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Microstructural evolution in near-metatectic Cu–Sn alloys

M. Stier, M. Rettenmayr *

Institut für Materialwissenschaft und Werkstofftechnologie, Friedrich-Schiller-Universität Jena, Löbdergraben 32, 07743 Jena, Germany

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ABSTRACT

Microstructures forming in the Cu–Sn system with alloy compositions close to the metatectic composition are characterized. A careful experimental procedure with a variety of holding temperatures and cooling rates allows for unambiguous interpretation of the solidified microstructures. The decay of the high-temperature γ-phase according to the metatectic reaction γ→ε+liquid could not be suppressed even by the highest available quenching rates. Different microstructural features are observed concerning the secondary ε-phase. For low and moderate cooling rates, ε is growing in columnar grains, surrounded by peritectic η-phase. For rapid quenching, secondary ε partially remelts and exhibits fine globulitic particles of η.

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1. Introduction

Metatectic reactions (also referred to as 'catatectic reactions' [1]) in binary alloy systems represent a non-variant equilibrium that has so far received relatively little attention. A remarkable feature is that a completely solid sample can partially melt upon cooling, as a solid phase will decay in a second solid phase and liquid. An example is the equilibrium at 640 °C in Cu–Sn system (Fig. 1).

Interestingly, metatectic equilibria are found in more than 50 binary phase diagrams, partly with technical relevance. Examples are Fe–Mn, Fe–S and Ag–In. A further subdivision of metatectic reactions into terminal, compound and mixed metatectics has been undertaken by different authors, e.g. Ferro et al. [3] or Wagner and Rigney [1]. The compound metatectic is based on the decomposition of an intermetallic compound with decreasing temperature. This type is relatively rare and occurs in less than ten systems, among others in Cu–Sn. Despite the widespread applications of this alloy system, on the Cu-rich side as structural material and on the Sn-rich side, e.g. as Pb-free solder material, only little is known about microstructure evolution of alloy compositions involving metatectic reactions, as the technically important alloys are not in the range >38–<60 wt% Sn.

Only few publications in the literature discuss the microstructure generated during metatectic reactions. Ferro et al. [3] exclusively analyze rare earth alloy systems. Lograsso and Hellawell [4] studied the microstructure evolution of two near-metatectic Cu–Sn alloys and correlated the microstructures with temperature evolution upon cooling. Relatively low cooling rates in a resistance furnace were applied. The metatectic microstructure is described as coarse grains of ε-phase and intergranular η-phase. There is an obvious orientation relationship between the ε grains. The metatectic reaction of a nominally metatectic alloy (42.5 wt% Sn) is detected by thermal analysis at temperature 650 °C, which is above the metatectic temperature (640 °C). This is explained by segregation in the high-temperature γ-phase due to slow back diffusion during solidification, which results in a lower Sn concentration in the core of the grains that decomposes to γ+ε at higher temperatures. Thermal and microstructural analysis in Ref. [4] is somewhat weakened by the fact that the initial microstructure before the metatectic reaction was not well defined. Also, the results are based on experiments with only few samples that leave some room for different interpretations.

In the present work, metatectic reactions and microstructures are studied in the Cu–Sn system. The microstructures at high temperatures prior to the metatectic reaction are carefully adjusted and characterized after rapid quenching. Small samples and a gradient furnace are used to impose temperature profiles that are variable to a large extent.

*Corresponding author. Tel.: +49 3641 947790; fax: +49 3641 947792.
E-mail address: M.Rettenmayr@uni-jena.de (M. Rettenmayr).

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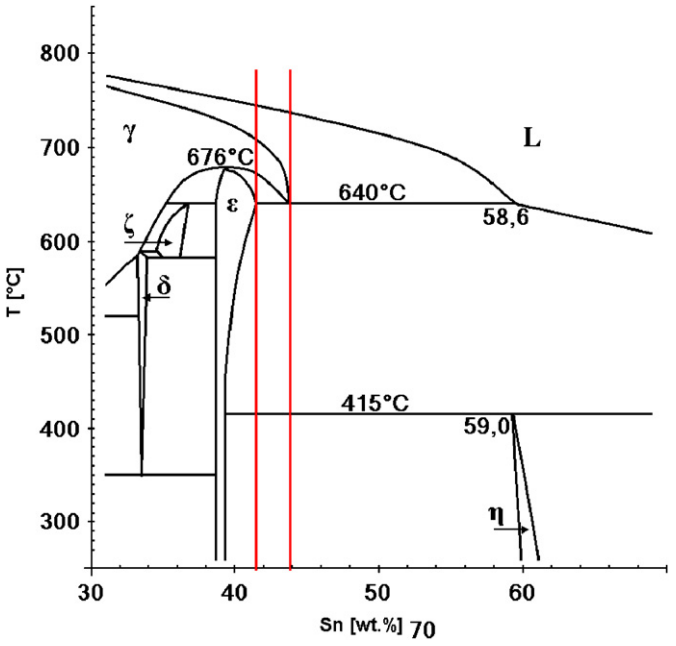

Fig. 1. Detail of the Cu–Sn phase diagram with metatectic equilibrium at 640 °C, after Refs. [2,7]; the initial concentrations of studied alloys are marked.

2. Experimental procedure

Following the work of Lograsso and Hellawell [4], the compound metatectic reaction is studied in the Cu–Sn system using an alloy close to the metatectic point Cu-41.5 wt% Sn.

Details about the experimental setup can be found in Refs. [5,6]. Defined initial microstructures are generated in the hot region of the gradient furnace at different homogenization temperatures for different times. Defined cooling rates between 0.05 and 0.12 K/s as well as quenching rates up to 250 K/s were applied. An application with controlled varying cooling rates is shown in Ref. [8].

The alloys were produced by melting the metallic elements Cu and Sn of 99.99% purity in an induction furnace. The alloys were of essentially uniform composition, as verified by EDX analysis. Cylindrical samples with diameter 8 mm and height 10–12 mm were machined and coated with an alumina-based ceramic adhesive. The adhesive acts as a (thin) crucible with good thermal contact to the sample, so that heat transfer from the furnace into the sample and from the sample into the cooling water is fast. A NiCr–Ni thermocouple was placed in the centre of the sample, and the thermal history was monitored throughout the experiments.

The samples were positioned and moved in a vertical furnace with ten independent heating zones. A linear thermal gradient of 1 K/mm between 500 and 800 °C was adjusted. The sample temperature was set by adjusting the sample position in the thermal gradient using a computer-controlled motor. A PID control was programmed for the temperature control, so that the sample temperature differs by $< \pm 0.2$ K from the chosen temperature. Holding temperatures are reproducible to 0.1 K.

The thermal history to which the samples were subjected is a combination of homogenization treatments at constant temperatures up to 4 h (if applicable up to two times at different temperature levels) followed by cooling at defined rates and/or finally quenching in streaming water. The samples were melted at 780 °C and homogenized in the γ region of the phase diagram at 660 °C. In some experiments, a prior annealing step was carried out in the two-phase-field γ+liquid at 710 °C. The rationale for this first annealing step is to coarsen the primary γ-phase and change its morphology from dendritic to globular, so that dendritic morphologies that are generated at lower temperatures can be clearly identified. The metatectic reaction that occurs at 640 °C thus starts from a well-defined microstructure with uniform composition in all of the present phases.

After quenching the samples were prepared metallographically by grinding and polishing. Etching is not necessary, as the low temperature phases ε and η exhibit a phase contrast both in the optical and the scanning microscopes.

The onset of phase transformations can clearly be seen in the cooling curves. Particularly the precipitation of the ε-phase from the γ-phase (at compositions left of the metatectic composition in the phase diagram in Fig. 1) is strongly exothermic and leads to a distinct recalescence if started at some undercooling [4]. While the recalescence could be detected for the experiments with defined cooling rate, the resolution of data acquisition is not fast enough to detect it during quenching. At very low cooling rates of up to 0.05 K/s precipitation of ε occurs without noticeable undercooling. Overall the metatectic reaction is exothermic, even though latent heat is needed for partial melting (about 20% in weight for pure γ) during the reaction. Calculations with FactSage and the COST2004 database yield a ΔH of 1850 J/mol, which means a latent heat release of about 1/7 of that of pure Cu during solidification.

3. Microstructural characterization

As predicted by the phase diagram, at room temperature all samples exhibit two-phase microstructures. Sample sections parallel and perpendicular to the cylinder axis did not show any distinct differences concerning the morphology of phases or phase fractions. Thus, anisotropy effects did not play any role during microstructural evolution. Phase analysis by XRD was not carried out, as EDX analysis in coarse microstructures confirms that the phase with the higher volume fraction (of approx. 90%) is the ε-phase Cu_3Sn (38 wt% Sn), and the one with the smaller volume fraction (of approx. 10%) is the η-phase Cu_6Sn_5 (60 wt% Sn). In the optical microscope, the ε-phase appears with a darker grey shade than η. A composition near the γ-phase (Cu_4Sn) was not found in the microstructure by EDX, indicating that the γ-phase could not be kept in a metastable state down to room temperature even at the highest available quenching rates.

The microstructures of the samples quenched from the single-phase region of γ exhibit mainly ε-phase with finely dispersed globular inclusions of η, see Fig. 2. The η inclusions are mostly uniformly distributed in ε. There are also areas of ε with a coarser length scale (effect of the solidification of the γ-phase), surrounded by a more or less closed layer of η.

The microstructures of the samples cooled from the γ region with a defined cooling rate of 0.12 K/s are significantly coarser than those of the quenched samples. The η 'inclusions' are not finely dispersed any more, see Fig. 3a. The ε-phase appears dendritic, the η-phase is situated in the interdendritic regions.

Annealing at 710 °C for solid–liquid coarsening of the primary γ-phase and afterwards at 660 °C for homogenization followed by quenching leads to a microstructure with bimodal length scale, see Fig. 3b. The structure of the former γ-phase is still clearly visible as coarse globular or very coarse dendritic. The products of the metatectic reaction are mainly seen in the region in between the primary coarse structures. Note that finely dispersed inclusions are also present in the coarse primary dendrites, but not resolved at the chosen low magnification.

The experiments with coarsened γ-phase show clearly that a columnar substructure is generated inside the γ-phase during the metatectic reaction. In Fig. 4a (sample with first solid–liquid

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