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ELECTRICAL RESISTIVITY AND POSITRON LIFETIME STUDIES OF PRECIPITATION EFFECTS IN Al-Cu-BASED ALLOYS

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The improved workability of the commercial automatic machine designed alloy Al-Cu-Bi-Pb is guaranteed by the presence of Pb. Nevertheless, the toxic element Pb reduces some of the alloy properties. Therefore new Pb-free machinable Al-based alloys are developed. The Al-Cu-Bi-Sn alloy belongs to these non-traditional materials. The contribution deals with the investigation of precipitation effects in Al-Cu-Bi-Sn alloy during step-by-step isochronal annealing up to 500°C after previous solution heat treatment by means of positron annihilation spectroscopy completed with electrical resistivity measurements and results of independent transmission electron microscopy studies. The used combination of experimental methods gives the possibility to detect separately the redistribution of Sn and Cu atoms in the matrix and to study the influence of vacancies on this process.

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1. Introduction

The development of new workable lead-free aluminium-based alloys [1, 2] is one of the current tasks in material science of light alloys. According to [3] it is possible to replace toxic lead in automatic machine designed aluminium alloys by non-dangerous tin keeping simultaneously the good workability of the alloy with respect to chip forming. Moreover the new Al-Cu-Bi-Sn alloy exhibits some improved properties, for example, a considerably improved strength at room temperature after previous artificial ageing compared to Al-Cu-Bi-Pb alloy.

Whereas, according to [4], the presence of Pb and Bi does not influence the decomposition sequence of supersaturated solid solution of Cu in Al (see e.g. [5]), the replacement of lead by tin changes this decomposition sequence essentially [4, 6]. The redistribution of solutes in solution treated Al-Cu-Bi-Sn alloy starts by the formation of fine Sn precipitates. The vacancies are strongly bound to

these particles and thus the number of the free vacancies enhancing the diffusion of the Cu atoms is reduced. Therefore, the decomposition of supersaturated solid solution of Cu is shifted to higher temperatures and starts by the formation of θ'-phase without the previous formation of Guinier–Preston (GP) zones typical of Al-Cu system.

Precipitation processes in Al-Cu-Bi-Sn and in commercial Al-Cu-Bi-Pb alloys were compared in [7] in the wide temperature range from room temperature up to 500°C. The aim of this work is the study of the precipitation of Sn and Cu atoms in Al-Cu-Bi-Sn alloy by means of positron annihilation spectroscopy (PAS). PAS with a high timing resolution allows obtaining separate information about the behaviour of vacancies and the redistribution of Sn and Cu atoms in the crystal lattice. Positron lifetime measurements are combined with electrical resistivity measurements and results of transmission electron microscopy (TEM) [7] are used for the interpretation purpose.

2. Experimental details

The material was prepared as the industrial casting in ALUSUISSE Děčín. This alloy contains (in wt.%) 4.6 Cu, 0.59 Bi, 0.36 Sn, 0.16 Fe, 0.06 Si, and 0.014 Pb. The extruded material was exposed to the solution heat treatment at 530°C for 1 hour finished by rapid quenching into water of room temperature. A calibration tension of 8% at room temperature and finally ageing at 140°C for 10 hours followed. The machined specimens for electrical measurements ($4 \times 6 \times 66$ mm^3, where the last number means the gauge length for electrical measurements) and PAS (targets of 9 mm in the diameter and 3 mm in the thickness) were solution heat treated at 525°C for 30 minutes and fast cooled in water. The subsequent isochronal annealing was carried out in steps of 20°C/20 min in the oil bath (up to 240°C) and in the furnace with argon atmosphere at higher temperatures.

Electrical resistivity was measured by the standard four-point method at 77 K with a dummy specimen in series enabling the corrections of temperature instability of the liquid nitrogen bath. The electrical circuit was composed from KEITHLEY devices. The resistivity measurements were completed with transmission electron microscopy by means of JEOL JEM 2000 FX electron microscope. The choice of positron lifetime measurements was done on the base of the measured annealing electrical resistivity curves.

The positron lifetime spectrometer is equipped with a coincidence system representing a modification of our fast-slow configuration, which was described in detail in [8, 9]. Its detector part, consisting of two BaF_2 cylinder scintillators ($\oslash$ 25×10 mm) coupled to PHILIPS XP2020/Q photomultipliers (PMT). The dynode timing signal from 10th dynode of PMT passes through the capacitor to the input of the constant-fraction differential discriminator (CFDD), which provides also the coarse energy selection of events. Output timing signals from CFDD activate the start and stop inputs of the time-to-amplitude converter (TAC). The energy signals from 9th dynode of PMT are first shaped by a passive RC-integration circuit and then passively summed. The sum of signals is amplified by the spectroscopy amplifier whose output is connected with timing single-channel anal-

yser (TSCA) adjusted at the sum of energies 511 keV (stop photon) + 1274 keV (start photon) in the case of ^{22}Na positron source. The output pulses from TSCA strobe the signal from the TAC. The output pulses from TAC are processed in an analogue-to-digital converter whose data output is connected to a histogramming memory operated by an auxiliary CAMAC controller. The complete electronics is built from commercially available modules produced by ORTEC, CANBERRA and C.E.S. The more detailed description of spectrometer will be published elsewhere [10].

Face-to-face detector geometry with common symmetry axis was used and a 2.5 mm thick Pb shielding was placed between the detectors. Two Helmholtz's coils serve as a protection against Earth's magnetic field. A carrier-free ^{22}NaCl ($\approx$ 1.3 MBq) deposited and sealed between 2 μm thick mylar foils was used as a positron source. The source was placed between two targets of the investigated material. The sandwich is located out of a common axis of detectors at a radial distance slightly greater than the radius of the scintillators (12.5 mm). All measurements were performed at room temperature. At least 9×10^6 counts were collected in each spectrum. The lifetime spectra were decomposed into the individual exponential components by means of a fitting procedure [11] based on the maximum-likelihood principle. Total FWHM of resolution function, composed of three Gaussians, was found in simultaneous fit to be 152 ps.

3. Results and discussion

The isochronal annealing curve of electrical resistivity and the isochronal annealing response of the relative intensities of positron lifetime components are shown in Figs. 1 and 2, respectively. According to the TEM results and the data discussed in [7], a slight local maximum of electrical resistivity at 100°C and a subsequent decrease in electrical resistivity (below 160°C) are caused by clustering of Sn atoms. This process ends by the vacancy-assisted formation of incoherent spherical β-Sn precipitates. Vacancies increase considerably the diffusivity of Sn in Al due to high binding energy of the vacancy to Sn atom [6]. The sharp drop of electrical resistivity above 160°C is caused by the appearance of fine plate-like semicoherent precipitates of the θ'-phase (Al_2Cu), which arise mainly by means of heterogeneous nucleation on β-Sn particles [6]. The coarsening of these precipitates takes place above 260°C followed by the transformation of the θ'-phase into the equilibrium incoherent θ-phase (Al_2Cu) at 320°C. The decrease in electrical resistivity is finished at 340°C and its subsequent growth is caused by the reconstruction of solid solution.

Despite two components with long lifetimes and low relative intensities, which originated from positron annihilation in source material, positron lifetime spectra were decomposed into two or three components depending on annealing temperature, see Fig. 2. Lifetimes of these components are denoted as τ_1, τ_2, τ_3. The component τ_1 is characterised by a short and inconstant lifetime varying between 45 and 76 ps and by a low relative intensity decreasing below 10% with increasing annealing temperature. This component comes from annihilations of non-localised positrons in the matrix. The lifetime τ_2 equals 229 ps (at 80°C) and 235 ps (at 120°C). These values are close to literature data for the lifetimes of

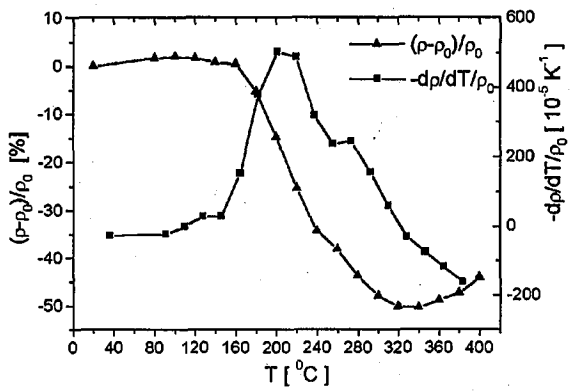

Fig. 1. Resistivity annealing curve together with its derivative. ρ_0 denotes the resistivity value in the as solution treated state.

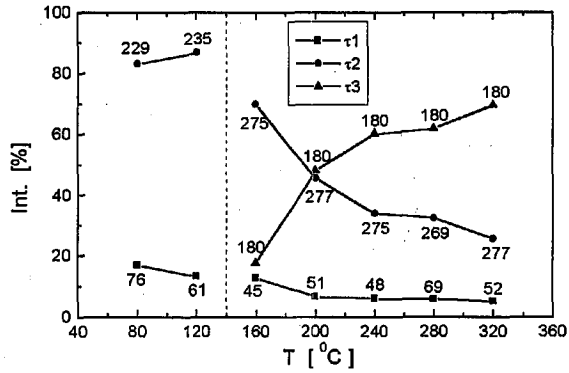

Fig. 2. Temperature dependence of relative intensities of positron lifetime components τ_1, τ_2 and τ_3. The numbers at different points denote the actual values of lifetimes.

positrons trapped at the vacancies in Al (240 ps, [12]). Therefore, it is likely that this component comes from the annihilation of positrons localised at the vacancies bound to Sn atoms. According to [6, 13] the existence of vacancy–Sn atom complexes is very probable in our specimens in the initial state and in the range of low annealing temperatures due to the strong binding energy between vacancy and Sn atom in Al with respect to the heat treatment of our specimens. At annealing temperatures above 160°C the lifetime component τ_2 is enlarged to 269–277 ps. We assume that in the temperature range 160–320°C this component could be related to positron annihilation at incoherent precipitates of the β-Sn, considering the strong positron affinity to the Sn precipitates in Al matrix [14]. The Sn precipitates act simultaneously as nucleation centres for semicoherent precipitates of the θ'-phase which were detected by means of PAS just at 160°C (see component τ_3 in Fig. 2) in agreement with electrical resistivity measurements and TEM observations [7]. Considering almost zero affinity of positrons to Cu precipitates in Al matrix [14] we ascribe this component to positron annihilations at the misfit dislocations of the θ'-phase precipitates. Therefore, the lifetime τ_3 was fixed as

180 ps during the spectra deconvolution according to results of our previous study of precipitation processes in Al–Cu system [9, 15]. It is shown in Fig. 2 that the relative intensity of the component τ_3 increases in the temperature range 160–320°C due to the θ'-phase volume fraction increase, in the perfect agreement with results of electrical resistivity measurements (Fig. 1) and TEM [7]. Consequently, the relative intensity of the component τ_2 decreases in this temperature range.

4. Conclusion

It was shown by means of PAS, resistivity measurements and TEM studies, that in solution heat treated Al-Cu-Bi-Sn alloy the vacancy-assisted formation of β-Sn particles takes place during the isochronal annealing below 160°C and the nucleation and growth of θ'-phase (Al_2Cu) on β-Sn particles occurs between 160°C and 320°C.

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