# Chemical Interaction of the In–Ga Eutectic with Al and Al-Base Alloys

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**Abstract**—The chemical interaction of the indium–gallium eutectic with Al and Al-base alloys is studied by x-ray diffraction, optical microscopy, and electron microscopy. Experimental data are presented that shed light on the reaction mechanism and the diffusion processes responsible for the subsequent disintegration of the material and its dissolution in water. Mechanical tests show that the activation of aluminum leads to a transition from plastic to brittle fracture.

**DOI:** 10.1134/S0020168506030083

## INTRODUCTION

There is now ample evidence that a liquid metal in contact with a solid metal diffuses into it [1, 2]. Al–Ga is known to be among the most convenient test systems for studying this effect [3, 4]. In particular, the rate of liquid gallium penetration into aluminum along its grain boundaries was reported to be as high as  $0.55-8.7 \mu m/s$  [5, 6].

Similar processes take place when aluminum is in contact with an indium–gallium alloy, but this system has been studied in less detail.

The purpose of this work was to study chemical interaction of the indium–gallium eutectic with Al and Al-base alloys using a number of physicochemical characterization techniques with the aim of gaining information about the mechanism of this interaction and the processes responsible for the subsequent disintegration of the material and its dissolution in water with the formation of hydroxides.

#### **EXPERIMENTAL**

We studied interaction of 7- to 10-mm-diameter pure-grade aluminum granules and  $5 \times 10 \times 15$ -mm plates of Al, Al–Ti, Al–Si, Al–Cu, and other aluminum alloys with the In–Ga eutectic (24 wt % In, melting point of 16°C [7]) in the liquid state (in what follows, this process will be called activation).

The phase composition of activated aluminum and the products of its reaction with water was determined by x-ray diffraction (XRD) with DRON-3 and HZG-4/A powder diffractometers. The surface morphology of the materials was examined on a Tesla BS-350 scanning electron microscope (SEM). We carried out a series of in situ experiments in order to assess the dynamics of the interaction between the liquid In–Ga alloy and the surface of aluminum granules. To this end, an In–Ga drop ( $\approx 3 \text{ mm}^3$ ) was spread over the surface of an Al granule precleaned with ethanol, and changes in the surface morphology of the granule were followed using electron microscopy after holding in the vacuum lock of the SEM at a pressure of  $\approx 1$  Pa or atmospheric pressure and 20°C for different lengths of time.

The morphology of the products of reaction between activated aluminum and water was examined on an EM-125 transmission electron microscope (TEM).

A sample of the AK5M-2 alloy (Cu 1.7, Si 4.57, Fe 0.95, Mg 0.58, Mn 0.27, Ti 0.05, Zn 0.7 wt %, the balance being Al; RF State Standard GOST 1583-93) prepared via crucible melting followed by natural cooling was examined by optical microscopy (MBI-15 microscope). To reveal the grain structure, the sample surface was polished, etched in the mixture of acids recommended in [8], and then degreased with ethanol. The sample ranged in grain size from 50 to 100  $\mu$ m.

To assess the effect of liquid In–Ga on the plasticity of bulk aluminum, activated aluminum specimens were tested in tension on an R-10 tensile testing machine.

#### **RESULTS AND DISCUSSION**

**SEM examination.** In examining the variation in the surface morphology of aluminum in response to activation, we took advantage of the fact that the backscattered electron signal in SEM depends on the conductivity of the material: lower conductivity areas on the specimen surface backscatter more electrons [9]. In SEM images, such areas appear lighter (Fig. 1). This allowed us to more accurately interpret our results for the multiphase system Al–In–Ga.

Electron-microscopic examination of the surface morphology of activated aluminum after holding in the vacuum lock of the SEM at low pressure for different lengths of time, up to 36 h, revealed no evidence of interaction between aluminum and liquid In–Ga.

After holding at atmospheric pressure, there were clear indications of interaction:

1. The surface of the In–Ga drop became rougher.

2. Areas that appeared bright when exposed to the electron beam were observed on the specimen surface.

3. The apparent specimen volume decreased substantially.

4. Both dark and light areas (compared to the unaffected surface) appeared on the aluminum surface near the In–Ga drop.

The first changes in surface morphology were observed 20–30 min after the drop had been applied to the granule. The changes became more pronounced with increasing holding time. After 20–25 h, the surface of the aluminum specimen was seen to have a loose microstructure.

Detailed analysis of SEM micrographs revealed a number of regular trends. In particular, with increasing holding time the fraction of light areas increased on both the aluminum and drop surfaces, as did the roughness of the drop surface. Some of the light areas on the aluminum surface were surrounded by darker areas. As mentioned above, the light areas in SEM micrographs are due to locally reduced conductivity. An interesting feature in the arrangement of the light areas is that they do not form a continuous zone near the In–Ga drop and often coincide with grains of the parent aluminum specimen. In the peripheral parts of the grains, we also observed narrow light areas, whereas the grain boundaries had relatively high conductivity, i.e., absorbed the electron beam better than the grain bulk (Fig. 2). Consequently, the In–Ga alloy forms an intergranular film, which seems to be responsible for the broadening of grain boundaries during activation, as observed in SEM micrographs.

**XRD examination.** Comparison of XRD data for aluminum activated with liquid In–Ga for 5 min and the XRD pattern of the parent aluminum specimen indicated that

(1) the lattice parameter of aluminum (0.405 nm) remained unaffected by the reaction between aluminum and liquid In–Ga to within  $\approx 0.05\%$ ;

(2) the width of XRD peaks from activated aluminum was equal to the instrumental broadening ( $\Delta 2\theta \approx 0.10^\circ$ );

(3) no reflections from additional phases emerged, except for a broad, weak line of the liquid In–Ga alloy.

INORGANIC MATERIALS Vol. 42 No. 3 2006



**Fig. 1.** Surface microstructure of aluminum after holding in the vacuum lock of the SEM at atmospheric pressure for 60 min; 600×.



**Fig. 2.** Liquid In–Ga film between aluminum grains (center) and the product of surface reaction between aluminum and liquid In–Ga, presumably, pseudoboehmite (left).

Thus, XRD results support the assumption that the liquid In–Ga alloy penetrates into the bulk of aluminum along grain boundaries, without changing its structure.

In subsequent experiments, activated aluminum was immersed in distilled water maintained at 20°C, which led to aluminum dissolution, the formation of aluminum hydroxides, and hydrogen release.

The XRD patterns of the samples prepared by reacting activated aluminum with water, followed by drying at 110°C, showed only reflections from aluminum hydroxides (pseudoboehmite and small amounts of bayerite and nordstrandite) and metallic indium (Fig. 3, scan 3). The likely reason is that indium is nonreactive with water [10], while gallium is oxidized by water and is probably then incorporated into the aluminum hydroxide lattice.



**Fig. 3.** XRD patterns of the samples prepared by reacting activated aluminum with water for (1) 1, (2) 3, and (3) 5 min, followed by drying at  $110^{\circ}$ C; PB = pseudoboehmite, In = metallic In, Al = metallic Al.

As mentioned above, we also activated several aluminum alloys, in particular the Al–2.5% Ti alloy, containing the intermetallic compound TiAl<sub>3</sub>. The activation process was accompanied by no significant anomalies. After subsequent reaction with water, XRD patterns showed reflections from TiAl<sub>3</sub>, pseudoboehmite (AlOOH), and bayerite (Al(OH)<sub>3</sub>).

Silumin (11.04% Si) was activated by a standard procedure. The activation product reacted rapidly with water. XRD patterns showed only weak reflections from Al, with no peaks from any silicon-containing compounds. After subsequent calcination in air at

550°C, XRD patterns showed peaks from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> (quartz).

The  $Al_{50}Cu_{50}$  alloy activated as described above differed markedly in reaction with water from the activation products in the Al–Ti and Al–Si systems. The alloy consisted of the intermetallic phase CuAl<sub>2</sub> and a trace amount of aluminum metal. Reacting the activation product with water, we obtained a dark, fine-particle precipitate. After drying, the precipitate consisted of the intermetallic phase CuAl<sub>2</sub> and small amounts of aluminum hydroxides.

**Characterization by optical microscopy.** The reaction between the activated aluminum alloy AK5M-2 and liquid In–Ga led to the formation of dark areas on the surface of AK5M-2. After 50–60 min, the dark areas extended 2–3 mm from the boundary of the liquid In–Ga alloy (Fig. 4). In addition, there were light areas corresponding to grain-boundaries and dark rounded particles less than 20  $\mu$ m in size. Similar results were obtained by examining the reaction between aluminum and liquid In–Ga by SEM and TEM (Fig. 5).

After 24 h of reaction, dark areas appeared on the surface, which had a dendritic microstructure. The reaction extended 10–15 mm into the alloy. The dark areas typically corresponded to grain surfaces, whereas the grain boundaries remained light. There were, however, zones where the reaction was more pronounced at grain boundaries and adjacent regions. Grain-boundary and near-boundary contrast changes also prevailed in the zone 18–20 mm from the liquid In–Ga alloy, but the reaction front did not reach the zone where the morphological changes in question occurred. Characteristically, the surface of the liquid In–Ga alloy changed from lustrous metallic to dull dark brown in appearance and became rougher, and the volume of the drop decreased by as much as 30–40%.



Fig. 4. Surface morphology of the AK5M-2 alloy after 60 min of reaction with the liquid In–Ga alloy; the dark area represents the reaction front;  $220\times$ .



**Fig. 5.** TEM micrograph showing the products of reaction between water and aluminum activated with liquid In–Ga; 80000×.

Holding for an additional five days under the same conditions produced no changes in the surface morphology of the sample.

If the In–Ga drop applied to the aluminum surface was not specially deformed, it did not wet the surface, even after holding for 3–5 days between 20 and 60°C.

In an earlier study [11], gallium was also assumed to be incorporated into the aluminum lattice in the course of diffusion. This accounts for the absence of diffraction peaks from gallium or its compounds in XRD patterns of the products of reaction between aluminum and liquid In–Ga. In addition to reflections from aluminum hydroxide, the XRD patterns showed only peaks from metallic indium. These findings can be interpreted in terms of the Hume-Rothery rule [12], according to which the solid solubility of two metals is limited if they differ in atomic radius by more than 14-15%. Using the atomic volumes  $\Omega$  reported by Barrett and Massalski [13] for different elements and the formula  $r_{\Omega} = (0.75 \Omega/\pi)^{1/3}$ , where  $r_{\Omega}$  is the Seitz radius, we obtain  $r_{\Omega} = 0.158$ , 0.164, and 0.184 nm for aluminum, gallium, and indium, respectively. Pilipenko [14] also gives the atomic radii of these elements, taken from three different sources. The average radii (in the same order as above) are 0.137, 0.130, and 0.164 nm. The considerable difference in atomic radius between In and Al (on average more than 15%) seems to be responsible for the insignificant indium solubility in aluminum, which is below 0.01 wt % according to Goldstein et al. [9]. At the same time, the gallium solubility in aluminum amounts to 21 wt % [15], in line with the small difference in atomic radius between these metals. The natural assumption that the particles seen in Fig. 4 consist of indium lends indirect support to the incorporation of gallium into the aluminum lattice and the formation of metallic indium.

The light areas seen along grain boundaries after the reaction with the liquid In–Ga alloy seem to represent microinhomogeneities due to additional phases consisting of foreign atoms that do not react with the alloy.

In the systems studied, the equilibrium angle  $\theta$ between the solid-liquid and liquid-vapor interfaces (contact angle) was close to 180°, attesting to a high surface tension at the interface between the solid and liquid metals and a nearly perfect nonwetting condition [16]. Spreading the In–Ga drop over the aluminum surface reduced the contact angle. For  $\theta$  approaching zero, the liquid must penetrate into the bulk of the solid metal along grain boundaries [17]. Moreover, according to Nikitin [2] embrittlement develops most frequently if the solubility of a liquid metal in a solid one is very low, which corresponds to indium dissolution in aluminum. In addition, the atomic volume of solid gallium is known to be 3.2% greater than that of liquid gallium [18], which may also contribute to the disintegration of aluminum and its alloys.

Mechanical tests. We carried out tensile strength tests on aluminum plates. Specimens that were not acti-



**Fig. 6.** Tensile strength of aluminum as a function of activation temperature.

vated with liquid In–Ga had a well-defined plastic zone. The regions of subsequent rupture were found to suffer a tensile strain, without cracking. The plastic strain of activated aluminum was substantially lower. In that case, the fracture surface was cracked and textured in a direction normal to the loading axis.

We also examined the tensile strength of aluminum as a function of activation temperature. In all instances, the activation time was 5 min. The results indicate that the diffusion rate decreases with decreasing temperature. The tensile strength of parent aluminum was 166 MPa, and that of aluminum activated at 17°C was 109 MPa. Raising the activation temperature to 25– 35°C reduced the tensile strength of aluminum to 50– 60 MPa (Fig. 6). Similar results were reported by Larikov *et al.* [19], who observed an increase in intrinsic stress as the temperature of reaction between aluminum and liquid gallium was raised.

#### CONCLUSIONS

The observed reaction between a liquid In–Ga alloy and aluminum, accompanied by changes in the surface morphology of aluminum, is associated with surface, grain-boundary, and volume diffusion. The relatively fast rate of reaction propagation is primarily due to surface and grain-boundary diffusion.

At low pressure, aluminum did not react with indium or gallium; at atmospheric pressure, we observed the formation of dielectric products, presumably aluminum hydroxides.

In the case of alloys containing an intermetallic phase (TiAl<sub>3</sub> or CuAl<sub>2</sub>), this phase did not react with water after activation and retained aluminum.

Mechanical tests showed that the activation of aluminum led to a transition from plastic to brittle fracture. Our results provide clear evidence for two forms of embrittlement by the liquid alloy: a low-temperature effect, related directly to the reduction in the surface energy of the solid metal in the presence of a molten coating, and an effect due to the diffusion-induced changes in the composition and, accordingly, mechanical properties of the solid material. The latter effect becomes more important at higher temperatures.

The activation of aluminum seems to be due to the disruption of the surface oxide layer under the action of the liquid alloy, leading to an increase in the effective reaction surface. Subsequent grain-boundary and volume diffusion of liquid In–Ga into aluminum or its alloys gives rise to the embrittlement of the material and drastically increases its reactivity with water.

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