

Crystallization Processes in Metallic Systems with Miscibility Gap in the Liquid State

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One of the most common preparation techniques for intermetallic compounds is the solidification of the phases from a homogeneous melt. The prepared phases are usually in equilibrium with the melt and it is often possible to grow large single crystals with very regular atomic arrangements and small amounts of defects. For the preparation of phases that do not segregate from the melt or in systems without homogeneous melt, the use of an additional metal with low melting temperature is one possible solution. Elements like tin, aluminum, gallium and zinc are often used as solvents because other components can be solved therein at accessible temperatures. Crystallization of compounds occurs from supersaturated melts. This so-called flux method is often applied for the preparation of refractory materials with very high melting temperatures. On this way they can be prepared at temperatures of several 100 K lower than the melting point. Important conditions for the flux method are the solubility of the educts in the liquid solvent and negligible solubility of the flux element in the products. Additionally, for high efficiency of preparation, the educts and solvents should not form competing phases to the target phase.

Several binary systems show coexistence of two liquid phases with different compositions at higher temperatures. Miscibility gaps in the liquid state are known, for example, for systems of alkaline- and alkaline-earth metals as Na-Mg, K-Mg, Na-Ca and also for several other systems with cadmium, zinc or lead. The aim of this project is to use the special conditions at a liquid-liquid interface for the preparation of intermetallic phases by the flux method. We present first results of investigations on the quaternary system (Pb,Co)-(Zn,Ge).

The Pb-Zn system shows two coexisting liquids with different compositions in large temperature ($420\text{ °C} < T < 798\text{ °C}$) and concentration ($0.5\text{ at.}\% < x_{\text{Zn}} < 93\text{ at.}\%$) ranges (Fig. 1). At higher temperatures ($T > 798\text{ °C}$), one homogeneous liquid exists in the complete concentration range [1]. The formation of the liquid-liquid interface is one of the main processes for these crystallization experiments. The process of separation of the coexisting

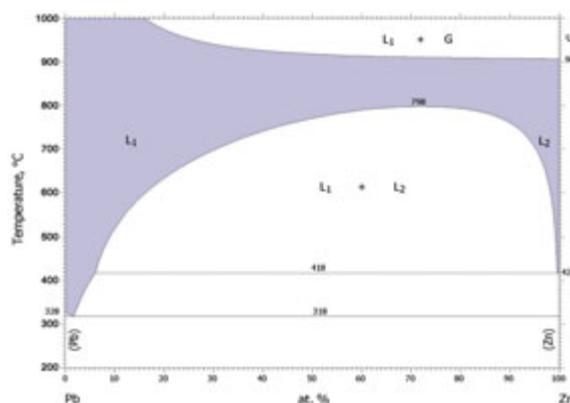


Fig. 1: Binary phase diagram of Pb-Zn [1].

liquids is dominated by the density differences of both liquids which can lead to an almost complete spatial separation and a stacked arrangement of both liquids. The separation is influenced by interaction at the phase boundaries which determines, for example, the concave or convex shape of the boundary and also by viscosity and process parameters like heating and cooling rates. We have prepared the microstructures of the solidified samples to investigate the phase distribution especially in the vicinity of the phase boundary originating from the miscibility gap in the liquid state. The

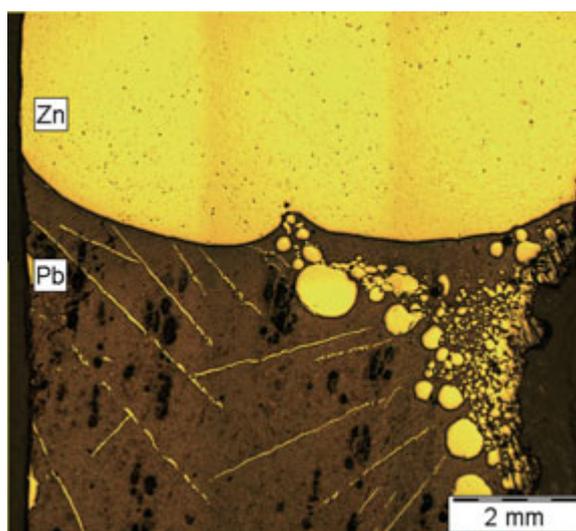


Fig. 2: Microstructure of a $\text{Pb}_{50}\text{Zn}_{50}$ alloy. The phase separation in Zn-rich (bright) and Pb-rich (dark) parts originates from the miscibility gap in the liquid state.

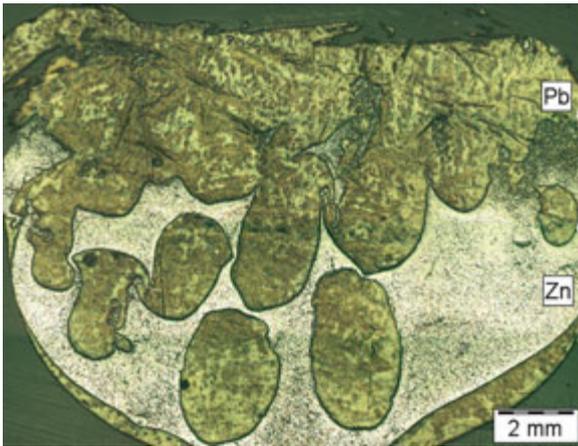


Fig. 3: Microstructure of a $Pb_{49}Co_1Zn_{49}Sn_1$ alloy showing droplet-shaped Pb-rich regions embedded in a Zn-rich matrix. The formation of the interfaces is strongly influenced by the Sn content.

microstructures of Pb-Zn samples show a spatial separation in one Pb-rich and another Zn-rich part with a very reproducible shape of the boundary (Fig. 2). The addition of a small amount of Sn alters the shape of the boundary and spatial distribution of the phases which reveals a quite different phase interaction via boundary in the presence of tin. The microstructure of the Pb-Zn alloy with small amounts of Sn and Co — prepared by a similar procedure as the binary Pb-Zn samples — shows large Pb-rich droplet-shaped parts embedded in a Zn-rich matrix (Fig. 3). In case of a miscibility gap in the liquid state, the spatial distribution of the liquid phases and the microstructure of the solidified sample are strongly influenced by dwell

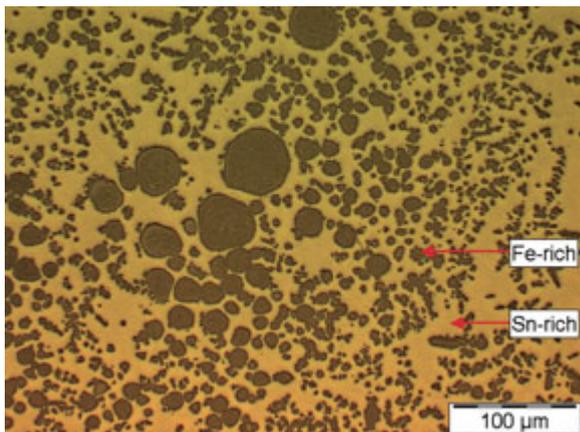


Fig 4: Microstructure of a $Fe_{50}Ga_{17}Sn_{33}$ alloy showing Fe-rich spheres surrounded by a Sn-rich matrix. The phase distribution is caused by the miscibility gap in the liquid state and fast solidification during the preparation process in the arc furnace.

time and cooling rates during the preparation process. As example, the microstructure of an $Fe_{50}Ga_{17}Sn_{33}$ alloy shows finely dispersed Fe-rich spheres within a Sn rich matrix originating from the miscibility gap in the liquid state and fast solidification in the arc-furnace (Fig. 4).

To investigate the crystal growth nearby the Pb-Zn liquid-liquid interface, we added small amounts of cobalt or germanium to according liquids with the aim to modify the local composition next to the interface. The partial processes in the binary systems Pb-Co and Zn-Ge were investigated by individual experiments.

The phase diagram of the binary system Pb-Co shows a solubility of less than 2 at.% Co in Pb rich melt up to the melting point of Co ($T_M = 1492$ °C). Hence, the distribution of Co should be determined mainly by the buoyancy of solid Co particles in the Pb melt. The microstructures of the Pb-Co samples confirm the displacement of smaller ($d = 10$ μm) and larger ($d = 100$ μm) Co particles from the bottom to the surface of the melt at 12 hours dwell time and 550 °C or 800 °C (Fig. 5). Shape and particle size are unaffected by this process.

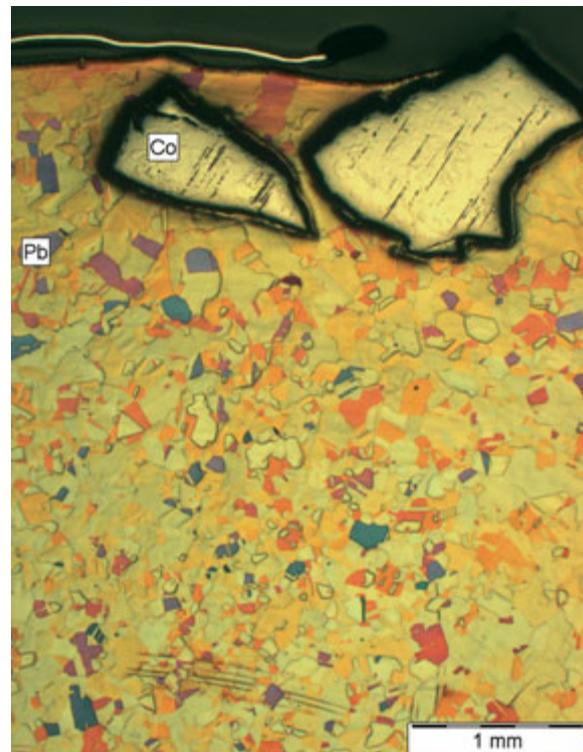


Fig. 5: Microstructure of a Pb sample with solid Co particles on the top surface. The Co particles are displaced from the bottom to the top surface during annealing at 850 °C for 12 hours.

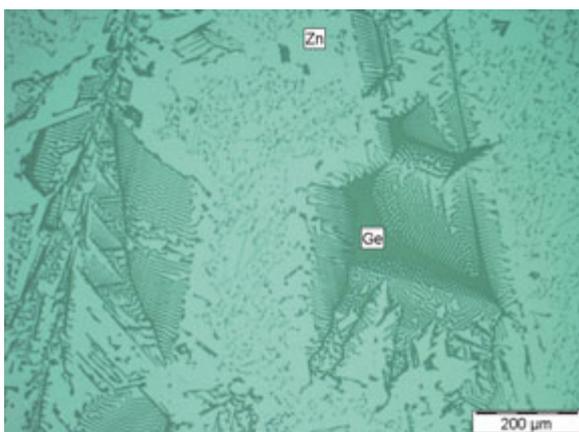


Fig. 6: Microstructure showing Ge crystals embedded in a Zn matrix.

The phase diagram of the Zn-Ge system shows the eutectic point at $T_E = 394$ °C and 5.2 at. % Ge and the solid phases of both elements with melting temperatures $T_M(\text{Zn}) = 420$ °C and $T_M(\text{Ge}) = 938$ °C. Our Zn-Ge samples exhibited a typical over-eutectic microstructure with agglomerates of Ge plates and finely dispersed Ge particles embedded in the Zn matrix (Fig. 6). The homogeneous distribution of both phases in the microstructure indicates the complete dissolution of the initial Ge particles in the liquid state at the same temperature and dwell time as it was used for the Pb-Co samples.

Identical preparation parameters — dwell time, heating-, cooling rates and concentration — were applied also for the investigation of the sample (Pb-Co)-(Zn-Ge), but all preparations are carried out at the temperature $T = 850$ °C. The samples were prepared in closed quartz ampoules with 10 mm diameter, 60 mm length, and nearly the same height of 12 mm for the Zn-rich and Pb-rich part after the annealing. This corresponds to masses of approximately 10 g Pb and 7 g Zn. The amount of 500 mg Co and 1 g Ge were added to the Pb-rich and Zn-rich parts, respectively. The microstructure of the quaternary sample is shown in Fig. 7a. It keeps the main features of the binary samples like the eutectic Ge – Zn arrangement, the concave shape of the Pb surface and large, parallel Zn layers on the Pb-rich side. The significant difference occurs by the formation of Co-containing phases on the Zn-rich side of the sample. The arrangement of phases next to the Pb-Zn interface is dominated by the formation of plate-like Ge crystals very close to the interface. However, a few small crystals of composition $\text{Co}_{61}\text{Ge}_{39}$ are found by means of scanning electron microscopy (SEM) and EDX analysis just “on” the interface (Fig. 7b). Additionally, very small particles ($d < 5$ μm) with the approximate composition $\text{Co}_6\text{Zn}_{94}$ are detected next to the interface in the Zn-rich matrix. The third and most frequently observed Co-containing phase forms large crystals and is distributed in a wide region of the Zn-rich side. These crystals show mostly hexagonal morphology and a composition in the concentration range $\text{Co}_{10}\text{Zn}_{87+x}\text{Ge}_{3-x}$ ($0 < x < 3$). It should be mentioned, that no excess Co particles are found, neither on the Pb-rich nor on the Zn-rich side. No new phases were found on the Pb-rich side.

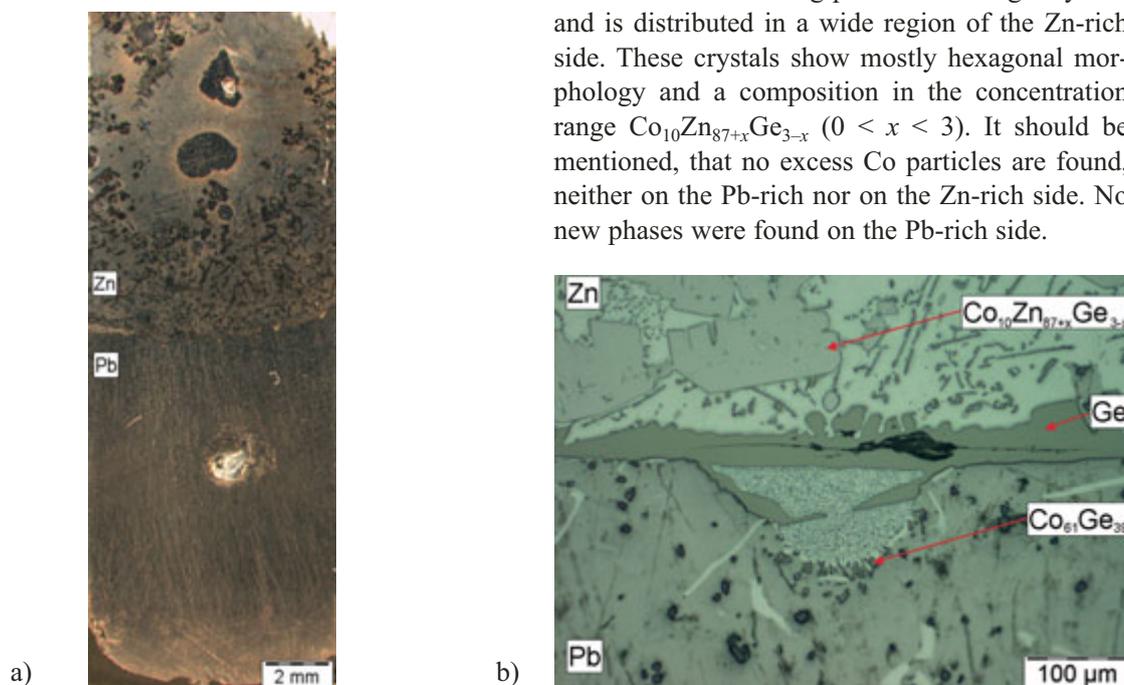


Fig. 7: a) Microstructure of a $\text{Pb}_{49}\text{Co}_1\text{Zn}_{49}\text{Ge}_1$ alloy. b) Phase distribution next to the Pb-Zn interface of the $\text{Pb}_{49}\text{Co}_1\text{Zn}_{49}\text{Ge}_1$ alloy.

The composition $\text{Co}_{61}\text{Ge}_{39}$ of some small crystals indicates the formation of the Co_3Ge_2 phase (Ni_2In type, Pearson code $hP6$, space group $P6_3/mmc$). Its formation seems to be possible only next to the Pb-Zn interface, because elsewhere the competing CoZn_x phases are strongly preferred. The composition of small crystals $\text{Co}_6\text{Zn}_{94}$ agrees with the binary CoZn_{13} phase (93 at.% Zn). Its peritectic temperature $T = 566$ °C is lower than the melting point of other binary Co-Zn phases. This could explain the rare formation of the phase on the interface. The hexagonal morphology as well as its composition $\text{Co}_{10}\text{Zn}_{87+x}\text{Ge}_{3-x}$ indicate the formation of the $\delta\text{-Co}_2\text{Zn}_{15}$ phase ($\text{Co}_{11.8}\text{Zn}_{88.2}$, Pearson code $hP60$, space group $P6_2$) [2] with small Ge solubility. The well shaped facets of the crystals and their wide distribution on the Zn-rich side gives strong hints on crystal growth from the melt.

The results of our metallographic investigations on the samples of the quaternary system (Pb,Co)-(Ge,Zn) shows the possibility to prepare the binary phase Co_3Ge_2 at the liquid-liquid interface of the Pb-Zn system. The buoyancy of Co particles on the Pb-rich side and the dissolution of the Co particles in Zn is effective at the applied annealing temperature $T = 850$ °C and leads to the formation of CoZn_x by-products.

References

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