THE CONTACT ANGLE BETWEEN Ag-BASED MELTS AND GRAPHITE SUBSTRATE AND THE TEXTURE EVOLUTION DURING THE SUBSEQUENT SOLIDIFICATION

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ABSTRACT

Ag based alloys are widely used in the modern brazing technologies for the substitution of tin-lead based alloys. In the present work the wetting ability between graphite substrate and diluted Ag-M (M: Cd, In, Sn, Sb) has been studied using the sessile drop method. The contact angle between the liquids and solid substrate was measured at 1200˚C. Subsequently the micro structure of the solidified drops was investigated applying X-ray diffraction (XRD) and transmission electron microscopic (TEM) measurements. A texture formation was found in the substrate/drop interface region. Comparing the values of the contact angles measured on the Ag-M samples with the degree of the texture determined by XRD it was found, that the contact angle is smaller the degree of texture higher.

Keywords: *wetting, Ag based alloys, microstructure, X-ray diffraction, transmission electron microscopy, contact angle, silver*

1. INTRODUCTION

In the last years some environmental and technological factors were pressing for the development of alternative lead-free brazing materials [1-3], including the Ag based alloys. Requirements of the sufficient wetting and the melting point lowering can be fulfilled by appropriate alloying. During soldering, molten alloy comes into contact and usually reacts with the substrate. The ability of the liquid alloy to spread on the substrate is crucial to the formation of a bond driven by the physical-chemical properties of the system. The contact angle represents a quantitative measure of wetting of a solid by a liquid. For characterisation of the liquid phase, knowledge of the surface tension is required.

In the present work the influence of Cd, In, Sn and Sb alloying elements was investigated on the wetting properties of Ag on graphite substrate. Systematic change of the wetting angle is expected, because the replacement of the Ag host metal of these elements effects a gradual change in the electron concentration, and calculations show that the electronic term for surface tension also depends on the electron density, i.e. on the e/a (electron/atom) ratio [4]. It was found, that adhesion between the substrate and melts do also contribute to the shape of melt drop. This reveals the wetting conditions depend on several, often controversial factors, and the surface tension of the liquid drops is one of the important parameters. Adhesion between the substrate surface and liquid alloys plays a remarkable effect on the wetting ability too.

2. MATERIAL AND METHODS

Alloys were prepared from high purity (4N) Ag, Cd, In, Sn, Sb respectively, using induction melting in cold crucible under inert (Ar) atmosphere. Content of alloying elements is 5at% in each case.

The polycrystalline graphite substrate was made from high purity porosity free base material. The substrates were mechanically polished to Ra=0.23±0.005 μm, r=1.009±0.0005. Surface roughness was determined using a 3D laser profilometer (Rodenstock RM600 surface topography measurement system).

Wetting experiments were performed in a sessile drop equipment [5]. 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 105 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 105 Pa during the measurements. Measurements were made at 1273, 1323, 1373, 1423 and 1473 K.

Microstructure of the solidified drops was investigated by X-ray diffraction measurements (XRD) using a Philips X'pert equipment and transmission electron microscopy (TEM) carried out with a Philips CM2

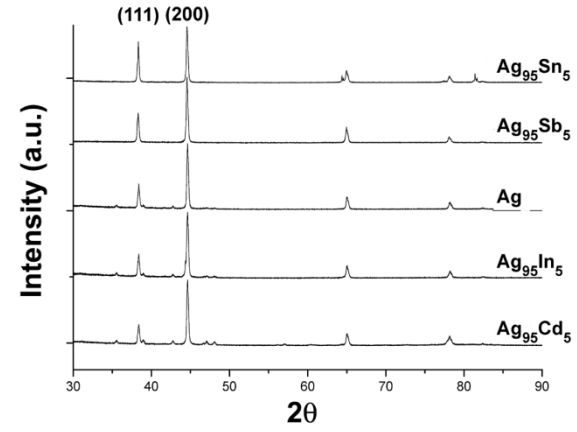
3. RESULTS AND DISCUSSION

3.1. XRD study of the drops characterised by different contact angle

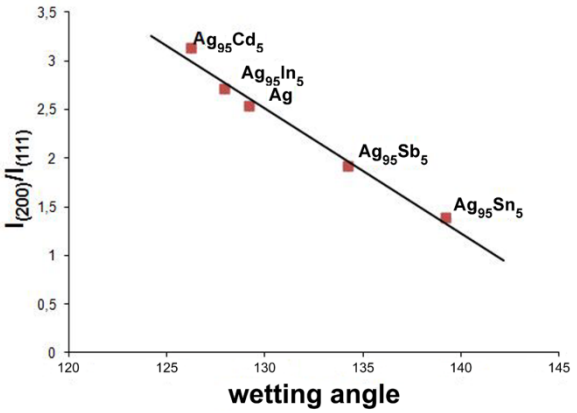
Wetting angle (Θ) measurements were performed on graphite substrate at 1200˚C for the pure Ag, AgCd5, Ag In5, Ag Sn5 and Ag Sb5 respectively [4]. In contrast with the predicted tendency the contact angle does not change monotonously with increasing electron density (e/a) caused by the alloying elements. The wetting angles detected in the case of samples alloyed with Cd and In are lower then, the pure Ag has, though their surface tension is higher in consequence of the increased e/a ratio. It means the surface tension is one of the important parameter only among other effects, like adhesion processes taking place at the substrate interface.

XRD patterns measured on the substrate side of the pure Ag and its alloys are plotted versus the experimentally determined wetting angle in Fig. 1a.

According to the ratio of the intensity maxima it can be established, that all of the investigated drops are characterised with a strong (100) texture near to the graphite substrate. This can be understood taking account the fact, that the size of the (200) lattice distances in Ag crystal is nearly the same as the (101) in the graphite. Comparing the values of contact angles measured at 1200C with the degree of the texture determined by XRD, it turned out the contact angle is smaller the degree of texture higher (Fig. 1b) The same tendency was found also in the case of Ag-Zn, Ag-Cu and Ag-Ga alloys [7].It means, that the better wetting properties (characterised by decreasing contact angle) are in strong correlation with the arrangements of the crystallites at the substrate. Via this preferential orientation favourable packing density is developed in contacting crystal planes, which can contribute to the interface energy minimization between the drop and graphite substrate. Enhanced surface diffusion, which plays an essential role in the development of preferential orientation, is promoted by the alloying elements.



(a)



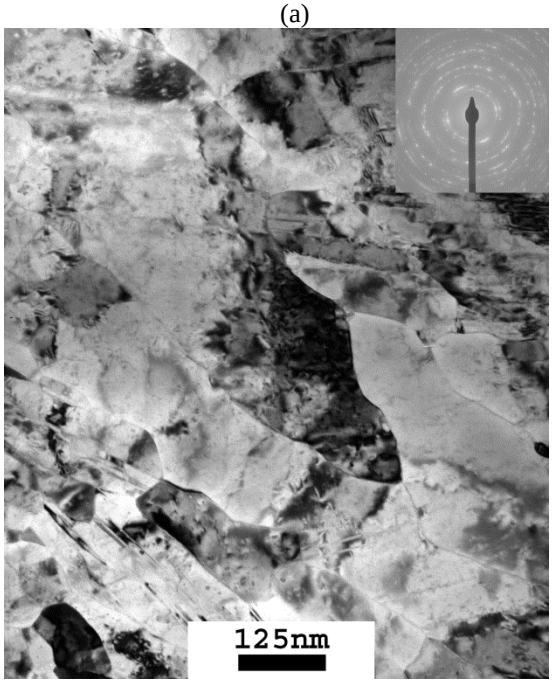
(b)

Fig. 1 XRD patterns measured on pure Ag and Ag alloyed with 5at.% of Cd, In, Sn or Sb samples at the substrate of the solidified drops (a), and the ratio of the measured intensity I(200) /I(111) versus wetting angle(b)

3.2. Microstructure of Ag-M drops

Cross-sectional TEM study revealed further details about the interface structure developed in drops near the substrate. The characteristic microstructure of the solidified drops can be seen in Fig. 2. Bright field TEM picture (See Fig. 2.a.) of pure Ag drop exhibits a 1μm wide layer with a polycrystalline structure at the graphite substrate. Crystallites of this layer have elongated shape parallel with the substrate (See Fig. 2.b.). This polycrystalline layer is supported by the texture formation in the vicinity of graphite/melt interface, and it is energetically favourable interface contact.

(a)



(b)

Fig. 2 Cross sectional bright field TEM image of the pure Ag drop near to the graphite substrate, a) in small magnification where arrow shows the place of the substrate, and b) a characteristic picture taken on the polycrystalline area in larger magnification

As an effect of alloying elements, the wideness of polycrystalline layer formed at graphite substrate decreases from In, -Cd, pure Ag, Sb, to Sn, which is in correlation with increasing values of wetting angles measured decreasing the wetting ability.

Inner part of the drop consists of large crystallites striped by twin lamellas parallel to each another. Selected

area diffraction analysis performed on this kind of faults proves that they are really twinned crystallites (See. Fig. 3).

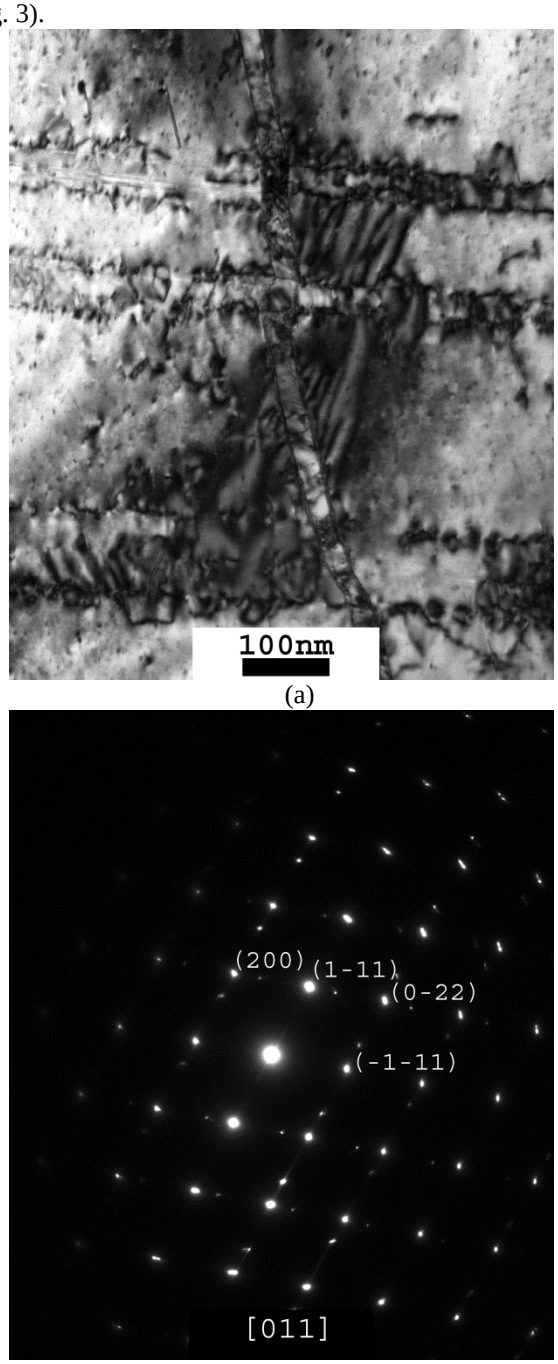


Fig. 3 Bright field image (a) taken on a "striped area" in Ag5%Sn, and its selected area diffraction pattern (b), show twinned crystallites

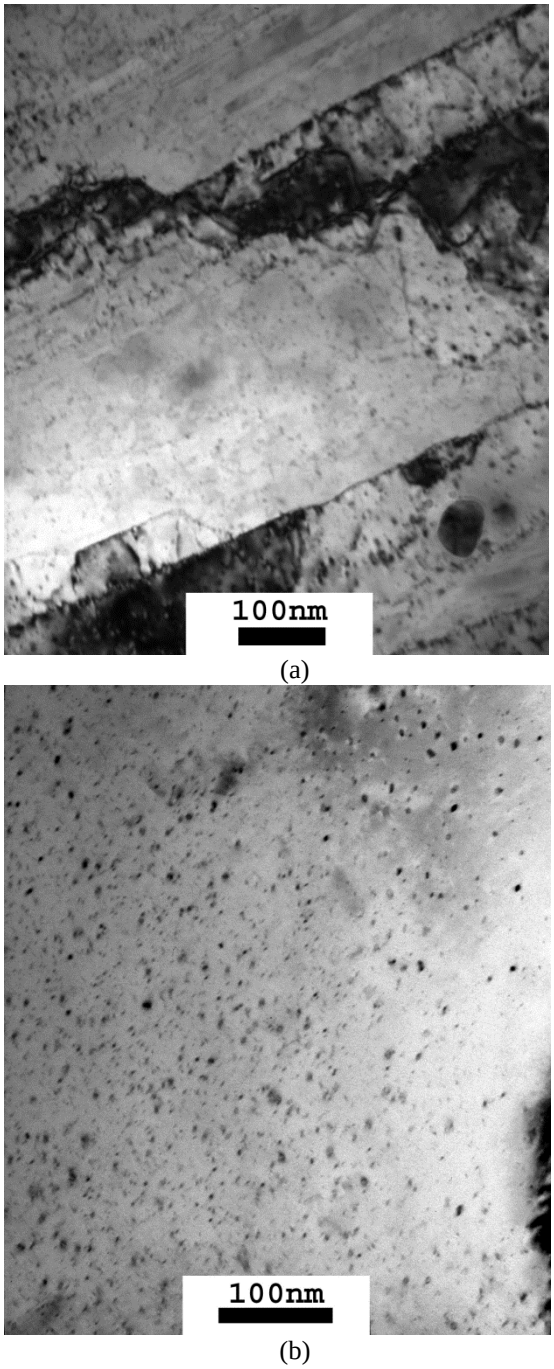


Fig. 4 A bright field TEM image, showing a large number of small dislocation-loops in the inner part of the a) pure Ag, and b) Ag5at%In drops

It was found that a large number of dislocation loops entrapped in the microstructure of drops after solidification (See. Fig. 4) and a large amount of the remaining energy stored in these loops. In low stacking fault energy Ag formation of these faults is favourable to decrease the strength during solidification of drop. As an effect of alloying elements the density of dislocation loops is much higher in the Ag alloys investigated (Compare Fig.4.a and Fig. 4.b). Most probably, the increased, number of dislocations loops were formed around the alloying atoms due to their attractive interactions.

The lattice defect structure is strongly influenced by different alloying elements. The density of twin lamellas increases parallel with the values of contact angles, and they are forming a grid like structure inside the drops (See: Fig. 5). Such a grid like structure of twins was not observable in the samples alloyed with In and In and Cd. According to our measurements the wetting angles do not change during solidification, which means that a larger amount of twin faults can reduce the inner strength in the samples with higher surface tension (Sn, Sb).

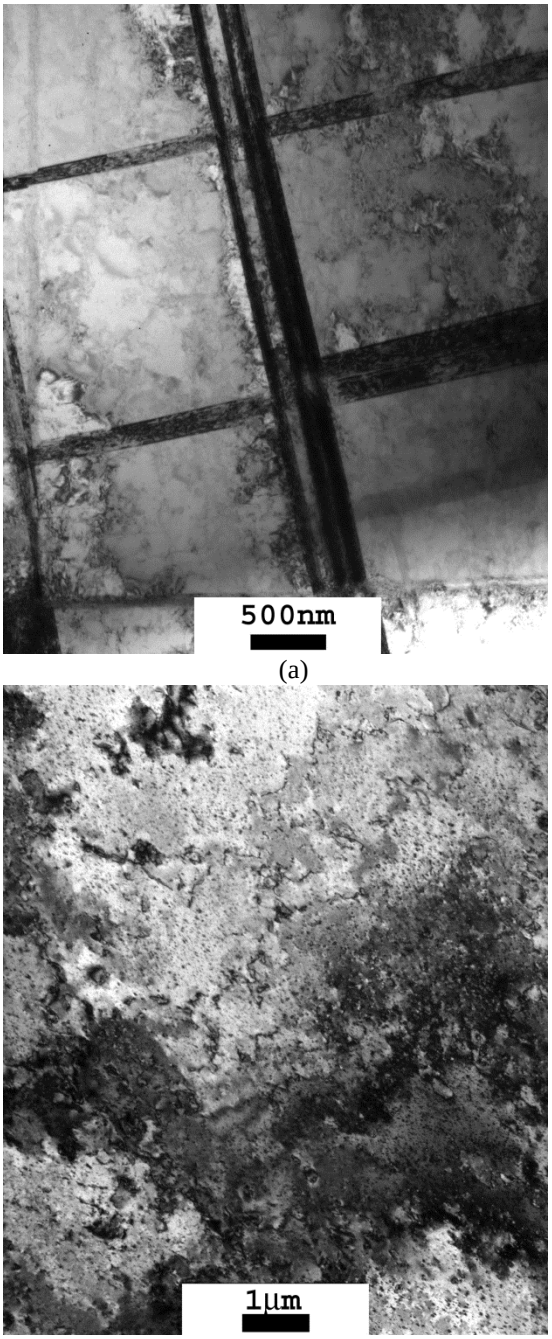


Fig. 5 TEM image taken on the inner part of a) Ag5%Sb and b) Ag5%Cd drops

4. CONCLUSIONS

From the analysis of the sample cross-sections the formation of an interface layer of textured polycrystalline phase with a thickness of some microns is desirable for the energetically favourable interface contact.

According to the TEM observations the density and the arrangement of stacking fault and twin lamellas formed inside of drops to reduce the strength during solidification are different in the investigated alloys.

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BIOGRAPHY

Zoltán Weltsch was born on 28.02.1985. In 2008 he graduated (MSc) at the department of Vehicles Manufacturing and Repairing at the Budapest University of Technology and Economics. Since 2008 he is working as a tutor with the Vehicles Manufacturing and Repairing. His scientific research and PhD theme are focusing on wetting ability between molten metals and ceramics.