

WETTING FEATURES OF AG-SN LIQUIDES AND THE PHASE STRUCTURE IN SOLIDIFIED STATE

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Abstract

We studied the evolving micro-structure and its correlation with the wetting features of the Ag-Sn alloys have been studied in the whole concentration range. The properties of the wetting contact angles show close correlations with the evolving phases during solidification. It was found that the quantity of saturation of some phases has great influence on the texture of the solidified drop.

Keywords:

wetting, contact angle, crystal orientation, texture, silver, tin

1. Introduction

One of the perspective families of lead-free solder alloy systems is based on the Ag-Sn binary system [1-4]. Among the many important physical and chemical properties of soldering alloys, the wettability represents a key parameter in the success of practical use. [5-10]. In the present paper, experimental results are presented directing the concentration dependence of the wettability of the liquid Ag-Sn alloy on graphite substrate.

In our previous experiments, we assessed that the contact angles between the drop and substrate don't change during the solidification, so the solid drop keeps its quantity. It was also experienced, that a strong, preferred <100> texture is developed near to the drop-graphite interface, which seems to be in correlation with the wetting mechanism. i.e., the evolution of special short range order in the solidified alloy hints to the pre-existing atomic ordering in the liquid which can be enhanced by a "cathalitic" influence of the graphite substrate. We actually studied the correlations between the micro-structural and wetting features of the solid drop in the whole concentration range of Ag-Sn alloy in this contribution.

2. Experimental

Alloys were prepared from high purity (4N) Ag and Sn, using induction melting in cold quartz crucible

under inert (Ar) atmosphere. The graphite substrate was made from high purity, porosity free base material. The substrates were mechanically polished to $Ra=0.23\pm0.005\text{ }\mu\text{m}$, $r=1.009\pm0.0005$. Surface roughness was determined using a 3D laser profilometer (Rodenstock RM600 surface topography measurement system).

Wetting experiments were performed in a sessile drop equipment [11], taking the methodological issues summarized by Sobczak et al [12] into account. The graphite substrate and the alloy were positioned into the furnace at ambient conditions. The pressure was then reduced to 0.1 Pa at room temperature in the chamber. The vacuum was then filled by a 10^{-5} Pa 99.999 % Ar gas. This procedure was repeated 3 times. Following this, the temperature was raised to 1273 K at a rate of about 4 K/s. Since only a small portion of the gas chamber is heated, the pressure around the droplet remains at about 10^{-5} Pa during the measurements. Measurements were made at 1273, 1323, 1373, 1423 and 1473 K.

The time dependence of the contact angle was measured from the moment of time the required temperature was stabilized. It was experienced, that the contact angle independent of the holding time after 1 minute duration at a given temperature (thermal equilibrium). Similar time-dependent graphs were obtained for other alloy compositions and temperatures (not shown here). Based that measurements after 2 minutes of holding time were used in this paper. As will be shown below, the Ag-Sn/C system is non-reactive and non-dissolutive. Consequently, the equilibrium shape is established within 1 s for such low viscosity liquids and non-reactive liquids [13-19].

The contact angle was determined by fixing the shape of the droplet optically, subsequently processed by self-made automatic evaluation software in the Matlab environment. Although the uncertainty of this software was below 1 degree, the total uncertainty of the measured values was $\pm 3^\circ$.

After the last measurement at 1473 K, the furnace was switched off and was left to cool to ambient temperature. This took about 40 minutes. After that, the furnace was dismantled and the sample was removed. The alloy sample was weighed before and after each experiment. The average weight loss was below 0.5 % for pure Ag and for all Ag-Sn alloys, except for pure Sn (1.5 %). The alloyed sample was mounted into a resin and one half polished. This half of the sample is used for additional investigations.

SEM investigations were carried out using JEOL-JSM25-SIII SEM equipment, in secondary electron imaging mode. The constituent elements were analyzed by a Bruker-Röntec EDS microanalysis system attached to the SEM. The excitation parameters were 25keV beam energy and 50-200 pA beam current. Quantitative results were obtained from the measured spectra by a non-standard QUANTAX P/B ZAF correction program. Additionally, XRD measurements were performed with a Philips X'Pert diffractometer and the profile fitting of the detected XRD patterns were carried out using the Pro'Fitt commercial program. The transmission electron microscopy (TEM) carried out with a Philips CM2.

3. Contact angle measurements

The solubility limit of Sn in Ag is below 10 at % around room temperature (See Fig. 1.). Within this limit solid solution is formed. Exceeding this concentration limit, the so called „ α and β ” Sn phases are stable, for which the crystal structure deviate from that for the a-solid solution.

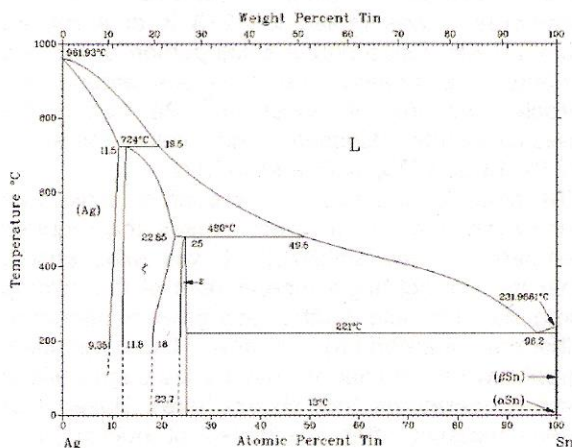


Figure 1. Ag-Sn equilibrium phase diagram [20]

The change of contact angles (on graphite substrate) as a function of Sn concentration (Fig. 2.) follows the appearance order of the balance phases pictured on the phase diagram, in case of alloys of different Ag-Sn concentration.

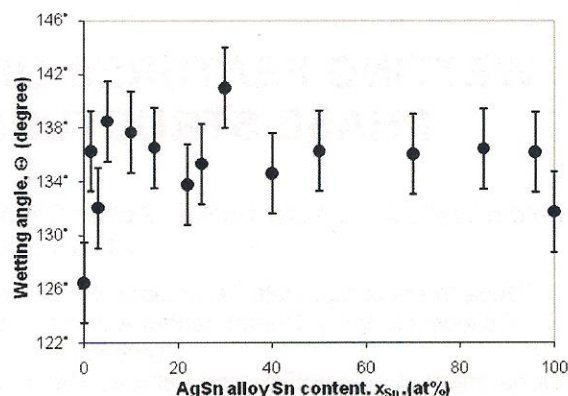


Figure 2. The concentration dependence of the measured contact angle at $T = 1373$ K

In the region below Sn content (up to 5%) the contact angles increase. This increase is not monotonic however local maximum exists at around 1.5%. Between 5% and 22% the contact angles decrease and, except the local minimum at 22%, it keeps the increase until a maximum at 30%. Rather small change can be detected between 40 and 100%, which fits the phase relation, because no new phase appears here. The ratio of phases changes only, required by the concentration change.

4. XRD measurement results

The XRD measurements were performed on the cut surface along the sheet illustrated in Fig. 3. supplying information about the coexisting phases.

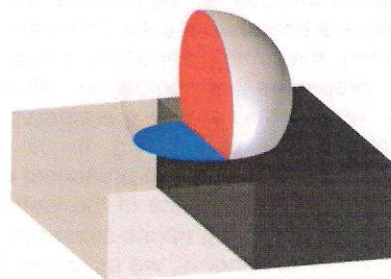


Figure 3. XRD measurements were performed between the substrate and the drop

In the Fig. 4. the XRD intensities are illustrated as a function of 2θ , measured on pure silver, $\text{Ag}_{98.5}\text{Sn}_{1.5}$, $\text{Ag}_{97}\text{Sn}_3$, $\text{Ag}_{95}\text{Sn}_5$ samples respectively.

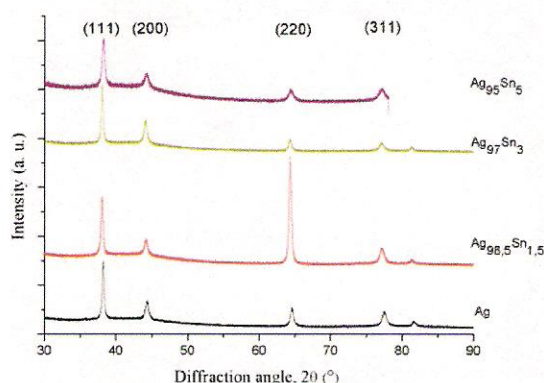


Figure 4. XRD results of Ag- Ag₉₅Sn₅ alloys

According to this Fig.3, the position of diffraction intensities fits to the pure silver's FCC structure in the investigated concentration range, supporting clearly the solid solution character of the solidified drops. The intensity scale of diffraction maximum are also supported by the reported data, published on appropriate powder patterns (ASTM 04-0783), showing, that the orientations of FCC grains are random.

The only exception is the Ag_{98.5}Sn_{1.5} sample, which has a definite <110> texture, because its (220) reflection is more intensive, than the (111). The reason of this unique orientation can be the consequence of preferential incorporation Sn atoms (in the surface layer). In case of higher Sn concentration the FCC structure (with Sn atoms replacing the Ag atoms), the controlled incorporation and the preferential orientation of the crystallites break off. Perhaps this structural change causes the noticed "anomaly" in the magnitude of contact angles, namely the local intensity maximum at Ag_{98.5}Sn_{1.5}. In this concentration range the contact angles are higher than that for the pure Ag, which is understandable if we consider the increased surface-tension (because of the sudden increase of electron density) caused by the Sn solute atoms.

In the Fig. 5. the XRD spectrums are depicted for Ag₉₀Sn₁₀ - Ag₇₅Sn₂₅ alloys.

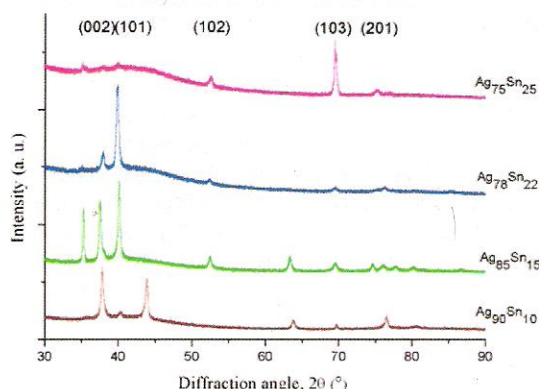


Figure 5. XRD results of Ag₉₀Sn₁₀ - Ag₇₅Sn₂₅ alloys
From the analysis of the, XRD patterns it can be seen, that the Ag₉₀Sn₁₀ sample has mainly FCC structure, so it has Ag(Sn) phase, but also contains a minimum of 1-2% Ag₄Sn phase too, because its most intensive reflections (101) and (103) appear in the XRD pattern. In the Ag₈₅Sn₁₅ sample the two kinds of crystallites coexist. In the case of Ag₇₈Sn₂₂ sample the detected intensity maximums fit the Ag₄Sn (ASTM, 29-1151) hexagonal structure. This phase is the so called ξ phase in literature (Fig. 1.). Lattice parameters are: a=0.2966 nm, b=0.4782 nm. The measured intensity scales fit the measured reference data taken on the powder pattern, showing that the orientation of grains are random. It is remarkable, that the appearance of this intermetallic phase decreases the contact angles, representing the improved wettability on the graphite substrate.

Comparing the XRD patterns of Ag₇₈Sn₂₂ and Ag₇₅Sn₂₅ alloys (Fig. 5.) the significant difference is obvious. In Ag₇₅Sn₂₅ Sn alloy the XRD measurements shows formation of new Ag-Sn phase (see on Fig. 5 and Fig. 6, XRD diagrams detected on Ag₇₅Sn₂₅ and Ag₇₀Sn₃₀ samples). The locations of intensity maximums fit the orthorhombic Ag₃Sn (ASTM, 04-0800) phase. Lattice parameters: a=0.2995 nm, b=0.5159 nm, c=0.5805 nm. Also this single phase was identified in the Ag₇₀Sn₃₀ sample, which indicates the +5% solid solubility of Sn in this phase. Comparing the XRD diagrams of the two samples, it is evident, that the additional Sn incorporation causes significant change in the peak intensities. The contact angles increases in this concentration range (between 25-30%.Sn). In consequence of the increasing electron density caused by increasing Sn content.

On Fig. 6 and 7 you can see the x-ray diffractograms measured on Ag₇₀Sn₃₀-Sn samples.

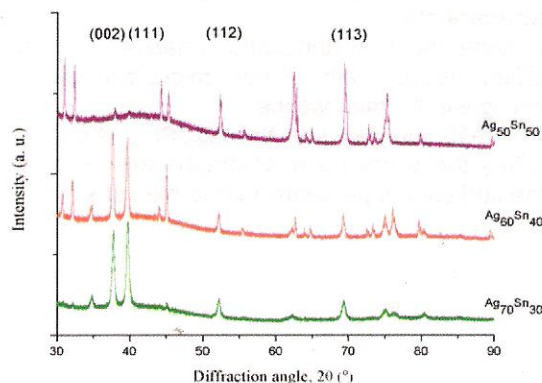


Figure 6. XRD results of Ag₇₀Sn₃₀ - Ag₅₀Sn₅₀ alloys

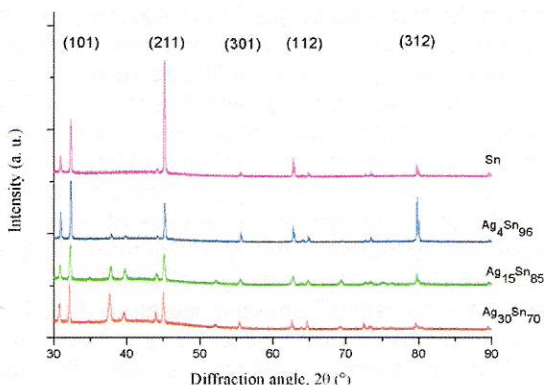


Figure 7. XRD results of $Ag_{30}Sn_{70}$ -Sn alloys

In the $Ag_{60}Sn_{40}$ sample the Sn element appears as additional, individual phase together with the Ag_3Sn compound phase resulting the decrease of contact angle. As the Sn concentration further increases, the detected intensity maximums came from the above mentioned two different phases, which scale changes progressively. The Sn parameters are: $a = 0.5831$ nm, $b = 0.3182$ nm (the scale can be defined from the XRD measurements as an analysis of the line profile). In the Ag_4Sn_{96} sample the Ag_3Sn phase is hardly detectable. The presented results fit qualitatively to the phase relations illustrated by the equilibrium phase diagram, so the progressive change of the contact angle can be explained based on this connection. The questions are, whether this connection can be developed into a more quantitative form, when the coexisting phases are defined quantitatively including also the determination of Sn content in the individual phases. For this purpose, scanning electro-microscopic measurements and EDAX micro-analyses are performed in the solidified drops including also homogeneity study.

5. Scanning electron microscopic (SEM) measurements

The component distributions analyzed in the solidified drops with X-ray micro-analysis in scanning electro-microscope.

In Fig. 8-10. you can see the $Ag_{90}Sn_{10}$, $Ag_{78}Sn_{22}$, $Ag_{50}Sn_{50}$ the scanning micrographs are recorded on the surface cut perpendicular to the substrate.

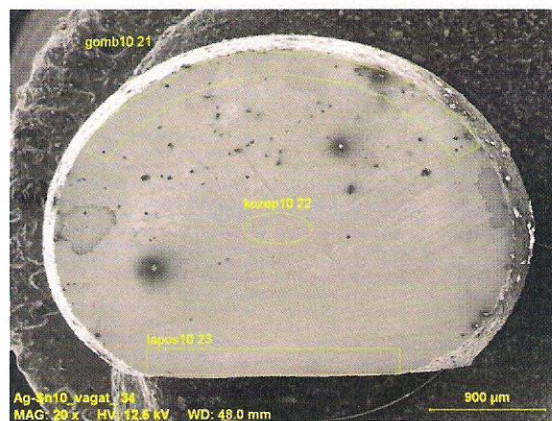


Figure 7. SEM picture from the $Ag_{90}Sn_{10}$ alloy drop

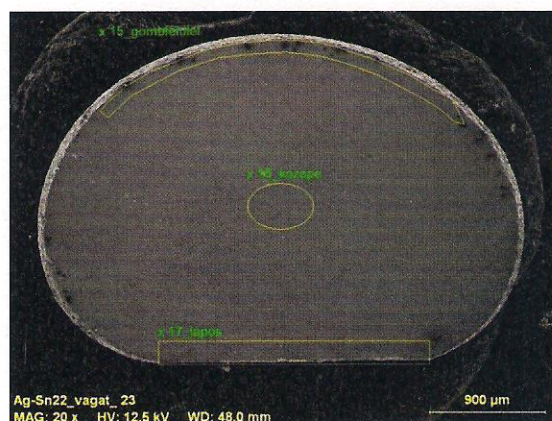


Figure 8. SEM picture from the $Ag_{78}Sn_{22}$ alloy drop

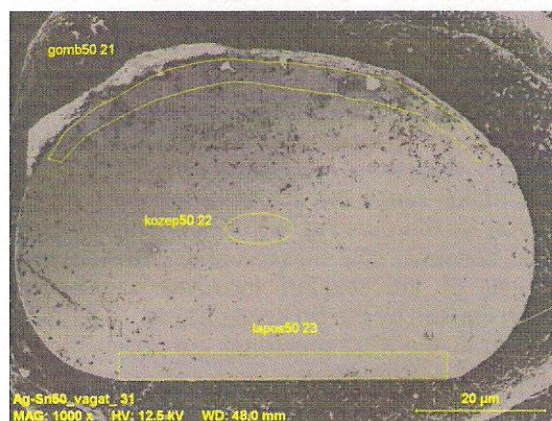


Figure 9. SEM picture from the $Ag_{50}Sn_{50}$ alloy drop

The results of the X-ray micro-analysis are collected in the Table 1. obtained, on the top, middle and bottom of the drop (see Fig.9.).

In case of $Ag_{90}Sn_{10}$ and $Ag_{50}Sn_{50}$ samples, the highest Sn concentration is detected in the middle of the drops, Contrary, in the $Ag_{78}Sn_{22}$ single-phased (Ag_4Sn) sample, the highest Sn concentration is found at the bottom of the drop.

Table 1. Results of the X-ray micro-analysis of $Ag_{90}Sn_{10}$, $Ag_{78}Sn_{22}$, $Ag_{50}Sn_{50}$ alloys

		bottom (at %)	middle (at %)	top (at %)
$Ag_{90}Sn_{10}$	Ag	89	87.2	88.4
	Sn	11	12.8	11.6
$Ag_{78}Sn_{22}$	Ag	72.7	74.1	74.2
	Sn	27.3	25.9	25.8
$Ag_{50}Sn_{50}$	Ag	42.6	38.2	42.4
	Sn	57.4	61.8	57.6

With the applied resolution during component analysis we could only reveal local concentration changing, without the detection so called phase separation in the $Ag_{50}Sn_{50}$ sample. The two other samples is homogeneous within the experimental error of measurements, which confirm the XRD results, indicating the single phase character of the $Ag_{78}Sn_{22}$ sample. (The role of second Ag_4Sn phase in the $Ag_{90}Sn_{10}$ sample is negligible, due to the low fraction). In Fig. 11. the X-ray map can be observed in the $Ag_{50}Sn_{50}$ sample

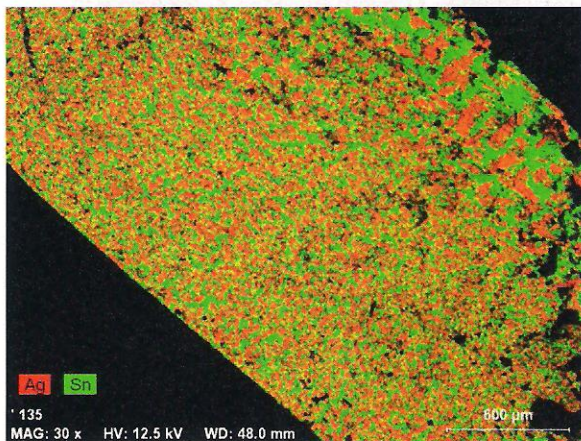


Figure 11. X-ray map of the $Ag_{50}Sn_{50}$ sample

The coarsening of Ag and Sn rich regions is more pronounced in the vicinity the top of the solidified drop, demonstrating clearly the intensive segregation as the solidification proceeds. Based on Fig. 11. one can conclude also, that solidification starts via heterogeneous nucleation at the melt-substrate interface.

When higher resolution is applied, the two-phase nature is obvious in the whole volume (inner part) of the solidified sample (Fig. 12.).

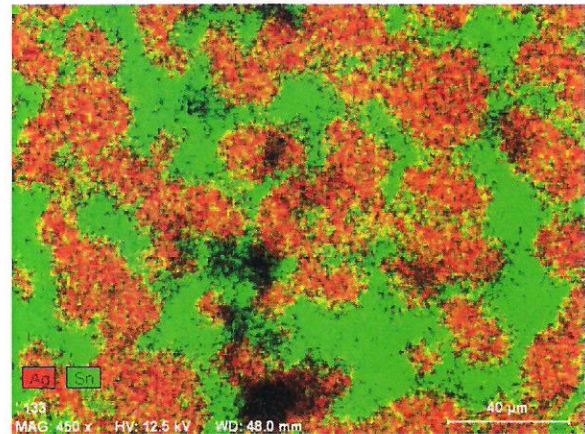


Figure 12. X-ray map of the $Ag_{50}Sn_{50}$ sample with higher resolution

Quantitative element analyses are also performed in selected areas of samples (see Fig. 12.). It was realized, that the concentration of Ag and Sn is slightly different in the "red and green" colored areas which means, that the Ag-content of the tetragonal Sn phase (detected with XRD) can slightly changes within a solubility limit.

In the Ag areas, the composition is actually ~74:26% Ag, which fits the composition of the orthorhombic Ag_3Sn intermetallic compound phase (detected with X-ray diffraction), although it has a minimum of ~1% Sn surplus.

6. Transmission electron microscopic (TEM) measurements

It was reported in previous paper, that the contact angles measured at 1473 K on liquid drop is nearly the same, as the measured values after solidification (room-temperature measurement). This means that the most favorable atomic arrangements have already been developed in liquid state prior to the formation of solid, crystalline nuclei at the interface. Our earlier result hints to the role of interaction between graphite and the drop, which shows that the evolution of pronounced texture around the interface vicinity of the graphite substrate has a close correlation with the contact angles which defines the drop's shape, and the wetting.

TEM measurements showed that, the inner tensions during chilling are deduced by the drop with a typical imperfection. The electro-microscope record (Fig. 13.) was made of the $Ag_{95}Sn_5$ drop's core, and its eye-catching, that the twin lamella (which deduce the inner tensions) and the small-angled limits model a perpendicular reticulated pattern.

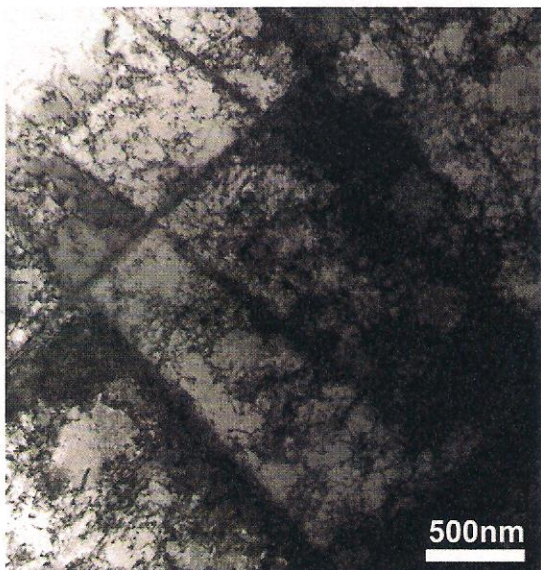


Figure 13. TEM picture from the $Ag_{95}Sn_5$ alloy

7. Conclusion

The evolving phases during solidifying in Ag-Sn alloys play an important role on changing the alloy's wetting features, which is not surprising, if we have a look at the drop's shape, which doesn't changes according to our measurements, so the order evolves during melt phase as a consequence of atomic interactions.

Our measurements pointed that not only the new phase brings significant changes in contact angles, but the saturation of different phases forming a solid solution.

Acknowledgement

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