

UNIVERSITY OF BELGRADE
TECHNICAL FACULTY BOR

**52nd International October Conference on
Mining and Metallurgy**



PROCEEDINGS

Edited by

Saša Stojadinović

and

Dejan Petrović

November 29th – 30th 2021

Bor, Serbia

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STUDY OF MICROSTRUCTURE AND THERMAL CONDUCTIVITY OF THE Ag–Bi–Sn ALLOYS

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Abstract

Five Ag–Bi–Sn ternary alloys with changeable tin concentration ranging from 12.8 to 75.1 mass% and nearly equal mass contents of silver and bismuth were investigated in this study. Microstructures of as-solidified alloy samples were examined using scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDS). The observed microconstituents were Ag₃Sn and (Bi) phases as well as ternary (Sn)+(Bi)+Ag₃Sn eutectic. The flash method was used for thermal diffusivity measurements in the temperature range from 25 to 100 °C. Based on the measured values of thermal diffusivity, thermal conductivity of the solid Ag–Bi–Sn alloys was obtained. Thermal conductivity of the studied Ag–Bi–Sn ternary alloys considerably increases with increasing tin concentration and slightly decreases with increasing temperature.

Keywords: Ag–Bi–Sn alloys, microstructure, ternary eutectic, thermal conductivity

1. INTRODUCTION

In the past few decades, Pb-free solders have made great development and several main kinds of Sn-based lead-free solders such as Sn–Ag, Sn–Zn, Sn–Bi, Sn–Cu, and Sn–Ag–Cu have been extensively studied [1–4]. In the majority of cases, there is still no universal Pb-free alternative and the selection of the soldering alloy is based on specific requirements of an application [4]. The ternary Sn–Bi–Ag alloys have been recognized to be important lead-free solder materials [3]. The Sn–35Bi–1Ag alloy is especially attractive because it has a melting point (178 °C) close to the traditional Sn–Pb eutectic solder (183 °C), excellent mechanical property and wettability [3].

The aim of the present study is to investigate relations between chemical composition, microstructure and thermal properties of the Ag–Bi–Sn alloys. For this purpose, five Ag–Bi–Sn alloys from a wide composition range were prepared by induction melting of pure Ag, Bi and Sn and characterized using several experimental techniques. Microstructure, phase morphology and thermal properties of the Ag–Bi–Sn alloys were examined. Microstructure of the samples was analyzed by SEM-EDS technique. Thermal diffusivity and thermal conductivity of the investigated alloys were determined by means of xenon-flash technique in the temperature range from 25 to 100 °C.

2. EXPERIMENTAL

All investigated alloy samples were prepared from Ag, Bi, and Sn (99.99 mass% purity) in an induction furnace under high-purity argon atmosphere. The average masses of the prepared ingots were about 5 g. The average loss of mass during melting of the samples was about 1 mass%. The microstructure was analyzed using scanning electron microscopy (SEM) in the backscattered electron (BSE) imaging mode using a TESCAN VEGA3 scanning electron microscope. The energy dispersive X-ray spectrometry (EDS) (Oxford Instruments X-act) was

employed for measurements of overall compositions and compositions of individual phases and the analysis was carried out with an accelerating voltage of 20 kV. The analyzed samples were prepared by classic metallographic procedure by polishing the specimens with diamond pastes without etching. The flash method was applied for determination of thermal diffusivity and thermal conductivity. This method was established by Parker et al. [5]. A xenon lamp (xenon-flash method) supplies an energy pulse to the front face of a thin disk specimen, and the temperature at the rear face is automatically recorded as a function of time. The thermal diffusivity is then determined according to the following equation suggested by Parker et al. [5]:

$$\alpha = \frac{1.37L^2}{\pi^2 t_{1/2}} = 0.1388 \frac{L^2}{t_{1/2}} \dots(1)$$

Thermal diffusivity was measured using Discovery Xenon Flash (DXF-500) instrument over a range of temperatures from 25 to 100 °C. The Ag-Bi-Sn samples (12.6 mm in diameter and 2 mm thick with plane-parallel ground end faces) were placed in a vacuum furnace and heated at a constant rate of 10 °Cmin⁻¹ to a measurement temperature. When the furnace temperature was sufficiently stable, the front surface of the specimen was heated by an energy pulse from the xenon lamp. Temperatures of the rear face of the samples were observed using the nitrogen-cooled IR detector (InSb sensor).

After the measurements of thermal diffusivity, thermal conductivity of the investigated samples was determined using the following fundamental relationship:

$$\lambda = \alpha \cdot \rho \cdot Cp \dots(2)$$

where λ is thermal conductivity (Wm⁻¹K⁻¹), α is thermal diffusivity (m²s⁻¹), ρ is density (kgm⁻³), and Cp is specific heat capacity (Jg⁻¹K⁻¹).

3. RESULTS AND DISCUSSION

3.1. Microstructure observation

The samples were characterized by SEM-EDS technique to examine microstructures, identify the microconstituents, and to measure their composition. The EDS data was acquired using area and point analysis. Firstly, the overall compositions of the alloy samples were determined by analyzing an as large as possible part of their surface. In order to determine the compositions of coexisting phases, each observed phase was analyzed at at least five different regions of the sample. Overall results of SEM-EDS analysis are given in Table 1. Examples of the microstructures are shown in Fig. 1.

Table 1 – Results of SEM-EDS analysis

Sample / mass%	Microstructure	Identified microconstituents	Composition/mass%		
			Ag	Bi	Sn
44.3Ag-42.9Bi-12.8Sn	Equiaxed Ag ₃ Sn grains in the (Bi) base	Ag ₃ Sn	75.4	2.2	22.4
		(Bi)	-	98.5	1.5
34.0Ag-33.4Bi-32.6Sn	Equiaxed Ag ₃ Sn grains, (Bi) dendrites and eutectic (Sn)+(Bi)+Ag ₃ Sn in the interdendritic regions	Ag ₃ Sn	75.1	-	24.9
		(Bi)	-	100.0	-
		(Sn)+(Bi)+Ag ₃ Sn eutectic	2.3	30.7	67.0
22.5Ag-23.9Bi-53.6Sn	Ag ₃ Sn and (Bi) dendrites and eutectic (Sn)+(Bi)+Ag ₃ Sn in the interdendritic regions	Ag ₃ Sn	75.2	-	24.8
		(Bi)	-	99.0	1.0
		(Sn)+(Bi)+Ag ₃ Sn eutectic	2.2	24.4	73.4
19.7Ag-18.5Bi-61.8Sn	Ag ₃ Sn and (Bi) dendrites with eutectic (Sn)+(Bi)+Ag ₃ Sn in the base	Ag ₃ Sn	75.6	-	24.4
		(Bi)	-	98.5	1.5
		(Sn)+(Bi)+Ag ₃ Sn eutectic	2.3	20.3	77.4
12.0Ag-12.9Bi-75.1Sn	Ag ₃ Sn and (Bi) dendrites with eutectic (Sn)+(Bi)+Ag ₃ Sn in the base	Ag ₃ Sn	75.5	-	24.5
		(Bi)	-	98.8	1.2
		(Sn)+(Bi)+Ag ₃ Sn eutectic	2.6	13.9	83.5

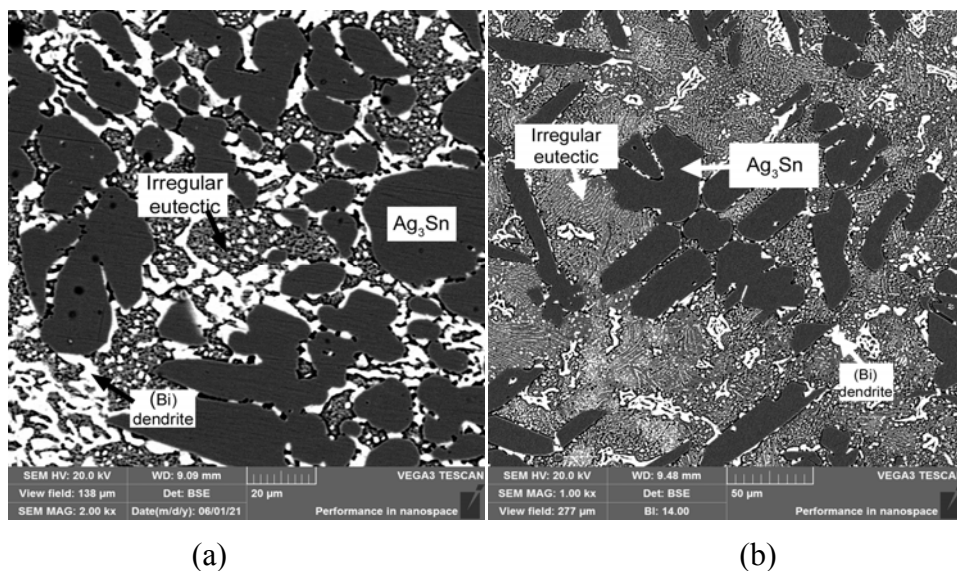


Figure 1. SEM image: (a) 34.0Ag-33.4Bi-32.6Sn alloy; (b) 22.5Ag-23.9Bi-53.6Sn alloy

3.2. Thermal conductivity measurements

The obtained values of density, thermal diffusivity, specific heat capacity and thermal conductivity for the solid Ag-Bi-Sn alloys in the temperature range from 25 to 100 °C are given in Table 2. Alloys densities were determined by using a buoyancy method based on the Archimedes' principle. Specific heat capacities of the studied alloys were calculated using thermodynamic parameters from [6]. The uncertainty for the thermal diffusivity measurements is ± 3% [4]. The total uncertainty for the thermal conductivity is estimated to be ± 6% [4].

4. CONCLUSION

The main conclusions of the present study may be summarized as follows:

The microstructure of studied alloys includes grains of Ag₃Sn and (Bi) phases and ternary eutectic mixture of (Sn) Ag₃Sn and (Bi) phases. Density decreases and specific heat capacity

increases with increasing Sn content. Thermal diffusivity and conductivity monotonically increase with increasing Sn content and slightly decrease with increasing temperature.

Table 2 – Density, specific heat capacity, thermal diffusivity, and thermal conductivity of the investigated Ag–Bi–Sn alloys in the temperature range 25-100 °C

Alloy /mass%	Temperature /°C	Density/ gcm ⁻³	Calculated specific heat capacity /Jg ⁻¹ K ⁻¹	Measured thermal diffusivity /mm ² s ⁻¹	Thermal conductivity /Wm ⁻¹ K ⁻¹
44.3Ag- 42.9Bi- 12.8Sn	25	9.73	0.183	8.00	14.24
	50	9.73	0.185	7.83	14.09
	100	9.73	0.187	7.65	13.92
34.0Ag- 33.4Bi- 32.6Sn	25	9.03	0.192	16.50	28.61
	50	9.03	0.194	16.23	28.43
	100	9.03	0.199	15.69	28.19
22.5Ag- 23.9Bi- 53.6Sn	25	8.19	0.201	25.86	42.57
	50	8.19	0.204	24.47	40.88
	100	8.19	0.21	23.43	40.3
19.7Ag- 18.5Bi- 61.8Sn	25	8.01	0.207	25.9	42.94
	50	8.01	0.211	24.80	41.91
	100	8.01	0.216	23.22	40.17
12.0Ag- 12.9Bi- 75.1Sn	25	7.73	0.213	27.80	45.77
	50	7.73	0.217	26.69	44.77
	100	7.73	0.223	24.89	42.91

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