Mechanochemical Synthesis of Intermetallic Compounds in the Gallium—Iridium System

**E. A. Pavlov[a, *], I. V. Chuprov[a], M. V. Nikulin[a], E. V. Mal'tsev[a], A. A. Pshenichnaya[a, b, **],
T. F. Grigoreva[c, **], E. A. Pastukhov[d, †], A. P. Skuratov[e], and N. Z. Lyakhov[c]**

[a]*OAO Krasnoyarsk Plant of Nonferrous Metals Named after V. N. Gulidov, Krasnoyarsk, 660027 Russia*
[b]*Kirensky Institute of Physics, Federal Research Center, Siberian Branch, Russian Academy of Sciences,
Krasnoyarsk, 660036 Russia*
[c]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences,
Novosibirsk, 630128 Russia*
[d]*Institute of Metallurgy, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620016 Russia*
[e]*Siberian Federal University, Krasnoyarsk, 660041 Russia*
*e-mail: E.Pavlov@krastsvetmet.ru
**e-mail: grig@solid.nsc.ru
Received December 20, 2017

Abstract—The interaction between a solid inert metal (Ir) and an active liquid metal (Ga) during mechanical activation in a high-energy planetary mill is studied by X-ray diffraction and scanning electron microscopy with EDS-apparatus for high-resolution energy dispersive X-ray microanalysis. The influence of mechanical activation conditions on the formation of Ga_xIr_y intermetallic compounds and Ga_xIr_y/Ir composites and on their solubility in various acids is investigated. Being a surfactant for iridium, gallium propagates along the grain boundaries of polycrystalline iridium particles during mechanical activaiton and, hence, sharply decreases their strength. As a result of strong mechanical deformation during activation, the contact surface area between the solid and liquid metals, where the intermetallic compounds form intensely, increases sharply. As a result of treatment of the products of mechanical activaiton by a mixture of concentrated hydrochloric and nitric acids, iridium (>30%) from passes into an acid solution and forms H_xIrCl_y complex compounds, which can interact with bases to form soluble complex salts.

INTRODUCTION

Iridium has unique physicomechanical properties, such as an extremely high density (22.65 g/cm³) and a high melting temperature (2454°C); therefore, even its small additions increase the strength, the hardness, and the melting temperature of other metals. The addition of 10% iridium to relatively soft platinum increases its hardness and strength limit almost three-fold. If the iridium content in an alloy increases to 30%, the hardness of the alloy increases weakly but the strength limit doubles, to 99 kg/mm². Small iridium additions to tungsten and molybdenum increase the strengths of these metals at high temperatures. The alloys of Ir with W and Th serve as materials for thermoelectric generators; the alloys of Ir with Hf are materials for fuel tanks in spacecrafts; the alloys of Ir with Rh, Re, and W are the materials of thermocou-

ples used at temperatures above 2000°C; and the alloys of Ir with La and Ce are the materials of thermal emission cathodes. Titanium—iridium alloys are the materials of pipelines operating in the ocean depths. An iridium layer several atoms thick covers the mirrors of the telescopes that receive X-rays [1].

Nanosized iridium is applied in the space industry as the material of electrochemical sensors for selective determination of toxic gases, catalysts in fuel elements, and film pastes in microelectronics [2].

The high corrosion resistance of iridium makes possible to use its alloys in aggressive media. A low iridium addition to titanium (0.1%) sharply increases its high acid resistance, and the same is true for chromium [3, 4]. The thermocouples consisting of iridium and an iridium—40% rhodium alloy reliably operate at high temperatures in an oxidation atmosphere. Thus, iridium is widely used in various industries [5].

† Deceased.

A promising method of producing ultradispersed high-purity metals can be their dissolution in acids followed by the formation of ammonium salts and reduction. Iridium is chemically inert; therefore, it is difficult to dissolve it, since it does not interact with mineral acids. The reactivity of iridium increases in the alloys of iridium with the metals or intermetallics to be dissolved in acid solutions [6].

Intermetallic compounds (IMC) and alloys dissolve faster than the inert metals entering in their compositions, especially in the presence of a large interfacial or grain boundary surface [6, 7]. The transformation of an inert metal into a soluble form becomes possible when one of the IMC (alloy) components is well dissolved. This effect is most pronounced for ultradispersed IMC, and one of the most promising methods of their production is mechanochemical synthesis.

The adsorption-active properties of a liquid metal with respect to most solid metals are manifested in interacting solid−liquid metal systems. The penetration of a liquid metal along grain boundaries in polycrystals sharply decreases their strength characteristics [8, 9]. The fracture energy of a polycrystalline metal in contact with a melt decreases by two orders of magnitude, which ensures a high rate of formation of a "fresh" solid metal surface. As a result of high wettability of the surface with a liquid metal, the metal again forms a solid−liquid metal contact surface, where IMC are synthesized [10]. As an inert metal, iridium is expected to interact with active liquid gallium, since some IMC in the Ir−Ga system form at a high temperature and pressure (Ga_9Ir_2, Ga_3Ir, Ga_5Ir_3, GaIr). However, the equilibrium Ga−Ir phase diagram has not yet been plotted [11]. The presence of several IMC in the Ir−Ga system allows us to assume that the enthalpy of mixing is negative and mechanochemical synthesis of these compounds is possible. Since Ga is well dissolved in acid solutions [12], it can be removed from the Ga_xIr_y IMC fabricated by mechanochemical synthesis, which increases the ability of iridium to dissolve in acids.

An analysis of the reported data demonstrates that the mechanochemical interaction in (Ir, Ru, Rh)−liquid gallium systems has not been studied; therefore, such an investigation is important.

The purpose of this work is to study the possibility of mechanochemical synthesis of Ga_xIr_y IMC and Ga_xIr_y/Ir composite materials in the Ga−Ir system and the possibility of acid separation of gallium from the synthesized IMC to transform iridium into a soluble form.

EXPERIMENTAL

We used GL-0 gallium and IA-1 iridium powder with a particle size of ~1.5 μm for experiments.

The mechanochemical synthesis of IMC in the system inert solid metal (iridium)−active liquid metal (gallium) was performed in a high-energy planetary ball mill.

To determine the degree of dissolution of initial gallium and iridium in mechanochemically synthesized Ga_xIr_y and Ga_xIr_y/Ir IMC, we treated them in a mixture of concentrated acids (60 mL HCl + 20 mL HNO_3) at a temperature of 75°C for 3 h. 1 g samples were weighed in 400 mL glasses on a Mettler Toledo RT 503 analytical balance with an accuracy of 0.001 g. Filtration was carried out in several stages using filters with pore sizes of 2−3 μm (two layers) and glass graduated cylinders to measure the volumes of filtrate and rinsing water. The solutions and the insoluble residues of the compounds were analyzed by a chemical analytical method and electron-probe microanalysis, respectively.

X-ray diffraction (XRD) analysis of the powders was carried out on an XPERT-PRO diffractometer using $CuK\alpha_1$ radiation (wavelength is 1.54051 Å) in the angular range $2\theta = 3.0131°−90.91°$ at the minimum step $2\theta = 0.001°$.

The morphological characteristics and the elemental composition of the initial iridium powder and the mechanochemically synthesized Ga_xIr_y and Ga_xIr_y/Ir IMC in the Ga−Ir system before and after treatment by a mixture of concentrated acids were studied with a JEOL 6601 LV (accelerating voltage was 20 kV, magnification was up to ×10000) scanning electron microscope (SEM) equipped with an energy dispersive X-ray microanalyzer (EDXM). The error of elemental analysis using EDXM was 0.2−0.3 wt %.

RESULTS AND DISCUSSION

Figure 1 shows the results of XRD investigation of the samples fabricated by the mechanochemical activation of an iridium−gallium powder mixture taken in the proportion to form the GaIr. The intermetallic GaIr phase is seen to form during activation for 2 min, which is indicated by the appearance of its weak diffraction lines along with the intense lines of Ir in an X-ray diffraction pattern (Fig. 1, curve *I*).

An electron-microscopic study of the samples after activation for 2 min demonstrates that the average sizes of the primary product particles of mechanochemical interaction (Fig. 2b) and the initial iridium powder particles (Fig. 2a) are close (1−2 μm), but the degree of agglomeration of the initial iridium particles is substantially higher.

According to EDXM data, the samples contain (wt %) 42−48 iridium, 40−42 gallium, and 1−2 iron.

At the initial stage, the major part of gallium covers iridium powder particles with a very thin layer, and the Ga_3Ir forms on the contact surface due to the fact that the enthalpy of mixing is about 7 kJ/mol (according to the Miedema calculation) [13−15]. According to

○ Ir [46-1044]
● GaIr [17-427]

GaIr [17-427]
Ir [46-1044]

(100) (111) (110) (200) (111) (200) (220) (210) (211) (311) (222)

2θ, deg
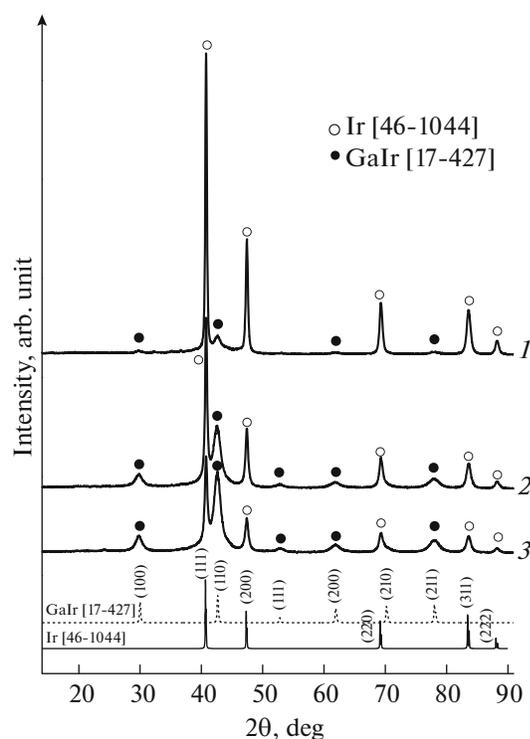
Fig. 1. X-ray diffraction pattern of the products of mechanochemical iridium–gallium interaction vs. the activation time: (*1*) 2, (*2*) 22, and (*3*) 32 min.

[16, 17], IMC with the maximum content of a low-melting-point metal should form on the contact surface between metals at the initial stage. Therefore, the Ga_3Ir should first form in the Ga–Ir system, the mechanochemical interaction of Ga_3Ir with Ir begins after the entire gallium has been spent, and IMC with a lower gallium form later [18]. Based on the XRD data, we assume that, after activation for 2 min, only a small part of Ga_3Ir transforms into GaIr via the mechanochemical reaction $Ga_3Ir + Ir \rightarrow GaIr$, since the reflections of GaIr in the X-ray diffraction pattern are weak (Fig. 1, curve *1*).

An increase in the activation time to 22 min leads to an increase in the intensities of all diffraction lines of the GaIr and to a decrease in the intensities of the lines of Ir (Fig. 1, curve *2*). Electron-microscopic studies showed that, after activation for 22 min, the average particle size is ~0.65 μm and the agglomerate size of 1–3 μm (Fig. 2c).

As follows from EDXM results, the Ir content increases insignificantly to 45–48 wt % and the gallium content decreases to 32–36 wt %. The iron content in the system increases to 5–6 wt % because of the milling of steel drums and balls during activation.

As the activation time increases to 32 min, the GaIr content in the system increases: its diffraction line intensities increase further. The Ir content decreases: the intensities of the strongest diffraction lines Ir (111)
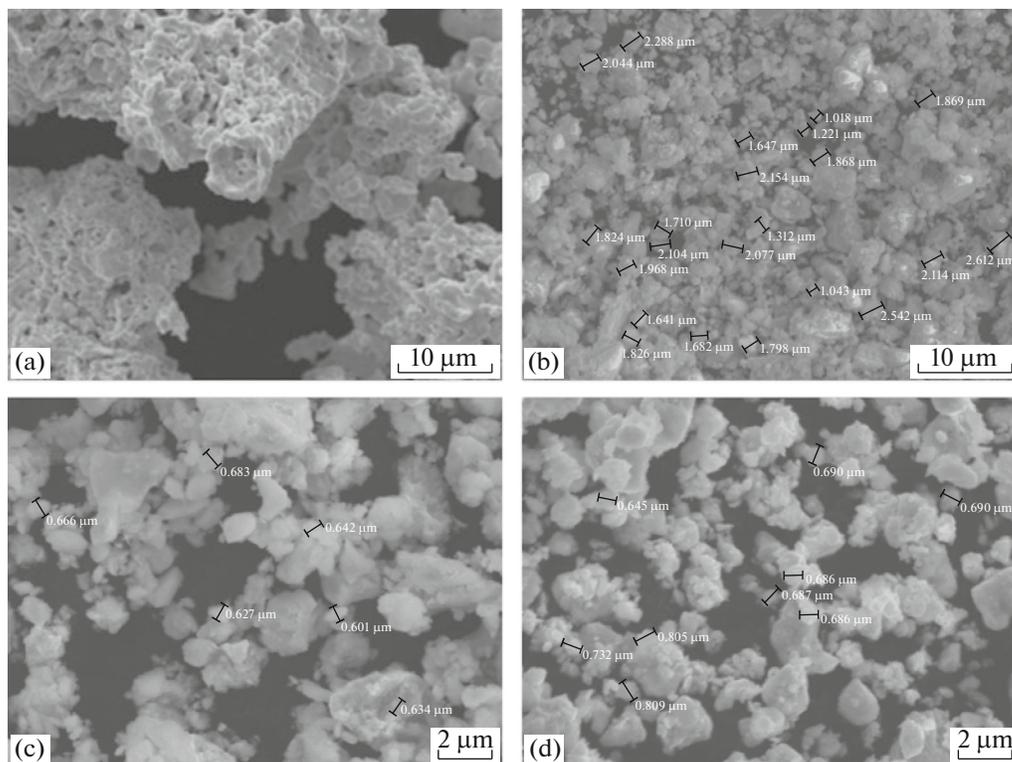
Fig. 2. SEM images of initial iridium particles (a) and Ir–Ga mixture activated for (b) 2, (c) 22, and (d) 32 min.
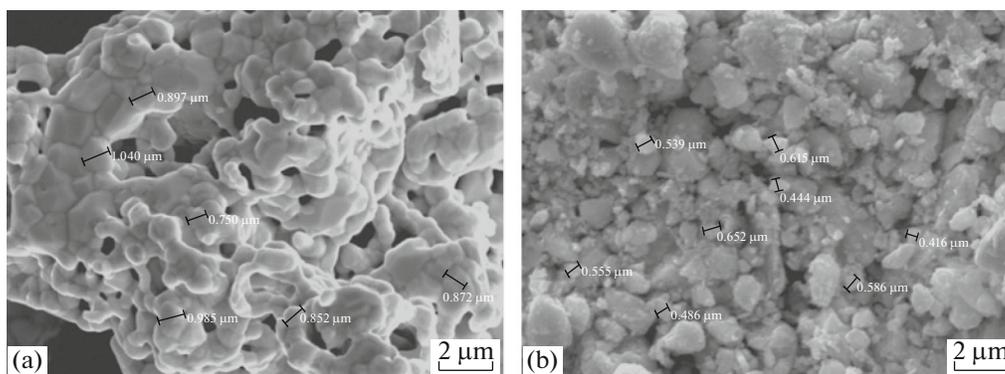
Fig. 3. SEM images of (a) insoluble initial iridium powder sediment and (b) Ir−Ga mixture activated for 32 min after acid treatment.

and GaIr (110) become almost the same (Fig. 1, curve *3*). According to EDXM data, the iridium content increases to 50−52 wt %, the Ga content decreases to 30 wt %, and the Fe content remains unchanged. According to SEM data, the average particle size remains almost the same (~0.7 μm) and the agglomerate size is 1−3 μm (Fig. 2d).

Preliminary experiments on the dissolution of initial gallium and iridium in the mixture of concentrated acids showed that gallium is fully dissolved in 40 min. A highly dispersed iridium powder with a particle size of 1.5 μm does not dissolve under these conditions and retains the morphological features of the initial iridium (Fig. 3a).

According to EDXM data, the elemental composition of iridium in the insoluble sediment is 100 wt %.

Since gallium is well dissolved in acid solutions [12] and iridium can actively pass into a soluble form after the extraction of Ga from Ga_xIr_y intermetallics [6], we studied the dissolution of the products of the mechanochemical interaction of iridium and gallium, namely, Ga_xIr_y intermetallics.

As the GaIr content in the composites increased, the solubility of iridium in an acid solution was shown to increase. For example, it was 24.82 wt % after mechanical activation for 22 min and increased to 31.12 wt % after 32 min. After the passage from the mechanical composite material into the acid solution, iridium is expected to undergo oxidation with the formation of a complex H_xIrCl_y acid.

The insoluble sediment after mechanical activation for 32 min is ultradispersed and has an average particle size of 400−500 nm; therefore, it is difficult to separate it from the solution (Fig. 3b). Filtration was performed in several stages through two filter layers with a pore size of 2−3 μm.

The agglomerated particles of the dried insoluble sediment contain ~80 wt % iridium and ~5 wt % gallium.

CONCLUSIONS

Using the Ga−Ir system as an example for metallic systems with platinum-accompanying metals, we showed that the problem of transformation of chemically inert iridium into a soluble form can be solved using mechanochemical synthesis of the intermetallic compounds of Ir with liquid Ga followed by the extraction of gallium from them into acid solutions. Being a surfactant with respect to iridium, liquid gallium propagates along the grain boundaries of polycrystalline iridium particles during activation and, hence, sharply decreases their strength. As a result, the contact surface between solid iridium and liquid gallium increases, which leads to active formation of IMC on it. Chemically active gallium was shown to pass from an IMC to a solution during treatment by a mixture of concentrated acids, the reactivity of iridium increases, and more than 30% of iridium transforms into a soluble form in the form of H_xIrCl_y ($H_2Ir^{4+}Cl_6$) complexes.

REFERENCES

1. A. Yermakov, P. Panfilov, and R. Adamesku, "The main features of plastic deformation of iridium single crystals," J. Mater. Sci. Lett. **9**, 696−697 (1990).
2. M. A. Dombrovskaya, D. G. Lisienko, E. D. Kubrina, A. S. Kazakov, and E. P. Aleksandrov, "Validation of spectral analysis of iridium for a metal nanopowder," Zavod. Lab. **81** (1-II), 62−64 (2015).
3. S. S. Hecker, D. L. Rohr, and D. F. Stein, "Brittle fracture in iridium," Metall. Trans. A **9** (4), 481−488 (1978).
4. N. I. Timofeev, A. V. Ermakov, V. A. Dmitriev, and P. E. Panfilov, *Fundamentals of Metallurgy and Tech-*

nology of Manufacturing Products from Iridium (UrO RAN, Yekaterinburg, 1996).

5. L. B. Hunt, "A history of iridium," Platinum Metals Review **31** (1), 32–41 (1987).

6. S. I. Ginzburg, N. A. Ezerskaya, I. V. Prokof'eva, N. V. Fedorenko, V. I. Shlenskaya, and N. K. Bel'skii, *Analytical Chemistry of Platinum Metals*, Ed. by I. P. Alimarin (Nauka, Moscow, 1972).

7. I. K. Kakovskii and Yu. M. Potashnikov, in *Kinetics of Dissolution* (Metallurgiya, Moscow, 1975), pp. 126–138.

8. R. C. Hugo and R. Hoagland, "In situ TEM observation of aluminum embrittlement by liquid gallium," Scripta Mater. **38** (3), 523–529 (1998).

9. R. C. Hugo and R. Hoagland, "Penetration of aluminum: in situ TEM observation at the penetration front," Scripta Mater. **41** (12), 1341–1346 (1999).

10. T. F. Grigoreva, A. P. Barinova, and N. Z. Lyakhov, *Mechanochemical Synthesis in Metal Systems* (Parallel', Novosibirsk, 2008).

11. *Phase Diagrams of Binary Metallic Systems: A Handbook*, Ed. by N. P. Lyakishev (Mashinostroenie, Moscow, 1997), Vol. 2.

12. R. V. Ivanova, *Chemistry and Technology of Gallium* (Metallurgiya, Moscow, 1973).

13. A. R. Miedema, "On the heat of formation of solid alloys (II)," J. Less-Common Met. **46** (1), 67–83 (1976).

14. A. R. Miedema, P. F. de Chatel, and F. R. de Boer, "Cohesion in alloys—fundamentals of a semi-empirical model," Physica B **100**, 1–28 (1980).

15. H. Bakker, "Miedema's semi-empirical model for estimating enthalpies in alloys," Mater. Sci. Briefings **1**, 1–80 (1988).

16. A. P. Savitskii, *Liquid-Phase Sintering of Systems with Interacting Components* (Nauka, Novosibirsk, 1991).

17. B. D. Summ and Yu. V. Goryunov, *Physicochemical Fundamentals of Wetting and Spreading* (Khimiya, Moscow, 1976).

18. S. P. Yatsenko, *Gallium. Interaction with Metals* (Nauka, Moscow, 1974).

Translated by K. Shakhlevich