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Structure AND Mechanical Properties of Al-Co-Cr-Fe-Mn-Ni-Si-V High-Entropy Films Obtained by Splat-Quenching

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The multicomponent films of Al-Co-Cr-Fe-Mn-Ni-Si-V high-entropy alloys obtained by splat-quenching from melt were investigated. Phase formation criteria for high-entropy alloys were considered. The films have a structure with body-centered cubic lattice. The value of lattice parameters of the investigated alloys suggests that the solid solutions are form on the base of Cr lattice, in view of its higher melting temperature. The positive influence of microstrains level and dislocation density on the microhardness values of splat-quenched high-entropy alloys has been established. Improved mechanical characteristics are ensured by the strong distortion of the crystal lattice due to the differences in atomic radii of the elements.

Keywords: multicomponent high-entropy alloy; structure; microhardness; splat-quenching.

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1. INTRODUCTION

The conventional development of new alloys is based on one or two elements as major constituents, and some other minor elements for the optimization of final properties. However in the last time, increasing industrial demands for various structural and functional metallic materials have stimulated the advent of new technologies and the development of multicomponent alloys. Recently a new class of materials known in the literature as multicomponent high-entropy alloys (HEA) was obtained [1]. High-entropy alloys are defined as solid solution alloys that contain more than five principal elements (usually from five to thirteen) in equal or near equal atomic percent. The basic principle of HEAs is the stabilization of solution phase by the significantly higher configurational entropy of mixing ΔS_{mix} compared to conventional alloys. The configurational entropy of mixing during the formation of regular solution alloy can be determined as

$$\Delta S_{mix} = -R\sum_{i=1}^{n} c_i \ln c_i \qquad (1.1)$$

c_i - atomic fraction of the i-th component, R - universal gas constant. Increasing of mixing entropy reduces the Gibbs free energy of the alloy and improves stability of the solid solution, in accordance with Gibbs equation

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (1.2)$$

Here ΔG_{mix} - the Gibbs potential, ΔH_{mix} - the mixing enthalpy. For the alloy where n is the number of components maximum mixing entropy is when they are mixed in equal atomic fractions.

Usually in HEA value of ΔS_{mix} is in the range of 12 - 19 J/(mol·K). Due to the high mixing entropy HEAs are solid solutions typically having simple crystal structures (FCC or BCC), but to avoid the appearance of brittle intermetallic compounds, complex microstructures and amorphous phases in the structure of alloys, some phase formation criteria are required to be completed. According to [2, 3], the Ω parameter can be used to estimate the phase composition of HEA.

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \qquad (1.3)$$

where T_m is the average melting temperature of alloy

$$T_m = \sum_{i=1}^{n} c_i (T_m)_i \qquad (1.4)$$

$$\Delta H_{mix} = \sum_{i=1, i\neq j}^{n} \Omega_{ij} c_i c_j \qquad (1.5)$$

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. Alloy components should not have large atomic-size difference, which is described by the parameter

$$\delta = 100\sqrt{\sum_{i=1}^{n} c_i \left(1 - r_i/\bar{r}\right)^2} \qquad (1.6)$$

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

According to [2] the HEA alloys for which Ω≥1.1 and δ≤6.6 can form the solid solutions without intermetallic compounds and amorphous phases. However, simple (not ordered) solid solutions form if -15 kJ/mol < ΔH_{mix} < 5 kJ/mol and δ≤4.6.

The other useful parameter is the valence electron concentration, *VEC*, which has been proven useful in determining the phase stability of high-entropy alloys [4,5]. VEC is defined by:

$$VEC = \sum_{i=1}^{n} c_i (VEC)_i \qquad (1.7)$$

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where $(VEC)_i$ - valence electron concentration (including the *d*-electrons)of the *i*-th element. As pointed in [5] at $VEC \geq 8.0$, sole FCC phase exists in alloy; at $6.87 \leq VEC < 8.0$, mixed FCC and BCC phases will co-exist and sole BCC phase exists at $VEC < 6.87$.

It has been reported that HEAs possess many attractive properties, such as high hardness, outstanding wear resistance, irradiation resistance, excellent high-temperature strength, good thermal stability and corrosion resistance [1, 6-13]. Improved mechanical characteristics are ensured by strong distortion of the crystal lattice due to the differences in atomic radii of the elements.

In this work effect of the value of mixing entropy and composition on the microhardness, phase composition and parameters of the fine structure of HEA films of Al-Co-Cr-Fe-Mn-Ni-Si-V alloy system is discussed (Mn and Si are added as minor elements to improve mechanical properties and corrosion resistance).

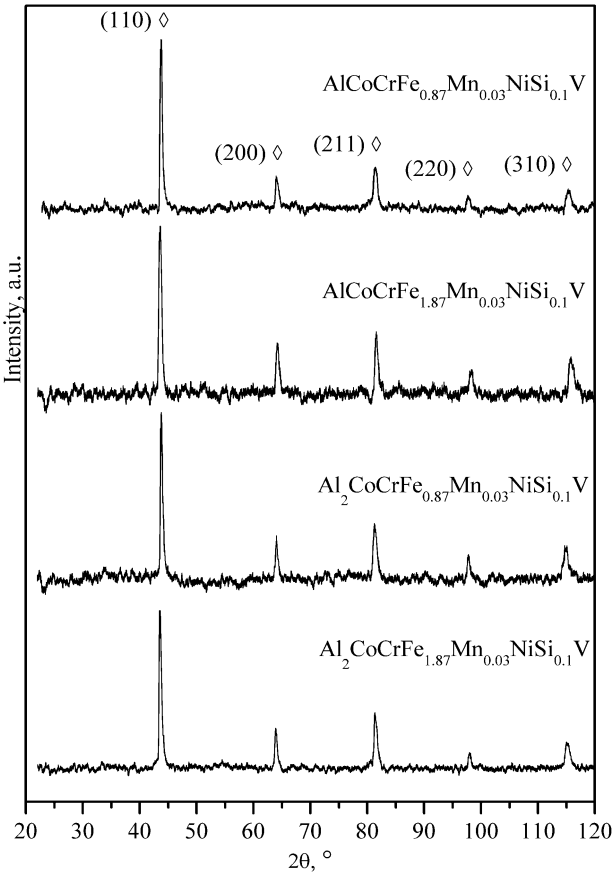

Fig. 1 – XRD patterns of splat-quenched HEA films of Al-Co-Cr-Fe-Mn-Ni-Si-V alloy system: ◊-BCC.

2. EXPERIMENTAL

The samples of Al-Co-Cr-Fe-Mn-Ni-Si-V high-entropy alloys were taken from the as-cast (cooling rate of ~ 10^2 K/s) ingots. The quenching from the molten state (splat-quenching, SQ) was performed 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 using a DRON-2.0 X-ray diffractometer in Cu *Ka* monochromatized radiation. The microhardness was measured on a PMT-3 microhardness-meter.

3. RESULTS AND DISCUSSION

Using the data listed in Tab.1 and Tab. 2., the following quantities are calculated for the HEA films (as listed in Tab. 3): ΔS_{mix}, ΔH_{mix}, δ, Ω and *VEC*.

The phase composition of investigated alloys, crystal lattice parameters and fine structure parameters (size of coherently scattering domains and microstrains) (Tab.4) were determined from the XRD patterns (Fig.1). The dislocation density (ρ) was obtained from the profile of the first diffraction peak. The microhardness values of Al-Co-Cr-Fe-Mn-Ni-Si-V HEA films are given in Tab. 5.

Table 1 – Atomic radii of elements and valence electron concentrations [4,10] of Al-Co-Cr-Fe-Mn-Ni-Si-V HEA films

	Al	**Co**	**Cr**	**Fe**	**Ni**	**V**	**Si**	**Mn**
Atomic radii, nm.	0.143	0.125	0.129	0.126	0.125	0.135	0.118	0.137
VEC	3	9	6	8	10	5	4	7

Table 2 – Values of ΔH_{mix}^{AB} (kJ/mol), calculated by Miedema's model [14]

Element	**Co**	**Cr**	**Fe**	**Ni**	**V**	**Si**	**Mn**
Al	-19	-10	-11	-22	-16	-19	-19
Co		-4	-1	0	-14	-38	-5
Cr			-1	-7	-2	-37	2
Fe				-2	-7	-35	0
Ni					-18	-40	-8
V						-48	-1
Si							-45

Table 3 – Values of ΔH_{mix}, ΔS_{mix}, δ, VEC and Ω of Al-Co-Cr-Fe-Mn-Ni-Si-V HEA films

Alloy	**ΔH_{mix}, kJ/mol**	**ΔS_{mix}, J/(mol·K)**	**δ**	**VEC**	**Ω**
$AlCoCrFe_{0.87}Mn_{0.03}NiSi_{0.1}V$	-17.04	15.52	5.18	6.76	1.6
$AlCoCrFe_{1.87}Mn_{0.03}NiSi_{0.1}V$	-14.6	15.18	4.96	6.94	1.84
$Al_2CoCrFe_{0.87}Mn_{0.03}NiSi_{0.1}V$	-18.98	15.07	5.78	6.22	1.3
$Al_2CoCrFe_{1.87}Mn_{0.03}NiSi_{0.1}V$	-16.81	14.97	5.66	6.45	1.48

Table 4 – Phase composition, size of coherently scattering domains (L), degree of distortion of the crystal lattice ($\Delta a/a$), and dislocation density (ρ) of investigated films

Alloy	**Phase composition**	**L, nm**	***Δa/a***	**ρ, cm^{-2}**
$AlCoCrFe_{0.87}Mn_{0.03}NiSi_{0.1}V$	BCC (a=0.2882 nm)	34±2	$3.8 \cdot 10^{-3}$	$2.6 \cdot 10^{12}$
$AlCoCrFe_{1.87}Mn_{0.03}NiSi_{0.1}V$	BCC (a=0.2879 nm)	25±2	$2.8 \cdot 10^{-3}$	$6.8 \cdot 10^{11}$
$Al_2CoCrFe_{0.87}Mn_{0.03}NiSi_{0.1}V$	BCC (a=0.2887 nm)	33±2	$1.8 \cdot 10^{-3}$	$5.4 \cdot 10^{11}$
$Al_2CoCrFe_{1.87}Mn_{0.03}NiSi_{0.1}V$	BCC (a=0.2881 nm)	33±2	$1.7 \cdot 10^{-3}$	$5.7 \cdot 10^{12}$

Table 5 – Microhardness (H_μ) of investigated films

Alloy	H_μ, MPa
$AlCoCrFe_{0.87}Mn_{0.03}NiSi_{0.1}V$	6900±300
$AlCoCrFe_{1.87}Mn_{0.03}NiSi_{0.1}V$	6200±300
$Al_2CoCrFe_{0.87}Mn_{0.03}NiSi_{0.1}V$	7500±300
$Al_2CoCrFe_{1.87}Mn_{0.03}NiSi_{0.1}V$	5600±200

The analysis of the XRD patterns allowed us to establish what the investigated HEA films have disordered body-centered cubic (BCC) structure. Indeed, from the analyses of Tab. 3 it is seen that the low value of *VEC* favours the formation of a BCC phase. Exception is the $AlCoCrFe_{1.87}Mn_{0.03}NiSi_{0.1}V$ alloy, for which the value of *VEC* lies in the range, where a face-centered cubic (FCC) + BCC mixture is favoured. But, as pointed in [15], if the value of *VEC* is close to the boundary values, predictions of the phase compositions sometimes not work.

Meanwhile from Tab.3 we can see that ΔH_{mix} has a large negative value favoring the formation of a intermetallic compounds, which are not observed experimentally. In our opinion the high cooling rate during the formation of thin SQ film should prevent it from possible separation and hinder the appearance of structures and phases typical for equilibrium as-cast states.

The values of lattice parameters of the investigated alloys suggests that the solid solutions are form on the base of Cr lattice (a =0.2884 nm), in view of its higher melting temperature.

High microhardness values of Al-Co-Cr-Fe-Mn-Ni-Si-V HEA films can be explained by the presence in the lattice of dissimilar atoms with different size, electronic structure and thermodynamic properties. This leads to significant distortion ($\Delta a/a$) of the crystal lattice. So SQ films have high level of microstrains and dislocation density, and, consequently the hardness of the films increases.

4. CONCLUSIONS

Based on the study of the Al-Co-Cr-Fe-Mn-Ni-Si-V HEAs, produced by splat-quenching from the melt, the following conclusions can be drawn:

1. Splat-quenched alloys exhibit only disordered BCC solid solution structure.
2. With the increase of cooling rate the level of microstrains, dislocation density and microhardness of Al-Co-Cr-Fe-Mn-Ni-Si-V HEAs increases.
3. Confirmed the leading role of the element with higher melting temperature as the basis for the formation of solid solution in the studied alloys. .

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