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Diffraction 'in-situ' study of Al-Cu-Fe-X quasicrystalline powders for thermal-sprayed coatings

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Structure and phase composition of Al-Cu-Fe-X (X = Cr, Sc) powders atomized by high-pressure water are investigated. As-atomized powders had two main phase components: a quasicrystalline phase of icosahedral symmetry (ψ) and lattice parameter $a_\psi = 0.63466(7)$ nm and a cubic phase (β), $a_\beta = 0.29236(3)$ nm. The relation of phase amounts depended on powder particle size. X-ray in-situ investigation (monochromatic $\text{CuK}\alpha$ radiation) in He environment of powders while heating revealed the occurrence in them of a complete phase transition $\beta \rightarrow \psi$ at temperatures of 550-600°C after 1 h holding. It was accompanied by lowering the ψ -phase lattice period to the value $a_\psi = 0.63167(2)$ nm. X-ray diffractometric analysis has shown the existence of the ψ -phase in the given powder sample to a temperature of 870 °C. Alloying Al-Cu-Fe powders by Sc and Cr led to changing the relation of amounts of ψ - and β -phases as well as of their lattice parameters in as-atomized condition and appearing new phase components at temperatures of 600-800°C in process of powder heating. The temperature functional dependence of the ψ -phase lattice period in $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{62,56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0,44}$ powders are established.

Keywords: quasicrystalline phase, in-situ X-ray investigation, Al-Cu-Fe system

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I. Introduction

Quasicrystals of Al-Cu-Fe system acquired a great interest also for practical use for the combination of their properties (low density about 4.5 g/cm³, high hardness of 6-10 GPa, high elasticity modulus to 200 GPa, high corrosion and wear resistance, low friction coefficient, lowered adhesion, low thermal conductivity combined with thermal expansion coefficient close by its value to metals (e.g. stainless steel) [1,2]), and for economical reasons as well. Directed alloying can intensify one or other property of Al-Cu-Fe quasicrystalline phase [3].

The quasicrystalline phase Al-Cu-Fe has no strict stoichiometric composition, but the region of its existence in the equilibrium diagram close to the composition $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ is rather narrow. The Al-Cu-Fe quasicrystalline phase is denoted usually as " ψ ". The melting temperature of this phase is 870°C, the region of its existence is the widest at 700°C. It should be noted that there are remarkable discrepancies in details of sections of the Al-Cu-Fe equilibrium diagram between works of various investigators.

II. Experimental procedures

A precise investigation was performed in monochromatic $\text{CuK}\alpha$ -radiation in DRON-UM1 diffractometer with Bragg-Brentano geometry ($R_d = 192$ mm). A graphite single crystal installed in diffracted beam was used as a monochromator. X-ray patterns were obtained in the conditions of step scanning in the angular interval $2\theta = 18-98^\circ$. The scanning step was of 0.05° , the exposure time in one point was of 3-9 s. X-ray high-temperature "in situ" investigation in the temperature interval of 20-900°C was performed with the help of the high-temperature attachment UVD-2000. During X-ray heating experiments the samples were kept flowing helium at a positive pressure of 20 kPa over atmosphere. The period of cubic lattice of the icosahedral phase in 6-dimensional space was calculated from the positions of three most intense diffraction peaks with Cahn indices (N,M) of (18,29), (20,32) and (52,84) [4]. The ψ -phase content in of alloys determined by the Sordelet graph [5] by the ratio of the intensities of X-ray peaks of the ψ -phase and β -phase. Handling of experimental data was carried out with using the program for full-profile analysis of X-ray spectra from a mixture of polycrystalline phase components Powder Cell 2.4 [6].

III. Experimental results and discussion

The investigation was carried out with powder samples of size fraction of $(-63+40)$ μm produced by atomizing with argon (sample 1) as well as with water (sample 2). In initial condition samples had the $(\psi+\beta)$ phase composition with the content of ψ -phase of 35 vol. % in sample 1 and of 60 vol. % in sample 2. The investigation in the temperature interval of 20-900°C has shown that at a temperature of 600°C in both of samples the phase transformation $\beta \rightarrow \psi$ proceeded. Already during the first 30 min. the intensity of X-ray peaks of the crystalline component in the sample 1 decreased 3.3 times, and further holding at higher temperatures (Fig. 1) did not lead to changing the intensity of diffraction

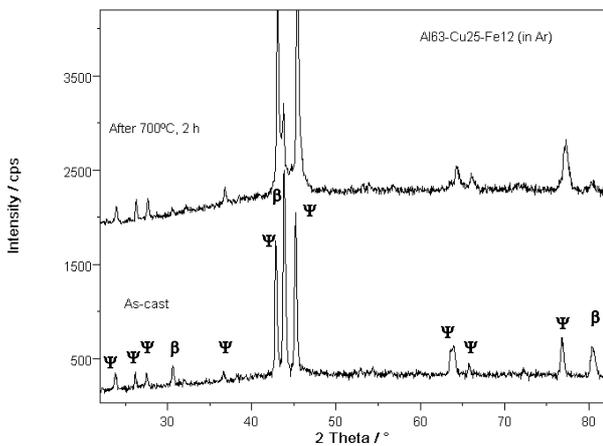


Figure 1. Fragments of X-ray diffraction patterns at 20°C of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powder (argon atomization) in initial condition and after holding for 2 h at 700 °C.

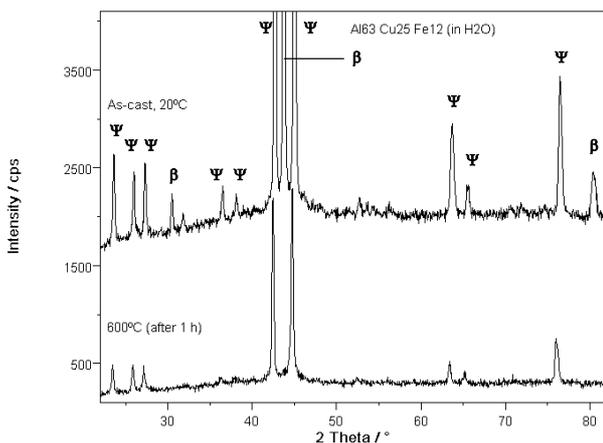


Figure 2. Fragments of X-ray "in situ" patterns of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powder (water atomization) in initial condition at 20°C and at 600°C (after holding for 1 h).

peaks. In the sample 2 the phase transformation $\beta \rightarrow \psi$ completed at 600 °C during 1 h (Fig.2). Therefore a detailed investigation was carried out with using powders of the type 2.

The investigation has shown that diffraction peaks of ψ -phase are registered right up to a temperature of 870°C (the temperature of ψ -phase melting). Heating the sample to 900°C led to their vanishing and appearing weak λ -phase peaks that is in accordance with the Al-Cu-Fe equilibrium diagram. The following cooling of the sample to 600°C led to appearing in places of ψ -phase peaks more diffuse peaks and to their splitting. A detailed analysis of this pattern together with literary data evidences to the formation in this sample of the approximant rhombohedral R-phase. A presence of about 10 vol. % of β -phase with increased elementary cell period is also fixed in this sample.

Obviously, the formation of the R-phase was caused by low cooling rate of the sample in the X-ray chamber in the temperature interval of 900-600°C that stipulated the appearance while crystallization of structures closer to the equilibrium diagram compared to rapidly cooled powder. At the same time after annealing at 600°C and cooling in the chamber in this sample the ψ -phase with lowered lattice period was obtained, as in sample 1.

Changing lattice periods for the quasicrystalline component with temperature and average thermal expansion coefficient of the ψ -phase (α_ψ) in the given temperature intervals are presented in Table. It is seen that the α_ψ changes very weakly to a temperature of 700°C, and in the premelting region (800-850°C) it increases more than 2 times.

Alloying with 0.44% Sc led to lowering the lattice parameters of both ψ and β phases in comparison to the non-alloyed powder: $a_\psi = 0.63298(3)$ nm and $0.63466(7)$ nm, $a_\beta = 0.29237(3)$ nm and $0.29270(9)$ nm, respectively (Table). From this fact we can make a conclusion that Sc enters into the composition of both phases. In addition, in X-ray patterns of these powders compared to the X-ray pattern of the non-alloyed powder two weak lines at 2θ angles of 20.5°, 29.05°, 41.53° and 46.71° appeared (Fig. 3). These lines disappeared after high-temperature annealing and can be a sign of the formation of the ternary Al-Cu-Sc intermetallic. Really, the analysis of angular position of these additional peaks has shown that they belong to a tetragonal phase AlCuSc ($a = 0.8688$ nm, $c = 0.5029$ nm) with structure of type ThMn_{12} [7]. It is shown that additional alloying of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy with a small amount of Sc significantly increased the ψ -phase content in the powder. Thus, the part of the ψ -phase with lowering powder particle size from 200 to 25 μm increased from 62 to 78 mass. % that is significantly higher compared to non-alloyed water-atomized powders (47...59 mass. %). Dependence lattice period of the ψ -phase with temperature (Table) for $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$ powders can be approximated in the form:

$$a_\psi(T) = 0.62982 + 4.75933 \cdot 10^{-6}T + 5.40485 \cdot 10^{-9}T^2$$

$$\text{and } a_\psi(T) = 0.62879 + 8.96279 \cdot 10^{-6}T + 8.77936 \cdot 10^{-10}T^2 \text{ respectively.}$$

Value of the period of quasicrystalline lattice (a_6) of ψ -phase and crystalline β -phase (a) for samples $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$ powder (water atomization) at various temperatures and average thermal expansion coefficient of the ψ -phase (α_ψ) in the given temperature intervals

Temperature, °C	$\text{Al}_{65}\text{Cu}_{25}\text{Fe}_{12}$		$\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$		
	$\psi - a_6, \text{nm}$	$\alpha_\psi \times 10^6$	$\psi - a_6, \text{nm}$	$\beta - a, \text{nm}$	$\alpha_\psi \times 10^6, \text{K}^{-1}$
20, as-cast	0.63466(7)		0.63298(3)	0.29237(3)	
600, 1h	0.63824(2)	17.9	0.63774(3)	-	17.1 (20-600 °C)
20 after 600	0.63167(2)		0.63149(4)	-	
200			0.63322(1)	-	15.2 (20-200 °C)
400			0.63522(2)	-	15.8 (200-400 °C)
600			0.63728(3)	-	16.2 (400-600 °C)
700	0.63944(3)	18.1	0.63832(4)	0.29674(5)	16.3 (600-700 °C)
800	0.64094(4)	23.5	0.63998(3)	0.29719(7)	26.0 (700-800 °C)
600 after 800			0.63696(5)	0.29633(4)	
850	0.64218(6)	38.7	0.64137(6)	0.29754(7)	43.4 (800-850 °C)
600 after 900	0.62890(9)		0.63160(9)	0.29650(8)	
20 after 900			0.62740(8)	0.29390(6)	

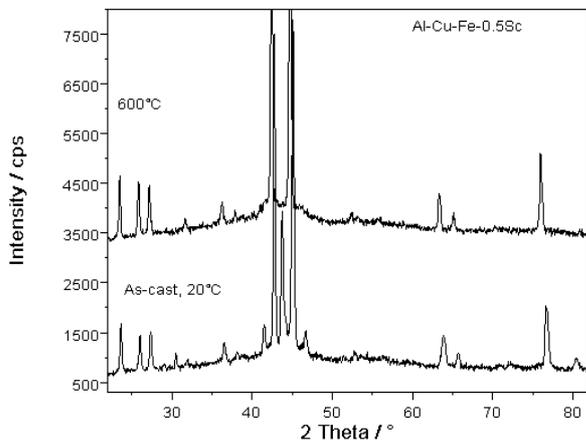


Figure 3. Fragments of X-ray “in situ” patterns of powder of alloy $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$ at 20 °C and at 600°C. Peaks at 2θ angles of 29.05°, 41.53° and 46.71° belong to intermetallic tetragonal phase AlCuSc ($a = 0.8688 \text{ nm}$, $c = 0.5029 \text{ nm}$) with structure of type ThMn_{12}

In alloys $\text{Al}_{66}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$ and $\text{Al}_{63.6}\text{Cu}_{17.3}\text{Fe}_{9.6}\text{Cr}_{9.5}$ the phase composition and structure differ from ones in powders Al-Cu-Fe-Sc . Thus, in the powder of alloy with 8 at. % Cr the phase composition $\psi+\beta$ was revealed. After its holding in the chamber of the high-temperature X-ray diffractometer at 600°C the O1-phase – a crystalline approximant of the decagonal quasicrystal [8],

appeared in the powder. The decagonal quasicrystalline phase together with ψ and β phases was revealed in the powder of alloy with 9.5 at. % Cr. After annealing both phases also transformed to the O1-phase.

IV. Conclusions

By means of X-ray investigation the atomized powders are shown to consist of a mixture of two phases: icosahedral quasicrystalline phase ψ and crystalline phase β with cubic lattice. The ψ -phase content in water-atomized powders is some percents higher than in argon-atomized powders. The temperature dependence of the parameter of the ψ -phase lattice in $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$ powders in the form of a second order polynomial that permits to calculate the thermal expansion coefficient of the ψ -phase at different temperatures.

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М.В. Карпець, Ю.В. Мільман

Дифракційне 'in-situ' вивчення квазікристалічних порошків Al-Cu-Fe-X для газотермічних покриттів

Досліджено структуру та фазовий склад порошків Al-Cu-Fe-X (X = Cr, Sc) одержаних диспергуванням розплаву водою високого тиску. Розпилені порошки містять дві основні фазові складові: квазікристалічну фазу ікосаедричної симетрії (ψ) з періодом ґратки $a_\psi = 0,63466(7)$ нм і кубічну фазу (β), $a_\beta = 0,29236(3)$ нм. Фазовий склад порошків залежить від їх зернистості. Рентгенівське in-situ дослідження (монохроматичне CuK α випромінювання) при нагріванні порошків в атмосфері гелію виявило протікання в них повного фазового перетворення $\beta \rightarrow \psi$ при температурах 550-600°C після витримки на протязі 1 години. Таке перетворення супроводжується зменшенням періоду ґратки ψ -фази до значення $a_\psi = 0,63167(2)$ нм. Дифрактометричне вивчення показало існування ψ -фази в досліджених порошках до температури 870°C. Легування порошків Al-Cu-Fe атомами Sc та Cr приводить до зміни співвідношення вмісту ψ - та β -фаз і їх періодів ґраток, а також появи нових фазових складових при температурах 600-800°C в процесі нагріву порошків. Встановлено функціональну залежність періоду квазікристалічної ґратки ψ -фази від температури в водорозпиленних порошках Al₆₃Cu₂₅Fe₁₂ і Al_{62,56}Cu₂₅Fe₁₂Sc_{0,44}.

Ключові слова: квазікристалічна фаза, рентгенівське in-situ дослідження, система Al-Cu-Fe.