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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

How the Tin Concentration Affects the Interactions of Intermetallic Compounds of the Cu–Sn System with Liquid Gallium and a Gallium–Tin Eutectic

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Abstract—Interactions in the copper–gallium–tin ternary system are studied. New phase formation involves the step of dissolution of solid copper alloys in a liquid phase. The induction period of tin segregation in an autonomous phase depends on tin concentration in the feed. The formation of solid solution of gallium in tin is suggested.

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Interactions of copper powders with liquid gallium are known to yield $CuGa_2$ immediately after they are mixed [1–3]. In interactions of copper with two-component gallium eutectics, the phase next after the intermetallic compound should be formed of the elements released from the eutectic:

$$Cu + (Ga + 12\%\ Sn) \rightarrow CuGa_2 + Sn,$$

$$Cu + (Ga + 24.5\%\ In) \rightarrow CuGa_2 + In.$$

It is pertinent that while the first phase ($CuGa_2$) appears immediately after the components are mixed , the next phase requires a certain time to be formed, that is, an induction period, after which its formation occurs very rapidly. The induction period provides enough time for most part of the $CuGa_2$ to form [4]. Similar results were obtained in studying the interaction of a solid solution of tin in copper with a liquid gallium–tin eutectic [5]. Presumably, the dissolution of the solid phase in the liquid phase occurs after mixing a solid copper powder with the liquid eutectic, and while $CuGa_2$ starts to form immediately, tin piles up in liquid gallium, thanks to its good solubility in liquid gallium and the absence of intermetallic compounds in the Ga–Sn system, and its crystallization starts only as gallium is consumed in intermetallic compound formation and once tin concentration in gallium reaches a certain critical value. This suggestion being true, an increase in tin concentration in the Cu–Sn–Ga system would shorten the induction period and increase the formation rate of the second phase.

The equilibrium phase diagram of the Ga–Sn system [6] teaches that, as tin is soluble in gallium, gallium is soluble in tin, too. In this case, the second phase can be formed as a solid solution.

This work studies the effect of the tin concentration in the initial Cu–Sn–Ga system on the formation rate and composition of the second phase during the interaction of mechanochemically synthesized intermetallic compounds of the Cu–Sn system with liquid gallium and a gallium–tin eutectic.

EXPERIMENTAL

Copper and tin intermetallic compounds of various compositions were prepared mechanochemically from appropriate mixtures of copper (PMS-1) and tin (POE) powders in an AGO-2 water-cooled high-power planetary mill in an argon atmosphere. The drum volume was 250 cm^3; ball diameter was 5 mm; ball load: 200 g; sample size: 10 g; drum rotation speed around a common axis: 1000 rpm.

Diffraction studies were carried out at the station of the 4th SR channel of the VEPP-3 storage ring at the Siberian Synchrotron Radiation Center, the Institute of Nuclear Physics, Siberian Branch of Russian Academy of Sciences. A method was used where a thin (0.4×0.4 mm) monochromatic beam ($\lambda = 0.3686$ Å) passes through a thin layer of the material and gives a diffraction pattern recorded by a flat area detector. The diffracted beam was detected by a detector system based on a MAR345 image plate detector (Marresearch).

Precision diffraction studies were carried out at the station of the 2nd SR channel using a parallel beam mode. Such studies gain high-precision data on the unit cell parameters of test samples.

Calorimetric studies were perform on a NETZSCH STA 409 PC/PG instrument under an

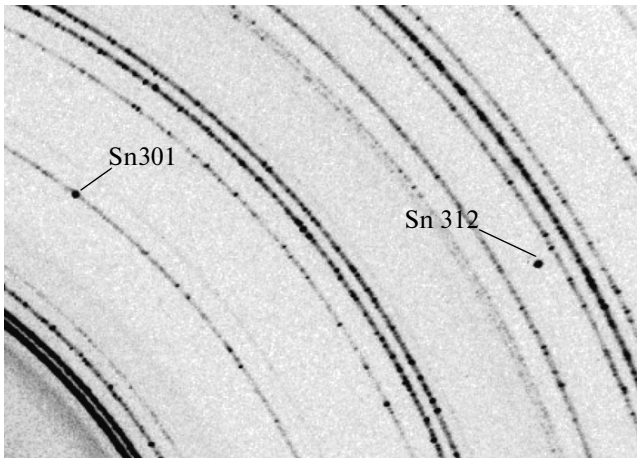

Fig. 1. Fragment of the diffraction pattern from the products of the interaction of the solid solution of gallium in tin with liquid gallium. All unlabeled reflections belong to intermetallic $CuGa_2$.

argon atmosphere in an Al_2O_3 crucible in the temperature range from room temperature to 290°C at a heating rate of 20 K/min.

RESULTS AND DISCUSSION

We have studied the interactions of samples having compositions of Cu + 20% Sn (supersaturated solid solution), Cu + 39% Sn (Cu_3Sn), and Cu + 61% Sn (Cu_6Sn_5) with gallium and a gallium–tin eutectic of composition Ga + 12% Sn. (Hereafter, all compositions are expressed in weight percent.)

The system having the least tin content of the solid-phase component (20%) was studied first. In agreement with the previous suggestion, tin would pile up in liquid gallium as the solid solution decomposition progresses; its concentration would also increase on account of gallium consumption in $CuGa_2$ formation.

In the case at hand, tin segregation into an autonomous phase occurred 30 h after the components were mixed (Fig. 1). In the diffraction pattern, the tin phase is represented by individual crystallites.

Though the reflections from tin are stronger than the reflections from intermetallic compounds, tin reflections are virtually undistinguishable from the background when the diffraction pattern is integrated over the diffraction angles. When integration is confined to the section in which a single reflection is positioned rather than integrating over the entire range of the angles, then this reflection will be well distinguishable on the resulting diffraction pattern. When the tin concentration in the Cu–Sn–Ga reaction system becomes higher on account of using a gallium–tin eutectic as the liquid phase (this means that tin is initially contained in the liquid phase), the induction period shortens considerably. In this case, tin is segregated into an autonomous phase 4 h after the components were mixed (Fig. 2).

Figure 3 displays data on the phase formation dynamics gained by fitting the integrated intensities of the relevant diffraction lines. This figure makes it clear that the reflection intensity first rises very rapidly after the induction period, but then drops also rapidly.

In elucidating how the increasing tin concentration in the solid phase component influences the process

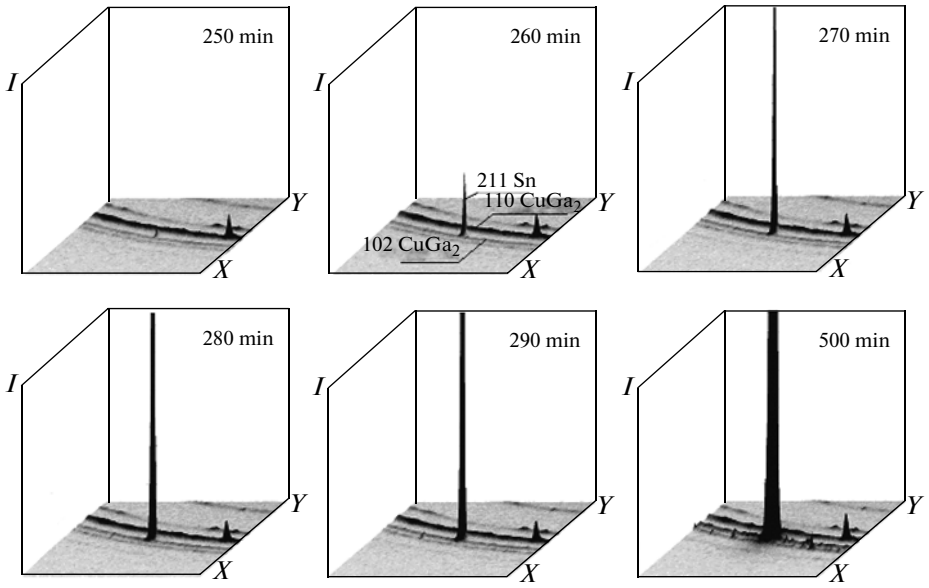

Fig. 2. Fragments of the diffraction patterns from the products of the interaction of the solid solution of gallium in tin with the gallium–tin eutectic recorded in various periods of time after mixing the components.

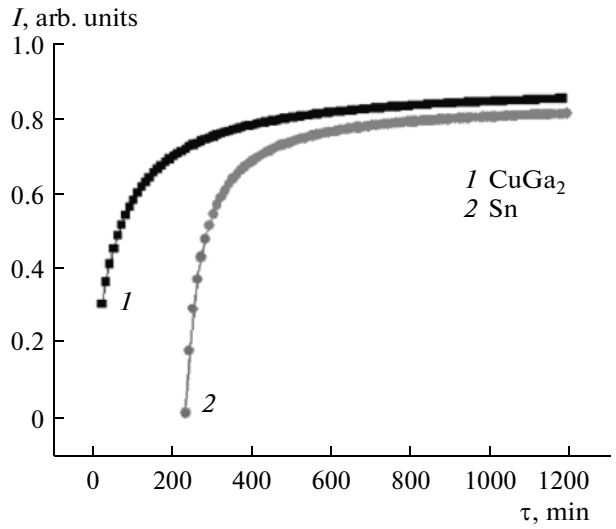

Fig. 3. Phase formation dynamics during the Cu(Sn) + $(Ga–Sn)_L$ = $CuGa_2$ + Sn reaction.

dynamics and the characteristics of the resulting phases, we used intermetallic compounds prepared by mechanochemical activation of copper with 39 and 61% tin as solid phase components.

The sample prepared by mechanochemical synthesis of the first composition is the Cu_3Sn intermetallic compound as identified by powder X-ray diffraction. The sample prepared from a Cu + 61% Sn mixture, comprises a single phase of the Cu_6Sn_5 intermetallic compound. The steps of mixing the components to a homogeneous material, applying this material to the holder of the goniometer head, adjustment, and exposure take about 10 min. Even the first diffraction pattern from the reaction products of Cu_3Sn with the gallium–tin eutectic measured after the component are mixed, shows reflections from $CuGa_2$ and tin (Fig. 4). Over time, the tin reflections increase in number, size, and intensity. In 10 h, all gallium from the eutectic melt is consumed in $CuGa_2$ formation and the chemical interactions in the system stop. The interactions

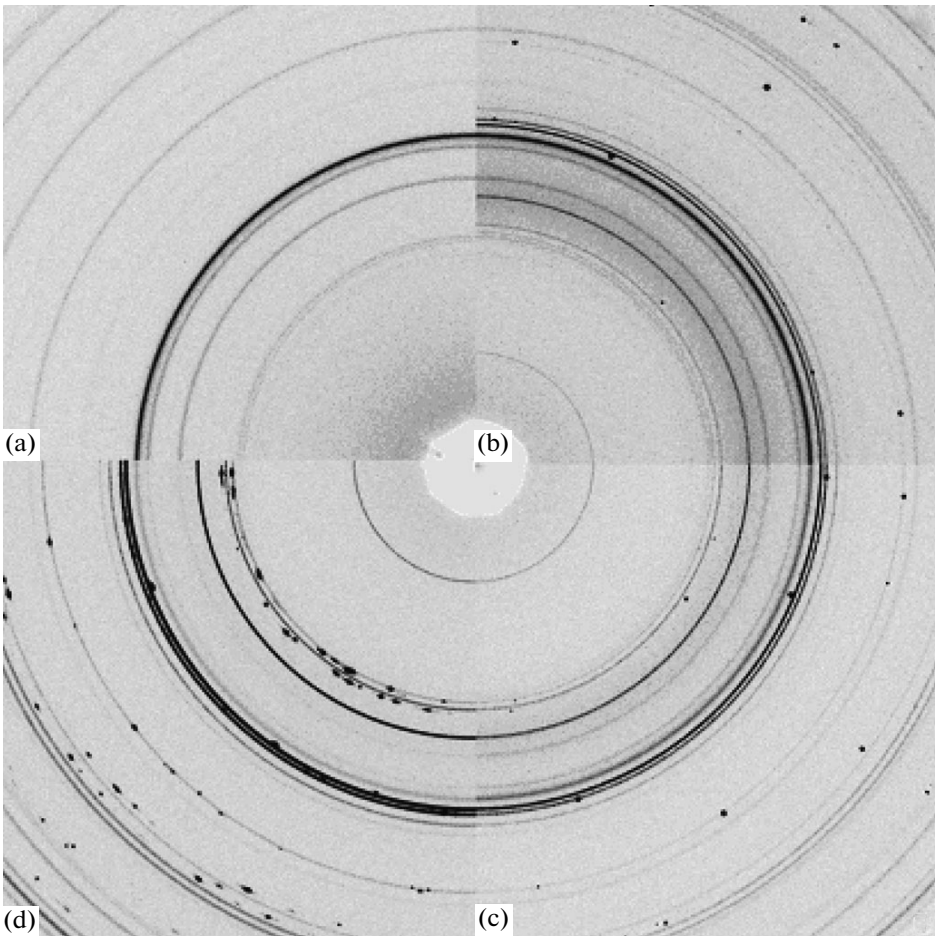

Fig. 4. Fragments of the diffraction patterns from the products of the interaction of a Cu + 39% Sn powder with the Ga + 12% Sn eutectic: (a) the initial mechanochemically prepared intermetallic compound and (b) 10 min, (c) 1 h, and (d) 10 h after mixing the components. All separate reflections belong to tin.

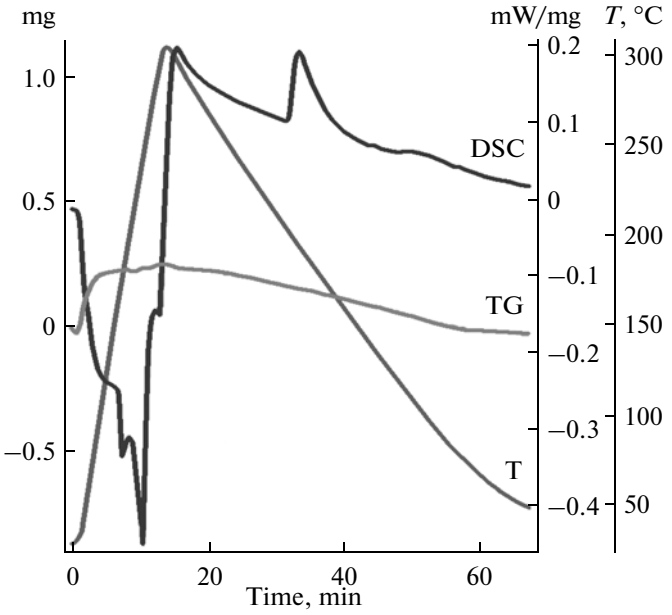

Fig. 5. Thermoanalytical curves for a (Cu + 20% Sn) + (Ga + 12% Sn) sample.

produce the new phases of intermetallic $CuGa_2$ and tin. The constituent phases of the reaction product have diverse particle sizes. Intermetallic $CuGa_2$ has particle sizes of at most 1 μm; tin has far coarser particles.

During the interaction of mechanochemically synthesized Cu_6Sn_5 with the liquid gallium–tin eutectic (that is, in a mixture having the highest tin concentration), $CuGa_2$ formation and tin segregation into an autonomous phase also occur starting with the very first minutes. The interaction rate is rather high, and 2 h after mixing no changes are observed in diffraction patterns. Initially extended reflections transform during the reaction to become separate and pointlike. Because the reflections from $CuGa_2$ form continuous rings, we may infer that the crystallize sizes are less than 0.1 μm.

Thus, while tin concentrations in the system are less than 20–30%, tin appears as an autonomous phase after some induction period. The reflections from both the intermetallic compound and tin have high intensities. The increasing tin concentration in the system shortens the induction period for the crystallization of a tin phase to become undetectable under our conditions. Reflections from both the tin phase and the intermetallic phase decrease in size.

For all systems studied, powder X-ray diffraction shows that the interaction products in the Cu–Sn–Ga system are mixtures of $CuGa_2$ and tin crystallites; however, thermal studies of these products, where chemical processes occurred at room temperature, show that four endotherms on the relevant thermoanalytical curves without considerable weight change (Fig. 5). The first appearing endotherm (~120°C) may be associated with melting of the solid solution of gallium in tin, and the further cascade with melting of tin and structural alterations in $CuGa_2$.

To verify the suggestion about the occurrence of the solid solution of gallium in tin in the product, we carried out precision measurements of the tin unit cell parameter. The resulting values ($a = 5.8063 \pm 0.0004$ Å, $c = 3.1697 \pm 0.0004$ Å) slightly differ from tabulated values ($a = 5.831$ Å, $c = 3.181$ Å).

The aforementioned two facts allow us to suggest that the solid solution of gallium in tin is formed as a second phase during the interaction of copper–tin alloys with gallium or the gallium–tin eutectic.

In summary, our studies have shown that the interactions of copper and tin intermetallic compounds with gallium and liquid gallium eutectics involve the dissolution of the intermetallic compounds in the liquid metal. The induction period preceding tin segregation into an autonomous phase shortens as the tin concentration in the system increases to disappear when the tin concentration reaches 40%. By the strength of calorimetric and X-ray diffraction data, we suggest that the second phase is the solid solution of gallium in tin.

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