Rev.Adv.Mater.Sci. 18(2008) 716-719

PHASE TRANSFORMATION SEQUENCE DURING INTERACTION MECHANOCHEMICALLY SYNTHESIZED SOLID SOLUTION WITH LIQUID EUTECTICS

T. F. Grigoryeva[1], A.I. Ancharov[1], V.F. Pindyurin[2], A.P. Barinova[1] and V.V. Boldyrev[1]

[1]Institute of Solid State Chemistry and Mechanochemistry Siberian Branch of Russian Academy of Sciences, Kutateladze 18, Novosibirsk 630128, Russia
[2]Budker Institute of Nuclear Physics of Siberian Branch of Russian Academy of Sciences, Ac. Lavrentiev Av, 11, Novosibirsk 630090, Russia

Received: March 29, 2008

Abstract. The reactions of copper-based Cu-In, and Cu-Sn solid solutions with liquid Ga-In and Ga-Sn eutectics have been studied in situ by synchrotron X-ray diffraction. At the same elements the phase composition of receiving materials depends on search of liberating components (liquid eutectics or solid solution).

1. INTRODUCTION

Solid metallic alloys interact with liquid metals in various fields of engineering, such as soldering, sintering involving a liquid phase, and metallurgical processes. These processes have been mainly studied for binary systems. In this work, we studied *in situ* the interaction between binary mechanochemically synthesized solid solutions and binary gallium eutectics by X-ray diffraction with the use of synchrotron radiation to find the phase formation sequence for the elements released.

It's known that liquid gallium reacts with copper ($Ga + Cu \rightarrow CuGa_2$), and the reaction ceases when gallium is consumed completely [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.

2. EXPERIMENTAL

In our preparations, we used copper powder, tin powder, gallium, indium, 80 wt.% Cu + 20 wt.% Sn solid solution (in what follows, Cu(Sn)), 80 wt.% Cu + 20 wt.% In solid solution (Cu(In), 88 wt.% Ga + 12 wt.% Sn eutectic (Ga-Sn), and 75.5 wt.% Ga + 24.5 wt.% In eutectic (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 [5].

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 Sibe-

Corresponding author: T. F. Grigoryeva, e-mail: grig@solid.nsc.ru

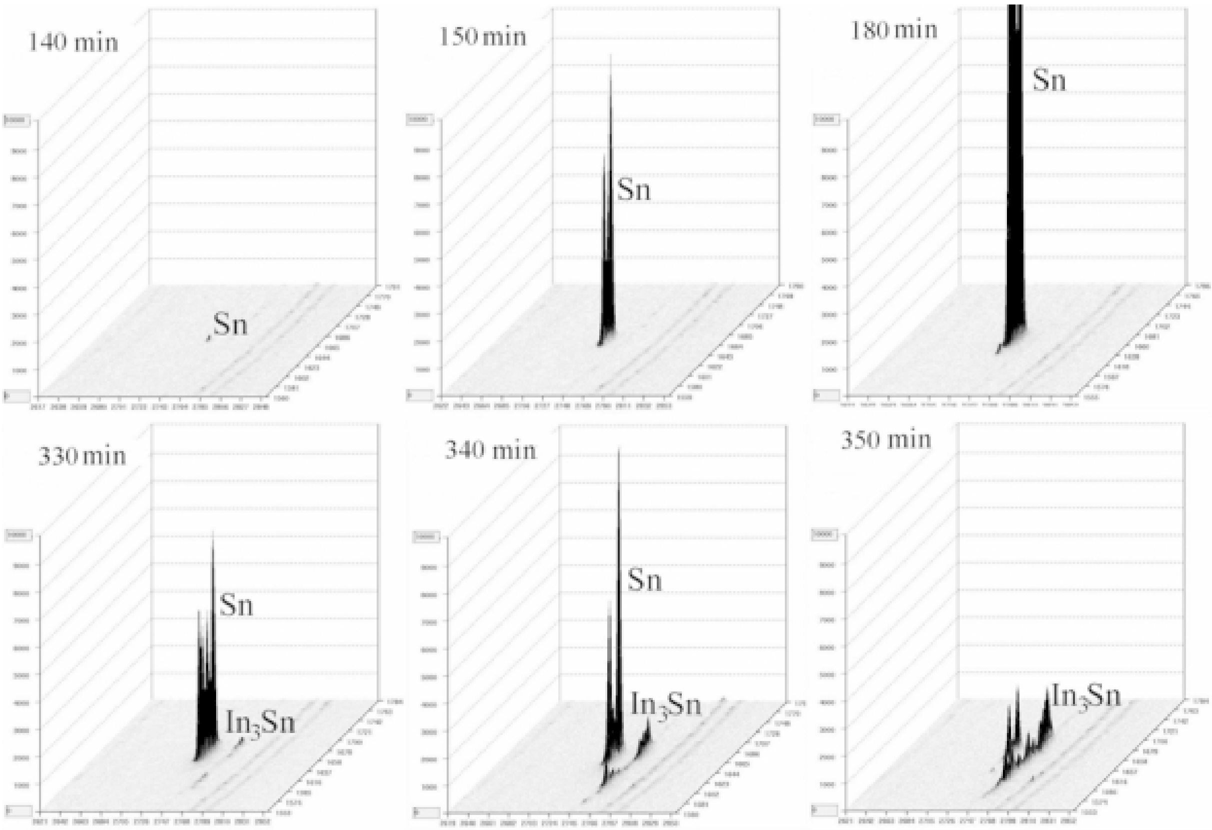

Fig. 1. Dynamics of the changes in the diffraction pattern after mixing of the powder of the mechanochemically synthesized solid solution of tin in copper with the liquid gallium–indium eutectic.

rian Synchrotron Radiation Centre (Budker Institute of Nuclear Physics, Siberian Branch, 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.

3. RESULTS AND DISCUSSION

Two systems were studied to reveal the specific features of the interaction of a solid solution with a liquid eutectic when two different elements become free in the system, with the same element leaving the liquid eutectic or the solid solution. These systems are the solid solution of tin in copper with the gallium–indium eutectic and the solid solution of indium in copper with the gallium–tin eutectic. In both systems, the $CuGa_2$ phase forms first, which is accompanied by the liberation of indium and tin. They can interact with each other, since this system contains two intermetallic compounds, namely, In_3Sn and $InSn_4$, according to the equilibrium phase diagram. However, each element can also solidify. Several chemical reactions are possible for this interaction:

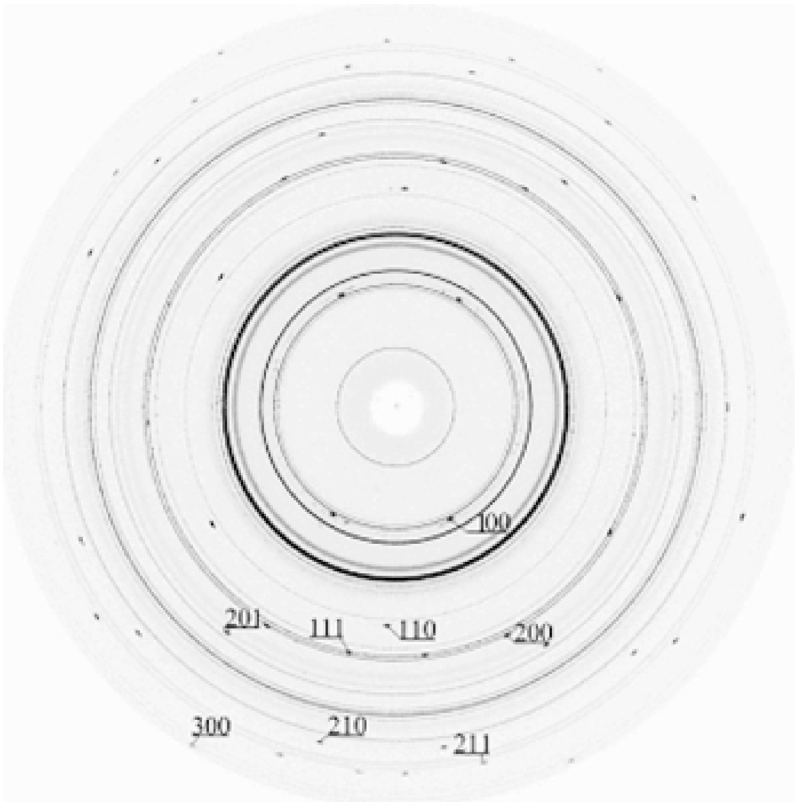

Fig. 2. Diffraction pattern of the sample produced by 24-h interaction of the Cu(In) solid solution with the Ga–Sn liquid eutectic. All indexed diffraction reflections belong to the $InSn_4$ intermetallic compound, and the other reflections correspond to $CuGa_2$.

$$\left.\begin{array}{c} \text{Cu 20 wt\% Sn} + \text{Ga 24.5 wt\% In} \\ \text{Cu 20 wt\% In} + \text{Ga 12 wt\% Sn} \\ \text{Solid solution} \quad \text{liquid eutectic} \end{array}\right\} \rightarrow \left\{\begin{array}{c} CuGa_2 + In_3Sn + Sn \\ CuGa_2 + InSn_4 + In \\ CuGa_2 + Sn + In \end{array}\right.$$

The X-ray diffraction study of a mixture of a mechanochemically synthesized Cu (Sn) solid solution with the gallium–indium eutectic shows that $CuGa_2$ grains grow within the first 140 min. Only after this process does a reflection from tin appear (Fig. 1). The intensity of this reflection increases rapidly. However, in 330 min, the intensity ceases to increase and begins to decrease. At the same time, a reflection from the In_3Sn intermetallic compound appears and begins to increase. The reflection from tin then disappears completely.

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. After 8 h, the intermetallic phase $InSn_4$ appeared (Fig. 2), while crystalline indium was still missing. The formation of the intermetallic phase $InSn_4$ lends support to the above assumption.

So, when a copper-based solid solution interacts with a liquid gallium eutectic, the composition of the products forming from the elements that are released upon the interaction of copper with gallium depends on the state of the element (solid or liquid). The second forming intermetallic phase should contain the highest content of the liquid element (i.e., of the element that enters into the eutectic rather than into the solid solution) regardless of the melting points of these elements.

ACKNOWLEDGEMENTS

The investigation has been performed within the integration program of Russian Academy of Science 8.15 “Development of production methods of chemical substances and creation of new materials” and within the integration project of Siberian Branch of RAS No 98 “Mechanocomposites are precursors for creation of materials with new properties”.

REFERENCES

[1] O.Tikhomirova, M.Pikunov, I.Marchukova, I.Tochenova and I.Izotova // *Fiziko-khimicheskaya mekhanika materialov* **5** (1969) 455, In Russian.

[2] O.Tikhomirova and M.Pikunov // *Svarochnoe proizvodstvo* **10** (1967) 16, In Russian.

[3] A.Ancharov, T.Grigoryeva, S.Nikitenko and M.Sharafutdinov // *Poverkhnost. Rentgenovskie, sinkhrotronnye i neitronnye issledovaniya* **7** (2002) 23, In Russian.

[4] A.Ancharov and T.Grigoryeva // *Nuclear Instruments & Methods in Physics Research A* **543** (2005) 139.

[5] E.Avvakumov, A.Potkin and O.Samarin, *A.C. USSR* № *975068. BI* **43** (1982), In Russian.