DOI 10.15421/331904

STRUCTURE AND CORROSION IN NaCl SOLUTION OF QUASICRYSTALLINE Al–Cu–Fe CAST ALLOYS AND THIN FILMS

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For the first time, quasicrystalline $Al_{60}Cu_{28}Fe_{12}$ films with 260 nm thickness cooled at 10^{12}–10^{14} K/s were produced by the modernized method of three-electrode ion-plasma sputtering. Films were deposited on NaCl substrate. The structure of as-sputtered films was investigated in comparison with that of as-cast specimens by methods of quantitative metallography, X-ray analysis, and scanning electron microscopy. Corrosion behavior in 5% NaCl aqueous solution was studied by potentiodynamic method and model tests. In the structure of the as-cast Al–Cu–Fe alloy, the quasicrystalline icosahedral i-phase was established to co-exist with λ-$Al_{13}Fe_4$, τ-AlCu(Fe), η-AlCu, and θ-Al_2Cu crystalline phases and occupy ~56 % of the alloy volume. The Al–Cu–Fe film contains dispersive quasicrystalline i-phase (~3 nm in size) that is stable up to 723 K. Corrosion of the as-sputtered Al–Cu–Fe film runs at the lower rate as compared with that of the as-cast alloy of the same composition. Model corrosion tests for 1, 2, 3, 4, 8 days with 5% NaCl solution at 293 K indicate that the investigated Al–Cu–Fe film remains virtually untouched by corrosion. No marks of pittings typical for as-cast Al–Cu–Fe alloys are observed on the film surface affected by saline solution.

Keywords: quasicrystalline icosahedral phase, as-cast alloy, thin film, NaCl aqueous solution, corrosion resistance.

Received 04.09.2019; Received in revised form 14.10.2019; Accepted 15.10.2019

1. Introduction

Due to their unique aperiodic long-range atomic order, quasicrystals exhibit a broad variety of physical, chemical, mechanical, and tribological properties that are unusual for metallic systems [1]. Quasicrystal-forming alloys consequently have high potential for applications like low-friction, corrosion- and wear-resistant coatings [2, 3]. The icosahedral quasicrystalline phase forming Al-Cu-Fe alloy has been extensively studied owing to the possibility of making bulk single quasicrystalline alloys. However, their extreme brittleness and complex solidification microstructure make it difficult to utilize this material in the bulk form [4].

The numerous methods of vapor deposition were developed to obtain thin quasicrystalline films on substrate materials [5, 6]. The Al–Cu–Fe films were deposited at various substrate temperatures in either the amorphous or the crystalline state or as a stack of elemental layers. The icosahedral quasicrystalline phase (i-phase) was obtained by subsequent annealing. Thin quasicrystalline Al–Cu–Fe films were also formed directly by such methods as sputtering or evaporation, without need for post-deposition treatments.

In deposition of quasicrystalline coatings, it is essential to monitor the rates of sputtered atoms which have a considerable dispersion not only in magnitude but also in direction. An acceleration of ions impinging on the target and, correspondingly, an increase in their kinetic energy by factors of 5 to 6 can be achieved by using a modernized method of ion-plasma sputtering [7, 8]. This method ensures a more uniform mixing of components upon their deposition on the substrates. The cooling rates for deposited films, estimated theoretically considering the time of atom relaxation, are within the range of 10^{13} to 10^{14} K/s. Thus, the structure of the films is formed in extremely nonequilibrium conditions.

The objective of this study is to obtain a quasicrystalline Al–Cu–Fe thin film using the modernized method of three-electrode ion-plasma sputtering and characterize the effect of rapid quenching on the structure and corrosion properties of as-sputtered coating.

2. Experimental procedure

As-cast alloy with a nominal composition of $Al_{65}Cu_{20}Fe_{15}$ (in atomic percent) cooled at a rate of 5 K/s was prepared by melting a mixture of high purity (99.99 %) Al, Cu, Fe in alumina crucibles [9]. As-sputtered $Al_{60}Cu_{28}Fe_{12}$ film was deposited on NaCl substrate by the modernized method of three-electrode ion-plasma sputtering [7, 8].

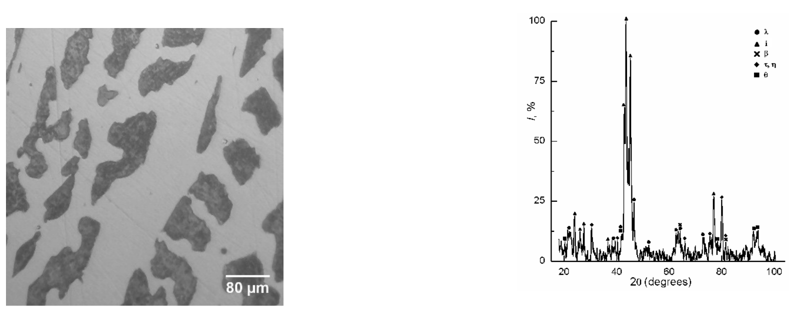
Phase constituents and phase morphology were characterized by light-optical microscopy (OM) using *NEOPHOT-2* device. The X-ray diffraction (XRD) examination of as-cast alloy was performed using *ДРОН-УМ-1* diffractometer with the Cu-K_α radiation to identify the existing phases of the powdered samples. Measurements were taken for a wide range of diffraction angles (2θ) ranging from 20° to 120° with a scanning rate of 5 deg/min. X-ray examinations of the as-sputtered film were conducted using URS-2.0 device with Co-K_α radiation.

Corrosion behavior was investigated in 5% NaCl aqueous solution (pH 6.9–7.0) at the temperature of 293±2 K. The electrochemical experiments were conducted by means of PI–50–1 potentiostat and PR–8 programmer using a three-electrode electrolytic cell. Platinum was selected as a reference electrode, silver chloride – as a working electrode. Model corrosion tests for 1, 2, 3, 4, 8 days in a 5% NaCl solution at 293±2 K were carried out with specimens 3.0×0.5 cm in size. The specimens were fully immersed in the saline solution. Testing under these conditions was assumed to be equivalent to a 5-years application in sea atmosphere.

3. Results and discussion

The examination by light-optical microscope of the as-cast $Al_{63}Cu_{25}Fe_{12}$ alloy cooled at 5 K/s reveals a multiphase structure (Fig. 1a). The primary λ-$Al_{13}Fe_4$ phase in the dendritic shape and small inclusions of β-AlFe(Cu) appear. The λ-phase is surrounded by layers of the quasicrystalline i-Al_6Cu_2Fe phase and subsequently by τ-AlCu(Fe), η-AlCu(Fe), and θ-Al_2Cu phases, which is consistent with the previous reports [9]. During conventional casting, the primary λ-phase is nucleated directly from the melt and grows into the liquid, and the β-phase is formed directly from the liquid or via a peritectic reaction between the primary λ and liquid. Afterwards, another peritectic reaction occurs, where the i-phase is formed. Further cooling to lower temperature encourages τ-, η-, and θ-phases to form in the inter-dendritic region of the i-phase. The θ-phase is the lowest-melting phase among present. Therefore, it is likely to be uniformly distributed throughout the very fine interphase regions.

The phase constitution of the as-cast $Al_{63}Cu_{25}Fe_{12}$ alloy was also confirmed by XRD pattern (Fig. 1b). The diffractogram indicates that the i- and λ-phases are dominant. Furthermore, several weaker reflections of minor phases can be seen in the diffractogram as well. The XRD pattern is not suitable to distinguish the τ- and η-phases in the solidification product, since they have similar CsCl-type cubic structure and lattice parameter.



a b

Fig. 1. As-cast quasicrystalline Al–Cu–Fe alloy: a – microstructure; b – X-ray pattern.

The Al–Cu–Fe film deposited onto the NaCl substrate is found to have nanoquasicrystalline icosahedral structure (Fig. 2a). The size of coherent scattering regions for Al–Cu–Fe film is ~3 nm. The quasicrystalline dispersive state of Al–Cu–Fe film is also deduced from XRD patterns (Fig. 2b). The peaks are close to the angles predicted for the icosahedral quasicrystalline phase. A high dispersion degree of i-phase is verified by a width of diffraction peaks. So, dispersive but not amorphous structure of coating is revealed.

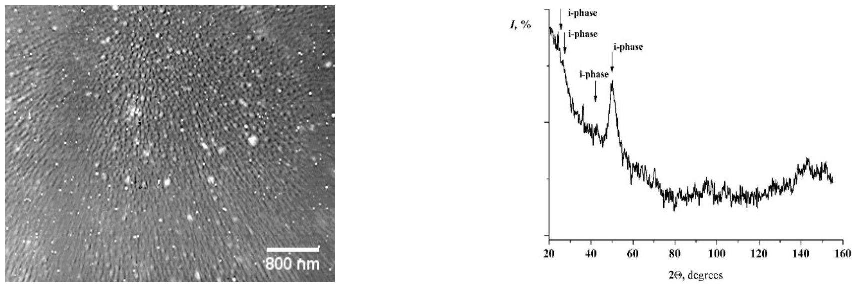


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Fig. 2. As-sputtered Al–Cu–Fe film: a – SEM-image; b – X-ray pattern.

With a change in the quasicrystalline structure of the as-sputtered Al–Cu–Fe film, its corrosion properties in 5% NaCl aqueous solution change as compared with those of the as-cast alloy (Fig. 3).

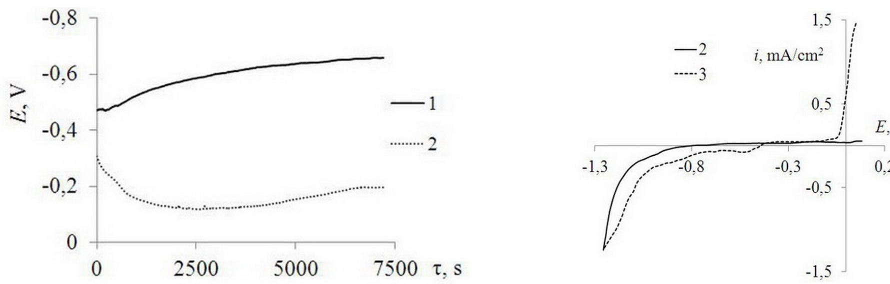

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Fig. 3. Corrosion in 5% NaCl aqueous solution:
a – (E,τ)-dependences obtained for as-cast Al–Cu–Fe alloy (1) and as-sputtered Al–Cu–Fe film (2);
b – polarization curves (1,3 – anode sweep; 2 – cathode sweep) for Al–Cu–Fe film at a rate of 1 mV/s.

For both the as-cast alloy and the as-sputtered film, corrosion potentials E reach permanent negative values in ~7000 s from the starting measurements. For the as-cast alloy the free corrosion potential equals to (–0.66) V, and that for as-sputtered film – (–0.20) V. This proves that an as-sputtered coating has higher resistance to corrosion in saline solution.

Model corrosion tests with 5% NaCl solution conducted at 293 K for 1–8 days show that the surface of the as-sputtered Al–Cu–Fe film remains virtually untouched by corrosion. The observed corrosion behavior of the deposited coating may be explained by the formation of protective oxide layer on the surface of the quasicrystalline icosahedral i-phase. Meanwhile, the as-cast quasicrystalline Al–Cu–Fe alloy as early as in 4 days exhibits severe corrosion with numerous pits appearing on their surface because of Fe and Al dissolution [10]. Thus, the Al–Cu–Fe film produced by sputtering reveals definite evidences for essential improvement in corrosion resistance due to the quasicrystalline nanostructure.

3. Conclusions

The quasicrystalline icosahedral $Al_{60}Cu_{28}Fe_{12}$ film is first deposited by the modernized three-electrode method of ion-plasma sputtering at cooling rates of 10^{12}–10^{14} K/s. Determination of a size of coherent scattering regions indicates that the quasicrystalline phase of the Al–Cu–Fe film is in a nanostructural state.

Raid quenching is shown to improve the corrosion resistance of the as-sputtered Al–Cu–Fe film in 5% NaCl aqueous solution as compared to that of the as-cast quasicrystalline Al–Cu–Fe alloy. The model corrosion test conducted at 293 K for 1 – 8 days indicates that the surface of the film is not susceptible to pitting corrosion.

References

1. **Stadnik, Z.M.** Physical Properties of Quasicrystals / Z.M. Stadnik. – Berlin Heidelberg: Springer-Verlag, 1999. – 438 p.

2. **Rudiger, A.** Corrosion behavior of Al–Cu–Fe quasicrystals / A. Rudiger, U. Koster // Mat. Sci. and Eng.: A. – 2000. – Vol. 294–296. – P. 890 – 893.

3. **Sukhova, O.V**. The influence of Si and B on the structure and corrosion properties of quasicrystal Al–Cu–Fe alloys in saline solutions / O.V. Sukhova, V.A. Polonskyy, K.V. Ustinova // Metallofiz. Noveishie Technol. – 2018. – Vol. 40, No. 11. – P. 1475 – 1487.

4. **Spyrydonova, I.M.** Thin films and composites based on quasicrystal Al–Cu–Fe alloy / I.M. Spyrydonova, O.V. Sukhova, G.V. Zinkovskij // Metall. Min. Ind. – 2012. – Vol. 4, No. 4. – P. 2 – 5.

5. **Shaitura, D.S.** Fabrication of quasicrystalline coatings: a review / D.S. Shaitura, A.A. Enaleeva // Crystallography Reports. – 2007. – Vol. 52, No. 6. – P. 945 – 952.

6. **Rampulla, D.M.** Oxidative and tribological properties of amorphous and quasicrystalline approximant Al–Cu–Fe thin films / D.M. Rampulla, C.M. Mancinelli, I.F. Brunell, A.J. Gellman // Langmuir. – 2005. – No. 6. – P. 4547 – 4553.

7. **Ryabtsev, S.I.** Structure and properties of ion-plasma-deposited films of Fe–(Ag,Bi) alloys / S.I. Ryabtsev // Phys. Met. Metallogr. – 2009. – Vol. 108, No. 3. – P. 226 – 231.

8. **Bashev, V.F.** Features of influence of thermal modes of cooling on processes of nonequilibrium crystallization of materials from the liquid state / V.F. Bashev, S.I. Ryabtsev, S. N. Antropov etc. // J. Physics and Electronics. – 2018. – Vol. 26, No. 2. – P. 45 – 50.

9. **Sukhova, O.V.** The effect of cooling rate on phase composition of quasicrystalline Al–Cu–Fe alloys doped with Si and B / O. V. Sukhova, K. V. Ustinova // Functional Materials. – 2019. – Vol. 26, No. 3. – P. 1 – 12.

10. **Sukhova, O.V.** Corrosion-electrochemical properties of quasicrystalline Al–Cu–Fe–(Si,B) and Al–Ni–Fe alloys in NaCl solution / O.V. Sukhova, V.A. Polonskyy, K.V. Ustinova // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2019. – No. 3. – P. 77 – 83.