Influence of Gd, Dy and Fe doping on electrochemical properties of Al$_{87}$Y$_{5}$Ni$_{8}$ amorphous metallic alloy

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Abstract: Corrosive properties of some Al-based amorphous metallic alloys (AMA) and the relationship between the AMA composition and nature of protective layers on the surface of alloys were studied. The complex of physico-chemical methods, namely the potentiometry, voltammetry, electrochemical impedance spectroscopy and electronic microscopy, has been used. It was shown that the influence of Dy doping on the same characteristics of alloys is opposite to that of Gd. It increases corrosion resistance of Dy-containing alloys in comparison to the reference Al$_{87}$Y$_{5}$Ni$_{8}$ alloy. Partial substitution of 4 at. % Ni by Fe causes further increase of corrosion resistance of Al$_{87}$Gd$_{5}$Ni$_{4}$Fe$_{4}$.

1. Introduction

Amorphous metallic alloys (AMA) of Al–Y–Ni-system are used in the precious electrotechnical devices due to their specific physico-chemical distinctions, which are caused by the inhomogeneity of chemical and phase composition, and also of possibility of interaction between components,. The AMAs of such type, doped by Y or the elements of lanthanum group, exhibits the magnetic and semiconductive properties. The doping elements, namely both rare-earth and transition metals, increase the mechanical stability of AMA, exactly their surface protection layers essentially. The mechanism of atomic ordering in the multicomponent AMA is connected with the change in its electronic structure [1, 2]. It is known that 4-f state is the most energetically favorable for the lanthanides regarding proximity of 4-f i 5-d states. Therefore in all cases, except for Gd, the 5-d' electron rises on the 4-f sublevel. Such electronic structure leads to their reactivity close to 3-d-metals. Lanthanides (especially Gd) are able to reacts with different metals, including Al, what leads for the formation of intermetallides under the certain conditions [3]. Rare-earth and transition metals doped AMA lightly oxidizes in the weak acid media with formation of protection oxides layers. Therefore the higher corrosion resistance of Al-based AMA with additives of rare-earth metals can be foreseen in advance, but high reactivity of Gd can be stipulated the partial dissolution of alloy [4]. Therefore the aim of this work is to study corrosive properties of some Al-based amorphous metallic alloys and a relationship between the AMA composition and nature of protective layers on the surface of alloys.

2. Experimental details and principles

The Al-Y-Ni amorphous ribbons of 30 μm thickness were produced by melt spinning with the following compositions: Al$_{87}$Y$_{5}$Ni$_{8}$, Al$_{87}$Y$_{5}$Gd$_{5}$Ni$_{4}$, Al$_{87}$Y$_{5}$Dy$_{5}$Ni$_{4}$, Al$_{87}$Gd$_{5}$Ni$_{4}$, Al$_{87}$Dy$_{5}$Ni$_{4}$, Al$_{87}$Gd$_{5}$Ni$_{4}$Fe$_{4}$ and Al$_{87}$Y$_{5}$Gd$_{5}$Ni$_{4}$Fe$_{4}$. The ribbons were produced in the Kurdyumov Institute of Metal Physics of the National Academy of Sciences of Ukraine (Kyiv).

The oxide films were formed on AMA surface during polarization of electrodes in 0.1 M NaCl aqueous solution. The process of the formation of passive layers was performed in Pyrex® (Radiometer No.1734) glass cell. The experiments were carried out in 0.1 M NaCl aqueous solution at room temperature with platinum as a counter electrode and SCE as a reference electrode. The exposed geometric surface area of working electrode was 1 cm$^2$. Steady-state polarization measurements as well as EIS experiments were conducted using Autolab®/PGSTAT20 with Frequency Response Analyser (FRA) and Differential Electrometer Amplifier (Eco Chemie B.V. the Netherlands),
combined with one of the software packages and controlled by IBM compatible PC. Micrographs of the surface were obtained with scanning electron microscope REMMA-102 using various magnifications.

3. Results and discussion

The investigation of AMA corrosion properties was carried out by the voltammetry method in the potential interval ±50 mV (figure 1) from the stable value of open circuit potential (φ) (figure 2) without failure of the structure of Stern’s double electric layer (figure 3).

Figure 1. Stern voltammetric curves of the Al-based AMA in 0.1 M NaCl aqueous solution: 1-\(\text{Al}_{87}Y_3\text{Ni}_{16}\), 2-\(\text{Al}_{87}\text{Gd}_5\text{Ni}_{18}\), 3-\(\text{Al}_{87}\text{Dy}_5\text{Ni}_{18}\), 4 \(\text{Al}_{87}\text{Y}_4\text{Dy}_1\text{Ni}_{20}\), 5-\(\text{Al}_{87}\text{Y}_4\text{Gd}_1\text{Ni}_{18}\)

Figure 2. Potentiometric curves of the Al-based AMA in 0.1 M NaCl aqueous solution: 1-\(\text{Al}_{87}Y_3\text{Ni}_{16}\), 2-\(\text{Al}_{87}\text{Gd}_5\text{Ni}_{18}\), 3-\(\text{Al}_{87}\text{Dy}_5\text{Ni}_{18}\), 4-\(\text{Al}_{87}\text{Y}_4\text{Dy}_1\text{Ni}_{20}\), 5-\(\text{Al}_{87}\text{Y}_4\text{Gd}_1\text{Ni}_{18}\), 6-\(\text{Al}_{87}\text{Y}_4\text{Gd}_1\text{Ni}_{18}\text{Fe}_4\)

Figure 3. The decrease of electric potential in the DEL (accordingly to Stern)
Partial and total substitution of Y by Gd decreases corrosion potential ($E_{\text{corr.}}$) and increases of corrosion current ($j_{\text{corr.}}$), polarization resistance ($R_p$) (see table). The influence of Dy doping on the same characteristics of alloys is opposite to that of Gd. It increases corrosion resistance of Dy-containing alloys in comparison to the reference alloy Al$_{87}$Y$_5$Ni$_8$. Partial substitution of 4 at. % Ni by Fe causes further increase of corrosion resistance of Al$_{87}$Gd$_5$Ni$_8$Fe$_4$ (see table). This effect is suppressed by partial substitution of Gd by Y in Al$_{87}$Y$_5$Gd$_5$Ni$_8$Fe$_4$. The corrosion resistance depends on layer thickness and especially on its sealing, therefore good the quality control of both parameters has maximum significance [5].

Table. Corrosion characteristics of the Al-based AMA in 0.1 M NaCl aqueous solution

| AMA          | $E_{\text{corr.}}, \text{V}$ | $j_{\text{corr.}}, \text{A}\cdot\text{cm}^{-2}$ | $R_p, \text{\Omega}$ |
|--------------|-------------------------------|-----------------------------------------------|---------------------|
| Al$_{87}$Y$_5$Ni$_8$ | -0.502                        | 5.79·10$^{-7}$                               | 1.81·10$^2$         |
| Al$_{87}$Y$_5$Gd$_5$Ni$_8$ | -0.612                        | 1.34·10$^{-7}$                               | 2.10·10$^2$         |
| Al$_{87}$Y$_5$Dy$_5$Ni$_8$ | -0.259                        | 1.16·10$^{-9}$                               | 1.55·10$^3$         |
| Al$_{87}$Gd$_5$Ni$_8$ | -0.481                        | 3.40·10$^{-8}$                               | 6.47·10$^3$         |
| Al$_{87}$Dy$_5$Ni$_8$ | -0.433                        | 1.94·10$^{-9}$                               | 7.74·10$^4$         |
| Al$_{87}$Gd$_5$Ni$_8$Fe$_4$ | -0.472                        | 5.39·10$^{-10}$                              | 1.26·10$^4$         |
| Al$_{87}$Y$_5$Gd$_5$Ni$_8$Fe$_4$ | -0.643                        | 1.35·10$^{-5}$                               | 4.53·10$^3$         |

The processes of electrochemical behaviour and of AMA have been studied by the cyclic voltammetry method in a 0.1 M NaCl aqueous solution during electrode polarization (figure 4).
The results of electrochemical studies, namely the forms of voltammetric curves (figure 4 b), indicated that the most stable to the electrode polarization is the partial Gd–Dy-doped (to 1%) Al–Y–Ni AMA-systems. AMAs doped by 4% of iron were the most sensitive for the polarization influence. The values of the currents of oxidation and reduction of Al$_{87}$Gd$_5$Ni$_4$Fe$_4$ and Al$_{87}$Y$_4$Gd$_1$Ni$_4$Fe$_4$ AMA-electrodes approach $10^{-3}$ mA·cm$^{-2}$ (figure 4 c). However, one can see from the voltammograms on the Fig. 4, the increase of the number of electrodes polarization cycles leads to the decrease of the values of oxidation current. The reason for such effect is the formation of stable oxides of metals, exactly aluminum (because its concentration on the surface is the largest) forms on the AMA surface (figure 5). The basic oxides of lanthanides Ме$_2$О$_3$ are characterized by high enthalpy of formation ($\Delta G^\circ$~1600 kJ·mol$^{-1}$). Therefore the formation of passivation oxide layers and the rate of their formation can be explained by the ionization energy $E_{\text{ion}}$ for Me$^0$→Me$^+$ transition, which is equal 5.986 eV, 7.635, 6.217, 6.12 and 6.82 eV for Al$^0$→Al$^+$, Ni$^0$→Ni$^+$, Y$^0$→Y$^+$, Gd$^0$→Gd$^+$ and Dy$^0$→Dy$^+$ transitions respectively. The decrease of ionic radius in the Y–Gd–Dy sequence leads to the compaction of amorphous surface layers (figure 5).

Figure 5. Micrographs of the AMA surface after polarization of samples in the 0.1 M NaCl aqueous solution: Al$_{87}$Y$_5$Ni$_8$ (a), Al$_{87}$Y$_4$Gd$_1$Ni$_8$ (b), Al$_{87}$Y$_4$Gd$_1$Ni$_4$Fe$_4$ (c) and Al$_{87}$Gd$_5$Ni$_4$Fe$_4$ (d)

Passivation ability of oxide layers on the AMA-electrodes was studied by electrochemical impedance spectroscopy method in a 0.1 M NaCl aqueous solution. The impedance model for the formation of oxide (AMA) | 0.1 M NaCl (aq.) and AMA | 0.1 M NaCl (aq.) phase boundary was chosen. The Bode curves (impedance and phase angle) (figure 6) indicate that the lowest resistance is typical for the Al$_{87}$Y$_5$Ni$_8$ AMA. This effect can be explained by the big radius of Y$^{3+}$ ion, which is equal to 0.097 nm and is the largest in comparison to all the radiuses of both atoms and other ions in the AMA composition. The porous oxide films with thickness <100 nm, where the ionization of metals proceeds, are formed on the three-component alloys surface | 0.1 M NaCl aqueous solution boundary.
It was confirmed by the EIS method that \((\text{Al}_{87}\text{Y}_{5}\text{Ni}_{8}) | 0.1 \text{ M NaCl (aq.)} \) boundary can be described by the simplest electric scheme (figure 7 a). The charge transfer resistance increases due to the substitution of Y on Gd or Dy from 2.9 to 7.3 \(\text{kOhm} \cdot \text{cm}^{-2}\).

**Figure 6.** Bode plots of \(\text{Al}_{87}\text{Y}_{3}\text{Ni}_{8} \) (1), \(\text{Al}_{87}\text{Dy}_{5}\text{Ni}_{8} \) (2), \(\text{Al}_{87}\text{Y}_{4}\text{Dy}_{1}\text{Ni}_{8} \) (3) amorphous alloy in the 0.1 M NaCl aqueous solution

**Figure 7.** Equivalent circuit for plots in Figure 6: circuit a – curves 1, 2; circuit b – curves 3

The corrosion resistance properties of surface layers upgrade with the decrease of atomic radius of rare-earth metal. Moreover, the double-stage process of charge transfer on the oxide (AMA) | 0.1 M NaCl aqueous solution / boundary (figure 6, curve 3) indicates that the oxide layer, which forms in the presence of the ions of two different rare-earth metals, generates a diffusion barrier, that isolates the AMA surface. As a result, the electric scheme of this boundary can be described by Warburg element (figure 7 b).

**Conclusion**

The Dy-doped AMA has the highest corrosion resistance. Simultaneous doping by two metals, namely by the Y and Gd, Y and Dy, Ni and Fe leads to the improvement of the protective properties of AMA surface layers. The mixed oxides of Al and doping elements take part in the formation of the protective surface layers. It was confirmed by the EIS method that mixed oxides of Al, Ni, Dy or Gd forms the dense surface layers, where the reversible diffusion of the electrolyte ions takes place, and limits the contact of the aggressive ions of the electrolyte with metallic AMA surface. The studied AMAs were disposed in the following order according to the increase of their corrosion resistance: \(\text{Al}_{87}\text{Y}_{4}\text{Dy}_{1}\text{Ni}_{8} > \text{Al}_{87}\text{Dy}_{5}\text{Ni}_{8} > \text{Al}_{87}\text{Gd}_{5}\text{Ni}_{8} > \text{Al}_{87}\text{Gd}_{1}\text{Ni}_{8} > \text{Al}_{87}\text{Y}_{4}\text{Gd}_{1}\text{Ni}_{8} > \text{Al}_{87}\text{Y}_{5}\text{Ni}_{8} > \text{Al}_{87}\text{Y}_{4}\text{Gd}_{1}\text{Ni}_{4}\text{Fe}_{4}\)

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