

Wetting Properties of Silver Based Alloys

Zoltán Weltsch, József Hlinka, Eszter Kókai

Abstract—The temperature dependence of wettability (wetting angle, Θ (T)) for Ag-based melts on graphite and Al_2O_3 substrates is compared. Typical alloying effects are found, as the Ag host metal is gradually replaced by various metallic elements. The essence of alloying lies in the change of the electron/atom (e/a) ratio. This ratio is also manifested in the shift of wetting angles on the same substrate. Nevertheless, the effects are partially smeared by other (metallurgical) factors, like the interaction between the oxygen-alloying elements and by the graphite substrate-oxygen interaction. In contrast, such effects are not pronounced in the case of Al_2O_3 substrates. As a consequence, Θ (T) exhibits an opposite trend in the case of two substrates. Crossovers of the Θ (T) curves were often found. The positions of crossovers depend on the chemical character and concentration of solute atoms. Segregation and epitaxial texture formation after solidification were also observed in certain alloy drops, especially in high concentration range. This phenomenon is not yet explained in every detail.

Keywords—Contact angle, graphite, silver, soldering, solid solubility, substrate, temperature dependence, wetting.

I. INTRODUCTION

SOLDERING is the most popular joint technique in microelectronic and optoelectronic industries which technologies are widely used in the vehicle industry [1]-[3].

Ensuring good wetting conditions between the solder material and the metallic parts to be joined is of great importance in these processes [4]-[11]. The Ag based alloys are particularly promising in this respect especially, when the world-wide trends in the replacement of lead-thin based alloys are considered [12]-[15].

The temperature dependence $\Theta(\Delta T)$ was compared and the results were interpreted on the basis of classic alloying effects, i.e. based on the change in electron concentration (e/a), which is also reflected in the shape of the appropriate phase diagrams.

II. EXPERIMENTAL CONDITIONS

Alloys were prepared from high purity (4N) Ag and Sn, using induction melting in quartz crucible under inert (Ar) atmosphere. The graphite substrate was prepared from high purity, porosity free base material. The substrates were mechanically polished to $R_a=0.23\pm 0.005 \mu\text{m}$, $r=1.009\pm 0.0005$, then the surface roughness was determined

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using a 3D laser profilometer (Rodestock RM600 surface topography measurement system).

The wetting experiments were performed in home-made equipment developed for sessile drop measurements. The graphite substrate and the alloy pieces were positioned into the middle of furnace at ambient conditions. The pressure was then reduced to 0.1 Pa at room temperature in the chamber. The vacuum was replaced by a 10^5 Pa 99.999 % Ar gas. This procedure was repeated 3 times. Subsequently, the temperature was raised to 1273 K using a heating rate of 4 K/s. Since only a small part of the gas chamber is heated, no pressure change could be detected in the chamber (10^5 Pa) during the measuring run, which was performed during the heating run at 1273, 1323, 1373, 1423 and 1473 K respectively.

The heating power has stopped around each measuring temperature. Two minutes holding time was applied before the measurement.

The contact angle was determined by measuring directly the profile of the drop. Self-made automatic software in the Matlab environment is used for fixing and processing the data. Though the uncertainty of this software is below 1 degree, the total uncertainty of the measured values is higher: $\pm 3^\circ$.

At the end of the measuring process at 1473 K, the furnace was switched off and cooled slowly to the ambient temperature (the whole cooling time is around 40 minutes). Subsequently the furnace was opened and the solidified sample was removed.

The vapour pressure of the sample components is different. Consequently, the preferential evaporation during the wetting angle measurements cannot be excluded.

III. THE INVESTIGATED ALLOYS (METALLURGICAL CHARACTERIZATION)

It is well known, that several correlations exist between the bulk physical properties and the shape of phase diagram in metallic systems. On the other hand it was also reported already in early papers that surface molar energy of liquid metals is in close connection with the heat of vaporization [16]. The correlation is similar with the melting point of the appropriate metals. It is also known that simple relation exists for the description of phase stability and the electron structure of simple alloys. The investigated alloys were selected on the basis of outline principles.

An additional motivation in the alloy selection was the simple solidification mechanism, i.e. the simple phase relation which is developed during the solidification.

All alloys (except the 10 at% Sb alloy) do form continuous series of solid solutions after solidification, i.e. only a single phase is formed from the molten state and no second phase

precipitation occurs at low temperatures.

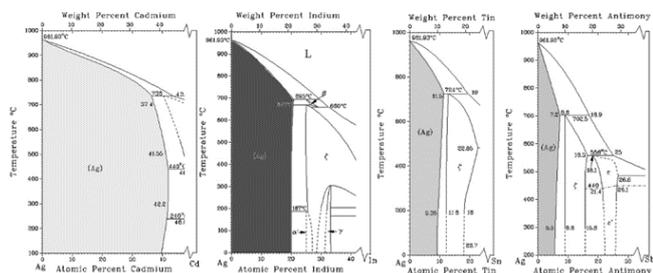


Fig. 1 The range of terminal (α)-solid solutions in Ag-Cd, Ag-In, Ag-Sn and Ag-Sb systems [17]

The shape of the appropriate phase diagrams (details from the Ag-rich sides) are collected in Fig. 1. The common feature is the tendency of solid solution formation at the Ag-rich sides during the solidification. The solidified alloys are not homogeneous however, in atomic scale, as the solute segregation occur. The degree of equilibrium segregation is reflected in the shape of the individual alloys. As the actual cooling rate is low, (see the experimental description) this segregation can be regarded as “equilibrium segregation”, so the concentration difference between the solid and the liquid does really represent the equilibrium distribution of the solute atoms in the solidified drop.

On the other hand it is clear, that the stability range of these α solid solutions are in close connection with the mentioned degree of segregation, which reflects the degree of difference between chemical potential of solutes between the contacting phases at a given temperature. The solubility limit can be explained on the basis of „electron phase” concept. Accordingly, the stability range of these solid solutions is governed by average valence electron concentration at the Fermi level of Ag. The upper limit of this concentration is around ($e/a \sim 1.36-1.59$) for the stability limit of α -solid solution in Ag. One can understand therefore, that alloying (partial replacement of Ag by these elements in the sequence Cd \rightarrow In \rightarrow Sn \rightarrow Sb leads to the narrowing of the α -phase region. The predictive power of this criterion is qualitatively supported by the well-known Hume-Rothery solubility rules in these alloys [18]. The appropriate changes in the bulk physical properties in solid state have been reported already in previous papers [19], [20].

IV. RESULTS

The wetting angle was measured in wide temperature range. The wetting angles are illustrated as a function of the melt overheating, (defined as $\Delta T = T_{obs} - T_{liq}$, where T_{obs} is the experimentally measured temperature, T_{liq} is the liquidus temperature for the alloy at the investigated concentration). The favour of this illustration is obvious, as the slope of liquidus is very different (see Fig. 1 the phase diagrams).

A. Ag-Cd, In, Sn, Sb System

Comparing Figs. 2, 3 the first remarkable finding is the opposite temperature dependence of the $\Theta(T)$ slope obtained

on the graphite and the Al_2O_3 substrates. It is also remarkable that the influence of the same solute atoms strongly depends on the melt superheat.

The results are collected in Figs 2, 3.

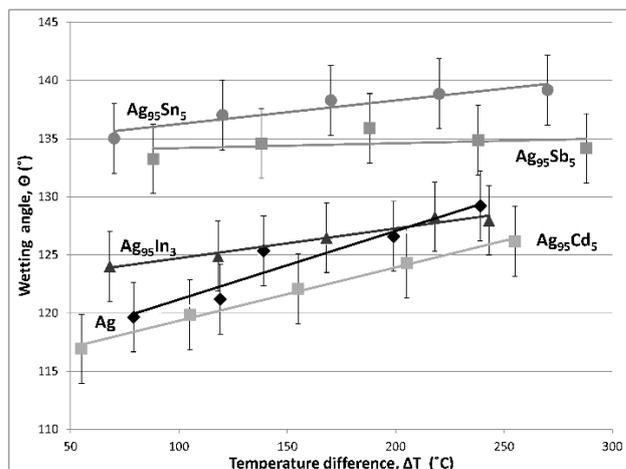


Fig. 2 Temperature dependence of the wetting angle of 5at% Ag-Cd, Ag-In, Ag-Sn, Ag-Sb and Ag liquids on graphite substrate

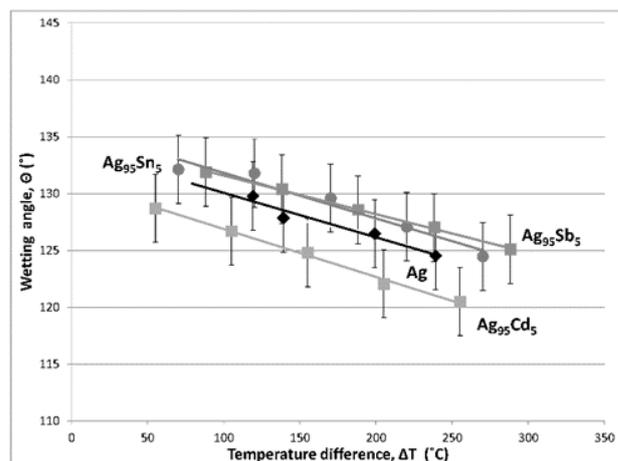


Fig. 3 Temperature dependence of the wetting angle of 5at% Ag-Cd, Ag-In, Ag-Sn, Ag-Sb and Ag liquids on Al_2O_3 substrate

As the phase-relations are very simple in these alloys (single phase nature of liquids and the solid solutions), one can suppose that the alloying induced by the electron concentration has a detectable impact not only in the stabilization of liquid state (melting point suppression) but also in the surface energy of the liquid drop. The magnitude of the wetting angle depends only indirectly on the total surface energy, which is composed from the drop/gas and the drop/substrate interface components [10].

The Summary of Observations is the Following:

The slope of $\Theta(T)$ for the pure Ag is positive on graphite, and negative on the Al_2O_3 substrates. This indicates the decreasing wetting ability of graphite, and the increase of Al_2O_3 versus the melt superheat, i.e. the Ag/graphite interphase formation is energetically unfavourable in the same

atmospheric circumstances, as the temperature increases (the interfacial energy increases) [16].

The influence of alloying elements on $\Theta(T)$ is also opposite in the case of two substrates. The shift (at a given superheating) increases with the solute concentration, as it is expected from the residual resistivity measurements.

Crossovers of the $\Theta(T)$ curves are often observed.

An influence of Cd addition is exceptional: generally opposite to that found in the case of other substituent (Θ decreases compared to the pure Ag). The lowering tendency is also typical on Al_2O_3 substrates. This general observation probably arises from the intrinsic property of Cd metal (exceptional high vapour pressure) [21].

This means that temperature dependence wetting ability is significantly modified by alloying elements. The existence of crossovers are probably associated with the different strengths of interactions between the Ag(Cd, In, Sn, Sb)-O in the melt, as it is expected from the Ellingham diagrams (Fig. 4).

The lowering tendency of Θ due to Cd addition observed both on the graphite and Al_2O_3 substrate is seen also in the case of Al_2O_3 substrates. This hints to the favour of melt/substrate interphase formation at the expense of melt/gas surface formation, when the Cd atoms are present in the melt drop. As it was mentioned above, the origin of this extraordinary behaviour can be attributed to the large heat of vaporization of Cd. It was reported that surface tension of metallic melts at their melting points depends on the heat of vaporization [21].

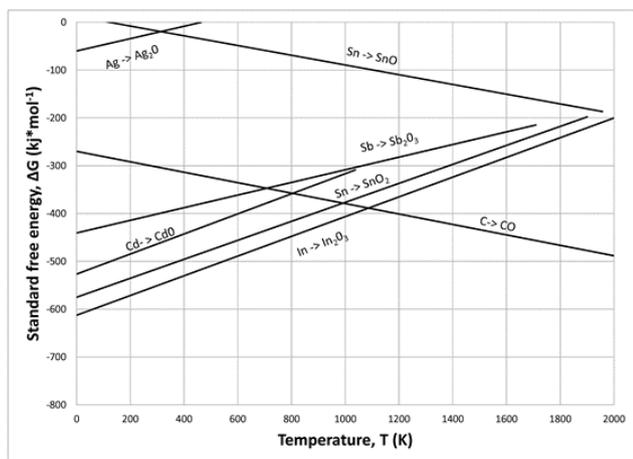


Fig. 4 Ellingham of the investigated systems [22]

As it was mentioned, the behaviour of Cd solvent is exceptional in the investigated systems:

$\Theta(T)$ usually decreases (especially at higher Cd content) which hints to increasing wettability due to the Cd addition. This tendency is particularly remarkable on the Al_2O_3 substrate. The wettability increase can be the indirect consequence of the high vapour pressure of Cd, the overwhelming majority of Cd exhausted from the liquid during the wetting experiments. Consequently on the reaction suppressed, the liquid/C interface formation is energetically favourable.

B. Ag-Cu, Ga, Zn System

The effect of alloying elements on $\Theta(T)$ is also visible in Fig. 5. While Θ is slightly increased due to the Zn and Cu replacement (the wetting ability decreases), the influence of Cu and Ga is opposite: Θ is lowered, hence the wetting ability increases nearly in the whole temperature range investigated. Another important feature of the curves is the different slope of their T-dependence. The highest is for the AgGa alloy, while the lowest is for Zn and Cu.

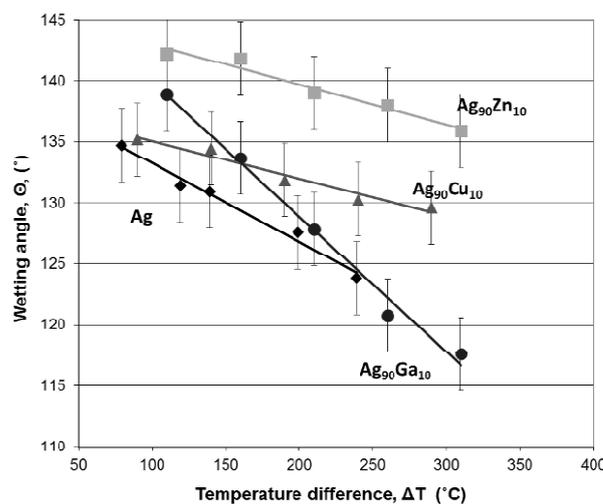


Fig. 5 The wetting angle for pure Ag, Ag(Cu10), Ag(Zn10) and Ag (Ga10) melt drops versus the temperature on graphite substrate

The existence of crossovers between Ag and Ag(Zn) as well as between Ag-Cu and Ag-Ga is also remarkable in the investigated systems. This means, that the wetting ability and its temperature dependence is significantly modified by the alloying elements in the Ag-based alloys. The temperature of the crossovers are not exactly the same, it is higher between the AgZn and pure Ag liquids. The existence of crossovers are probably are associated with the different shape of the appropriate phase diagrams, mainly due to the different concentration partitioning between the liquidus and solidus curves. The Ag-Ga alloy exhibits the highest degree of partitioning (Fig. 6). Another remarkable observation is, that $\Theta(T)$ is nearly the same for the pure Ag and the Ag (Zn), which is probably also connected with the low degree of concentration partitioning between the liquidus and solidus in the Ag(Zn) alloy, as well as the wide solubility range of Zn in the Ag (see Fig. 6).

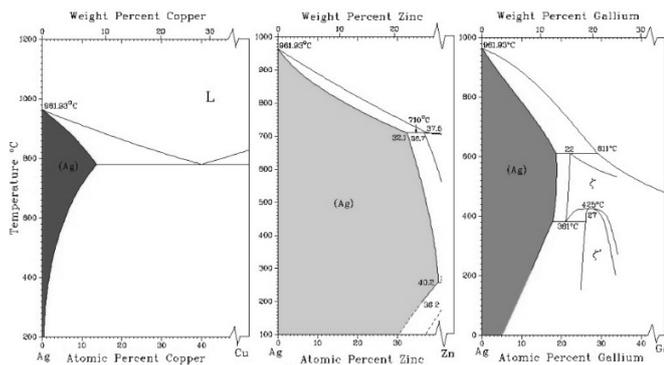


Fig. 6 The concentration range of terminal (α)-solid solutions in Ag-Cu, Ag-Zn and in Ag-Ga systems [17]

V. CONCLUSION

The temperature dependence of wetting angle is measured on graphite and Al_2O_3 substrates for various Ag-based melts, in which the composition is systematically changed by the controlled replacements of host metal by metallic substituent.

Wetting conditions of the investigated alloy drops depend on several, often controversial factors. The resulting surface-tension vectors manifest itself in the equilibrium value of contact angle. The contact angle representing the wettability between the substrate material and the sessile drop decreases with increasing temperature for simple liquids, like in the case of pure Ag melts, when the chemical interaction is negligible (present investigations with pure Ag). On the other hand, when alloying elements are dissolved in the host metal, local (temperature dependent) local deviations may occur either around the free surface or in the substrate/melt interface layer.

It was found, that the temperature dependence of the wetting angle is opposite for the two substrate materials in the pure Ag and the investigated solid solutions.

As a consequence, crossovers exist between the individual Θ (T) curves as a function of melt overheating. This means that at least two opposite factors exist in the temperature dependence of wetting ability of these alloy melts, indicating that the induced bulk alloying changes are often smeared by other metallurgical effects; like substrate melt interaction.

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REFERENCES

[1] M. Judd, K. Brindley, *Soldering in Electronics Assembly*. 2nd ed., Newnes, Oxford, UK, 1999.
[2] K. N. Tu, *Solder Joint Technology: Materials, Properties, and Reliability*. Springer, NY, USA, 2007.
[3] C. C. Fu, C. C. Chen, "Investigations of wetting properties of Ni-V and Ni-Co alloys by Sn, Sn-Pb, Sn-Cu, and Sn-Ag-Cu solders", *Journal of the Taiwan Institute of Chemical Engineers*, 42., 2011.
[4] M. Erinc, P. J. G. Schreurs, G. Q. Zhang, M. G. D. Geers. "Microstructural damage analysis of SnAgCu solder joints and an

assessment on indentation procedures," *Journal of Materials Science: Materials in Electronics*, Volume 16. 2003.

[5] K. L. Lin, C. L. Shih, "Wetting interaction between Sn-Zn-Ag solders and Cu," *Journal of Electronic Materials*, Volume 32. 2003.
[6] F. Dömötör, "Complex diagnostics of the cutting process of metal composite structures," *9th Danubia-Adria Symposium on Advances in Experimental Mechanics* Beograd, 2012
[7] L. J. Matienzo, R. R. Schaffer, "Wetting behaviour of eutectic tin/lead solder and fluxes on copper surfaces," *Journal of Materials Science* Volume 26/3. 1991.
[8] B. Vehovszky, P. Kamasa, J. Kovác, ZS. Fogarassy. "Complex Study of H-induced Structural Rearrangements in FeZr Glasses," *Materials Science Forum*, Vol. 729. 2013.
[9] L. R. Garcia, W. R. Osório, L. C. Peixoto, Am Garcia. "Wetting Behavior and Mechanical Properties of Sn-Zn and Sn-Pb Solder Alloys," *Journal of Electronic Materials*, Volume 38/11. 2009.
[10] G. Kaptay. "Classification and general derivation of interfacial forces, acting on phases, situated in the bulk, or at the interface of other phases," *J.Mater.Sci* 40. 2005.
[11] P. Baumli, G. Kaptay. "Wettability of carbon surfaces by pure molten alkali chlorides and their penetration into a porous graphite substrate," *Mater Sci Eng A*. 495. 2008.
[12] M. Abtew, G. Seldavuray, *Mater. Sci. Eng.* 27. 2007.
[13] W.H. Zhong, Y.C. Chan, M.O. Alam, B.Y. Wu, J.F. Guan. "Effect of multiple reflow processes on the reliability of ball grid array (BGA) solder joints," *Journal of Alloys and Compounds*. 414. 2006.
[14] J. Hlinka, Z. Weltsch, "Relation between the Wetting Property and Electrical Conduction of Silver-Gold (Ag-Au) Alloys" *Periodica Polytechnica Transportation Engineering*, 41/2. 2013.
[15] P. Casey, M. Pecht, *Proceedings of the Fourth International Symposium of EMP*, Taiwan, 2002.
[16] B. C. Allen, "Surface Tension in Liquid Metals," *Liquid Metals (Chemistry and Physics)*, INC., New York. 1972.
[17] Alloy Phase Diagrams Centre. ASM International, Materials Park, OH. 2006.
[18] W. Hume-Rothery, *Phase Stability in Metals and Alloys*. McGraw-Hill Publ. Co., New York, 1967.
[19] H. O'Neill, *Hardness measurements of metals and alloys*. Chapman and Hall Ltd. 1967.
[20] S. Flügge, *Encyclopedia of Physics*, Volume XIX. Electrical Conductivity, Springer-Verlag, 1956.
[21] F. D. Richardson, *Physical Chemistry of Melts in Metallurgy*. Academic Press London, New York Volume 2. 1974.
[22] DoITPoMS, University of Cambridge, http://www.doitpoms.ac.uk/tlplib/ellingham_diagrams