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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Structural Transformations in Mechanochemical Synthesis of Solid Solutions in the Cu–Ga System

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Abstract—Formation of solid solutions in the copper–gallium system under mechanical activation is considered as an example of a mechanochemical interaction between a solid metal and a liquid metal.

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Analysis of published data shows that there are almost no reports devoted to the mechanochemical interaction of a solid metal and a liquid one. However, previous studies of the mechanochemical interaction in the Cu–Hg system have shown that the mechanochemical synthesis in systems of this kind is exceedingly efficient: this is indicated by the high rates of mechanochemical reactions difficultly performable in the solid state mode, synthesis of supersaturated solid solutions possessing a high excess free energy, and a number of other specific features characteristic of the mechanochemical interaction in this system [1–3].

It is known that liquid metals are the most effective surfactants with respect to solid metals and the dispersion of solid metals in the presence of those in the liquid state is markedly facilitated [4].

The good wettability of a solid metal by a liquid one provides a large area of the contact surface between the reagents. At a sufficient amount of the solid phase, almost the entire surface of the solid-phase component is involved in the contact, whereas in interaction of solid phase, the contact surface area constitutes 10–5–10–4 of the total area [5].

The aim of the study was to examine the mechanochemical interaction in the system constituted by solid copper and liquid gallium at a small content of the liquid phase (concentration range of solid solutions).

EXPERIMENTAL

The mechanochemical synthesis in the copper–gallium system from powdered copper PMS-1 and gallium [GOST (State Standard) 12797–77] was performed in an AGO-2 high-energy water-cooled planetary ball mill in the atmosphere of argon (drum volume 250 cm^3, ball diameter 5 mm, charge 200 g, weighed portion of a sample being treated 10 g, revolution rate of drums about the common axis ~1000 rpm).

An X-ray phase analysis was made using a URD-63 diffractometer equipped with a graphite monochromator (CuKα radiation).

The X-ray diffraction studies were carried out in situ[1] by the method in which a pencil beam (0.4 × 0.4 mm) of monochromatic radiation (λ = 0.3686 Å) is passed through a thin layer of a sample and yields a diffraction pattern recorded by a planar 2D detector. In the case in

[1] The study was carried out at a station of the 4th synchrotron radiation beamline of VEPP-3 storage ring at the Siberian center of synchrotron radiation, Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences.

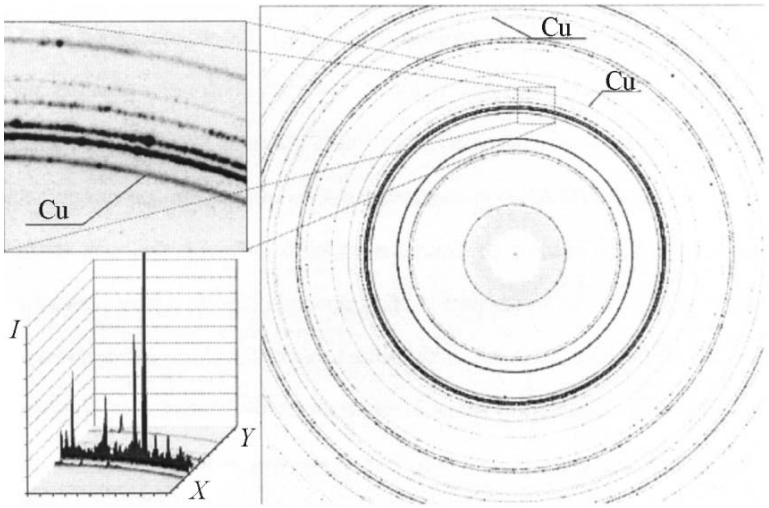

Fig. 1. X-ray diffraction pattern of the reaction product of powdered copper with liquid gallium, measured 2 days after mixing the components. Right panel: general view of the diffraction pattern; left panel: selected fragment in magnified 2D and 3D representations. Unmarked reflections belong to the intermetallide $CuGa_2$.

question, this was done using a detector system based on a Marresearch MAR-345 storage screen.

Precision X-ray diffraction studies were carried out using the method of recording in parallel beams.[2] The high degree of monochromatization was provided by a double silicon monochromator cutting off the fluorescent radiation from the diffracted beam and acting as a narrow slit with an angular resolution equal to the width of the rocking curve of the crystal used (~0.001°). The precision diffraction studies provided a high-accuracy information about the lattice constants of the phases under study.

Electron-microscopic studies were performed on a JSM-T20 electron microscope and JEM-2010 and JEM-400 high-resolution electron microscopes.

According to the equilibrium phase diagram, there are several intermetallic compounds and a rather wide concentration range of solid solutions in the Cu–Ga system [6]. In the interaction of its components, chemical reactions can occur to give any of the intermetallic phases present in the system. The enthalpies of mixing were calculated for alloys of the corresponding compositions by the Miedema method [7–9]. The enthalpies of the reactions in the Cu–Ga system, considered in the study, are negative:

$$\text{Cu} + 10\ \text{at\% Ga} \rightarrow \text{Cu(Ga)} - \text{solid solution},$$
$$\Delta H^\circ_{\text{form}}\ (\text{Cu} + 20\ \text{at\% Ga}) = -9\ \text{kJ mol}^{-1}; \qquad (1)$$

$$\text{Cu} + 20\ \text{at\% Ga} \rightarrow \text{Cu}_9\text{Ga}_4 + \text{Cu},$$
$$\Delta H^\circ_{\text{form}}\ (\text{Cu} + 34\ \text{at\% Ga}) = -13\ \text{kJ mol}^{-1}; \qquad (2)$$

$$\text{Cu} + 20\ \text{at\% Ga} \rightarrow \text{CuGa}_2 + \text{Cu},$$
$$\Delta H^\circ_{\text{form}}\ (\text{Cu} + 66\ \text{at\% Ga}) = -11\ \text{kJ mol}^{-1}. \qquad (3)$$

If the components, powdered copper and liquid gallium, are mixed at a temperature of 37°C without mechanical activation (MA), an intermetallide $CuGa_2$ is formed immediately after the mixing and there remains an unreacted part of copper. According to experimental observations, only reaction (3) proceeds to complete consumption of gallium. The growth rate of the intermetallide $CuGa_2$ is the highest in the first 20 min. Then, the growth rate gradually decreases. The process is complete in 48 h. By that time, the interaction with copper results in that the whole initial amount of gallium disappears to give the intermetallide $CuGa_2$ as the synthesis product. The X-ray diffraction pattern obtained using a 2D X-ray detector (see Fig. 1) provides information about the sizes of crystallites present in the sample. It can be seen that the width of the reflections associated with the resulting intermetallide $CuGa_2$ is many times more than that of the reflections for the starting copper powder. In addition, the reflections constituting a diffraction ring show a wide scatter of the diffracted radiation intensities. It is known that, if the crystallite size exceeds 0.1–1 μm, separate points, rather than continuous rings, will be observed in the diffraction pattern. Thus, it can be concluded that the crystallite

[2] The studies were carried out at a station of the 2nd synchrotron radiation beamline.

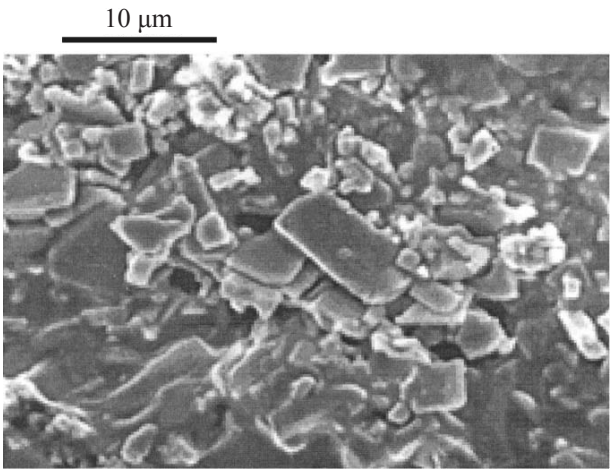

Fig. 2. Micrograph of the reaction product of powdered copper with liquid gallium, two days after mixing the components.

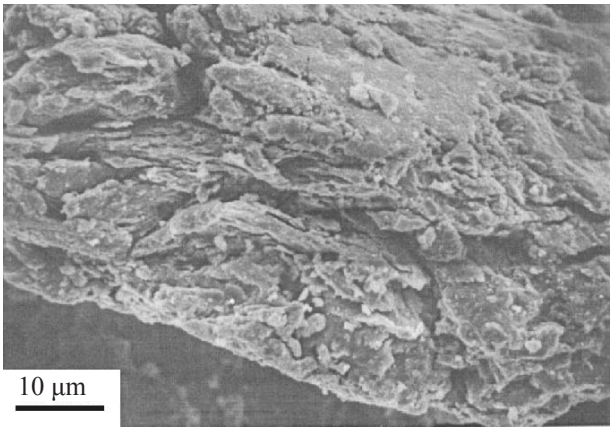

Fig. 3. Micrograph of a (Cu + 20 at % Ga) sample 10 s after activation.

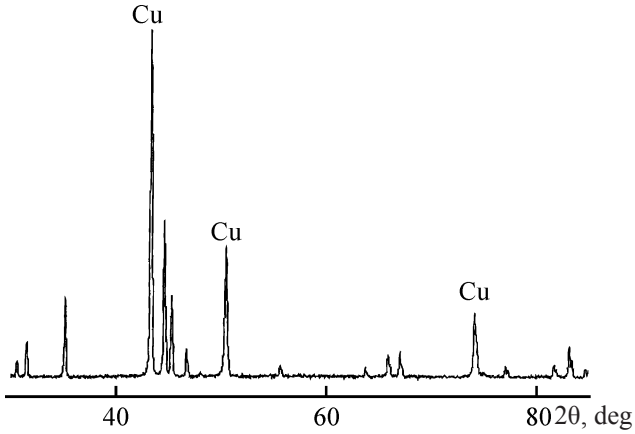

Fig. 4. X-ray diffraction pattern of a mixture of powdered Cu + 20 wt % Ga subjected to MA for 10 s. (θ) Bragg angle; the same for Fig. 5. Unmarked reflections belong to $CuGa_2$.

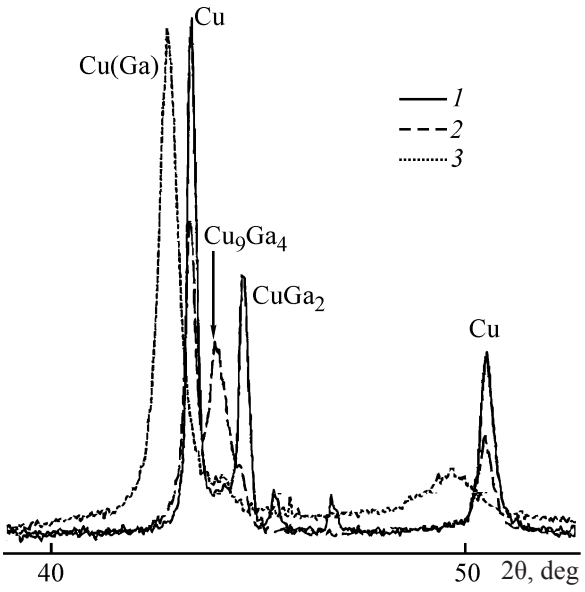

Fig. 5. X-ray diffraction pattern of a mixture of powdered Cu + 20 wt % Ga subjected to MA for (*1*) 1, (*2*) 3, and (*3*) 20 min.

size of the intermetallide $CuGa_2$ being formed may also exceed 0.1–1 μm.

An electron-microscopic image of the product formed in the interaction of copper with liquid gallium (Fig. 2) shows that the sample is for the most part composed of particles 1–5 μm in size, with separate particles being as large as 10 μm. The particles mostly have an irregular shape and are probably composed of several crystallites misoriented with respect to one another.

The part of copper unreacted with gallium remains in the pure form. Subsequent keeping at the same temperature for a month does not change the phase composition of the mixture, despite that only the region of solid solutions corresponds to its equilibrium state. The chemical interaction of powdered copper with liquid gallium without MA in a mixture formulated so as to obtain a solid solution yields only an intermetallide with the highest content of gallium, despite the excess of copper. Under the MA conditions, the interaction of powdered copper with liquid gallium yields the intermetallide $CuGa_2$ already in 10 s (Fig. 3). In the process, its content in the mixture corresponds to that amount which is formed without MA only after several hours of keeping. The diffraction reflections from the phase formed indicate that it is in the crystalline state, with the size of the X-ray coherent scattering regions also exceeding 100 nm.

The lattice constants ($a = 0.2827$ nm, $c = 0.5824$ nm) of the compound $CuGa_2$ synthesized by mechanical doping

are close to tabulated values (tetragonal lattice, a = 0.2836 nm, c = 0.5843 nm). The diffraction lines of copper are almost not broadened, whereas their intensity somewhat decreases. The lattice constant of copper also remains unchanged and close to tabulated data (a = 0.36151 nm). Electron-microscopic studies demonstrated that particles of the product formed after 10 s of MA of a Cu + 20 at % Ga mixture have micrometer sizes and lamellar structure (Fig. 4). Upon an increase in the activation time to 20 s, the morphology of the product remains nearly unchanged, although an X-ray phase analysis demonstrates that, during this time, almost the whole amount of gallium is consumed to give the intermetallide $CuGa_2$.

The subsequent MA is accompanied, by the end of the first minute, by the appearance of the Cu_9Ga_4 phase, with the intensity of reflections from both the $CuGa_2$ phase and copper starting to decrease (Fig. 5). After 3 min of activation, the Cu_9Ga_4 phase is preserved according to the diffraction pattern, whereas the diffraction reflections from the intermetallide $CuGa_2$ disappear nearly completely. The intensity of the diffraction reflections from copper markedly decreases. However, the angular positions of the lines remain unchanged, which indicates that no copper-based solid solutions are formed (Fig. 5).

The lattice constant of the intermetallide Cu_9Ga_4 synthesized by mechanical activation, equal to 0.8731(3) nm, corresponds to a Ga content of 33%. The X-ray coherent scattering regions in this intermetallide are substantially smaller (16–18 nm) than those for the compound $CuGa_2$.

The formation rate of the intermetallide Cu_9Ga_4 is substantially lower than that of the $CuGa_2$ phase. Further activation leads to a decrease in the intensity of diffraction reflections from the compound Cu_9Ga_4 and gives rise to reflections indicating that copper-based solid solutions are formed. The amount of the solid solution gradually grows, and in 20 min, the product of the mechanical activation is a solid solution with a fcc lattice and trace amounts of the Cu_9Ga_4 phase. The noticeable increase in the width of the reflections from the solid solution points to its variable composition. The average lattice constant of the solid solution is 0.3667 nm (for pure copper, a = 0.3615 nm). An electron diffraction analysis demonstrated that the product formed is to a solid solution, in agreement with X-ray diffraction data. High-resolution micrographs show stacking faults and microdistortions.

CONCLUSIONS

(1) On mixing powdered copper with liquid gallium, taken in amounts from which a (Cu + 20 at % Ga) solid solution should be formed, an intermetallide, $CuGa_2$, is obtained and there remains unreacted copper.

(2) In mechanical activation of a similar mixture, a series of successive reactions is observed. The first stage, formation of the intermetallide $CuGa_2$ (ΔH_{form}= –11 kJ mol^{-1}), continues to complete consumption of gallium (1 min). The second stage, formation of the intermetallide Cu_9Ga_4 (ΔH_{form} = –13 kJ mol–1) continues to complete consumption of the intermetallide $CuGa_2$ (3 min). The third stage, formation of a solid solution (ΔH_{form} = –9 kJ mol^{-1}), ends in complete consumption of the intermetallide Cu_9Ga_4 (20 min). All the phases formed belong to the low-temperature part of the equilibrium phase diagram of the Cu–Ga system.

(3) Despite that the enthalpy of mixing in the Cu–Ga system is negative for all the concentration regions, a stage-by-stage analysis shows that the final stage of the mechanochemical interaction of copper and gallium is the formation of a solid solution from the most stable intermetallic phase.

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