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Thin Films and Composites Based on Quasicrystal Al–Cu–Fe Alloy

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The structure and properties of Al–Fe–Cu and Al–Fe–Cu–Sc quasicrystal alloys have been investigated applying the methods of metallography, X-Ray analysis, transmission and focused-beam electron microscopy, differential thermal analysis (DTA), and electrical resistivity method. The cast and ion-plasmous sprayed alloys or composites having Al (industrial), Al–6Mg, Al–7Si, and Al–5Cu binders strengthened with $Al_{65}Cu_{20}Fe_{15}$ filler have been studied. The Al–Cu–Fe and Al–Cu–Fe–Sc have been assumed to show promise as advanced resistance alloys. Macroheterogeneous composites strengthened with the quasicrystal filler can be obtained by furnace infiltration that ensures strong adhesion of structural constituents.

Keywords: QUASICRYSTALS, COMPOSITES, THIN FILMS, ION-PLASMOUS SPRAYING, FURNACE INFILTRATION, AL–FE–CU ALLOYS

Introduction

Nano and quasicrystal materials make a deep interest in recent years. The first samples of the quasicrystal phases have been found in rapidly cooled binary systems: the icosahedral and decagonal phases in Al-Mn alloys and dodekagonalnaya phase in Ni-Cr alloys. These phases are metastable, like most known quasicrystals. But later stable icosahedral quasicrystals have been described in the ternary system Al-Cu-Li, and nowadays it has been invented a lot of stable icosahedral and decagonal phases. As a rule, the formation of stable quasicrystals run in ternary and quaternary alloys. Among the systems based on aluminum alloys can be identified Al-Cu-Fe, Al-Pd-Mn and Al-Pd-Re with a highly ordered icosahedral phases or Al-Pd-Mn, Al-Co-Cu and Al-Co-Ni alloys with stable decagonal phases.

The term quasicrystal comes from the quasiperiodicity properties, observed in above-listed alloys based on aluminum; there were found forbidden rotational axes of symmetry 5, 8, 10 and 12 orders. In other words, the quasicrystal is a crystal with long-range order in the atoms arrangement and without periodicity. For icosahedral quasicrystals are observed symmetrical forms, such as dodecahedron and triacontahedron, and also more complex polyhedrons with many faces. The grinding is also observed in decagonal quasicrystals, and direction of their periodic axes coincides with the direction of preferential growth, which leads to a columnar dendritic form of quasicrystals.

Today, quasicrystals are got by quenching from the liquid state – directly and by crystallization of amorphous quenched samples – mechanically alloyed with an ultra thin grinding source components, conventional hardening, reactive diffusion and, finally, condensation from the vapor phase. There are 2 ways of getting quasicrystals in the last case. The direct formation of quasicrystals from the vapor, the crystallization from the amorphous phase and multilayer plotting of pure elements with subsequent annealing.

Unusual combination of properties, such as low friction, high wear resistance, corrosion resistance, low surface tension are characteristic for quasicrystals. Most of these properties provides using of quasicrystalline alloys in products of modern technology. Therefore, there are shown the structure and properties of quasicrystalline alloy Al-Cu-Fe to create a film and composite materials with special properties.

Experimental technique

Thanks to metallographic analysis, X-ray studies, transmission and scanning electron microscopy, differential thermal analysis (DTA) and method of constructing polyterm resistance studied the structure and properties of Al-Fe-Cu and Al-Fe-Cu-Sc alloys. Studied alloys, obtained by casting at cooling rate 10-1000 °C/s and high efficient cooling rates (10^{12}-10^{14}), implemented with upgraded ion-plasmous sputter [1]. Composition of alloys fit the stoichiometric composition quasicrystal phase $Al_{65}Cu_{20}Fe_{15}$.

Cast alloys were got from double ligature Al-Cu, Al_3Fe and $Al_{30}Sc$. Their composition is controlled by spectral and X-ray fluorescence analysis. For samples sputtering was used a type-setting target of pure components and ligature with scandium. Scandium in the amount of 0.5% by weight were administered, thanks to the results of investigation [2], which reported that microalloying of Sc provide the formation of quasicrystal ψ-phase. For the production of composite materials, it was used cast alloy $Al_{65}Cu_{20}Fe_{15}$, dividing into pellet irregular size 1.0-3.0 mm. Al ligaments were used such as: technical aluminum, Al-6% Mg, Al-7% Si and Al-5% Cu. Impregnation method continued in the furnace for 30-60 minutes at 700-750 °C.

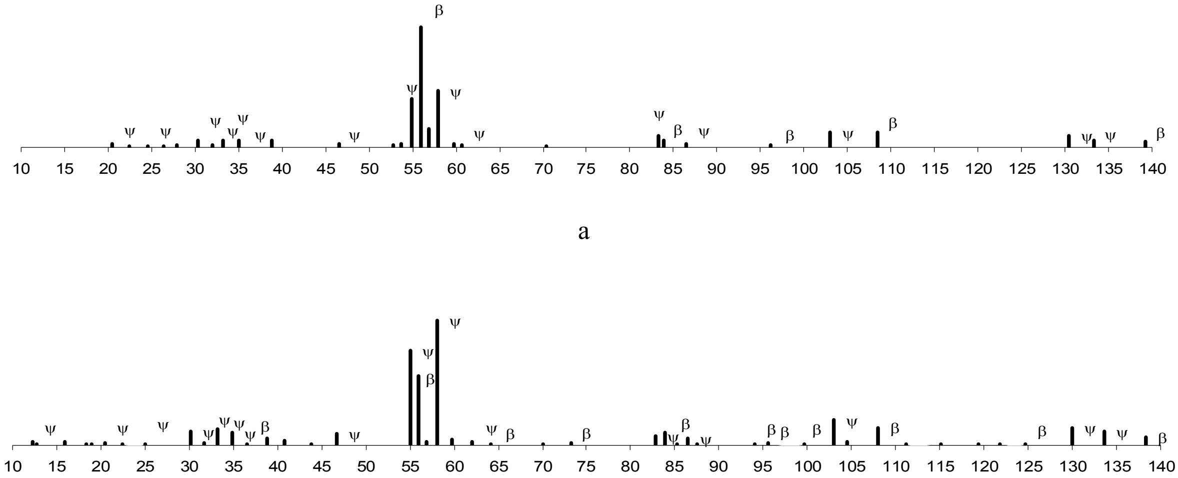
Results and discussion

Prepared cast alloys, according to the control of their composition, are notable for noticeable liquation, which, does not exceed the deviation of the composition, provided for the various melts. This is confirmed by the results of metallography. Alloy structure $Al_{65}Cu_{20}Fe_{15}$ biphasic and consists of an icosahedral quasicrystal ψ-phase (iso) and crystalline cubic phase based on FeAl (β-phase) in approximately equal proportions (**Figure 1**).

Figure 1. Microstructure of Al-Cu-Fe alloy, ×1000

At the rising of cooling rate from 10 to 1000 °C/s, quantity of ψ-phase increases by 10-15%. In alloyed samples with Scandium, amount of quasicrystal phase is less, than in unalloyed. X-ray structure analysis (XSA) totally proves results of metallography. The structure of alloys doesn't have a noticeable texture (for all explored samples ratio of intensity of phase lines in limit of one's connection isn't changed). It helps to sum up level of sample quasicrystality to the intensity of lines ψ- and β-phases. Thanks to DTA it's found, that the max rate of reduction β-phase in ψ-phase, during heating for Al-Fe-Cu alloys, is in range 350-725 °C. Annealings after 8 hours at 800 °C lead to the noticeable increasing of ψ-phase (most of all for unalloyed Sc alloy). But after decreasing the annealing temperature to 600 °C, on the contrary, scandium alloy becomes virtually quasicrystal (no β-phase), and unalloyed is still far from the state reached at 800 °C. Thus, the modification of Sc reduces the transition temperature of Al-Fe-Cu alloys to the state with the maximum number of quasicrystal phase.

Conducted by transmission and scanning electron microscopy and X-ray structure studies, comparative analysis of films of both systems showed that in the freshly sputter state the mixture is formed next dispersed phases: quasicrystal ψ-phase and β-crystalline phase. Evaluation of area sizes of coherent scattering (ECS) by Selyakov-Scherrer formula shows that they are within 3.11 nm and 1.5-6 nm. Thus, the introduction of Sc increases the dispersion of the structure. After heating under vacuum to 750 °C the size of the ECS increases more than twice and the number of quasicrystal phase increases. It indirectly confirms the variation of surface resistivity of films of Al-Cu-Fe system during continuous heating: negative temperature coefficient of resistance (TCR), a fast increasing in the nominal value at the temperature of phase transition to the R_S $6 \cdot 10^7$ ohms / square (**Figure 3**). For films of Al-Cu-Fe-Sc system this effect is much weaker. TCR values for films of Al-Cu-Fe system are ($-2 \cdot 10^{-4}$ °C^{-1}), and for the films of Al-Cu-Fe-Sc system – ($-4 \cdot 10^{-4}$ °C^{-1}).



a

b

Figure 2. Stroke radiographs (Fe-K$_\alpha$ radiation) of Al-Fe-Cu alloy: *a* – cast; *b* – annealing during 8 hours at 800 °C

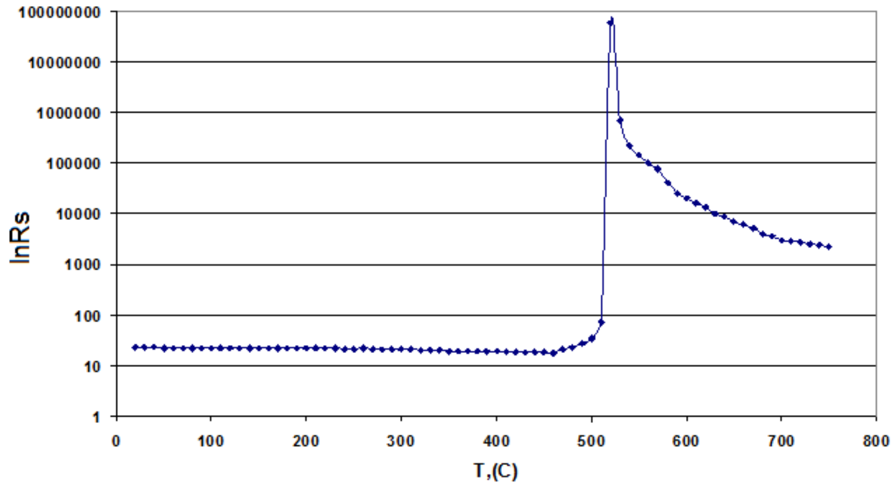
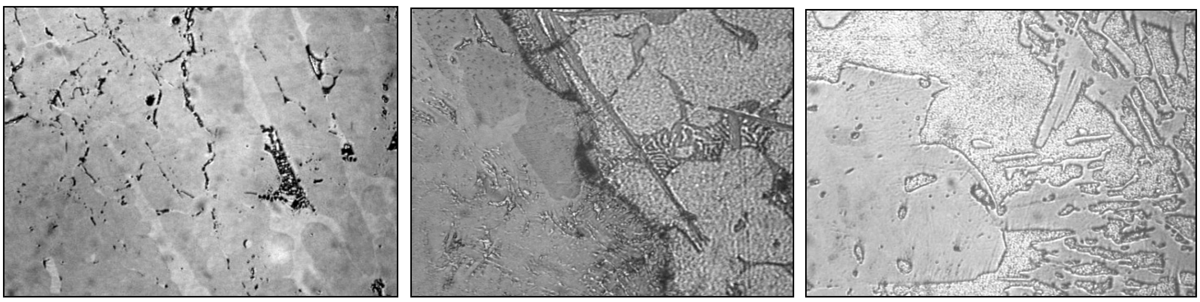


Figure 3. Change in the surface resistivity of films Al-Cu-Fe



a b c

Figure 4. Microstructure of composite materials, obtained by the free impregnation with ligament: *a* – Al-Mg (×800); *b* – Al-Cu (×1000); *c* – Al (×1000)

Composite materials based on the quasicrystal alloy $Al_{65}Cu_{20}Fe_{15}$ are characterized by a uniform distribution of granules along the section of the filler material (**Figure 4**). Filler Al-Cu-Fe in the structure of composite materials is 50-60 vol. %. Samples of composite materials, alloy-impregnated ligament Al-Mg, Al-Si and Al-Cu, are characterized by a porosity of up to 40 vol. %, and the highest value of this characteristic has the sample with a ligament of Al-Si. The content of quasicrystal phase in the structure of the filler after the impregnation of the composite material is practically unchanged.

Impregnation of composite materials at the interface between the filler and the molten ligaments Al-Mg, Al-Si and Al-Cu contacts occurred processes of interaction, leading to the preferential dissolution of the crystal β-phase (**Figure 4a, b**). As a result, micro hardness of the matrix and filler near the interface changes (**Table 1**). These results can be explained by diffusion in the filler component of ligament, namely: magnesium, silicon or cuprum. Despite on the flow of processes of contact interaction, the presence of a sufficiently large number of pores on the interfaces of the investigated composite materials reduces their reliability.

Table 1. Results of the determination of the micro hardness of interfaces in composite materials with quasicrystal filler Al-Cu-Fe (GPa)

Alloy-ligament	Matrix		Filler	
	near interface	away from interface	near interface	away from interface
tech. Al	0,79 ± 0,08	1,17 ± 0,09	6,46 ± 1,02	6,36 ± 0,32
Al–Mg	0,62 ± 0,09	0,38 ± 0,06	4,11± 0,99	5,13 ± 1,08
Al–Cu	1,06 ± 0,13	0,91 ± 0,30	4,11 ± 0,68	3,69 ± 0,59

In the case of the impregnation granules of quasicrystal filler $Al_{65}Cu_{20}Fe_{15}$ by ligament of technical aluminum, number of pores, cracks and other defects of lack of fusion at the interface decrease significantly (**Figure 4b**). Porosity of the material is average 10-12%. At the interface between filler and aluminum matrix observed areas of contact interaction with width 50-100 microns. Their appearance is caused by the dissolution of the crystalline phase β-phase in the molten ligament during impregnation. Structural and phase composition of the filler near the interface with the matrix is almost unchanged. On the part of the matrix appears conglomerate of phases based on aluminum and iron. By diffusion of cuprum and iron from the filler in aluminum ligament its micro hardness near the interface decreases, and micro hardness of filler increases.

Conclusions

Thus, high values of electrical resistance of quasicrystal phase, provide the ability to create a composition of metal and quasicrystalline phases with close to zero value for the thermal coefficient of resistance. The high thermal stability of these compositions show perspective of investigated films of Al-Cu-Fe and Al-Cu-Fe-Sc systems for creating resistant alloys.

Furnace impregnation method, first used for macro heterogeneous composite materials, reinforced with quasicrystal filler allows to provide reliable adhesion of structural components. During impregnation, processes of contact interaction can be controlled thanks to different stability of quasicrystal and crystalline phases of filler considering influence of molten ligament.

References

1. Bashev V.F., Dotshenko F.F., Miroshnichenko I.S. *The Physics of Metals and Metallography*. – 1992. – V. 73. – No. 2. – P. 152-156.
2. Karpets M.V., Milman Yu.V. *Physics and Chemistry of Solid State*. – 2005. – V. 6. – No. 2. – P. 203-206.

Пленочные и композиционные материалы на основе квазикристаллического сплава Al–Cu–Fe

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С помощью металлографического анализа, рентгенофазовых исследований, просвечивающей и растровой электронной микроскопии, дифференциально-термического анализа (ДТА) и методом построения политерм сопротивления изучали структуру и свойства квазикристаллических сплавов систем Al–Fe–Cu и Al–Fe–Cu–Sc. Исследовали сплавы, полученные литьем, при ионно-плазменном напылении и композиционные материалы: литой сплав $Al_{65}Cu_{20}Fe_{15}$ – связки на алюминиевой основе, а именно: технический алюминий, Al–6%Mg, Al–7%Si и Al–5%Cu. Показаны перспективность пленок систем Al–Cu–Fe и Al–Cu–Fe–Sc для создания сплавов сопротивления и возможность получения макрогетерогенных композиционных материалов, упрочненных квазикристаллическим наполнителем, методом печной пропитки, с надежной адгезией структурных составляющих.