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NEW SUBSTANCES, MATERIALS, AND COATINGS

Elemental and Phase Composition, Morphology, and Chemical Features of the Surface of Al–Ni Alloys in Contact with Liquid Ga–In Eutectic

A. B. Arbuzov[a], **V. A. Drozdov**[a, b*], **N. N. Leont'eva**[a], **A. V. Shilova**[a], **T. V. Kireeva**[a], **M. V. Trenikhin**[a], **and A. V. Lavrenov**[a]

[a] *Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences, Omsk, 644040 Russia*

[b] *Omsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Omsk, 644024 Russia*

**e-mail: drozdov@ihcp.ru*

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Abstract—A set of aluminum–nickel alloys has been studied. The elemental composition of the samples has been determined by atomic emission and atomic absorption spectrometry. X-ray diffraction analysis has revealed that the alloying of the metals leads to the formation of Al_3Ni and Al_3Ni_2 intermetallic compounds, while a portion of Al remains in a metallic phase. The local chemical composition and surface morphology of the original alloys and the alloys activated with the liquid Ga–In eutectic have been studied by scanning electron microscopy and X-ray microanalysis. It has been shown that the original alloys are characterized by a pronounced morphological heterogeneity of interfacial regions in the near-surface layers. It has been found that the studied Al–Ni alloys are activated by the liquid Ga–In eutectic; however, one of the alloy components—the Al_3Ni intermetallic compound—does not undergo significant morphological and chemical changes in contact with the liquid eutectic.

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INTRODUCTION

The coming into contact of metallic Al with liquid Ga–In eutectic leads to effective destruction of the near-surface oxide layers and the penetration of the eutectic components into the bulk of the metal; these processes bring aluminum into a highly reactive state with respect to proton-donor and organochlorine molecules. In the scientific literature, this state of aluminum is referred to as "activated aluminum" [1, 2]. It has been previously found that activated aluminum can be used in catalysis for in situ synthesis of catalyst systems composed of activated metallic Al and organochlorine compounds [3]. In addition, the used approach makes it possible to activate other aluminum-containing alloys, in particular, Al–Cu [4, 5].

It is known [6, 7] that the addition of nickel compounds to aluminum chloride complexes contributes to the formation of propylene and butene dimers. However, detailed studies of the physicochemical state of Al–Ni systems, particularly the stages of their coming into contact with the activating liquid Ga–In eutectic, have not been conducted. The functional catalytic properties of these materials have hardly been studied at all.

The aim of this study was a detailed examination of the elemental and phase composition and morphological and chemical characteristics of the surface of Al–Ni alloys in contact with the liquid Ga–In eutectic.

EXPERIMENTAL

The alloys were prepared from nickel and aluminum in which the content of the basic substance was no less than 99.99 wt %. The alloying was conducted as follows. Aluminum was placed in a graphite crucible and heated in an induction furnace to a temperature of 1200°C. After that, nickel was added to the melt. The molten mass was poured into a chill mold or a steel mold and then air cooled.

The liquid Ga–In eutectic (containing 76 wt % Ga) with $T_{melt} = 16°C$ was used as an activator of the Al–Ni alloys.

The dissolution of the Al–Ni alloys for elemental analysis was conducted as follows. A weighed portion of the alloy sample of up to 0.5 g was placed in a 250-mL beaker; a mixture of acids (20 mL of HCl (1 : 1) and 20 mL of HNO_3 (1 : 1)) was added under heating. The resulting solution was transferred into a 50-mL measuring flask, and the volume of the solution was adjusted to the mark with bidistilled water. The Ni and

Table 1. Elemental and phase composition of the studied Al–Ni alloys

No.	Phase composition and relative fraction of identified phases	Element content, wt %	
		Ni	Al
1	Al	–	No less than 99.99
2	Al Al_3Ni (22.0 wt %)	6.9 ± 0.2	92.2 ± 0.6
3	Al Al_3Ni (78.5 wt %) Al_3Ni_2 (3.6 wt %)	32.8 ± 0.7	69.2 ± 1.1
4	Al Al_3Ni (75.8 wt %) Al_3Ni_2 (1.5 wt %)	34.6 ± 1.5	65.2 ± 1.2
5	Ni	No less than 99.99	–

Al contents were determined by atomic absorption spectrometry (AAS) on a Shimadzu AA-6300 instrument and by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an Agilent Varian 710-ES instrument.

The phase composition of the Al–Ni alloys was identified by X-ray diffraction (XRD) analysis. The studies were conducted on a Bruker D8 Advance powder X-ray diffractometer. Recording was conducted in monochromatic CuK_α radiation ($\lambda = 0.15418$ nm) in the following modes: scanning pitch, 0.05°; signal acquisition time, 10 s/point; and filament voltage and current, 40 kV and 40 mA, respectively. The recorded XRD patterns were interpreted using the ICDD PDF-2 powder diffraction database. The relative fraction of the identified phases was determined from experimental diffraction patterns by the Rietveld method.

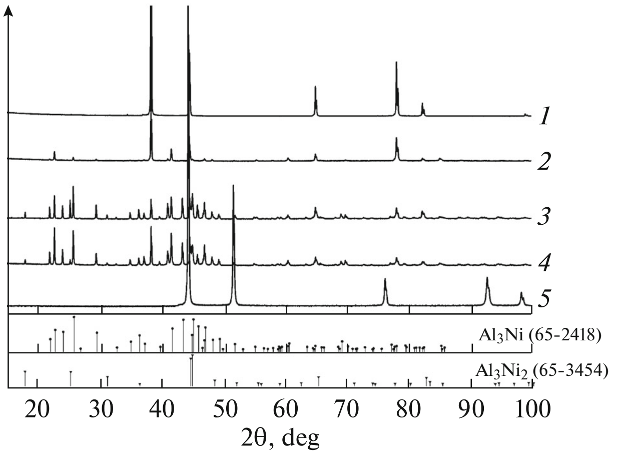

Fig. 1. XRD patterns of the studied aluminum–nickel alloys: (*1*) 99.99 wt % Al, (*2*) 6.9 wt % Ni, (*3*) 32.8 wt % Ni, (*4*) 34.6 wt % Ni, and (*5*) 99.99 wt % Ni.

The surface morphology and local elemental composition of the Al–Ni samples were studied by scanning electron microscopy (SEM) and X-ray microanalysis (energy dispersive X-ray spectroscopy (EDS)) on a JEOL JSM-6610LV electron microscope equipped with an Oxford Instruments INCAx-act attachment. The samples used in the study had the shape of plates with dimensions of 14 × 14 mm. The sample thickness was 2 mm. The resulting samples were polished with an abrasive material (SiC) with a particle size of up to 1 μm. After that, the samples were subjected to SEM and EDS studies.

The interaction of the liquid Ga–In eutectic with the resulting Al–Ni alloys was studied directly in the chamber of the JSM-6610LV electron microscope at room temperature for 3 h. A eutectic droplet with a weight of ~1 g was placed on the central portion of the surface of the test alloy plate. To provide a more effective wetting of the Al–Ni alloy surface, it was subjected to the mechanical action of a metal needle (scratching).

Elemental chemical analysis was conducted radially extending from the interface between the Ga–In eutectic droplet and the Al–Ni alloy across the alloy surface at 400-μm intervals. For the samples containing regions of different morphologies, each of the regions was separately analyzed by EDS.

RESULTS AND DISCUSSION

Table 1 summarizes the data on the elemental content of Al and Ni and the relative fraction of the identified phases of the original Al–Ni alloys.

Figure 1 shows the diffraction patterns of the studied Al–Ni alloys. It is evident that, in the alloy with a low nickel content, the main phase is metallic aluminum. With an increase in the nickel concentration to 32–35 wt %, the Al_3Ni intermetallic compound becomes the main phase in these alloys.

Table 2. X-ray microanalysis data (EDS) for the studied Al–Ni alloys

No.	Alloy		Element content, wt %		Al/Ni atomic ratio
			Ni	Al	
1	Ni		100.0	–	–
2	6.9 wt %	A*	9.4	90.6	9.6
		B**	6.6	93.4	14.2
3	32.8 wt %	A	43.7	56.3	2.8
		B	1.1	98.9	190.9
		C***	58.7	41.3	1.5
4	34.6 wt %	A	43.4	56.6	2.8
		B	2.9	97.1	72.8

* Region A: well-crystallized particles.
** Region B: dark portion.
*** Region C: slightly rounded particles that appear brighter in contrast.

Study of the Surface Morphology and Chemical Composition of the Original Al–Ni Alloys

The electron microscopic (EM) images of the resulting Al–Ni alloys show regions that differ in contrast ratio (Figs. 2a–2c). This finding suggests that the surface structure of the prepared aluminum–nickel alloys is heterogeneous. Thus, for Al–Ni alloys with a low nickel content (6.9 wt %), regions comprising particles with a size of no more than 3 μm are observed (Fig. 2, region A). Al–Ni alloy samples with a higher Ni content (32–35 wt %) are characterized by significant morphological heterogeneity of the surface (Figs. 2b, 2c). The EM images show well-crystallized particles (region A) located against the background of a dark portion (region B) and, in some cases, slightly rounded particles that appear brighter in contrast (region C).

The results of X-ray microanalysis of the alloy surface in regions A, B, and C are shown in Table 2. It is evident that the chemical composition of the Al–Ni alloy containing 6.9 wt % Ni almost completely corresponds to the volume content measured by AAS and ICP-AES (Tables 1, 2). Note that the local chemical composition of the surface of regions A showed a high Ni content (Table 2). Comparison of the SEM and EDS data with the XRD analysis data suggests that the particles of the Al_3Ni intermetallic compound are distributed in the near-surface layers of the metallic aluminum.

An increase in the Ni content leads to a significant increase in the chemical heterogeneity of the studied Al–Ni alloys. Thus, for the alloys containing 32.8 and 34.6 wt % Ni (Table 2), the near-surface layers are mostly enriched in Ni. For these regions, the Al/Ni atomic ratio is ~2.8, which is substantially close to the value of the stoichiometric Al_3Ni intermetallic compound. For the Al–Ni alloy containing 32.8 wt % Ni, other regions were found (Fig. 2b, regions C); according to local microanalysis (Table 2), in these regions, the Al/Ni atomic ratio is ~1.5, which corresponds to the value of the stoichiometric Al_3Ni_2 intermetallic compound. In the same samples (Table 2, nos. 3–4, regions B), regions with a lower Ni content—about 1–3 wt %—were observed (Figs. 2b, 2c). Taking into account the XRD data, it can be assumed that, in these samples, regions B correspond to the metallic Al phase.

Thus, according to SEM and EDS, the heterogeneity of the surface of the studied Al–Ni alloys is mostly attributed to the presence of the Al_3Ni intermetallic compound particles distributed in the near-surface layers of metallic Al.

Study of the Morphological and Chemical Features of the Surface of Al–Ni Alloys in Contact with the Liquid Ga–In Eutectic

After a 60-min contact of the liquid Ga–In eutectic with the aluminum–nickel alloy containing 6.9 wt % Ni, a front of propagation of the eutectic components was observed on the surface of the test alloy (Fig. 3a). The linear size of this front was 1.36 mm. After a 100-min contact of the studied alloys, the size of the front of propagation of the eutectic components was as large as 2.94 mm from the Ga–In eutectic droplet (Fig. 3b). According to the results, it was found that the rate of propagation of the liquid Ga–In eutectic components over the surface of the Al–Ni alloy containing 6.9 wt % Ni is 0.04 mm/min. Figure 3c shows the distribution of the Ga–In eutectic components from the droplet–alloy interface to the edge of the Al–Ni alloy. It is evident that the concentration of the liquid Ga–In eutectic components linearly decreases from the contact zone to the edge of the Al–Ni alloy; that is, the Ga/In ratio significantly deviates from the eutectic proportion. Note that the propagation of the front of the eutectic components was accompanied by the forma-

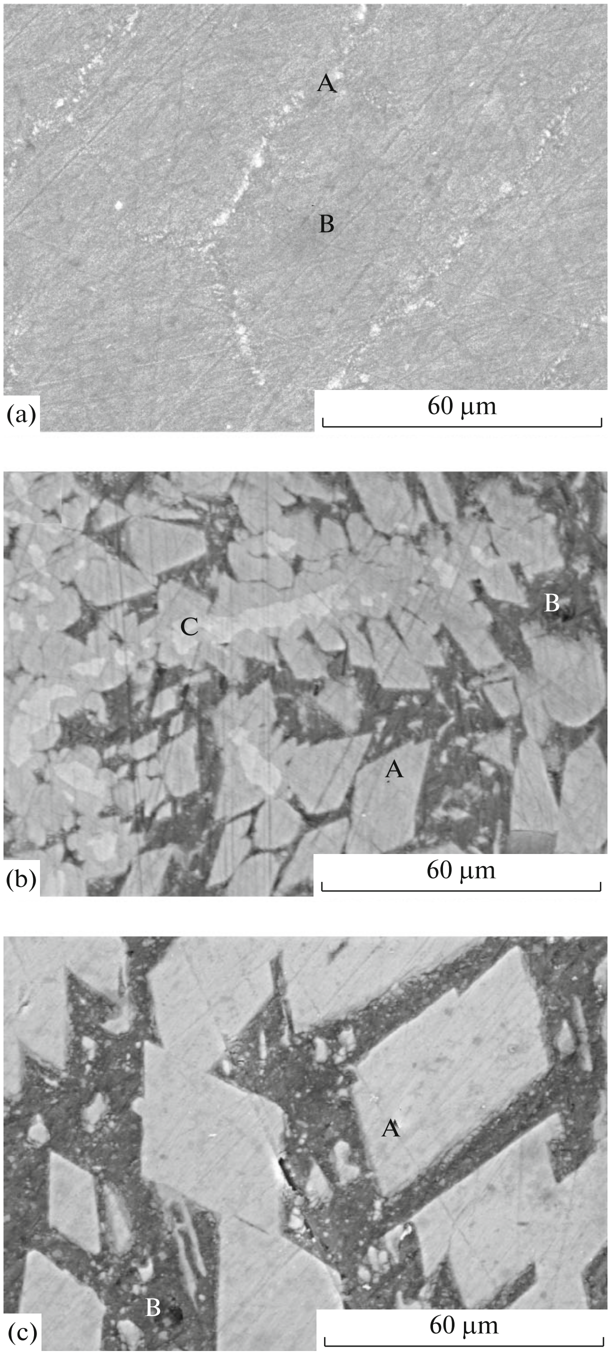

Fig. 2. EM images of the surface of the aluminum–nickel alloys: (a) 6.9, (b) 32.8, and (c) 34.6 wt % Ni.

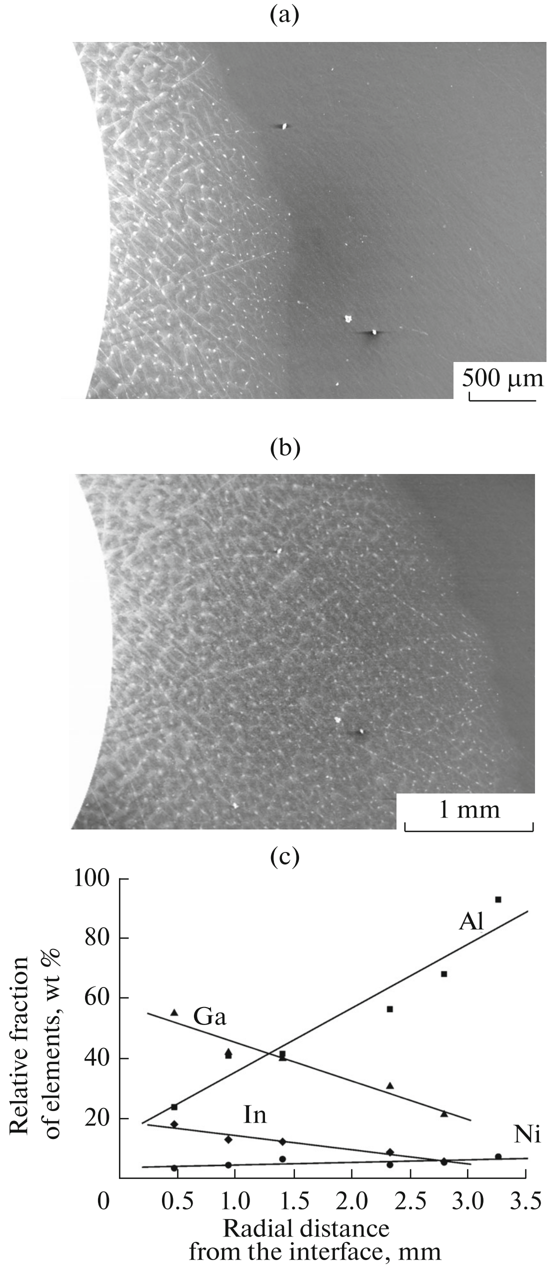

Fig. 3. EM images of the surface of the Al–Ni alloy containing 6.9 wt % Ni (dark region) after contact with the liquid Ga–In eutectic (light region) for (a) 60 and (b) 100 min; (c) plots of the content of the Al, Ni, Ga, and In elements on the surface of the Al–Ni alloy containing 6.9 wt % Ni in a radial direction from the interface (contact time of 100 min).

tion of bright particles with a size of 10–20 μm that were mostly composed of indium (>90 wt %). After a 3-h period in which the studied systems are in contact, the concentration of the Ga–In eutectic components significantly increases.

The observed effects were previously described for the contact of the liquid Ga–In eutectic with metallic Al [2]. We believe that the surface propagation of the liquid eutectic components is one of the first stages of the activation of aluminum alloys; it is accompanied by segregation of the passivation oxide layer [8].

Dissimilar results were obtained for the contact of the liquid Ga–In eutectic with Al–Ni alloys containing high nickel concentrations (32–35 wt % Ni). Despite the long-term interaction of the contacting alloys (3 h), data on the surface morphology and composition hardly differ from the data for the original Al–Ni alloys. Thus, in the contacting regions of the Al–Ni/Ga–In system corresponding to the Al_3Ni intermetallic compound, the gallium content remains low (~1 wt %) and unchanged throughout the entire contact time. However, in the surface regions with a low nickel content (Figs. 2b, 2c, regions B), the gallium concentration abruptly increases; after 3 h, it is ~20 wt %. In addition, signals of indium are recorded in these regions. The Ga/In concentration ratio already deviates from the eutectic proportion; the observed distribution of the eutectic components over the surface of the Al–Ni alloy is extremely heterogeneous in this region.

Thus, it has been found that the studied Al–Ni alloy samples that contain, in addition to the identified phases of intermetallic compounds, a significant amount of metallic Al are activated with the liquid Ga–In eutectic. The Al_3Ni and Al_3Ni_2 intermetallic compounds do not undergo substantial morphological and compositional changes when in contact with the liquid eutectic.

CONCLUSIONS

A systematic study of the elemental and phase composition, morphology, and local content of components on the surface of the contacting Al–Ni alloy–liquid Ga–In eutectic system has been conducted.

Compared to Al–Cu alloys containing $Al_9Cu_{11.5}$ and Al_2Cu intermetallic compounds, Al–Ni alloys containing Al_3Ni and Al_3Ni_2 intermetallic compounds undergo a more effective activation with the liquid Ga–In eutectic. This feature is attributed to the presence of a metallic aluminum phase in the studied samples, a phase that contributes to the development and occurrence of activation in these microheterophase systems.

These systems can be activated because Al exhibits a high chemical affinity for the liquid Ga–In eutectic, which subsequently leads to the destruction of the eutectic and the formation of solid solutions based on aluminum and gallium.

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