UDC 669.018+ 539.216.2

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EFFECT OF Al AND Si ADDITIONS AND COOLING RATES ON PHASE COMPOSITION AND PROPERTIES OF CuFeMnNi ALLOY

The multicomponent high-entropy alloys of Cu-Fe-Mn-Ni system with Al and Si additions in the as-cast and splat-quenched state are investigated. Electronic, thermodynamic, and atomic-size criteria of phase formation in high-entropy alloys are considered. Simple solid solutions with a face-centered cubic structure are obtained in all of the splat-quenched alloys. The as-cast alloys also have a simple face-centered cubic structure, with the exception of $CuFeMnNiSi_{0.5}$, in which the intermetallic phases are found. The values of lattice parameters of the investigated alloys indicate that solid solutions are formed on the base of γ-Fe lattice, taking into account its higher melting temperature. The positive influence of microstrains level and dislocation density on the microhardness values of alloys are established. The obtained results clearly indicate also a strong dependence between the measured microhardness and content of Si and Al additions, thus improved mechanical characteristics are obviously ensured by the strong distortion of the crystal lattice due to the differences in atomic radii of elements.

Keywords: high-entropy alloy, structure, phase composition, microhardness, splat-quenching.

Досліджено багатокомпонентні високоентропійні сплави системи Cu-Fe-Mn-Ni із домішками Al и Si у литому стані та при гартуванні з рідини. Розглянуто вплив термодинамічних та розмірних параметрів, а також параметрів електронної структури на фазовий склад високоентропійних сплавів. Встановлено, що сплави, загартовані з рідини мають однофазну структуру, в якій наявні прості тверді розчини із гранецентрованою кубічною (ГЦК) решіткою. Литі сплави також являють собою прості тверді розчини типу ГЦК, за виключенням сплаву $CuFeMnNiSi_{0.5}$, у якому наявні також інтерметалічні фази. Значення параметрів решітки вказують на те, що в якості основи для формування твердих розчинів слід розглядати решітку γ-Fe, як елемента з найбільшою температурою плавлення. Показано, що збільшення рівня мікронапружень та густини дислокацій сприяють підвищенню механічних характеристик досліджених сплавів. Отримані результати також вказують на чітку залежність між величиною мікротвердості та вмістом Al та Si. Таким чином, підвищення міцності відбувається завдяки значному викривленню кристалічної решітки внаслідок відмінності атомних радіусів елементів.

Ключові слова: високоентропійний сплав, структура, фазовий склад, мікротвердість, гартування з рідкого стану.

Исследованы многокомпонентные высокоэнтропийные сплавы системы Cu-Fe-Mn-Ni с добавками Al и Si в литом и жидкозакаленном состояниях Рассмотрено влияние термодинамических и размерных параметров, а также параметров электронной структуры на фазовый состав высокоэнтропийных сплавов. Установлено, что жидкозакаленные сплавы имеют однофазную структуру, в которой присутствуют простые твердые растворы с с гранецентрированной кубической (ГЦК) решеткой Литые сплавы также представляют собой простые твердые растворы типа ГЦК, за исключением сплава $CuFeMnNiSi_{0.5}$, в котором присутствуют также интерметаллические фазы. Значения параметров кристаллической решетки указывают на то, что основой для формирования указанных твердых растворов является решетка γ-Fe, как элемента с наибольшей температурой плавления. Показано, что повышение уровня микронапряжений и плотности дислокаций способствуют повышению механических характеристик исследованных сплавов. Полученные результаты также показывают четкую зависимость между величиной микротвердости и содержанием Al и Si. Таким образом, повышенные прочностные характеристики обусловлены сильным искажением кристаллической решетки вследствие различий в атомных радиусах элементов.

Ключевые слова: высокоэнтропийный сплав, фазовый состав, структура, микротвердость, закалка из жидкого. состояния.

1. Introduction

In 2004, a new alloy concept, "multi-principal-element alloys" (MPEA's) or "high-entropy alloys" (HEA's) was proposed and investigated through increased experimental studies [1]. Such alloys usually contain from 5 to 13 major elements in equiatomic or near equiatomic concentrations (5 to 35%). Due to the high mixing entropy multicomponent alloys typically consist of simple solid solutions with a BCC or FCC lattices. At the same time, through purposefully selection of the HEA components an alloy comprised of simple solid solution with a high plasticity and very hard and brittle intermetallic compounds (intermetallic phase, σ-phase, Laves phase) can be prepared. Also the study results concerning high-entropy metallic glasses and alloys with shape memory are published [2,3]. HEA's are characterized by the unique structure and properties, such as high hardness, outstanding wear resistance, irradiation resistance, excellent high-temperature strength, good thermal stability, and corrosion resistance [1,4].

This paper is devoted to investigation of structure and properties of multicomponent alloys of Cu-Fe-Mn-Ni system with Al and Si additions. In order to establish the influence of the composition and the cooling rate of the melt on the microhardness and phase composition the as-cast and splat-quenched alloys were investigated.

2. Experimental details

The samples of Al- and Si- modified Cu-Fe-Mn-Ni high-entropy alloys were prepared by a laboratory Tamman furnace in the flow of argon and poured into a copper mold (cooling rate of ~ 10^2 K·s^{-1}). The quenching from the molten state (splat-quenching, SQ) was performed with using the well-known technique of melt spinning, i.e., spreading of melt droplets on the internal surface of a rapidly rotating copper cylinder. The rate of cooling as estimated from the thickness of the obtained foils was ~10^5–10^6 K/s. The XRD studies were carried out with using a DRON-2.0 X-ray diffractometer in Cu $K\alpha$ monochromatized radiation. The patterns were processed using a MAUD software [5]. The microhardness was measured with a PMT-3 microhardness-meter at a load of 200g.

3. Results and discussion

3.1. Electronic, thermodynamic and atomic-size criteria of phase formation in high-entropy alloys

High-entropy alloys usually characterizing by entropy of mixing ΔS_{mix} and mixing enthalpy ΔH_{mix}. But in order to describe the phase composition of HEA's, some empirical criteria were proposed, namely atomic-size difference which is described by the parameter δ, valence electron concentration *VEC*, and the thermodynamic Ω parameter, correlates the melting point, entropy of mixing, and the enthalpy of mixing. The definitions of these parameters were considered in many papers [1]. But these empirical criteria for prediction of phase composition were developed and tested with using as-cast HEA's, which often contain non-equilibrium phases, so they are not always conclusive [6].

Recently it has been established that the difference in atomic sizes affects the topological instability of atomic packing [7]. It was suggested that atoms with the maximum and minimum radii play a crucial role in determining the stability of the packing in high-entropy alloys. The solid angles of packing for the atoms with the smallest ω_S and highest ω_L sizes were chosen [7] to describe the effects of the atomic packing in HEA's quantitatively.

$$\omega_S = 1 - \sqrt{\frac{\left(r_S + \overline{r}\right)^2 - \overline{r}^2}{\left(r_S + \overline{r}\right)^2}}\ , \tag{1}$$

$$\omega_L = 1 - \sqrt{\frac{\left(r_L + \overline{r}\right)^2 - \overline{r}^2}{\left(r_L + \overline{r}\right)^2}}\ . \tag{2}$$

Here r_S and r_L are the atomic radii of smallest and largest atoms respectively, $\overline{r} = \sum_{i=1}^{n} c_i r_i$, r_i – the atomic radius, c_i – atomic fraction of the *i*-th component.

Then, the normalized parameter of packing state was defined as the ratio between the solid angles for the atoms with smallest and largest sizes.

$$\gamma = \frac{\omega_S}{\omega_L}. \tag{3}$$

As pointed out in [7], the Hume–Rothery rule of 15% of the atomic size difference in binary alloys corresponds to a critical value of packing misfitting of γ = 1.167. The critical value of γ = 1.175 can distinguish the simple solid solution alloys and alloys with intermetallic compounds [7].

In [8] a new approach for the phase selection in HEA's, which takes into account both enthalpy and entropy terms of the competing phases, was proposed. If the enthalpy ΔH_{IM} and the entropy ΔS_{IM} of formation for intermetallic compounds are related with mixing ones

$$\Delta H_{IM} = k_1 \Delta H_{mix}\,, \tag{4}$$

$$\Delta S_{IM} = k_2 \Delta S_{mix}\,, \tag{5}$$

then the thermodynamic condition for the formation of a solid solution phase at a temperature *T* from the Gibbs equation [8] is

$$\Delta H_{mix} - T\Delta S_{mix} < \Delta H_{IM} - T\Delta S_{IM}\ . \tag{6}$$

Here $\Delta H_{IM} = \sum_{i=1}^{n}\sum_{j>i}^{n} 4\Delta H_{ij}^{IM} c_i c_j$, ΔH_{ij}^{IM} are enthalpies of formation of binary intermetallics.

Thus by considering the parameter

$$k^{cr}(T) = 1 - \frac{T\Delta S_{mix}}{\Delta H_{mix}}\left(1 - k_2\right), \tag{7}$$

the condition for suppression of IM phases at a temperature *T* can be defined as $k^{cr}(T) > k_1$ for HEA's with negative values of ΔH_{mix} and $k^{cr}(T) < k_1$ for HEA's with positive values of ΔH_{mix}.

Using the data from [9-12], the set of above mentioned parameters are calculated for the listed in Tab.1 HEA's of Cu-Fe-Mn-Ni system with Al and Si additions, namely, ΔS_{mix}, ΔH_{mix}, ΔH_{IM}, δ, *VEC*, Ω, α, γ, k_1 and k^{cr} (Tab. 2).

Table 1

Nominal chemical compositions of investigated HEA's, at.%

Alloy	Al	Cu	Fe	Mn	Ni	Si
CuFeMnNi	-	25	25	25	25	-
$Al_{0.44}$CuFeMnNi	10	22.5	22.5	22.5	22.5	-
$CuFeMnNiSi_{0.25}$	-	23.53	23.53	23.53	23.53	5.88
$CuFeMnNiSi_{0.5}$	-	22.22	22.22	22.22	22.22	11.12

Table 2

Thermodynamic, electronic, and atomic-size parameters of investigated HEA's

Alloy	ΔH_{mix}, kJ/mol	ΔH_{IMi}, kJ/mol	ΔS_{mix}, J/(mol·K)	δ	VEC	Ω	γ	k_1	k^{cr}(300)
CuFeMnNi	2.75	-2.77	11.52	3.68	9.0	6.72	1.104	-1.01	0.50
$Al_{0.44}$CuFeMnNi	-2.54	-15.69	13.07	4.72	8.4	7.89	1.158	6.17	1.62
$CuFeMnNiSi_{0.25}$	-5.26	-10.88	12.7	4.11	8.71	3.88	1.174	2.07	1.29
$CuFeMnNiSi_{0.5}$	-11.57	-17.23	13.14	4.42	8.44	1.48	1.175	1.49	1.14

It should be noted that, in accordance with the calculated values of ΔS_{mix} the majority of the alloys studied in this paper formally must be attributed to medium entropy alloys [1], however, taking into account the evaluation of the minimum entropy of mixing for the HEA's $\Delta S_{mix} \geq 11$ J/(mol·K), given in [13], many researchers consider such alloys as high-entropy [14].

3.2. Structure and mechanical properties of Cu-Fe-Mn-Ni system HEA's with Al and Si additions

The phase composition of the investigated alloys, crystal lattice parameters, and the fine structure parameters (size of coherently scattering domains and microstrains) (Tab.3) were determined from the XRD patterns (Fig. 1, 2). The dislocation density ρ was obtained from the profile of the first diffraction peak.

From the results of analysis of the XRD patterns it is apparent that all the as-cast samples, except the $CuFeMnNiSi_{0.5}$ one, have similar reflections of simple FCC solid solutions. This is consistent with the results of [14] for the CuFeMnNi alloy. The $CuFeMnNiSi_{0.5}$ alloy has a complicated phase composition, there two simple FCC solid solutions together with intermetallic FeSi and $FeSi_2$ phases are presented. This result is not unexpected since from Tab. 3 it is seen that ΔH_{mix} for this alloy has a large negative value favoring the formation of intermetallic compounds. The parameter γ also nearly reaches the critical value of 1.175. As for the thermodynamic k_1 and k^{cr} parameters, according to a ratio between them (Tab. 2), in all studied HEA's the formation of intermetallic compounds might be expected. At the same time nominal chemical compositions of all investigated alloys were chosen so that their *VEC* values were favored to the formation of a FCC phase. These factors put together leads to the formation of a mixture of FCC and intermetallic phases in $CuFeMnNiSi_{0.5}$ alloy only. Yet taking into accounts the thermodynamic criteria [8], in all investigated HEA's annealed at $T \sim 0.6T_{melting}$ together with non-equilibrium phases decomposition one should expect the formation of ordered intermetallic phases. It should be noted that the study of the fine structure of as-cast HEA's by the methods of high-resolution electron microscopy usually shows the presence of nanosized intermetallic precipitates [15].

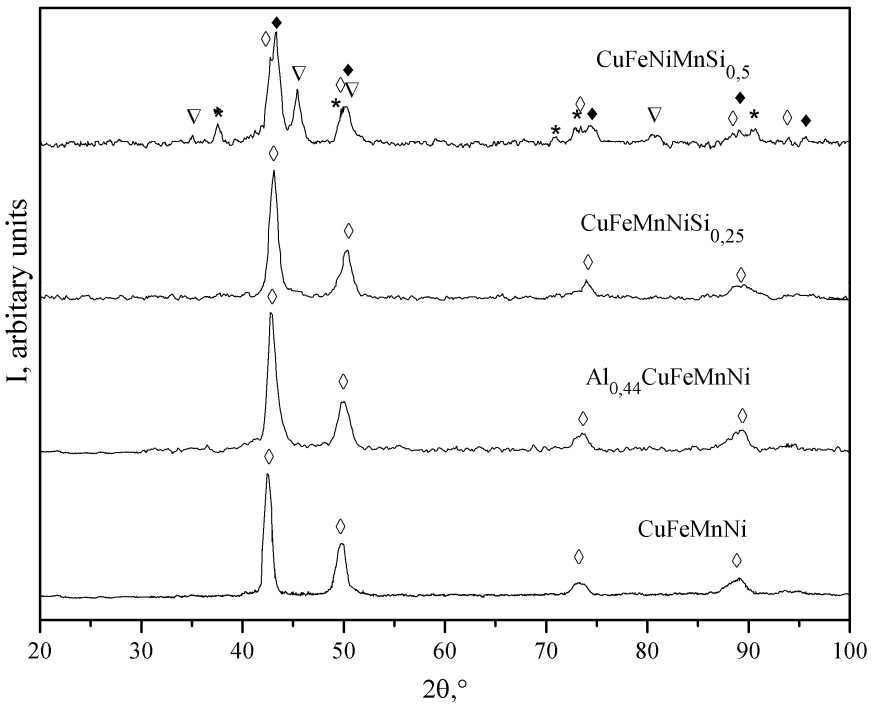

Fig.1. XRD patterns of as-cast HEAs of Al-Cu-Fe-Mn-Ni-Si alloy system: ◊-FCC1, ♦- FCC2 , ∇-FeSi, *- $FeSi_2$.

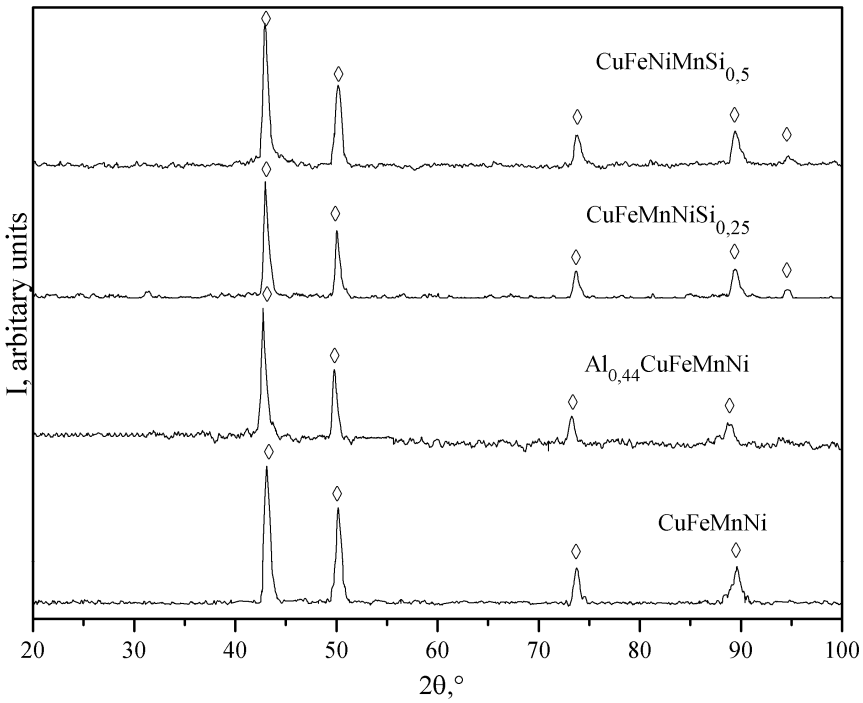

Fig.2. XRD patterns of splat-quenched HEAs of Al-Cu-Fe-Mn-Ni-Si alloy system: ◊-FCC.

Meanwhile the XRD patterns of SQ alloys do not have superlattice reflections and consequently SQ HEA's contain only disordered FCC phases. In our opinion, the high cooling rate during the formation of thin SQ foil should prevent it from non-equilibrium phase decomposition and hinder the appearance of structures and phases typical for as-cast and equilibrium states.

Taking into account the values of lattice parameters of the investigated alloys, one can suggest that the solid solutions are formed on the base of γ-Fe lattice (a = 0.3572 nm [16]), in view of its higher melting temperature.

Table 3

Phase composition, size of coherently scattering domains (L), degree of distortion of the crystal lattice ($\Delta a/a$), dislocation density (ρ) and microhardness (H_μ) of investigated alloys

Alloy	Phase composition	L, нм.	L, nm	ρ, cm^{-2}	$\Delta a/a$	H_μ, MPa
As-cast $Al_{0.44}CuFeMnNi$	FCC (a=0.3645 nm)	14±2	$5.9\cdot10^{-3}$	$2.6\cdot10^{12}$	5.9·10-3	2000±200
SQ foil $Al_{0.44}CuFeMnNi$	FCC (a=0.3619 nm)	30±3	$2.4\cdot10^{-3}$	$6.3\cdot10^{11}$	2.4·10-3	1600±100
As-cast $CuFeMnNiSi_{0.5}$	FCC (a=0.3660 nm)+ FCC (a=0.3620 nm)+ $FeSi + FeSi_2$	18±2 18±2	$2.3\cdot10^{-3}$	$1.6\cdot10^{12}$	2.3·10-3	3300±200
SQ foil $CuFeMnNiSi_{0.5}$	FCC (a=0.3646 nm)	30±3	$2.0\cdot10^{-3}$	$6\cdot10^{11}$	2.0·10-3	2200±200
As-cast $CuFeMnNiSi_{0.25}$	FCC (a=0.3642 nm)	16±2	$4.5\cdot10^{-3}$	$2.2\cdot10^{12}$	4.5·10-3	3000±200
SQ foil $CuFeMnNiSi_{0.25}$	FCC (a=0.3634 nm)	32±3	$2.5\cdot10^{-3}$	$5.5\cdot10^{11}$	2.5·10-3	2500±200
As-cast CuFeMnNi	FCC (a=0.3641 nm)	20±2	$4.4\cdot10^{-3}$	$1.35\cdot10^{12}$	4.4·10-3	1400±100
SQ foil CuFeMnNi	FCC (a=0.3632 nm)	31±3	$2.3\cdot10^{-3}$	$5.6\cdot10^{11}$	2.3·10-3	1000±100

High microhardness values of Cu-Fe-Mn-Ni system alloys with Al and Si additions can be explained by the presence of the dissimilar atoms of elements with different size, electronic structure and thermodynamic properties in the crystal lattice. This leads to a significant distortion ($\Delta a/a$) of the crystal lattice. Consequently the hardness of the alloys increases. As seen from Tab. 3, microhardness of the SQ alloys is lower than that of the as-cast alloys. This result is not surprising, since the microstructure and the phase composition of the as-cast alloy after decomposition is in a more equilibrium state, with the presence of hard and brittle intermetallic compounds, while highly non-equilibrium SQ alloys yields lower level of microstrains and dislocation density. The obtained results clearly indicate also a strong dependence between the measured microhardness and content of Si and Al additions, with a positive trend of microhardness as the Si content increases.

4. Conclusions

We found that all the as-cast alloys except the $CuFeMnNiSi_{0.5}$ have simple single-phase FCC structure while $CuFeMnNiSi_{0.5}$ alloy has a complicated phase composition, there two simple FCC solid solutions together with intermetallic FeSi and $FeSi_2$ phases are presented. All the splat-quenched HEA's contain only disordered FCC phases. With the increase of cooling rate, the level of microstrains, dislocation density, and microhardness of Al-Cu-Fe-Mn-Ni-Si HEA's decreases. The Al and Si additions have a positive effect on the microhardness of Cu-Fe-Mn-Ni system HEA's.

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Received 20.05.2016