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POSITRON ANNIHILATION IN INTERNALLY OXIDIZED COPPER

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The positron lifetimes in internally oxidized polycrystalline copper, annealed at different temperatures, were measured. It was found that the dispersed alumina particles act as positron traps. Estimation of concentration of defects was made in the frames of the trapping model.

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1. Introduction

In many cases there is a necessity of materials which combine high electrical and thermal conductivity with mechanical strength. The latter must retain at comparatively high temperatures.

In general, the strengthening is a result of some obstacles of any kind, present in material, which hinder dislocation motion. Such barriers are, for example, the Guinier–Preston zones, second-phase precipitates etc., which may be formed during quenching or (and) ageing of oversaturated solid solutions.

In internally oxidized alloys, the dislocation motion barriers are highly dispersed oxides of elements less noble than the matrix. In copper such elements are aluminum, magnesium and silicon [1].

It is well established that positrons are effective probe for studying vacancy--type defects (see for example [2]). In some cases the study of precipitation in metals by positron annihilation technique is also possible [3].

The aim of the present study is to elucidate the defect structure of oxide-dispersion-strengthened copper alloy prepared by hard plastic deformation of internally oxidized copper in the Department of Metal Science, Technical University, Russe.

2. Material

The sample material was obtained from 99.9% copper. After internal oxidation of Cu–Al(0.3 wt%) alloy for 8 h at 950°C, the samples were plastically deformed by pressure to reduce the thickness by $\varepsilon = 75\%$. The volume fraction of alumina is $\approx 1.4\%$. The size of the alumina particles is ≈ 0.1 μm.

Some characteristics of the material are shown in Table I (H_V is the Vickers

TABLE I

H_V	HMV	D [Å]	$\Delta\alpha/\alpha$	ρ [cm^{-2}]
113–115	≈ 150	636	0.0012	1.86×10^{11}

hardness (load $P = 5$ kgf), HMV — microhardness ($P = 50$ gf), ρ — dislocation density). The effective diameter D of particles and microstrain $\Delta\alpha/\alpha$ were determined by X-ray diffraction.

3. Experimental details

Two identical samples with dimensions $10 \times 10 \times 1$ mm were used in this study. A ^{22}Na radioactive source, sealed between two thin (0.723 mg/cm^2) kapton foils, was sandwiched by the samples.

The positron lifetime spectrometer used is based on a fast-slow type coincidence circuit and provides about 240 ps time resolution (FWHM).

Analysis of lifetime spectra was performed by the program POSITRONFIT-EXTENDED [4]. About 1.2×10^6 counts were accumulated for each spectrum. The samples were measured 4 to 8 times. Corrections for source lifetime components were made.

The measurements were carried out at room temperature in as-received samples and after 1 hour annealing of the samples successively at 100, 240, 300 and 430°C in air.

The 3γ probability was measured in as-received samples with a HPGe spectrometer (energy resolution at the 514 keV gamma line of ^{85}Sr — 1.2 keV) by the so-called "peak-peak" method [5].

Before each measurement the samples were cleaned by picking in nitric acid.

4. Results and discussion

The parameters (lifetimes and intensities) obtained by three-component fit of lifetime spectra are considerably dispersed. The longest lifetimes τ_3, however, remain constant in the error limits. Because of this, we tried a three-component analysis with the fixed value of τ_3, obtained in as-received samples. The results are shown in Table II.

TABLE II

Lifetimes, intensities and mean lifetime yielded from three-exponential fit of lifetime spectra; $\tau_3 = 2240$ ps — fixed.

Treatment	τ_1 [ps]	I_1 [%]	τ_2 [ps]	I_2 [%]	τ_3 [ps]	I_3 [%]	$\bar{\tau}$ [ps]
1	184(1)	87.2(6)	437(8)	9.6(5)	2241(18)	3.2(1)	274(3)
2	184(1)	97.4(4)	412(33)	2.1(3)	2240	0.39(9)	197(2)
3	129(1)	85.4(6)	277(5)	12.7(9)	2240	0.37(6)	156(2)
4	118.3(8)	89.5(5)	276(4)	10.2(5)	2240	0.22(2)	139(1)
5	119.7(9)	87.9(6)	285(1)	11.8(5)	2240	0.28(5)	145(2)

1 — as-received samples, 2 — one-hour annealing at 100°C, 3 — one-hour annealing at 240°C, 4 — one-hour annealing at 300°C, 5 — one-hour annealing at 430°C.

It is evident from the experimental results and their comparison with the theoretical ones [6] that the defect concentration in the as-received and annealed at 100°C samples is such that all the positrons annihilate in trapped states.

These states and the corresponding lifetimes, in our opinion, are as follows:

(i) Alumina particles — τ_3.

As Hirsch et al. [7] have shown, the internal oxidation of dilute Cu–Al alloys produces a fine dispersion of alumina particles in the matrix. On the other hand, the value of τ_3 is of the order of 2 ns and it is characteristic of pick-off annihilation of *o*-Ps. While in metals positrons annihilate without formation a bound e^+–e^- state, such state in Al_2O_3 is well established [8]. Therefore, this component can be attributed to positron annihilation in alumina precipitates. Moreover, as the probability of 3γ annihilation is equal to zero in 3σ-error limits in as-received samples, one could state that, namely, *ortho*-positronium is formed in alumina particles and pick-off annihilation takes place.

The conclusion that alumina particles act as positron traps is consistent with the observation of Alam et al. [9] that the heat treatment of dilute Al–Mg alloy in the presence of any amount of oxygen in the annealing atmosphere causes great changes in the parameters of positron annihilation.

It is well established [1] that with the increase in annealing temperature, two processes, namely recrystallization of the matrix and coagulation of alumina particles take place. This leads to the increase in interparticle distance. If the distance between alumina particles becomes greater than the diffusion path of positrons in copper, the probability of the positron trapping at the precipitates will decrease. This is consistent with I_3 changes after annealing of the samples.

(ii) Vacancies connected with dislocations, dislocation loops and border regions between alumina particles and matrix — τ_1.

We suppose that τ_1 can be considered as apparent lifetime of a mixture of three unresolved components due to positron annihilation in three different types

of traps, created during the internal oxidation and subsequent deformation of the samples.

1. During the oxidation all Al is removed from the solid solution and, therefore, some purification of the matrix takes place [1]. On the other hand, however, there remain vacancies on the previous Al sites. At room and higher temperatures, these vacancies are mobile and become trapped at dislocations. Annealing of the samples at 240°C removes these traps.

2. The dislocation structure generated by plastic deformation and associated with alumina particles consists predominately of prismatic loops. The number of these loops decreases rapidly with the temperature in the range of 30–230°C [7] which can be connected with fast decrease in τ_1 after annealing of the samples at 240°C.

3. Due to the considerable size of the alumina particles ≈ 0.1 μm, they have lost coherency, presumably by generation of interface dislocations at the temperature of precipitates formation. During the cooling, the difference between thermal contraction coefficients of the particles and of the matrix causes further misfit strains. The effect of particles coagulation during annealing of the samples is the same.

Due to the above mentioned behavior of these three types of traps during annealing of the samples, the shortest lifetime component τ_1 in the cases 3, 4 and 5 can be interpreted as apparent lifetime of a mixture of two unresolved components due to positron annihilation in the bulk of the matrix and in the border regions between alumina particles and matrix.

(iii) Vacancy clusters — τ_2.

The values of the second component τ_2 presume the presence of vacancy clusters in the samples. The sizes of these clusters decrease as the annealing temperature increases. Annealing at 100°C leads to considerable decrease in concentration of voids without changing their sizes. Annealing at 240°C leads to the dissociation of some of them. Subsequent annealing keeps practically unchanged sizes and concentration of clusters.

In the frame of the trapping model [10] for the cases of two and three different types of defects the following estimations were made.

(i) After 430°C annealing of the samples.

$$\tau_b = 126 \text{ ps}, \quad k_{cl} = 1.8 \times 10^7 \text{ s}^{-1}, \quad k_{AP} = 0.5 \times 10^9 \text{ s}^{-1},$$

where τ_b is the bulk lifetime, k_{cl} and k_{AP} are the positron trapping rates for vacancy clusters and alumina particles respectively. The specific trapping rate in the clusters is $\mu_{cl} = N\mu_v$, where $N = 4$ is the number of vacancies in this case, $\mu_v = 4.93 \times 10^{-9}$ cm^{-3} s^{-1} [11] is the specific trapping rate for a vacancy in copper. Using the upper value for k_{cl}, the cluster concentration was estimated to be $C_{cl} = 2.5 \times 10^{16}$ cm^{-3}.

(ii) As-received samples.

$$k_d = 2.83 \times 10^{11} \text{ s}^{-1}, \quad k_{cl} = 31.4 \times 10^9 \text{ s}^{-1} \ (N = 20),$$

$$C_{cl} = 3.2 \times 10^{17} \text{ cm}^{-3}, \quad k_{AP} = 10.6 \times 10^9 \text{ s}^{-1}.$$

$k_d = \mu_d \rho$ is the positron trapping rate for dislocations ($\mu_d = 1.51$ cm^2 s^{-1} [11]).

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