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# Activation of Al-Fe Alloys by Liquid Ga-In Eutectics for the *in situ* Formation of Catalytic Aluminium Chloride Complexes\*

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## Abstract

Samples of Al–Fe alloy of composition of  $(2.15\pm0.08)$  mass %, admixtures of not more than 0.2 mass %, were studied. It was demonstrated by XPA that the intermetallide of composition Al<sub>3.2</sub>Fe and polycrystalline aluminium were formed at alloying of metals. The interaction of Al–Fe alloy samples with liquid Ga–In eutectics was studied by scanning electron microscopy and energy-dispersive X-ray spectroscopy. It was found that Al–Fe alloy became activated slower by liquid Ga–In eutectics than polycrystalline aluminium and Al–Ni alloys. The intermetallide phase of Al<sub>3.2</sub>Fe composition does not undergo significant chemical changes. It was demonstrated by multiple frustrated total internal reflection IR spectroscopy that aluminium chloride complexes of various compositions were *in situ* formed during the interaction of activated samples of Al–Fe alloy with *tert*-butyl chloride. The complexes showed catalytic properties.

**Key words:** Al=Fe alloy, Ga=In eutectic, activation, scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray phase analysis, IR spectroscopy, IR spectra of multiple frustrated total internal reflection (MFTIR), *tert*-butyl chloride, and catalytic aluminium chloride complexes

## INTRODUCTION

Lately, activated aluminium has been regarded as a promising material in the area of catalysis and unconventional energetics [1-10]. Thus, by subjecting metallic aluminium to mechanical grinding with metals oxides [1], graphite [2], gallium and its alloys [3, 4], as well as by alloying with gallium, indium, bismuth, tin [5] and iron [6, 7], materials reactive in relation to water are obtained. By acting on metallic aluminium by crystalline I<sub>2</sub> [8], organoaluminum compounds [9] and liquid Ga–In alloy [10], a material reactive in relation to organochlorine compounds is formed. In the latter cases, in situ alumochloride complexes that are active in apparently important catalytic transformations of alkanes and olefins are formed: oligomerization, isomerization, and alkylation. It is known that selectivity of these reactions increases when adding compounds of copper, nickel, iron *etc.* [11, 12].

In this regard, the *in situ* preparation of alumochloride complexes containing transition metals ions from appropriate alloys based on aluminium activated, for example, by liquid Ga–In eutectics is of scientific interest. It was earlier detected that Al–Cu and Al–Ni alloys become activated by liquid Ga–In eutectics [13,

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14]. This work investigates the interaction of Al–Fe alloy with liquid Ga–In eutectics.

## EXPERIMENTAL

Al-Fe alloy was obtained by alloying of aluminium of purity of not less than 99.9 mass % and 10895 E electrotechnical unalloyed steel according to State Standard GOST 11036-75 in a graphite crucible under the flux layer at a temperature of 1573 K. The molten mass was stirred, was poured into a metal mould, and cooled in air.

Elemental analysis of Al–Fe alloy was performed using a Varian 710-ES Inductively Coupled Plasma Optical Emission Spectrophotometer (Agilent Technologies). For this, sample weights of the mass of 0.1-0.2 g were dissolved in 20 mL of HCl (1 : 1) os. ch. (extra pure) reagent grade with the addition of 1 mL of H<sub>2</sub>O<sub>2</sub>. In the resulting solutions, the content of Fe and impurities (Cu, Mn, Si) was determined.

X-ray phase analysis (XPA) of Al–Fe alloy samples was performed using a Bruker D8 Advance Powder X-ray diffractometer. Shooting was carried out in monochromatized  $CuK_{\alpha}$  radiation ( $\lambda = 0.15418$  nm) in the following modes:  $0.05^{\circ}$  scan step, signal accumulation time in 10 s point, voltage, and 40 kV and 40 mA filament current, respectively. The obtained diffractograms were unscrambled using ICDD PDF-2 powder diffraction databases.

The morphology and local elemental composition of the surface of Al–Fe alloy samples were studied by methods of scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) using a JEOL JSM-6610LV microscope with an INCAx-Act attachment (Oxford Instruments).

The interaction process of liquid Ga-In eutectics with Al-Fe alloy samples was studied directly in a camera of a JSM-6610LV electron microscope upon contact of the components from 0.5 to 36 h at room temperature. Discs with a diameter of 14 mm and a thickness of 2 mm were used as samples in this case. A drop of Ga-In eutectic of a volume of ~0.2 mL was applied to the central part of the plate surface of the test the alloy sample. The surface of Al-Fe alloy sample was subjected to mechanical influence (scratching) by a metal needle for more effective wetting by Ga–In eutectics.

Elemental chemical analysis was conducted radially from contact boundary drops of Ga–In eutectics – Al–Fe alloy sample along its surface with an interval up to  $400 \,\mu$ m.

The reactivity of Al–Fe alloy activated by liquid Ga–In eutectics was studied by IR MFTIR spectra. An activated sample was placed into an IR MFTIR cell filled with *tert*-butyl chloride. Afterwards, difference spectra of repeatedly frustrated total internal reflection spectroscopy began to register using a Nicolet 5700 IR-FT spectrometer (Thermo Fisher Scientific) in a spectral range of 400–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and the number of spectra accumulation of 32 with an interval of 2 min.

#### **RESULTS AND DISCUSSION**

According to inductively-coupled plasma atomic absorption spectrometry results, the iron content in the investigated alloy  $(2.15\pm0.08)$  mass %, the total content of admixtures (Cu, Mn and Si) – not more than 0.2 mass %. Little intense signals that correspond to the phase of the intermetallic compound of  $Al_{3.2}$ Fe composition were observed on diffractograms of investigated Al–Fe alloy samples in addition to reflexes of the polycrystalline aluminum phase.

An electron microscope image of a surface area of Al-2.15 mass % Fe alloy is presented in Fig 1. Using SEM and EDS methods it was found that the sample surface was non-homo-



Fig. 1. Electron microscopic image of the surface area of Al=2.15 mass % Fe alloy.

geneous and presented by well-faceted crystals of the intermetallic compound  $Al_{3.2}Fe$  with linear dimensions of 0.5–25 µm distributed in polycrystalline aluminium. According to the known literature data, such a morphology of intermetallic compound  $Al_{3.2}Fe$  crystals is driven by a preferential crystallographic orientation of its faces in the areas of <010> or <011> [15].

Afterwards, studying the interaction of Al– Fe alloy samples with liquid eutectics directly in the electron microscope chamber. Thus, the propagation front of the eutectic components (Fig. 2, *a*) after 100 min of contact of Al–2.15 mass %. Fe alloy with liquid Ga–In eutectics at a distance of ~1 mm from the contact area was observed. After 70 min, it increased by ~1.6 mm (see Fig. 2, *b*). Based on the experimental data obtained, the propagation rate of the *v* eutectic components that amounted to 0.02 mm/min for this Al–Fe alloy was assessed. Three hours after the contact, a Ga/In ratio deviates from the eutectic proportions (see Fig. 2, c). At a distance of ~0.5 mm from the contact zone, the formation of ball-shaped particles with dimensions of  $10-20 \ \mu m$  corresponding to indium metal was additionally registered on the surface. After 4 h of contact of the reagents, the eutectics components penetrated the near-surface layers of polycrystalline aluminium along the boundaries of grains with the sizes up to 1  $\mu m$ .

According to the XPA data, after 36 h of contact of the investigated sample of Al–Fe alloy with liquid Ga–In eutectics, the reflexes of the intermetallic compound of  $Al_{32}$ Fe composition are preserved on diffractogram, which points out at its resistance to the effect of eutectics.





Fig. 2. Electron microscop images of a drop of the Ga-In eutectic applied to a sample of Al-2.15 mass % Fe alloy, at activation time of 100 (*a*) and 170 min (*b*); *c* - dependencies of the content of Al, Fe, Ga, In along the alloy surface in the direction from the edge of a droplet of the eutectics at activation time of 170 min.

Similar phenomena being the major stages of the preparation of the reactive material that obtained in the literature the name "activated aluminium" was observed by us at the interaction of the liquid eutectics and alloys of Al–Ni in [14, 16]. One can suppose that Al–2.15 mass % Fe alloy containing phases of polycrystalline aluminium and the intermetallic compound  $Al_{3.2}$ Fe is also activated by liquid Ga–In eutectics mainly on account of aluminium activation by forming activated alloy Al–Fe.

By comparing propagation rates of the eutectics components obtained for Al–Ni alloys studied earlier [14] and metal aluminium [17], the following row was constructed: Al (v > 0.05mm/min) > Al–Ni (6.9 mass % Ni, v = 0.04mm/min) > Al–Fe (2.15 mass % Fe, v = 0.02mm/min), where v is propagation rate of the front of the eutectics components.

Thus, results obtained by SEM and EDS methods indicate that the investigated Al=2.15 mass % Fe alloy is slowly activated by liquid Ga=In eutectics in comparison with aluminium and Al= Ni alloy. The intermetallic compound  $Al_{3.2}$ Fe does not undergo significant chemical changes.

Nevertheless it is important that such an activated alloy interacts with liquid *tert*-butyl chloride.

At the initial time of the reagents contact, a change in their colour and bubbling are not observed. After 10 min, the shiny surface of activated Al-Fe alloy became dim; though no changes in difference IR MFTIR spectra were observed. After 8 h contact of the reagents, the sample surface acquired a black colour, the liquid medium did not change the colour. At the same time, in the differential IR MFTIR spectrum, the appearance of a broad absorption band in the  $470-750 \text{ cm}^{-1}$  spectral region was observed. It gained a clear maximum at 615 cm<sup>-1</sup> in 947 min after the beginning of contact of the reagents (Fig. 3). According to the literature data, this adsorption band corresponds to the stretching vibrations of Al-Cl bonds of the molecular form AlCl<sub>3</sub> [18]. The intensity of the observable adsorption band slowly increased before the time of contact of the reagents of 1157 min (see Fig. 3, spectrum 4). After this time, in difference IR MFTIR spectra, a sharp reduction in the adsorption band at 558 cm<sup>-1</sup> referred to the stretching vibrations of C-Cl bonds of tert-butyl chloride molecules was observed (see Fig. 3). Simultaneously, a new intense adsorption band at  $489 \text{ cm}^{-1}$ appeared indicating stretching vibrations of Al-Cl bonds in tetrahedral  $AlCl_4^-$  ions [19]. Addition-



Fig. 3. Differential IR MFTIR spectra of the in situ the dynamics of the interaction of activated Al-2.15 mass % alloy Fe with liquid *tert*-butyl chloride at various contact times (min): 847 (1), 947 (2), 1037 (3), 1157 (4), 1177 (5), 1197 (6), 1209 (7), 1221 (8), 1231 (9), 1237 (10), 1241 (11), 1249 (12), 1259 (13), 1267 (14).

ally, the appearance of low-intensity adsorption bands at 528 and 589 cm<sup>-1</sup> that refer to vibrations of Al–Cl bonds of binuclear  $Al_2Cl_7^-$  ions and  $AlCl_4^-$  ions of  $C_{3v}$  symmetry was observed in difference IR MFTIR spectra [20, 21].

Note that activated Al–Fe alloy does not entirely interact with liquid *tert*-butyl chloride even at a long time of contact. The conversion degree ( $\alpha$ ) of the investigated alloy is 40.9 %.

#### CONCLUSION

Thus, the present work demonstrates that liquid eutectic activates Al–Fe alloy primarily due to activating the region in polycrystalline aluminum itself. The phase of the intermetallic compound  $Al_{3,2}$ Fe is herewith stable and does not undergo chemical and morphological transformations. Herewith, the components of the eutectics propagate along the surface of aluminium matrix with a rate of ~0.02 mm/min, which is lower than for samples of aluminium and Al–Ni alloys.

Activated Al–Fe alloy is reactive towards *tert*-butyl chloride. According to IR MFTIR spectra data, ion and molecular catalytic alumochloride complexes are *in situ* formed in the reaction medium.

To reduce the formation time of activated Al-Fe alloy further studying the effect in temperature on the interaction of liquid Ga-In eutectics with samples of Al-Fe system.

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