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Chemical Interaction of Cu–In, Cu–Sn, and Cu–Bi Solid Solutions with Liquid Ga–In and Ga–Sn Eutectics

A. I. Ancharov[a], T. F. Grigorieva[a], S. V. Tsybulya[b], and V. V. Boldyrev[b]

[a] *Institute of Solid-State Chemistry and Mechanochemistry, Siberian Division, Russian Academy of Sciences, ul. Kutateladze 18, Novosibirsk, 630128 Russia*

[b] *Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia*

e-mail: ancharov@mail.ru

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Abstract—The reactions of copper-based Cu–In, Cu–Sn, and Cu–Bi solid solutions with liquid Ga–In and Ga–Sn eutectics have been studied in situ by synchrotron x-ray diffraction. The results indicate that the dynamics of the process and the phase composition, grain size, and microstructure of the resulting materials depend on the components of the solid solution and eutectic.

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INTRODUCTION

Chemical interaction of powdered metals and alloys with liquid gallium eutectics is basic to diffusion-hardening solders. In such multicomponent systems, several intermetallic phases form in parallel or in sequence, influencing the phase formation process and the properties of the resulting material. For example, in the reaction of gallium metal (t_m = 29.9°C) or gallium-containing eutectics with metal (copper, nickel, and other) powders at ≃35°C, the first to form is an intermetallic phase with the highest possible gallium content. The reaction proceeds until this phase is fully consumed [1–4]. If a gallium eutectic is used as the liquid metallic phase, the transfer of gallium from the eutectic to the forming intermetallic phase is accompanied by the liberation of the other component of the eutectic. Also, if the solid phase is an alloy rather than a pure metal, one component of the alloy reacts with gallium, while the other is liberated. As a result, there are free metals from the eutectic and alloy, which may also react to form an intermetallic compound.

Analysis of the literature indicates that this issue has not yet been addressed in sufficient detail. The formation sequence of intermetallic compounds in systems containing several intermetallics is unclear, and the factors governing this process are as yet not understood. It is unclear whether the metals liberated from the eutectic and alloy will crystallize or will react directly. Will the resulting phases undergo phase transitions? How will those components noninteracting with the other elements crystallize in the presence of the intermetallic compounds formed? Will the components liberated in this process influence the formation of the intermetallic compounds that appear first?

In this paper, we report in situ studies of reactions between copper-based solid solutions and liquid gallium eutectics and analyze the effects of the components present on the dynamics of the process and the phase composition, grain size, and microstructure of the resulting materials.

EXPERIMENTAL

In our preparations, we used copper powder (PMS-1), tin powder (POE), gallium (RF Standard GOST 12797-77), indium (RF Standard GOST 10297-94), bismuth (Technical Specifications TU 6-09-3616-82), 80 wt % Cu + 20 wt % Sn solid solution (in what follows, Cu⟨Sn⟩), 80 wt % Cu + 20 wt % In solid solution (Cu⟨In⟩), 90 wt % Cu + 10 wt % Bi solid solution (Cu⟨Bi⟩), 88 wt % Ga + 12 wt % Sn eutectic (L_E(Ga–Sn)), and 75.5 wt % Ga + 24.5 wt % In eutectic (L_E(Ga–In)). The solid solutions were prepared by mechanical alloying in a water-cooled AGO-2 high-energy planetary ball mill under an argon atmosphere, using 250-cm^3 grinding vials and 5-mm-diameter balls. The ball load was 200 g, and the sample weight was 10 g. The rotation rate of the supporting disk was ≃1000 rpm.

Reactions between powder solid solutions and liquid eutectics were studied by synchrotron x-ray diffraction (SXRD) using radiation from the fourth beamline at the VEPP-3 storage ring at the Siberian Synchrotron

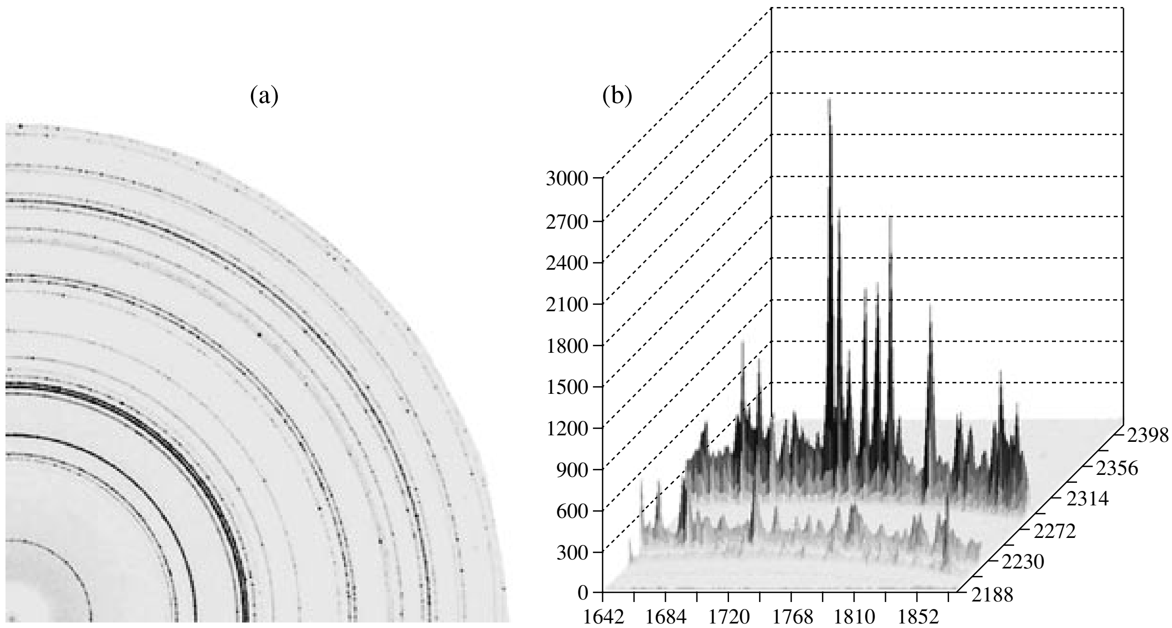

Fig. 1. Portions of the SXRD pattern from the alloy prepared by reacting solid copper and liquid gallium: (a) 2D diffraction pattern, (b) 3D representation of the diffraction pattern; *X* and *Y* are pixel coordinates in the detector system, and *Z* is the observed intensity in arbitrary units.

Radiation Centre (Budker Institute of Nuclear Physics, Siberian Division, Russian Academy of Sciences). At a wavelength $\lambda = 0.368$ Å, most diffraction peaks are situated at small diffraction angles and can be recorded using a 2D x-ray detector array. We used a Marresearch mar345 image plate detector and 0.4×0.4 mm x-ray beam. The sample–detector distance was 400 mm, the pixel size 0.1×0.1 mm, and the image plate diameter 345 mm. The read-out time at the smallest pixel size and largest scanned plate diameter was within 2.5 min, and the exposure time was 7.5 min. In this way, the formation of intermetallic compounds was monitored at 10-min intervals for a total of 24 h. The intersection of diffraction cones with the detector plate produces a set of concentric circles. In contrast to conventional diffractometers, which record only a narrow strip of the entire diffraction pattern, a plate detector records the entire diffraction pattern. Keeping the sample immobile, one can follow reflections from individual crystallites and evaluate their size and preferential alignment.

RESULTS AND DISCUSSION

First, we studied the reaction between copper powder and liquid gallium. As shown earlier [1–7], the product of this reaction is the intermetallic phase $CuGa_2$. SXRD examination showed that the forming $CuGa_2$ ranged very widely in crystallite size, as evidenced by the spots and arcs in Fig. 1a. The average crystallite size is difficult to evaluate from our data, but the material obviously consisted of both fine, poorly crystallized particles and large crystals (Fig. 1b).

In the reactions between the copper-based Cu–Sn solid solution and Ga–Sn eutectic and between the copper-based Cu–In solid solution and Ga–In eutectic, the liberated component is the same element.

In the former system, the reaction follows the scheme

$$Cu\langle Sn\rangle + L_E(Ga\text{–}Sn) \longrightarrow CuGa_2 + Sn.$$

The intermetallic compound $CuGa_2$ forms immediately after mixing the components, while reflections from Sn emerge 4 h after the beginning of the process, when the copper and gallium are, for the most part, bound. The intensity of these reflections then rises very rapidly (Fig. 2). After 24 h, the product consists of rather fine intermetallic particles (arcs in Fig. 3a) and large Sn crystals (spots in Fig. 3a). The corresponding diffraction pattern shows rather strong reflections from Sn and substantially weaker reflections from the intermetallic phase (Fig. 3b).

Our results indicate that the formation of the intermetallic compound is influenced by the liberated component. The crystallite size of the first-formed intermetallic compound ($CuGa_2$) is substantially smaller than that of Sn, with insignificant scatter. Since the reflections from Sn are far stronger than those from the starting powder, it is reasonable to assume that Sn crystallizes from a liquid phase.

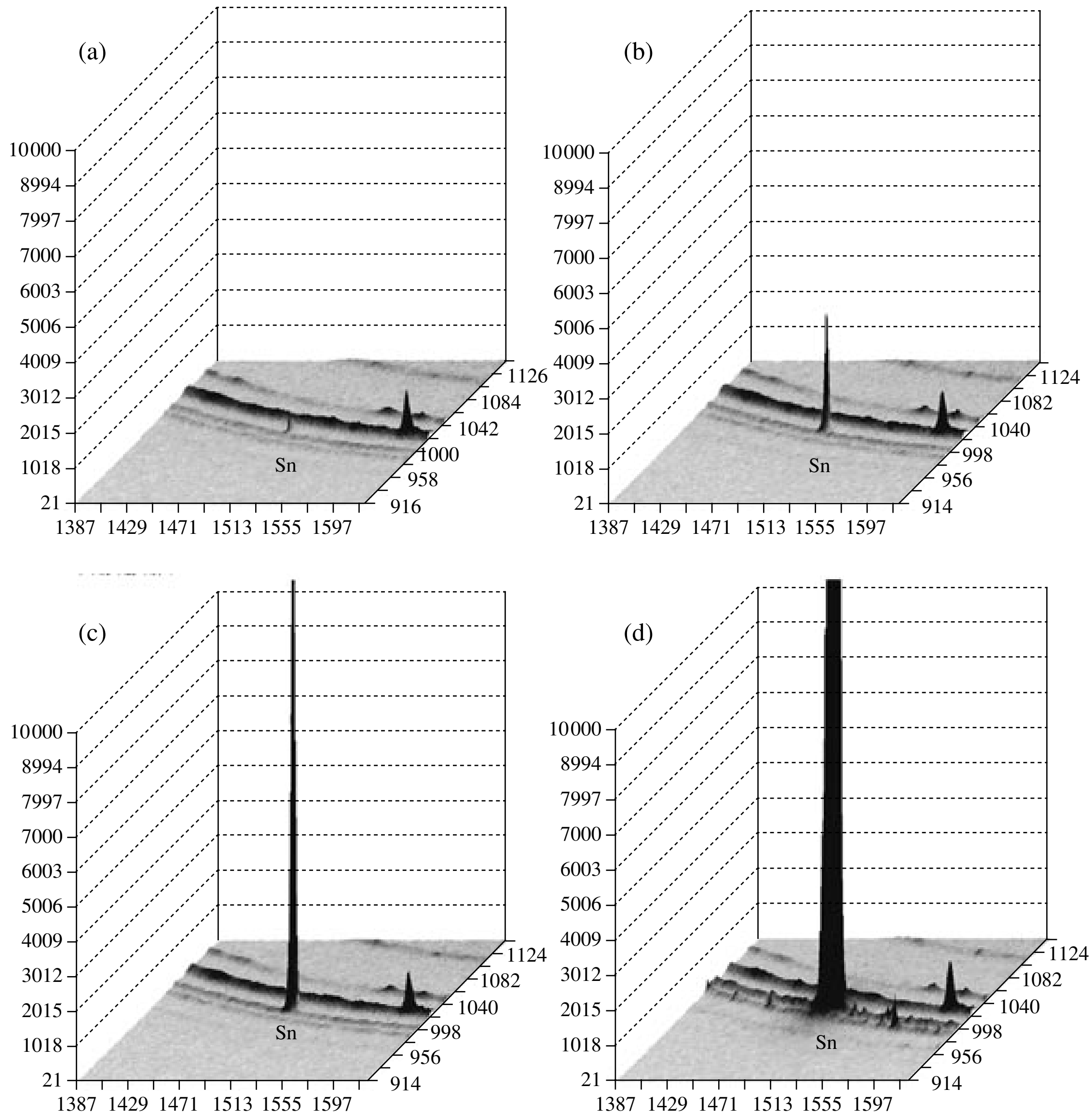

Fig. 2. Portions of SXRD patterns illustrating the time evolution of the reaction between a copper-based Cu–Sn solid solution and the liquid Ga–Sn eutectic; the time after mixing the components is (a) 250, (b) 260, (c) 270, and (d) 500 min; the same designations as in Fig. 1.

A similar effect was observed in the latter system, where the reaction followed the scheme

$$Cu\langle In\rangle + L_E(Ga\text{–}In) \longrightarrow CuGa_2 + In.$$

The intermetallic compound $CuGa_2$ was detected by SXRD immediately after mixing the mechanochemically synthesized solid solution Cu⟨In⟩ with the Ga–In eutectic and remained the only detectable phase during the first 230 min of reaction. Next, the diffraction pattern showed a reflection from indium (Fig. 4a), whose intensity then increased rapidly (Fig. 4). After 11 h, the reaction product consisted of microcrystalline $CuGa_2$ and coarse indium crystallites.

Thus, we obtained similar results in the two solid solution–liquid eutectic systems: the first to form is a microcrystalline intermetallic compound; then, after an induction period, the metal resulting from the reaction between copper and gallium appears. The metallic phase consists of much coarser grains in comparison with the starting powder and primary (intermetallic) phase.

To analyze reactions between a solid solution and liquid eutectic in systems where two different components are liberated, the same component being liberated from the liquid eutectic in one system and from the solid solution in the other system, we examined the reactions between the copper-based Cu–Sn solid solu-

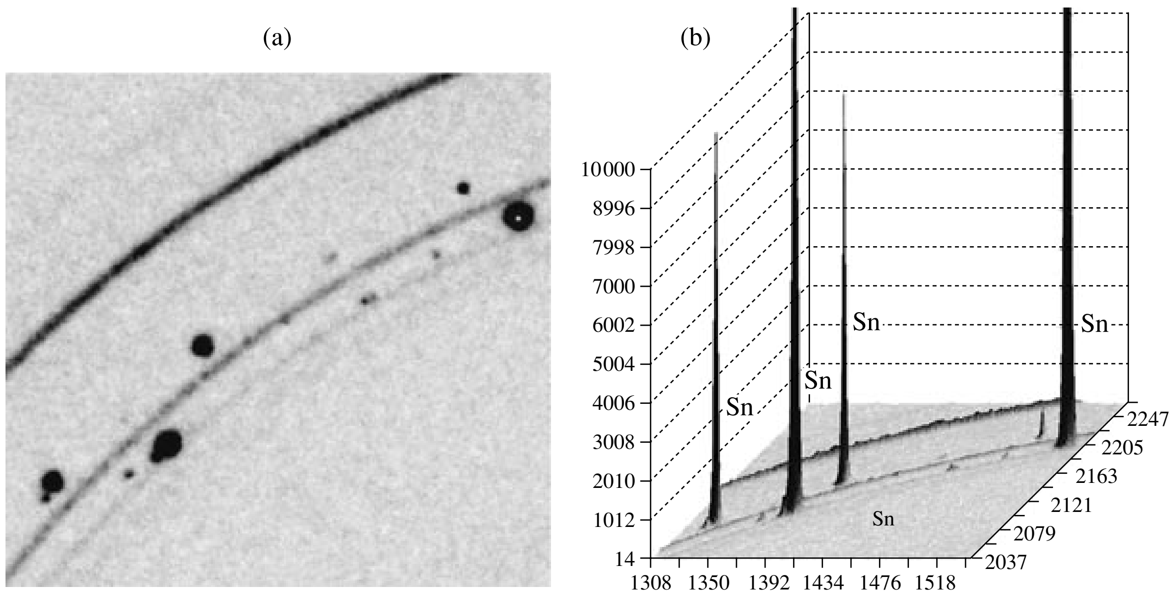

Fig. 3. Portions of the SXRD pattern from the end product of the reaction between a copper-based Cu–Sn solid solution and the liquid Ga–Sn eutectic; the same designations as in Fig. 1.

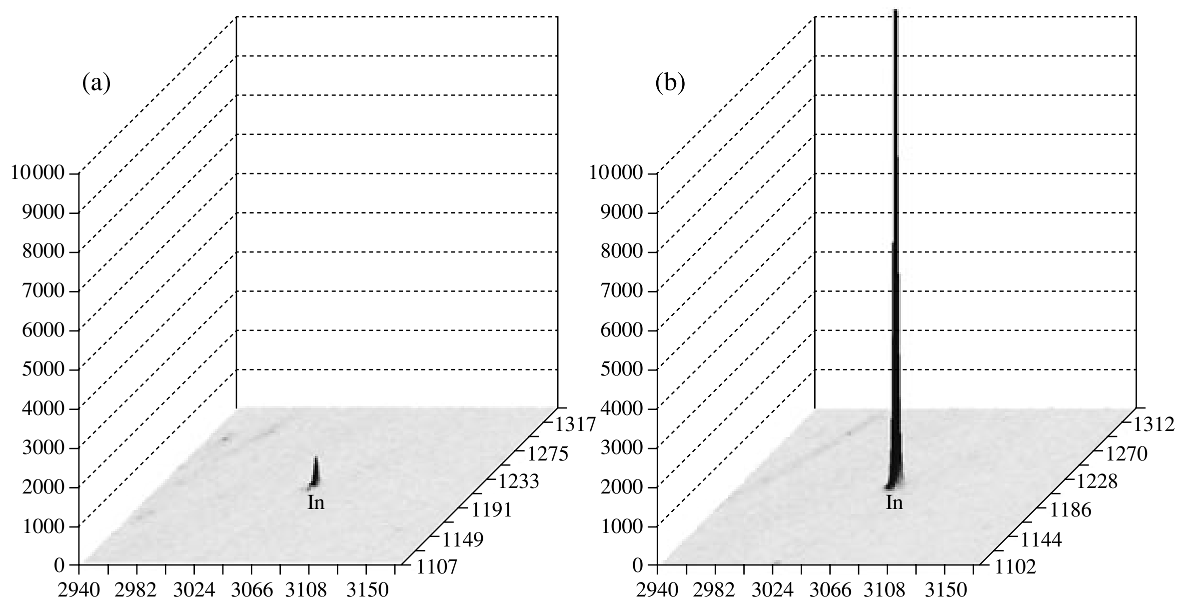

Fig. 4. Portions of SXRD patterns illustrating the time evolution of the reaction between a copper-based Cu–In solid solution and the liquid Ga–In eutectic; the time after mixing the components is (a) 210 and (b) 230 min; the same designations as in Fig. 1.

tion and Ga–In eutectic and between the copper-based Cu–In solid solution and Ga–Sn eutectic.

In both systems, the first to form, immediately after mixing, is $CuGa_2$. The liberated indium and tin may react with one another since, according to the equilibrium In–Sn phase diagram, this system contains two intermetallic compounds: In_3Sn and $InSn_4$. Indium and/or tin may also crystallize with no reaction. Thus, the following chemical reactions are possible in these systems:

$$\left.\begin{array}{l}\mathrm{Cu}\langle\mathrm{Sn}\rangle + L_E(\mathrm{Gu{-}In})\ \ (1)\\ \mathrm{Cu}\langle\mathrm{In}\rangle + L_E(\mathrm{Ga{-}Sn})\ \ (2)\end{array}\right\}$$

$$\longrightarrow\left\{\begin{array}{l}\mathrm{CuGa_2 + In_3Sn + Sn}\\ \mathrm{CaGa_2 + InSn_4 + In}\\ \mathrm{CuGa_2 + Sn + In.}\end{array}\right.$$

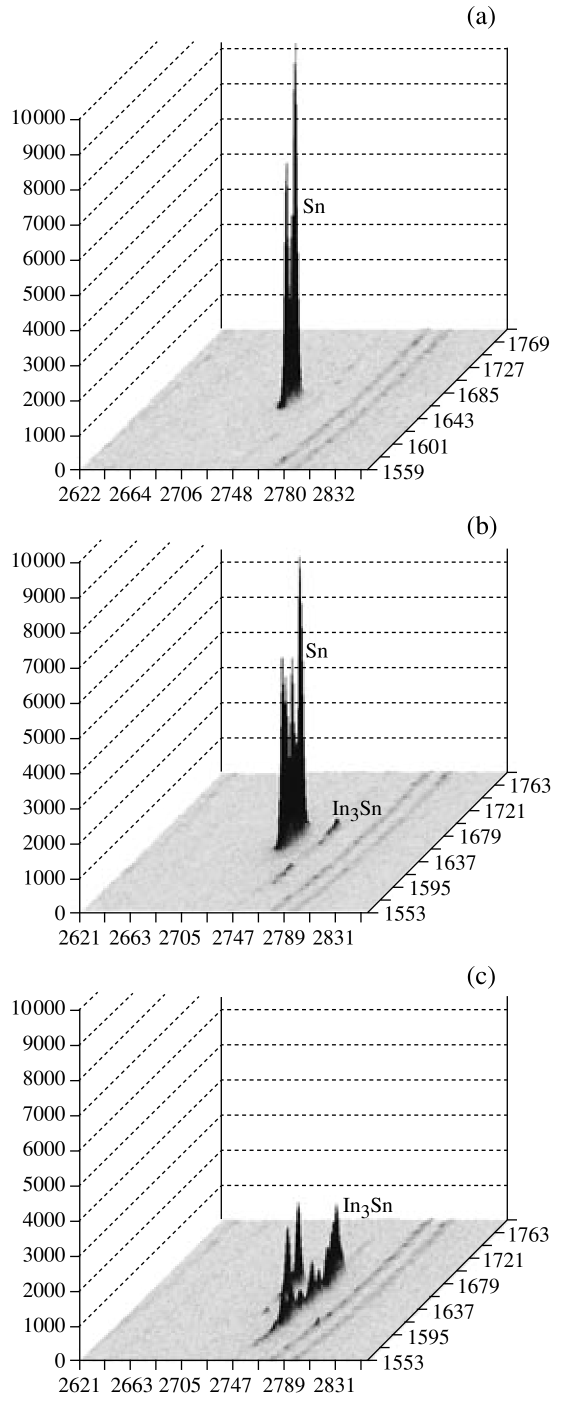

Fig. 5. Time evolution of the SXRD pattern after mixing powder of the mechanochemically synthesized copper-based Cu–Sn solid solution with the liquid Ga–In eutectic; reaction time of (a) 150, (b) 330, and (c) 350 min; the same designations as in Fig. 1.

In the former system, SXRD showed only grain growth of the intermetallic compound $CuGa_2$ during the first 140 min of reaction. After 140 min, a reflection from Sn emerged, and its intensity then increased rapidly (Fig. 5a). After 330 min, however, its intensity began to drop (Fig. 5b), and a reflection from the intermetallic compound In_3Sn emerged. Subsequently, its intensity increased, while the reflection from Sn vanished altogether (Fig. 5c). The disappearance of the reflection from Sn may be due to a tilt of the crystallite, resulting in a deviation from the Bragg angle. To rule out this effect, we took a diffraction pattern while rocking the sample by 15°. The diffraction pattern showed reflections from the intermetallic compounds $CuGa_2$ and In_3Sn but not from Sn.

Calculations indicate that the Sn could not be entirely bound in the intermetallic compound In_3Sn: since the reaction mixture contains roughly equal amounts of indium and tin, only part of the Sn could participate in the formation of the intermetallic compound. Therefore, most of the Sn was undetectable by SXRD.

Sn is liberated from the solid solution concurrently with the formation of the intermetallic compound $CuGa_2$ and can be detected by SXRD after 2 h of the reaction between the solid solution and eutectic, i.e., after most of the copper from the solid solutions has reacted with gallium to form $CuGa_2$. It is reasonable to assume that the Sn dissolved in the liquid gallium eutectic and that the rapid increase in the intensity of the reflections from Sn was due to its crystallization from the melt. The same is suggested by the large size of the Sn crystallites.

Free indium must appear in the system after all of the gallium is bound in $CuGa_2$. The absence of reflections from indium even after all of the gallium is combined with copper may be due to indium adsorption in the form of a thin, "liquidlike" layer on the surface of the $CuGa_2$ formed.

It is well known that the reaction between solid and liquid metals leads to the formation of an intermetallic phase which is richer in the component that is in the liquid (or liquidlike) state.

Therefore, in the case of liquid (or liquidlike) Sn, the forming intermetallic phase must be richer in Sn. To validate this assumption, we investigated the reaction between the copper-based Cu–In solid solution and liquid Ga–Sn eutectic. In this reaction, the liberated elements are the same as above, but indium is liberated from a solid phase, while tin, from the liquid eutectic as copper and gallium react to form the intermetallic compound $CuGa_2$.

SXRD examination showed that the intermetallic phase $CuGa_2$ appeared immediately after mixing the copper-based Cu–In solid solution with the liquid Ga–Sn eutectic. The intensity of the reflections from $CuGa_2$ increased very rapidly, and neither indium nor tin were detected during the first several (>8) hours of reaction.

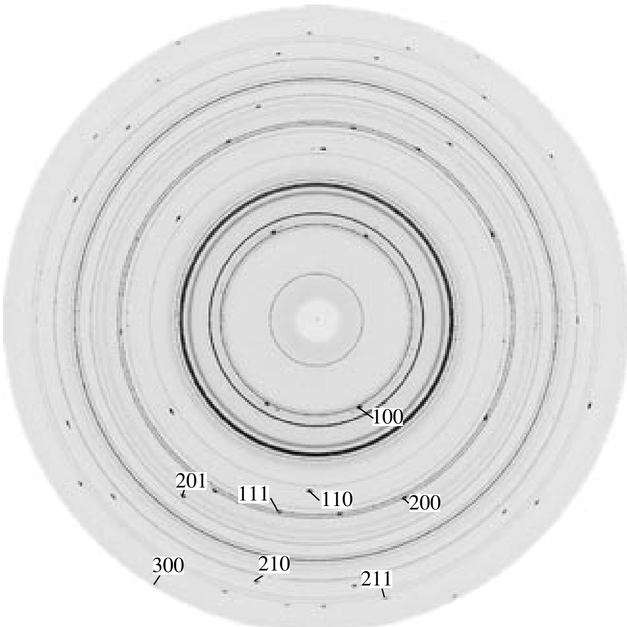

Fig. 6. SXRD pattern of the sample prepared by reacting a copper-based Cu–In solid solution with the liquid Ga–Sn eutectic for 24 h; the indexed rings are from the intermetallic phase $InSn_4$; the others are from $CuGa_2$.

After 8 h, the intermetallic phase $InSn_4$ appeared (Fig. 6), while crystalline indium was still missing. The formation of the intermetallic phase $InSn_4$ lends support to the above assumption.

Similar results were obtained for a mixture of the copper-based Cu–Bi solid solution and liquid Ga–Sn eutectic. In this system, several reactions are also possible:

$$\mathrm{Cu}\langle \mathrm{Bi}\rangle + L_E(\mathrm{Ga{-}In}) \longrightarrow \begin{cases} \mathrm{CuGa_2 + Bi + In}, \\ \mathrm{CuGa_2 + BiIn_2}, \\ \mathrm{CuGa_2 + BiIn + In}. \end{cases}$$

According to SXRD data, the reaction products in this system are bismuth metal and the intermetallic phases $CuGa_2$ and $BiIn_2$ (Fig. 7). This phase composition suggests that, like in the above system, indium is present in the form of a surface layer on intermetallic particles and may react with crystalline bismuth to form an indium-rich phase.

We also investigated a system in which the metals being liberated during $CuGa_2$ formation do not form intermetallic phases. The metals must then crystallize with no reaction:

$$\mathrm{Cu}\langle \mathrm{Bi}\rangle + L_E(\mathrm{Ga{-}Sn}) \longrightarrow \mathrm{CuGa_2 + Bi + Sn}.$$

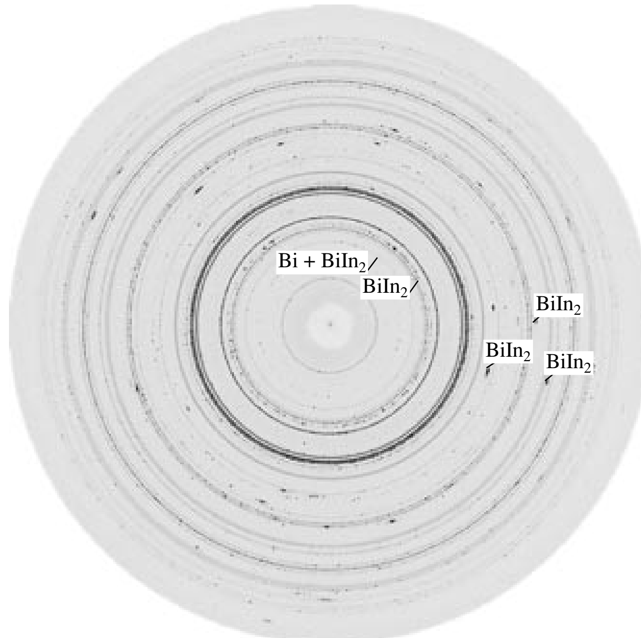

Fig. 7. SXRD pattern of the sample prepared by reacting a copper-based Cu–Bi solid solution with the liquid Ga–In eutectic.

The formation of $CuGa_2$ in this system must be accompanied by Bi and Sn liberation, since the Bi–Sn phase diagram has no intermetallic compounds. Indeed, SXRD results show that the reaction products in this system are $CuGa_2$, Bi, and Sn (Fig. 8).

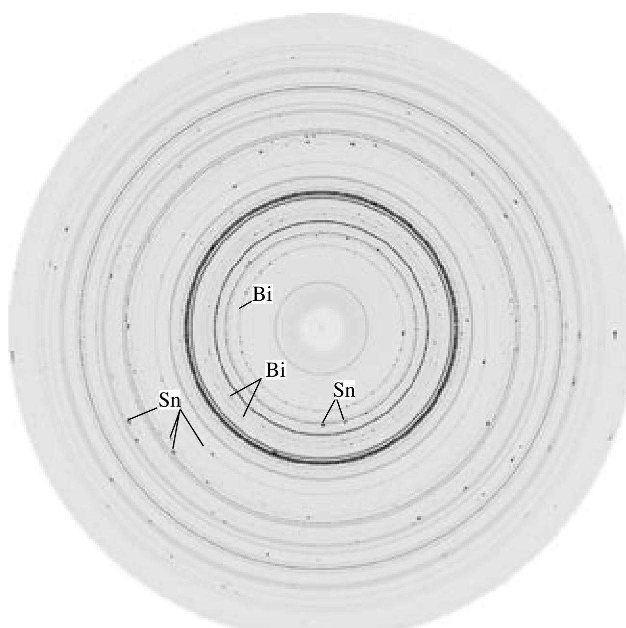

Fig. 8. SXRD pattern of the sample prepared by reacting a copper-based Cu–Bi solid solution with the liquid Ga–Sn eutectic.

CONCLUSIONS

Our results demonstrate that the intermetallic phase $CuGa_2$ resulting from the reaction between copper and liquid gallium ranges widely in crystallite size. In all of the reactions between a binary solid alloy and liquid eutectic, the first to form is fine-particle $CuGa_2$. The intermetallic phase forming at a later stage of the reaction consists of much coarser grains in comparison with the starting powder and primary intermetallic phase.

The present results on the reactions between the copper-based Cu–Sn solid solution and Ga–In eutectic, copper-based Cu–In solid solution and Ga–Sn eutectic, and copper-based Cu–Bi solid solution and Ga–In eutectic indicate that the second-formed intermetallic phase is richer in the element that was in the liquid phase (in the eutectic) in the starting mixture, independent of the melting points of the elements present.

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