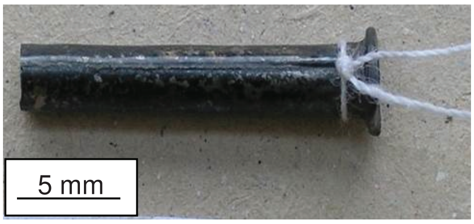

Figure 5 Sample of $Fe_4CrCuMnNi$ after exposition in corrosive solution

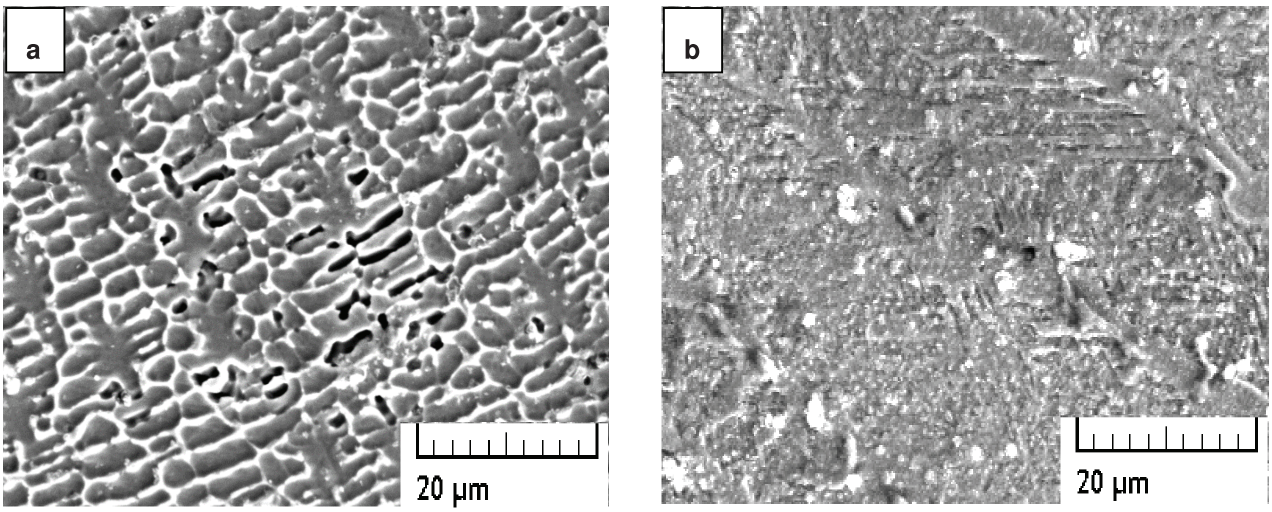

Figure 6 Micrographs of studied alloys a) $Fe_{2.5}CrCuMnNi$, b) $Fe_4CrCuMnNi$

Elements forming investigated alloys mostly represent segregation ones and maximal grain boundaries/inter-dendritic (ID) enrichment was observed in alloy $Fe_{2.5}CrCuMnNi$, which showed 2.5 time higher concentration of segregation elements. Revealed enrichments in both alloys are summarized in **Table 1**. From it follows, that segregation of Cu and Mn were maximal in both alloy types unlike Ni with minimal segregation which is rather homogeneously distributed in alloys. The same trend was reported by Ren et al [11].

Table 1 Maximal enrichment of inter-dendritic and/or dendritic (DR) areas vs basic material (wt. %)

Element	Cr	Cu	Mn	Ni
$Fe_{2.5}CrCuMnNi$	16DR	>50	28	5
$Fe_4CrCuMnNi$	5	29	20	9

Figure 7 demonstrates fracture surfaces of both studied alloys after tensile test. Alloy $Fe_{2.5}CrCuMnNi$ showed fracture surface with lower portion of porosity and noticeable central shrink-hole unlike samples dedicated for metallographic analysis (see **Figures 6a, b** and **7a - d**). Fracture surface was slightly more fine-grained than in case of the alloy $Fe_4CrCuMnNi$, which demonstrated more balanced fracture surface than the second alloy as it from **Figure 7 a, c** follows. In fracture surface of the HEA of $Fe_{2.5}CrCuMnNi$ type partially dimple morphology was observed (**Figure 7a, b**).

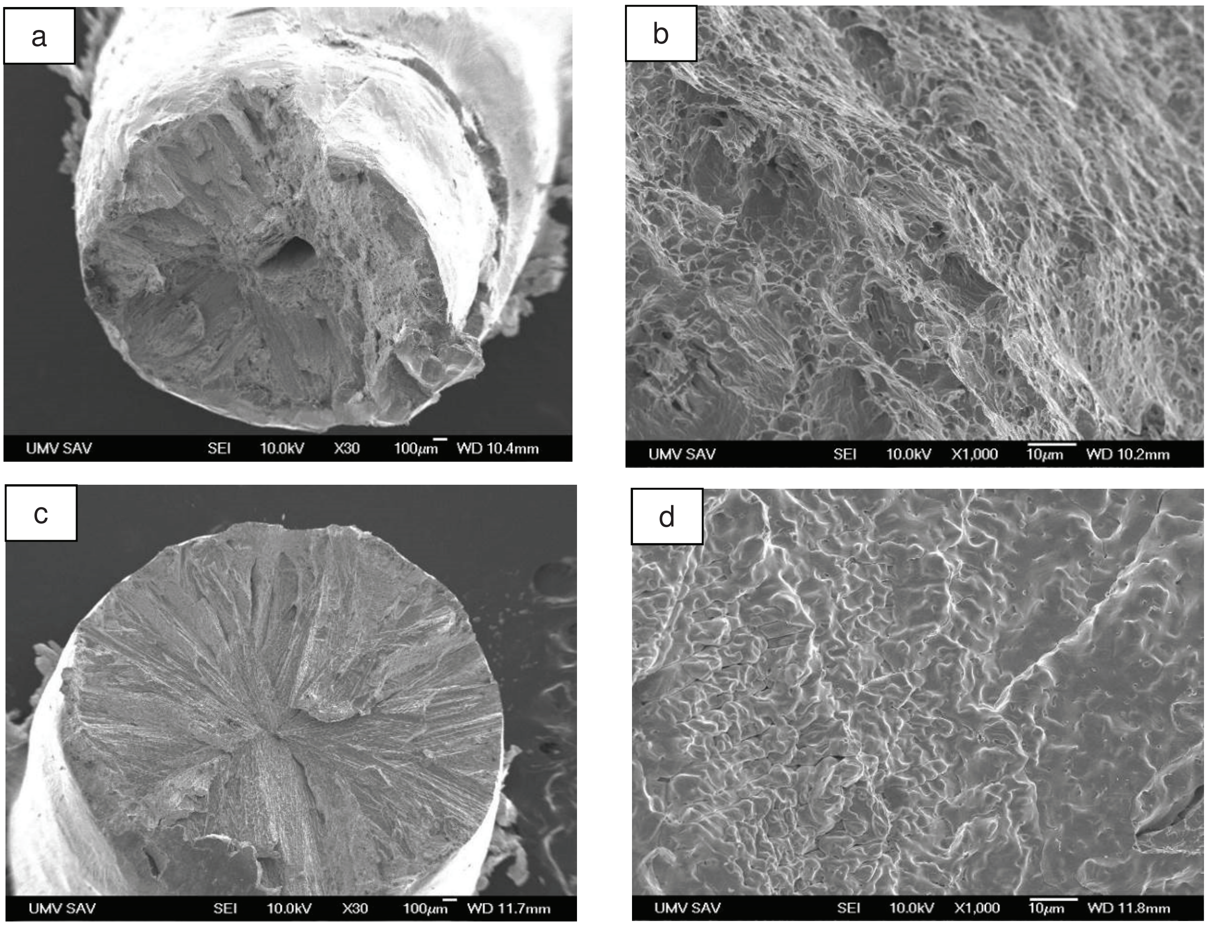

Figure 7 Fracture surfaces of tensile test samples a) and b) $Fe_{2.5}CrCuMnNi$, c) and d) $Fe_4CrCuMnNi$

4. CONCLUSIONS

Two types of five component high entropy alloys (HEAs) with two levels of Fe contents (50 and 80 wt. %) in cast state at ambient temperature were investigated. Presented Fe content replaced Co in CoCrCuMnNi alloy.

The rest elements always showed equivalent portions. According Ni and Cr equivalents, $Fe_{2.5}CrCuMnNi$ should consist of FCC and BCC phases, while $Fe_4CrCuMnNi$ alloy of BCC phase only.

Tensile strength was slightly higher in case of HEA of $Fe_{2.5}CrCuMnNi$ type, while the alloy of $Fe_4CrCuMnNi$ type showed generally higher micro-hardness values on average. Detected disproportions trends between tensile strength and micro-hardness values could be elucidated by uneven porosity, which was e.g. in sample of $Fe_4CrCuMnNi$ alloy very fine and regularly distributed as it was revealed in case of exposed material in corrosive solution bubbled with H_2S (hydrogen induced cracking), unlike the $Fe_{2.5}CrCuMnNi$ material used for tensile test, where greater central shrink-hole was observed. Fracture surfaces of $Fe_4CrCuMnNi$ alloy was slightly course-grained in comparison with HEA of $Fe_{2.5}CrCuMnNi$ type, which partially showed dimple morphology. Higher segregation enrichment was observed in alloy $Fe_{2.5}CrCuMnNi$ containing 2.5 time higher portion of segregation elements. Maximal segregation showed Cu and Mn in inter-dendrite areas. After HIC exposition, hydrogen resistance of $Fe_4CrCuMnNi$ alloy was excellent and none defects were revealed both inside of extremely small samples and on its surface. Similar trend could be awaited in case of $Fe_{2.5}CrCuMnNi$. Verification of phase structures using synchrotron will be followed.

ACKNOWLEDGEMENTS

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