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MICROSTRUCTURE AND MECHANICAL PROPERTIES OF NEW MULTICOMPONENT HIGH-ENTROPY ALLOYS

The multicomponent high-entropy alloys CoCrCuFeNiSn$_x$ (x=0,5;1) were investigated. Alloys were found to have two-phase (FCC + BCC) structure. No intermetallic phase formations were observed. The lattice constant of both the FCC and BCC phases increased with increasing content of the Sn atoms. Furthermore, increase of Sn content led to formation of BCC lattice-type phase B2 (ordered solid solution). Both of the alloys displayed a typical cast dendritic structure. Energy dispersive spectrometry revealed a segregation of Cu and Sn in the interdendritic space. Investigated alloys were found to exhibit high microhardness and excellent resistance to anneal softening. Their microhardness after annealing at 1000°C for 5 hours and cooling in the furnace remained almost the same. It was established that increasing of Sn content in the alloy has a positive effect on microhardness as by increasing the degree of elastic deformation of the crystal lattice, due to the large size of substituting Sn atoms, and by forming the ordered B2 phase.

Keywords: multicomponent high entropy alloy, structure, microhardness.

Впервые исследованы многокомпонентные высокоэнтропийные сплавы CoCrCuFeNiSn$_x$ (x=0,5;1). Установлено что сплавы имели двухфазную ОЦК+ГЦК структуру, интерметаллические фазы не обнаружены. Параметры решетки как в ОЦК так и в ГЦК фазах возростали с увеличением содержания Sn. Кроме того, увеличение содержания Sn приводило к формированию упорядоченного твердого раствора со структурным типом B2 на основе ОЦК фазы. Изученные сплавы демонстрировали типичную дендритную структуру. При помощи энергодисперсионного рентгеновского спектрометра обнаружена сегрегация атомов Cu и Sn в междендритное пространство. Исследованные сплавы демонстровали высокие значения микротвердости и устойчивость к смягчению путем отжига. Значения микротвердости сплавов оставались практически неизменными после отжига в течении 5 часов при температуре 1000°С и последующего охлаждения в печи. Установлено, что увеличение содержания Sn в сплаве оказывало позитивное влияние на величину микротвердости как благодаря увеличению степени упругой деформации кристаллической решетки из за большого размера замещающих атомов Sn, так и благодаря формированию упорядоченной фазы B2.

Ключевые слова: высокоэнтропийный сплав, структура, микротвердость.

Вперше досліджені багатокомпонентні високоентропійні сплави CoCrCuFeNiSn$_x$ (x=0,5;1). Встановлено що сплави мали двофазну ОЦК+ГЦК структуру, інтерметалічні фази не виявлені. Параметри решітки як в ОЦК так і в ГЦК фазах зростали зі збільшенням вмісту Sn. Крім того, збільшення вмісту Sn спричиняло формування впорядкованого твердого розчину зі структурним типом B2 на основі ОЦК фази. Досліджені сплави демонстрували типову дендритну структуру. За допомогою енергодисперсійного рентгенівського спектрометра виявлено сегрегацію атомів Cu та Sn у міждендритний простір. Досліджені сплави демонстрували високі значення мікротвердості та стійкость до пом'якшення шляхом відпалу. Значення мікротвердості сплавів залишались практично незмінними після відпалу впродовж 5 годин за температури 1000°С та наступного охолодження у пічці. Встановлено, що збільшення вмісту Sn у сплаві мало позитивний вплив на величину мікротвердості як завдяки збільшенню ступеня пружної деформації кристалічної решітки спричиненого великими розмірами атомів заміщення Sn, так і завдяки формуванню впорядкованої фази B2.

Ключові слова: високоентропійний сплав, структура, мікротвердість.

Introduction

Up to present time, the traditional strategy for developing alloys is to select one or two elements as principal components for primary properties and other minor elements incorporated for definite microstructure and properties. In the 1960-1990's many researchers have explored a wide range of bulk amorphous alloys based on at least three different components with significantly different atomic radii [1]. However, the design principles of the above alloys are still limited to the use of matrices containing a high concentration of one or two elements. The main reason for limiting the number of basic elements is the expected formation of a large number of brittle intermetallic compounds and complex microstructures in the structure of alloys. Recently some studies have developed a new thermodynamic approach to design alloys with multiprincipal metallic elements [2, 3] As a result, a new class of materials known in the literature as multicomponent high-entropy alloys (MHA) has been obtained. MHAs generally have at least five principal elements with the concentrations of each of them between 5 and 35 at.% (equiatomic or near-equiatomic concentrations being better). Alloys with multiprincipal elements tend to be thermodynamically stable because of their high entropy of mixing. Due to the high mixing entropy these equiatomic multicomponent alloys are observed to form solid solutions with simple crystal structures (FCC or BCC), without detectable intermetallic compounds or ordered phases. MHA's were first explored by Yeh et al., the results were published in 2004 [2]. For the past few years, a number of multicomponent alloys were obtained and studied. A unique structure and a complex of promising properties, such as hardness, wear resistance, oxidation resistance, corrosion resistance and high thermal stability [4-8] characterize these alloys. Improved mechanical characteristics are ensured by the strong distortion of the crystal lattice due to the differences in atomic radii of the elements. The higher the entropy of mixing, the more pronounced these characteristics of the alloy. This thermodynamic approach to the design of a multicomponent alloy allows to define a priori the number of elements and their relationship, and partly to evaluate the phase and structural state after crystallization. However, this approach cannot be a unique solution for the problem of choosing the specific alloying elements to obtain required characteristics. For this reason, basing on data like mixing entropy to assess MHA properties, it is need to specify the composition of the alloy empirically. Most of MHA's were designed with using such metals as Al, Ti, Cr, Fe, Co, Ni and Cu. In this paper effect of the value of mixing entropy and composition on the microhardness, phase composition and parameters of the fine structure of multicomponent alloys $\mathrm{CoCrCuFeNiSn}_x$ (x=0,5;1) in the as-cast (cooling rate of ~ 10^3 $\mathrm{K \cdot s^{-1}}$) state has been firstly investigated.

Materials and methods

Cast ingots of the alloys with multiprincipal metallic elements were polished and electrochemically etched for observation. The microstructures of the as-cast samples were studied using an optical microscope and scanning electron microscope (SEM) REMMA - 102-02. The chemical compositions of these cast alloys were analyzed by SEM energy dispersive spectrometry. X-ray diffraction (XRD) was carried out on a DRON -2.0 in monochromatic copper radiation. The microhardness was measured on a PMT-3 microhardness-meter at a load of 200 g. Selection of the components for investigated alloys was performed basing on the following considerations.

In accordance with the Gibbs equation

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}. \tag{1}$$

Here ΔG_{mix} - the Gibbs potential, ΔH_{mix} - the enthalpy and ΔS_{mix} - entropy of mixing, which is determined from the equation

$$\Delta S_{mix} = -R\sum_{i=1}^{n} c_i \ln c_i \ , \tag{2}$$

c_i is an atomic fraction of the *i*-th component, *R* is an universal gas constant. Increasing of mixing entropy in accordance with Eq. (1) reduces the Gibbs free energy of the alloy and improves the stability of the solid solution. For the alloy where *n* is the number of components maximum mixing entropy is when they are mixed in equal atomic fractions. However, in practice, is not always possible to achieve the desired alloy properties by simply mixing the components in the equiatomic ratio. In this regard, additional criteria have been developed for carrying out selection of alloy elements [9,10]:

1. The value of the entropy of mixing should not be less than 12 J/(mol·K)).
2 . Enthalpy of mixing should be in the range from -15 kJ/mol to 5 kJ/mol. Too high enthalpy of mixing leads to the segregation of the individual components of the alloy, too low leads to the formation of complex structures and intermetallic compounds. The value of ΔH_{mix} is determined by the formula

$$\Delta H_{mix} = \sum_{i=1, i\neq j}^{n} \Omega_{ij} c_i c_j \tag{3}$$

where the regular melt-interaction parameter between *i*-th and *j*-th elements $\Omega_{ij} = 4\Delta H_{mix}^{AB}$, and ΔH_{mix}^{AB} - mixing enthalpy of binary liquid AB alloy.

3. Alloy components should not have large atomic-size difference. It is necessary for the formation of simple substitution solid solutions (δ ≤ 4,6, where δ- parameter characterizing the difference in atomic radii of the alloy components). For the ordered solid solutions, δ is required to be in the range of 4.6 ≤δ ≤ 6.5.

$$\delta = 100\sqrt{\sum_{i=1}^{n} c_i \left(1 - {r_i}/{\bar{r}}\right)^2} \tag{4}$$

where $\bar{r} = \sum_{i=1}^{n} c_i r_i$, r_i - the atomic radius of the *i*-th element.

Mixing enthalpies and atomic radii of charging elements and their concentration in the alloys investigated in this paper are shown respectively in Tab.1 and Tab. 2. Values of ΔH_{mix}, ΔS_{mix} and δ, calculated using the equations (2) – (4) for alloy CoCrCuFeNiSn$_{0.5}$ are: ΔH_{mix} = 4.23 kJ/mol, ΔS_{mix} = 14.69 J/(mol·K), δ = 7.08. For alloy CoCrCuFeNiSn$_1$: ΔH_{mix} = 4.89 kJ/mol, ΔS_{mix} = 14.89 J/(mol·K), δ = 8.95. Thus, the parameter δ for the alloys exceeds the recommended limit, but, as pointed out in [12], this criterion appears to require some clarification.

The significantly larger atomic radius of tin should have a positive impact on the value of microstrains and mechanical characteristics of the materials (in particular, the microhardness H_μ). The value of microstrains is evaluated from the degree of distortion of the crystal lattice ($\Delta a / a$). In this paper, the level of microstrain and the value of the dislocation density were estimated from the broadening of the diffraction peaks.

Table 1

Atomic radii of elements and nominal chemical compositions of CoCrCuFeNiSn$_x$ alloys

	Co	Cr	Cu	Fe	Ni	Sn
Atomic radii, nm.	0.125	0.129	0.128	0.126	0.125	0.158
Composition of CoCrCuFeNiSn$_{0.5}$, at.%	18.18	18.18	18.18	18.18	18.18	9.1
Composition of CoCrCuFeNiSn$_1$, at.%	16.67	16.67	16.67	16.67	16.67	16.67

Table 2

Values of ΔH_{mix} (kJ/mol), calculated by Miedema's model [12]

Element	Cr	Cu	Fe	Ni	Sn
Co	-4	6	-1	0	0
Cr		12	-1	-7	10
Cu			13	4	7
Fe				-2	11
Ni					-4

Results and discussion

The phase composition of the investigated CoCrCuFeNiSn$_x$ alloys, crystal lattice parameters and the fine structure parameters (coherent scattering areas and microstrains) were determined from the XRD patterns. The dislocation density (ρ) was obtained from the profile of the first diffraction peak. XRD analysis allowed us to establish what CoCrCuFeNiSn$_{0.5}$ and CoCrCuFeNiSn$_1$ alloys have two-phase (FCC + BCC) structure. With increase in Sn content increases the tendency to form a BCC lattice-type phase B2 (CsCl).

Results of XRD analysis are shown in Tab. 3, from which it is seen that increasing of Sn content in the alloy has a positive effect on microhardness as by increasing the degree of elastic deformation of the crystal lattice, due to the large size of substituting Sn atoms, and by forming the ordered B2 phase. The lattice constant of both the FCC and BCC phases increased with increasing content of the Sn atoms.

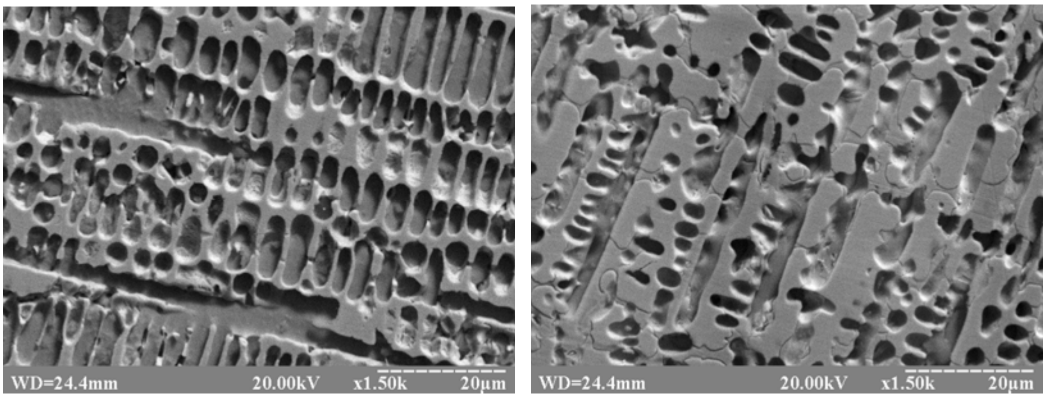
MHA were also found to exhibit excellent resistance to anneal softening. Tab. 3 shows that their microhardness after annealing, even at 1000°C for 5 hours and cooling in the furnace, remains almost the same.

Table 3

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

Alloy	Phase composition	*L*, nm	$\Delta a/a$	H_μ, MPa	H_μ, MPa (after heat treatment)	ρ, sm^{-2}
CoCrCuFeNiSn$_{0.5}$	FCC (a=0.3586 nm)+ BCC (CsCl-type, a=0.2979 nm)	L_{FCC}=37±2 L_{BCC}=27±2	$1.8\cdot10^{-3}$	3500±200	3800±200	$4.2\cdot10^{11}$
CoCrCuFeNiSn$_1$	FCC (a=0.3600 nm)+ BCC (CsCl-type, a=0.2981 nm)	L_{FCC}=19±2 L_{BCC}=21±2	$2.3\cdot10^{-3}$	4000±200	3900±200	$1.6\cdot10^{12}$

Fig. 1 is a secondary electron image of the as-cast CoCrCuFeNiSn$_{0.5}$ and CoCrCuFeNiSn$_1$ alloys subjected to electrochemical etching. Both of the alloys display a typical cast dendritic structure. Energy dispersive spectrometry revealed a segregation of Cu and Sn in the interdendritic space (Tab.4). The interdendritic space of CoCrCuFeNiSn$_1$ alloy can be divided into two phases of different composition.



a b

Fig.1.Microstructures of the CoCrCuFeNiSn$_{0.5}$ (a) and CoCrCuFeNiSn$_{1}$ (b) alloys

Table 4

Chemical compositions of as-cast CoCrCuFeNiSn$_x$ alloys

Alloy		Element, %					
		Co	Cr	Cu	Fe	Ni	Sn
CoCrCuFeNiSn$_{0.5}$	Dendrite	22.87	20.63	6.65	26.54	17.07	6.24
	Interdendrite	2.33	0.65	36.92	2.01	15.04	43.05
CoCrCuFeNiSn$_1$	Dendrite	20.73	15.88	7.50	22.50	13.92	19.47
	Interdendrite	1.56	0.24	42.14	0.76	9.14	46.16
		4.91	1.28	10.63	2.48	18.97	61.73

Conclusions

The investigated multicomponent CoCrCuFeNiSn$_x$ alloys reveal the presence of simple crystal structures, i.e. FCC solid-solution and BCC solid-solution phases. No intermetallic phase formation has been observed in these alloys.

In CoCrCuFeNiSn$_x$ alloys revealed the presence of segregation microinhomogeneity within interdendrite space.

For the investigated alloys increase of Sn content leads to formation of ordered solid solution phase B2.

The alloy microhardness increase with Sn content increasing. Such a fact can be explained not only by the increased strengthen effect of lattice strain caused by the lattice sites occupation of Sn, but also by the ordering into the B2 phase. This conclusion is because the microhardness increased with increasing degree of ordering in the solid solution.

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