

## Structure, Electrical and Corrosion Properties of Quasicrystalline Al–Cu–Fe–Sc Thin Films

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For the first time, quasicrystalline  $Al_{66.5}Cu_{20}Fe_{13}Sc_{0.5}$  films with 200-260 nm thickness cooled at  $10^{12}$ - $10^{14}$  K/s were produced by modernized method of three-electrode ion-plasma sputtering. Films were deposited on NaCl or glass-ceramic substrates. The coatings have been analyzed with X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Electrical resistivity was measured by four-probe method. Corrosion behavior in 3 %, 5 % and 16 % NaCl aqueous solutions was studied by potentiodynamic method and model tests. The deposits have nanoquasicrystalline icosahedral structure. As Sc added, the size of coherent scattering regions is found to decrease from 3 nm to 1.6 nm. Measurements of electrical resistivity during heating show that the investigated Al–Cu–Fe–Sc film is stable up to 623 K. Additions of Sc to Al–Cu–Fe film reduce thermal stability of quasicrystalline phase. The decrease in the quasicrystal-forming ability of the *i*-phase is expressed by the reduced transition temperature that is 100 K lower as Sc is added. Post-annealing treatment for 3 h at 873 K reveals that the resultant microstructural size tends to be coarser, and the coherent scattering regions increase by a factor of two. Additions of Sc to Al–Cu–Fe film made it less susceptible to corrosion in saline solutions. Corrosion of the as-sputtered Al–Cu–Fe–Sc film proceeds at the lowest rate, but after annealing it shows highest corrosion rate. With concentration of sodium chloride in saline solutions increasing from 3 % to 16 %, the values of free corrosion potentials are found to shift to more negative values. Model corrosion tests for 1, 2, 3, 4, 8 days with 5 % NaCl solution indicate that all the investigated films remain virtually untouched by corrosion. No marks of pittings typical for as-cast Al–Cu–Fe alloys are observed on the surface affected by saline solution.

**Keywords:** Ion-plasma sputtering, Quasicrystalline Al–Cu–Fe–Sc films, Electrical resistivity, Corrosion.

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### 1. INTRODUCTION

Unique structure and unusual properties of quasicrystalline alloys make them attractive materials for potential industrial applications. Among them, Al–Cu–Fe alloys have great importance because of their thermal stability, easy availability and the favorable cost of the alloying elements [1]. Besides, these alloys have many attractive properties, such as high hardness, low coefficient of friction, oxidation and corrosion resistance, which have not been observed for crystalline alloys [2]. However, these properties can only be used for technological applications in the form of reinforcement particles in metal matrix composites [3] or coatings [4] to circumvent their extreme brittleness.

The numerous methods of vapor deposition were developed to obtain thin quasicrystalline films on substrate materials [5]. 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 [6]. This method ensures a more uniform mixing of components upon their deposition on the substrates. The cooling rates for deposited films, theoretically estimated 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 extra non-equilibrium conditions.

The objective of this study is to obtain quasicrystalline Al–Cu–Fe–Sc thin films using modernized method of three-electrode ion-plasma sputtering and characterize the effect of adding Sc on the structure, electrical and corrosion properties of as-sputtered coatings.

### 2. EXPERIMENTAL

Quasicrystalline coatings were deposited on NaCl or glass-ceramic substrates by modernized method of three-electrode ion-plasma sputtering [6]. As targets, parallelepipeds were used with a dimension of  $20 \times 20 \times 5$  mm made of pure components (99.99 %) and separated by barrier cells performing like electrostatic lens. The initial nominal compositions of the targets used for sputtering were  $Al_{60}Cu_{28}Fe_{12}$  and  $Al_{66.5}Cu_{20}Fe_{13}Sc_{0.5}$  (at. %). The compositions were chosen considering the compositional range of the quasicrystalline icosahedral phase formation [1] and available data of stabilizing *i*-phase by Sc additions to the Al–Cu–Fe alloys [7]. The deposits were 200 to 260 nm thick.

The sputter-deposited coatings were analyzed with

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optical microscopy (OM, NEOPHOT, Germany), X-ray diffraction (XRD, URS-2.0 with Co-K $\alpha$  radiation, Russia), transmission electron microscopy (TEM, EMMA-2U, Russia), scanning electron microscopy (SEM, JSM-6490LV, Japan), energy dispersive X-ray spectrometer (EDS, INCA Energy 450, Japan).

Electrical resistivity ( $R$ ) of quasicrystalline films deposited on glass-ceramic substrate was determined by a four-probe method at heating rate of 18 K/min in vacuum ( $\sim 1.3$  mPa). Corrosion behavior was investigated in 3 %, 5 %, 16 % NaCl aqueous solutions ( $pH$  6.9-7.0) at the temperature of  $293 \pm 2$  K. The electrochemical experiments were conducted by means of PI-50-1 potentiostat and PR-8 programmer using three-electrode electrolytic cell. Platinum was selected as the reference electrode, silver chloride – as the working electrode. Model corrosion tests for 1, 2, 3, 4, 8 days in a 5 % NaCl solution at  $293 \pm 2$  K were carried out with specimens  $3.0 \times 0.5$  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 Al-Cu-Fe-Sc film deposited onto the NaCl substrate is found to be quasicrystalline. EDS measurements show that within the estimated error of  $\pm 1$  % the results agree with the expected concentration of Cu and Fe as compared with the elemental target composition (Fig. 1, Table 1). A deficiency of Al in the film may relate to selective oxidation of this element. Studies of quasicrystal oxidation have shown that a passivating aluminum oxide layer is formed on the surface by extraction of the Al from the near surface region of the film [8]. EDS measurements show that composition of the film varies only slightly over the rather large sample area.

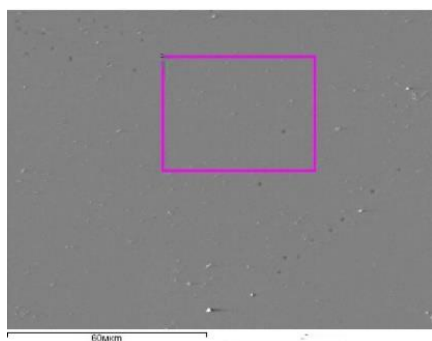
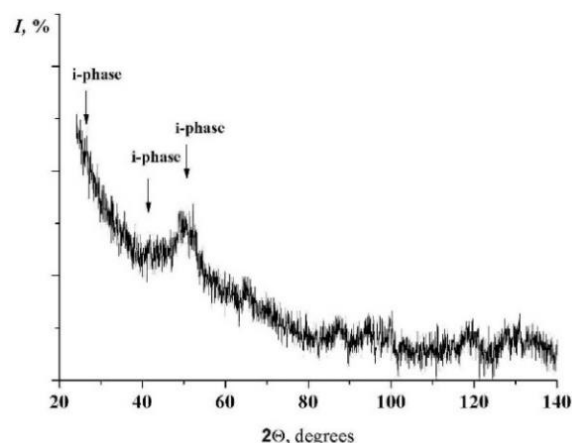


Fig. 1 – SEM of as-sputtered Al-Cu-Fe-Sc film

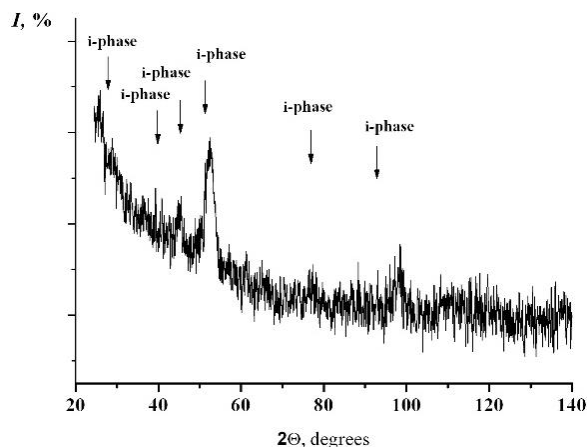
Table 1 – Elemental analysis of Al-Cu-Fe-Sc film

Element	Atomic %
O	16.14
Al	32.73
Sc	0.76
Fe	15.55
Cu	27.76
additions of Si, Ti, Mg	7.06
Total	100

The quasicrystalline dispersive state of Al-Cu-Fe-Sc film is deduced from XRD patterns (Fig. 2a, Table 2). 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. TEM measurements also confirm this state (Fig. 3). The diffraction lines of relatively small width are seen in TEM pattern. So, dispersive but not amorphous structure of material is revealed. Separate reflections are not observed here in microdiffraction mode which indicates ultra-small dimensions of quasicrystals as well. Thus, TEM shows that the film consists of isolated quasicrystalline nanoparticles at the given composition and deposition conditions.



a



b

Fig. 2 – XRD patterns of as-sputtered (a) and post-annealed (b) Al-Cu-Fe-Sc films

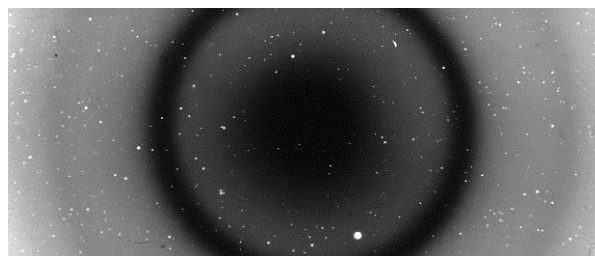


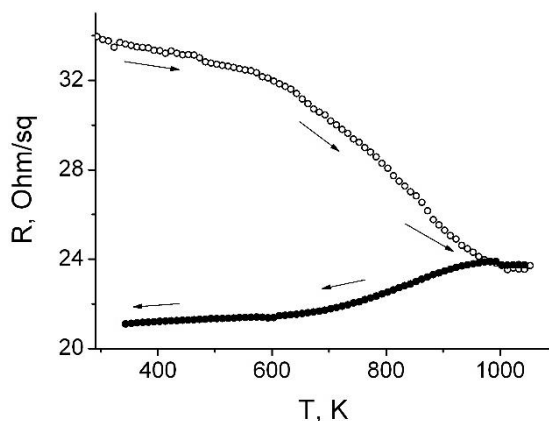
Fig. 3 – TEM of as-sputtered Al-Cu-Fe-Sc film

**Table 2** – XRD analysis of Al–Cu–Fe–Sc film before and after annealing for 3 h at 873 K

as-sputtered film			post-annealed film			ASTM cards
$I, \%$	$\theta, \text{degrees}$	$d_{hkl}, \text{nm}$	$I, \%$	$\theta, \text{degrees}$	$d_{hkl}, \text{nm}$	
25	12.7	0.4071	25	12.2	0.4236	–
10	13.9	0.3726	10	13.8	0.3752	0.3735
50	19.5	0.2682	25	19.6	0.2668	0.2446
–	–	–	50	22.9	0.2300	0.2108
100	25.6	0.2071	100	25.6	0.2071	0.206
10	37.0	0.1487	10	37.98	0.1455	0.1454
			15	46.035	0.12450	0.12430

The size of coherent scattering regions for Al–Cu–Fe–Sc film is  $\sim 1.6$  nm and that for Al–Cu–Fe film is  $\sim 3$  nm. This means that additions of Sc to the Al–Cu–Fe coating favors the increase in a dispersion degree of the quasicrystalline i-phase. Both films have nanoquasicrystalline icosahedral structure.

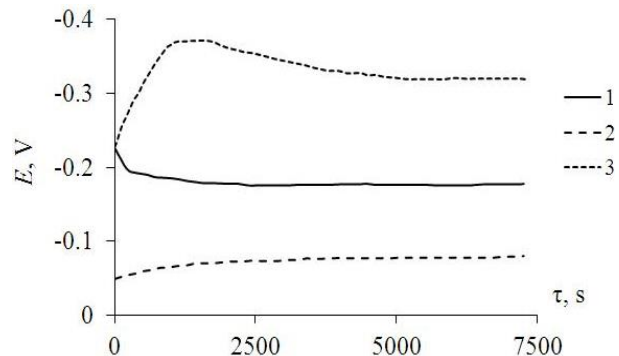
In the heating procedure with a rate of 18 K/min, measurements of electrical resistivity show that the Al–Cu–Fe–Sc film is stable up to 623 K (Fig. 4), whereas the Al–Cu–Fe film is stable up to 723 K. Over a temperature range of 293–623 K, the slight reversible change in a resistivity of the Al–Cu–Fe–Sc film is observed which indicates that no phase transformations take place (Fig. 4). As the temperature is raised from 623 to 673 K, irreversible decrease in electrical resistivity evidences that the structure of the Al–Cu–Fe–Sc film starts to change. Temperature coefficient of resistance is of negative value of  $(-2 \cdot 10^{-4}) \text{ K}^{-1}$  which relates to quasicrystalline structure of the Al–Cu–Fe–Sc film. With following increase in temperature above 673 K, electrical resistivity continues to reduce. On the whole, the resistivity values for the film decrease by a factor of about 1.5 with temperature raising from 293 to 1003 K. It is also worth noting that in our studies additions of Sc do not stabilize i-phase which is contradictory to earlier studies [8]. The starting temperature of the icosahedral phase transformation turns out to be 100 K lower when Sc is added. This effect is most probably due to the increase of the Sc content in the icosahedral phase.

**Fig. 4** – Temperature dependence of electrical resistivity for Al–Cu–Fe–Sc film

The observed changes in electrical resistivity of the deposits during heating are consistent with the change of their nanostructure [9]. After annealing for 3 h at 873 K, the Al–Cu–Fe–Sc film exhibits coarser structure.

Post-annealing treatment reveals that coherent scattering regions of quasicrystalline icosahedral phase become  $\sim 6$  nm in size, so a twofold increase in size is observed as compared to that of as-sputtered film. In X-ray patterns, additional diffraction peaks appear after annealing (Fig. 2b). All the peaks can be identified as icosahedral single phase. Diffraction peaks become narrow, their intensity increases. In addition, most of the peak positions are shifted towards lower angles (Table 2) because of the effect of thermal relaxation and volume diffusion of components in the films.

With the change in quasicrystalline nanostructure not only electrical resistivity but also corrosion properties change. Fig. 5 shows  $(E, \tau)$ -dependences obtained in 5 % NaCl aqueous solution for as-sputtered Al–Cu–Fe and Al–Cu–Fe–Sc films or post-annealed Al–Cu–Fe–Sc film.

**Fig. 5** –  $(E, \tau)$ -dependences obtained in 5 % NaCl aqueous solution for as-sputtered Al–Cu–Fe (1), as-sputtered Al–Cu–Fe–Sc (2) and post-annealed Al–Cu–Fe–Sc (3) films

For as-sputtered films free corrosion potentials reach a permanent negative value in 2400 s from starting measurements but for post-annealed film doped with Sc this value turns out to be achieved for twice longer period. This proves that post-annealed coating has lower resistance to corrosion in saline solutions. The values of free corrosion potential as a measure of the corrosion resistance are summarized in Table 3.

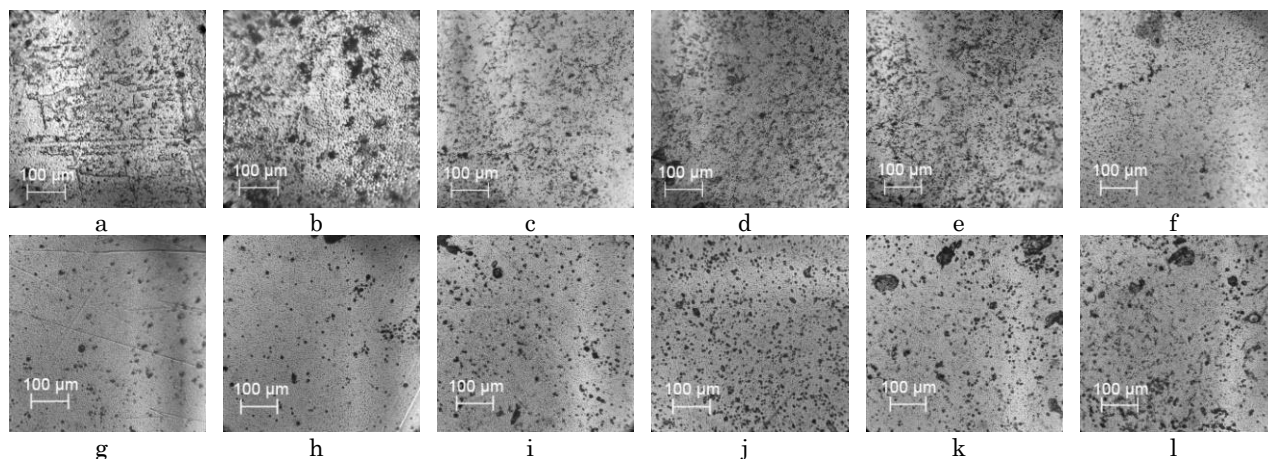
**Table 3** – Free corrosion potentials (in V) of investigated films in aqueous NaCl solutions of different concentrations ( $C_{\text{NaCl}}$ )

Film	$C_{\text{NaCl}}, \%$		
	3 %	5 %	16 %
as-sputtered Al–Cu–Fe	– 0.12	– 0.14	– 0.27
as-sputtered Al–Cu–Fe–Sc	– 0.08	– 0.11	– 0.19
post-annealed Al–Cu–Fe–Sc	– 0.32	– 0.30	– 0.31

The increase in chloride-ion concentration is seen to result in shift of the potentials to more negative values. It is noteworthy that in saline solutions the free corrosion potentials of as-sputtered Al–Cu–Fe–Sc coating are the least negative among the studied films but the potentials for post-annealed Al–Cu–Fe–Sc film are the most negative which is reflected in its lowest corrosion resistance.

Model corrosion tests with 5 % NaCl solution show that the differences in the corrosion of as-sputtered and post-annealed Al–Cu–Fe–Sc films are less pronounced. The microstructure of their surface does not depend on the length of time and remains virtually untouched by

corrosion (Fig. 6). The observed corrosion behavior of the deposited coatings may be explained by the formation of protective oxide layer on the surface of the quasicrystalline icosahedral phase. Meanwhile, as-cast quasicrystalline Al–Cu–Fe alloys as early as in 4 days exhibit severe corrosion with numerous pits appearing on their surface because of Fe and Al dissolution [10]. Thus, Al–Cu–Fe–Sc films produced by sputtering reveal definite evidences for essential improvement in corrosion resistance due to the quasicrystalline nanostructure. The as-sputtered Al–Cu–Fe–Sc film shows the best corrosion performance in saline solutions.



**Fig. 6** – Surface of as-sputtered (a-f) and post-annealed (g-l) Al–Cu–Fe–Sc films before test (a,g) and after holding in 5 % NaCl solution for 1 day (b, h), 2 days (c, i), 3 days (d, j), 4 days (e, k), 8 days (f, l)

#### 4. CONCLUSIONS

The quasicrystalline icosahedral  $\text{Al}_{66.5}\text{Cu}_{20}\text{Fe}_{13}\text{Sc}_{0.5}$  films were first deposited by modernized three-electrode method of ion-plasma sputtering on NaCl or glass-ceramic substrates at cooling rates of  $10^{12}$ – $10^{14}$  K/s. Determination of a size of coherent scattering regions indicated that the quasicrystalline phase of the Al–Cu–Fe–Sc films was in nanostructural state, with size reduction upon Sc addition. The measurements of an electrical resistivity of the depositions showed that the Al–Cu–Fe–Sc film is stable up to the temperature of 623 K which is 100 K lower than that for the Al–Cu–Fe film. This means that additions of Sc decrease the stability of the

i-phase. Post-annealing treatment for 3 h at 873 K revealed a twofold increase of the size of coherent scattering regions of i-phase.

Additions of Sc were shown to improve the corrosion resistance of the as-sputtered Al–Cu–Fe–Sc film in NaCl aqueous solutions as compared to Al–Cu–Fe one. The noblest free corrosion potential was measured for as-sputtered Al–Cu–Fe–Sc film and the most negative for post-annealed Al–Cu–Fe–Sc film. Free corrosion potentials determined in NaCl aqueous solutions of various concentrations were shifted to more noble values with concentration of chloride-ion decrease. Model corrosion test conducted at 293 K for 1–8 days indicated that the surface of the films was not susceptible to corrosion.

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**Структура, електричні та корозійні властивості квазікристалічних тонких плівок Al–Cu–Fe–Sc**

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Квазікристалічні плівки номінального складу  $\text{Al}_{66.5}\text{Cu}_{20}\text{Fe}_{13}\text{Sc}_{0.5}$  товщиною 200-260 нм, охолоджені зі швидкістю  $10^{12}\text{-}10^{14}$  К/с, були вперше отримані модернізованим методом триелектродного іонно-плазмового напилення. Плівки осаджували на підкладки, виготовлені з NaCl або сіталу. Покриття аналізували за допомогою рентгеноструктурного аналізу (РСА), скануючої електронної мікроскопії (СЕМ) та трансмісійної електронної мікроскопії (ТЕМ). Електричний опір вимірювали чотиризондовим методом. Корозійну поведінку в 3 %, 5 % та 16 % водних розчинах NaCl вивчали за допомогою потенціодинамічного методу та модельних випробувань. Осаджені плівки мають наноквазікристалічну ікосаедричну структуру. Після додавання Sc розміри ділянок когерентного розсіювання зменшуються з 3 нм до 1,6 нм. Вимірювання електричного опору під час нагріву вказують на те, що досліджена плівка Al–Cu–Fe–Sc стабільна до температури 623 К. Додавання Sc до плівки Al–Cu–Fe знижує термічну стабільність квазікристалічної фази. Зменшення формуючої здатності квазікристалічної і-фази проявляється в зниженні температури фазового переходу на 100 К у разі додавання Sc. Після відпалу протягом 3 годин за температури 873 К спостерігається укрупнення результуючої структури, при цьому розміри ділянок когерентного розсіювання збільшуються в два рази. Введення Sc до складу плівки Al–Cu–Fe сприяє збільшенню її корозійної тривкості в сольових розчинах. Корозія свіжонапиленої плівки Al–Cu–Fe–Sc відбувається з найменшою швидкістю, однак після відпалу ця плівка кородує з найбільшою швидкістю. Зі збільшенням концентрації натрій хлориду в сольових розчинах з 3 % до 16 %, величини стаціонарних потенціалів корозії зміщуються в бік більш негативних значень. Модельні корозійні випробування протягом 1, 2, 3, 4, 8 дб показують, що всі досліджені плівки практично не кородують у 5 % розчині NaCl. Після перебування в сольовому розчині на поверхні плівок не виявлено слідів пітінгової корозії, характерної для литих сплавів Al–Cu–Fe.

**Ключові слова:** Іонно-плазмове напилення, Квазікристалічні плівки, Електричний опір, Корозія.