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Quasicrystalline Al-Cu-Fe and Al-Cu-Co alloys for corrosion-resistant coatings

The corrosion properties of quasicrystalline $Al_{63}Cu_{25}Fe_{12}$ and $Al_{65}Co_{20}Cu_{15}$ alloys in HCl, H_2SO_4 , HNO_3 , and H_3PO_4 aqueous acidic solutions (pH=1.0) were investigated in this work. In all acidic media, the $Al_{65}Co_{20}Cu_{15}$ alloy forming decagonal quasicrystals showed higher resistance to corrosion than the $Al_{63}Cu_{25}Fe_{12}$ alloy forming icosahedral quasicrystals.

Introduction.

Corrosion resistance is of special importance for many applications [1]. Usually, corrosion depends on the chemical composition and microstructure of the alloys [2]. The discovery of quasicrystals creates new opportunities for the development of corrosion-resistant materials. Quasicrystals define a new class of materials characterized with aperiodic crystallographic order [3]. Due to their special structure, quasicrystals exhibit unique surface properties such as high microhardness, low surface energy, low friction coefficient, excellent oxidation resistance etc. The shortcomings of quasicrystals are related to extreme brittleness in bulk form. However, the combination of excellent physical and mechanical properties makes them potential for surface applications.

Quasicrystalline phases are observed in over a hundred alloy systems. Among such systems are the ternary Al-Cu-Fe and Al-Cu-Co alloys that are known to yield quasicrystalline phases after slow solidification. In the Al-Cu-Fe, an icosahedral phase (ψ -phase) is formed, which is aperiodic in three dimensions [4]. In the Al-Cu-Co, a decagonal phase (D-phase) is revealed, which is aperiodic in two dimensions and periodic along the third dimension [5].

The corrosion resistance of quasicrystalline Al-Cu-Fe alloys in acidic solutions is determined to be good due to the formation of a thin passivation layer on the surface [6,7]. The surface morphology indicates homogeneous dissolution of the alloys followed by redeposition of copper. Selective corrosion of Al and Fe combined with volume diffusion of Cu was also assumed as corrosion mechanism. The studies conducted in sulphuric acidic environments of different concentrations (the pH values of 3 and 5) indicated that the corrosion behavior of the Al-Cu-Fe quasicrystalline alloys was not influenced by the quasicrystallinity but by the composition of phases present in the structure. The phases with high Cu content remained virtually untouched by corrosion, but the phases with low Cu content were susceptible to corrosion due to the more noble electrode potential of Cu as compared with that of Al or Fe [6-9]. Corrosion mainly occurred near the phase boundaries by the galvanic mechanism.

To the authors' knowledge, the influence of acids on corrosion behaviour of the quasicrystalline Al-Cu-Co alloys has not been comprehensively studied in the literature despite their envisaged applications as corrosion-resistant coatings.

The properties of the decagonal quasicrystals exhibit a qualitative difference from those of the icosahedral materials. This implies that the corrosion properties of decagonal and icosahedral quasicrystals may be very different. From the point of view to their application, it is necessary to conduct comparative study on the corrosion behavior of icosahedral and decagonal quasicrystalline phases of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloys in acidic solutions of HCl , H_2SO_4 , HNO_3 , and H_3PO_4 .

Experimental procedure.

The quasicrystalline $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloys were prepared from chemically pure components (99.99 %) by casting in graphite crucibles. The cooling rate of the alloys was 5 °C/s. The average chemical composition of the alloys was examined by atomic absorption spectroscopy method using Sprut CEP-01-M device. The microstructure of the alloys was studied by light-optical microscope Neophot. Quantitative metallography was carried out with structural analyzer Epiquant. X-ray diffraction (XRD) analysis was done to identify the existing phases on an X-ray diffractometer ДРОН-УМ-1 with Cu-K_α source.

Corrosion behaviour was investigated by gravimetric method after holding the analyzed alloys for 1–4 hours in chloric, sulphuric, nitric or orthophosphoric acidic solutions (pH=1.0). Solutions were freshly prepared from distilled water and pure grade chemicals. The corrosion tests were carried out at a temperature of 20 ± 2 °C. The pH value of the corrosion media was measured with ionometer EB-74. After immersion in solutions, the specimens were weighed in a WA-21 analytical balance with errors smaller than 0.1 mg. The corroded surface of the alloys exposed to the acids was examined by scanning electron microscope PEM-106И (SEM).

Results and discussion.

Metallographic and XRD investigations indicate that in the structure of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy primary dendrites of λ -phase ($\text{Al}_{13}\text{Fe}_4$) are formed surrounded by the shells of icosahedral ψ -phase that crystallizes via peritectic reaction $\text{L} + \lambda \rightarrow \psi$ [5]. The relative content of the quasicrystals amounts to ~55 vol. %. Crystalline β -phase ($\text{Al}(\text{Cu}, \text{Fe})$) and θ -phase (Al_2Cu) are located at the boundaries of the ψ -phase.

Three phases are identified in the structure of the $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy [7]. Quasicrystalline decagonal D-phase crystallizes in the form of columnar dendrites via peritectic reaction between the primary $\text{Al}_4(\text{Co}, \text{Cu})_3$ phase and the liquid. The relative amount of the quasicrystals reaches ~65 vol. %. The residual liquid solidifies with forming $\text{Al}_3(\text{Cu}, \text{Co})_2$ phase.

During corrosion tests of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloys in the investigated acidic media, the appearance of the samples changes which is visually revealed as surface darkening or discoloration. This result can be interpreted by the formation, from a strong initial dissolution of the alloys, of corrosion products which block the surface. This layer formation is consistent with the change in color of the samples observed during the immersion. Besides, when subjected to aqueous acidic solutions, gas evolution takes place on the specimens' surface, most intensively in the HCl solution for the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy and in the H_3PO_4 solution for the $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy. Such effect is usually caused by selective dissolution of alloy components since they must have left the alloys as gaseous reaction products.

Gravimetric measurements evidence that the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy corrodes much faster than the $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy in the nitric solution (Table 1). The mass of the

Al₆₃Cu₂₅Fe₁₂ alloy continuously decreases, but that of the Al₆₅Co₂₀Cu₁₅ alloy – increases. At that, for the Al₆₃Cu₂₅Fe₁₂ alloy, the greatest specific mass loss occurs after 1 hour of testing, meanwhile for the Al₆₅Co₂₀Cu₁₅ alloy – after 3 hours.

Table 1.

Specific mass change (in g/sq m) vs. corrosion time for Al₆₃Cu₂₅Fe₁₂ and Al₆₅Co₂₀Cu₁₅ alloys in the aqueous acidic solutions (pH=1.0)

Acid	Alloy	Corrosion time			
		1 hour	2 hours	3 hours	4 hours
HNO ₃	Al ₆₅ Co ₂₀ Cu ₁₅	0.03	0.10	0.33	0.98
	Al ₆₃ Cu ₂₅ Fe ₁₂	0.00	-19.53	-17.16	-28.99
HCl	Al ₆₅ Co ₂₀ Cu ₁₅	0.75	1.31	3.80	4.58
	Al ₆₃ Cu ₂₅ Fe ₁₂	37.62	1.32	-30.69	-24.75
H ₂ SO ₄	Al ₆₅ Co ₂₀ Cu ₁₅	-0.20	-3.02	-5.60	-5.89
	Al ₆₃ Cu ₂₅ Fe ₁₂	-1.11	-7.50	-23.33	-54.72
H ₃ PO ₄	Al ₆₅ Co ₂₀ Cu ₁₅	-0.80	-3.10	-7.53	-8.18
	Al ₆₃ Cu ₂₅ Fe ₁₂	18.89	12.22	3.33	-6.11

In the chloric acidic solution, the mass of the Al₆₃Cu₂₅Fe₁₂ alloy specimens increases during first two hours of testing and then begins decreasing, while the mass of the Al₆₅Co₂₀Cu₁₅ alloy specimens is all the time on the rise (Table 1). In the solution of chloric acid, the mass of the Al₆₃Cu₂₅Fe₁₂ alloy changes most intensively after 1 holding hour and that of the Al₆₅Co₂₀Cu₁₅ alloy – after 2 hours of testing. The described changes of specimens' mass by corrosion may relate to different rate ratios of dissolution and accumulation of corrosion products on the surface.

In the corrosion tests with the sulphuric acidic solution, the attack on both alloys is relatively severe, their mass continuously decreases, whereas the greatest specific mass loss of the Al₆₅Co₂₀Cu₁₅ alloy is less by an order of magnitude than that of the Al₆₃Cu₂₅Fe₁₂ alloy (Table 1). The specific mass change by corrosion of the Al₆₃Cu₂₅Fe₁₂ alloy is biggest after 3 hours of testing, and that of the Al₆₅Co₂₀Cu₁₅ alloy – after 1 hour.

The mass of the Al₆₅Co₂₀Cu₁₅ alloy affected by orthophosphoric acid solution only decreases, while the mass of the Al₆₃Cu₂₅Fe₁₂ alloy increases for 3 hours and then decreases which may relate to dissolution of both corrosion products and alloy components (Table 1). For Al₆₃Cu₂₅Fe₁₂ alloy, the biggest specific gain of mass occurs during first hour of testing, and for Al₆₅Co₂₀Cu₁₅ alloy, the biggest specific loss of mass is observed after two hours of exposure to orthophosphoric acid.

The specific mass change of the Al₆₃Cu₂₅Fe₁₂ alloy after 4-hour staying in the investigated acidic media increases in the following order: H₃PO₄→HNO₃→HCl→H₂SO₄. At that, the Al₆₅Co₂₀Cu₁₅ alloy exhibits the sequence: HNO₃→HCl→H₂SO₄→H₃PO₄. Comparison of the gravimetric results proves that the Al₆₅Co₂₀Cu₁₅ alloy that forms decagonal D-quasicrystals is superior in all the investigated solutions. Cobalt in the composition of the Al₆₅Co₂₀Cu₁₅ alloy clearly

retards the attacks in the acidic environments, but iron in the composition of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy leads to an active accelerated corrosion.

After immersion in the most aggressive solution of the sulphuric acid, on the surface of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy, examined by SEM, the areas of uneven acidic attacks are observed (Fig. 1, a). The crystalline λ -phase is stronger attacked, this is due to a susceptibility of the phases enriched by iron to corrosion. So, the iron is weak component in the corrosion of the alloy in sulphuric acid. In contract, the iron-poorer ψ -phase is less attacked than the λ -phase. Besides, corrosion is located along the ψ - λ and ψ - (β,θ) phase boundaries where more defects may form.

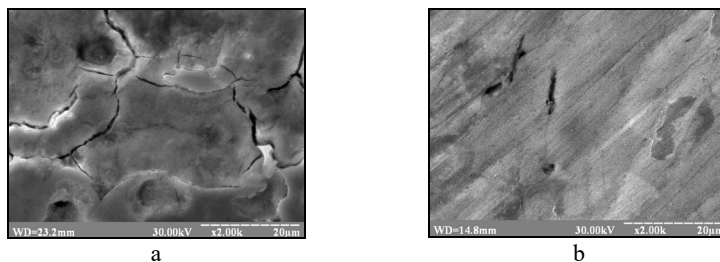


Fig. 1. SEM-images of the studied alloys after 4 holding hours in sulphuric acidic solution: a – $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy; b – $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy

On the surface of the $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy, the areas of strong acidic corrosion are not revealed after staying for 4 hours in the sulphuric acidic solution (Fig. 1, b). The alloy quite homogeneously dissolves where quasicrystalline D-phase and crystalline $\text{Al}_4(\text{Co,Cu})_3$ phase are located. Meanwhile, crystalline $\text{Al}_3(\text{Cu,Co})_2$ phase dissolves at a noticeably higher rate. This phase has the lowest cobalt content and, also, may be more defective because it crystallizes last from the residual liquid. Hence, cobalt promotes the resistance to corrosion of the phase constituents of the $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy under conditions where the passive oxide layer, formed on the surface in the sulphuric acidic solution, may be destroyed locally or uniformly.

Thus, scanning electron microscopy confirms that the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy shows indications of more active enhanced attack of sulphuric acidic solution, compared to the $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy. The attacks by the acid are suppressed by Co present in the alloy composition. Such attacks occur only locally, resulting in a lower mass loss and so lower corrosion rate. Hence, cobalt is favorable for the corrosion resistance of the alloys in the investigated acidic environments.

Conclusions.

Corrosion tests of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy, forming quasicrystalline icosahedral phase, show that after first holding hour in the nitric and sulphuric acidic solutions the mass of specimens does not noticeably change, but in the chloric and orthophosphoric acidic solutions the mass increases due to accumulation of corrosion products on the surface. After 4 hours of testing the mass of the alloy specimens changes most intensively in the H_2SO_4 solution and least intensively in the H_3PO_4 solution. The alloy surface exposed to acidic attacks dissolves nonhomogeneously. In the structure, iron-rich λ -phase and phase boundaries are preferentially attacked.

The $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy, in which quasicrystalline decagonal phase is formed, is less corroded in all the investigated acidic solutions, compared to the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy. The specimens' mass gradually increases in the solutions of chloric and nitric acids, especially in the HCl solution. After staying in the solutions of sulphuric and orthophosphoric acids, the specimens' mass, on the contrary, decreases, in the H_3PO_4 solution to a greater extent. The alloy surface exposed to acids rather homogeneously dissolves except for areas where boundaries of crystalline $\text{Al}_3(\text{Cu},\text{Co})_2$ phase are located which corrode at a higher rate. Compared to $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy, corrosion propagation of $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy is more uniform.

The studies on the behavior of the investigated alloys in the acidic media (pH=1.0) reveal the most severe corrosion of iron-rich phases in the structure of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy or cobalt-poor phases in the structure of the $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy. Therefore, the decagonal quasicrystalline phase of the $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy which contains cobalt exhibits enhanced corrosion resistance compared to the icosahedral quasicrystalline phase of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy which contains iron. The $\text{Al}_{65}\text{Co}_{20}\text{Cu}_{15}$ alloy may be used as coatings for effectively improving corrosion resistance since this alloy behaves relatively inert in the acids compared to the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy.

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