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Positron Annihilation Spectroscopy in the Evaluation of Microstructure of Cast Copper and Copper-Aluminum Alloys during Isochronal Annealing

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Isochronal annealing was carried out for cast Cu, Cu-5wt.%Al, Cu-10wt.%Al, and Cu-20wt.%Al alloys in the range of 423-1173 K. The annealing behavior was followed by positron annihilation lifetime spectroscopy (PALS). Microhardness (H_v) has been measured and used for comparison. The microstructure variations were observed by optical and scanning electron microscopy. Three stages were distinguished for all samples in the behavior of average lifetime (τ_{av}) and H_v. In the first stage (room temperature to 573 K), τ_{av} and H_v reach extremely high values for Cu-20wt.%Al compared with other alloys. The analysis of the first stage indicates anneal softening for cast Cu and Cu-5wt.%Al and anneal hardening for Cu-10wt.%Al and Cu-20wt.%Al. The second stage (573-873 K) is characterized by a maximum of τ_{av} at 673 K followed by a decrease up to the end of the stage for cast Cu, Cu-5wt.%Al (the highest maximum), and Cu-10wt.%Al; a slight change is observed for Cu-20wt.%Al. The change in H_v is notable only for Cu-10wt.%Al and Cu-20wt.%Al, and indicates that τ_{av} is sensitive to the change that occurred in the bulk material, while H_v shows the general behavior of the surface of the material. The third stage (873-1173 K) is characterized by near saturation for both τ_{av} and H_v, indicating complete recrystallization for cast Cu, Cu-5wt.%Al, and Cu-10wt.%Al and complete softening for Cu-20wt.%Al. Recrystallization is shifted to higher temperatures by increasing the amount of Al in Cu. The analysis of positron lifetime presents evidence of the existence of three-dimensional (3D) defects in addition to one-dimensional defects, so a modification to the simple trapping model is needed when considering inhomogeneous trapping.

Keywords Al bronze, cast Cu, grain size, lifetime parameters, microhardness, positron annihilation

1. Introduction

Copper aluminum alloys (Al bronze) are finding increasing applications in many industrial areas. The specific combination of properties often provides a unique engineering material, and future growth in their use is expected due to the ever-increasing demand for maintenance-free service (Ref 1, 2).

Copper alloy castings can be used in applications that require superior corrosion resistance, high thermal or electrical conductivity, good bearing surface qualities, or other special properties. Casting makes it possible to produce parts with shapes that cannot be easily obtained by fabrication methods such forming or machining (Ref 1). The mechanical properties of Al bronze (face-centered-cubic; fcc) depend mainly on the Al content (Ref 3).

Besides the traditional methods for inspection of the microstructure using techniques such as optical microscopy, scanning and/or transmission electron microscopy, microhardness, tensile testing, etc., nondestructive positron annihilation lifetime spectroscopy (PALS) has been used with great success for the same purpose (Ref 4-6).

The lifetime of positrons trapped in a defect depends on the average electron density (i.e., the lower the electron density, the longer is the lifetime). So each type of defect gives rise to a characteristic positron lifetime τ_i. Each defect exhibits a characteristic decay exponential, the slope of which equals the annihilation rate (τ_i^{-1}) for that particular defect.

It was found that the annihilation of a free positron in Cu (τ_1) has a lifetime in the range of 110-122 ps (Ref 7, 8). In the presence of defects such as monovacancies, dislocations, and dislocation loops, the lifetimes may increase up to 180 ps (Ref 9). In a porous sample like a cast alloy, it is important to consider the positrons that are most likely thermalized and how the annihilation characteristics are influenced by pores, voids (vacancy agglomerates), or grain boundaries, which also act as trapping sites (Ref 10). The lifetime of positrons trapped in three dimensions (voids) increases with the size of the voids to about 500 ps (Ref 6, 9).

The aim of this study was to use PALS to study the microstructure variations as a function of isochronal annealing of cast Cu and Al-bronze containing various amounts of Al (5, 10, and 20 wt.%).

2. Experimental

2.1 Material

The chemical composition of cast Cu and cast Cu-Al alloys[1] used in this investigation is shown in Table 1. The specimens were isochronally annealed for 1 h at 423-1173 K with an accuracy ±2 °C. The samples were left to cool in the oven to avoid quenching effects.

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[1] Supplied from Griffin England.

Table 1 Chemical composition of commercial pure Cu and Al-bronze

Material	Cu	Fe	Si	Mg	Mn	Al	Pb	P	Ni
Cu	bal	0.015	…	…	…	…	0.005	0.007	…
Cu-5wt.%Al	bal	0.5	<0.003	0.00066	<0.003	5	0.082	…	0.18
Cu-10wt.%Al	bal	0.5	<0.003	<0.003	0.5	10	0.1	…	0.8
Cu-20wt.%Al	bal	0.5	<0.003	<0.003	1.5	20	<0.002	…	1.2

After polishing, the specimens were etched in a solution of $FeCl_3$ (5 g), HCl (50 ml), and H_2O (100 ml). Metallographic observations were carried out optically for different positions in the sample to characterize the microstructure at different stages of the heat treatment. Some photomicrographs were taken using scanning electron microscopy (SEM).

2.2 Microhardness Measurements

Hardness measurements were performed using a Vickers microhardness tester. An applied load of 50 g was used with a dwell time of 10 s. Ten readings were taken for each sample, and the average and standard deviations were calculated.

2.3 PAL Measurements

In conventional positron annihilation experiments, the positrons are injected into a sample from a radioactive source (e.g., ^{22}Na), which emits positrons with mean energy of a few hundred keV. The injected positrons slow down to thermal energies in about 10^{-12} to 10^{-11} s by ionization and excitation of the atoms in the solid. During thermalization, the positrons penetrate the metal to a depth of about 100 μm or less. Thus, the positrons are used as a probe for the bulk material in such measurements (Ref 5).

For PAL measurements, a radioactive ^{22}Na positron source with activity ~20 μCi was deposited on a kapton foil and sandwiched between two identical samples. The positron emission is followed by a 1.274 MeV photon, which serves as the signal for the positron birth. The lifetime is, thus, the time delay between the 1.274 and 0.511 MeV (i.e., the annihilation of the positron) gamma quanta and is measured by the conventional fast-fast coincidence system using two plastic scintillation detectors. By measuring the time difference between the two signals, the positron lifetime can be measured. The time resolution of the spectrometer (i.e., the full width at half-maximum; FWHM) is 230 ps measured by a ^{60}Co source. The count rate in the lifetime spectrum is ~100 counts/s. The measured lifetime spectrum consists of 5×10^6 counts. The measurements of lifetime spectra were carried at room temperature (RT) and were analyzed with PATFIT (Ref 11) after subtracting the background.

At some time δt (distributed from zero up to some hundreds of pico seconds) after positron injection into the metal, the positron will annihilate with an electron yielding two γ rays. The distribution of the δt values measured in the lifetime experiment yields information reflecting total electron density. The presence of defects in a material leads to trapping of the positron and an increase in the observed positron lifetime relative to the free positron. The results of PAL experiments on materials containing defects that trap positrons are normally analyzed in terms of the two-state trapping model (Ref 12). This model assumes that at time t, the positron exists in one of only two states: the bulk or Bloch state, and the defect-trapped state, in relative concentrations $n_b(t)$ and $n_d(t)$, respectively, with $n_d(0) = 0$. This model can be described by a set of coupled differential equations:

$$\frac{dn_b}{dt} = -n_b\lambda_b - n_b k \quad \text{(Eq 1)}$$

$$\frac{dn_d}{dt} = +n_b k - n_d\lambda_d \quad \text{(Eq 2)}$$

where k is the trapping rate:

$$k = \frac{I_2}{I_1}(\lambda_b - \lambda_d)$$

and λ_b and λ_d are the annihilation rates in the bulk and in the defect, respectively. The solution of these equations leads to a lifetime spectrum with two exponential components of the lifetimes: τ_1 and τ_2 with intensities I_1 and I_2. Thus,

$$\tau_1 = (\lambda_b + k)^{-1} \text{ and } \tau_2 = \lambda_d^{-1} \quad \text{(Eq 3)}$$

and relative intensities:

$$I_1 = 1 - I_2 \text{ and } I_2 = k(\lambda_b - \lambda_d + k)^{-1} \quad \text{(Eq 4)}$$

3. Results

3.1 Microstructures of the Tested Cast Alloys

The microstructures of the cast alloys are shown in Fig. 1, 2, and 3. The microstructure of pure Cu at RT is fine grained, whereas for Cu-5wt.%Al, cored α is observed. For Cu-10wt.%Al, the alloy possesses a $(\alpha + \gamma_2)$ structure that consists of ductile α and brittle γ_2. Cu-20wt.%Al (like an Al bronze with >15wt.%Al) possesses the brittle γ_2 phase. This structure is similar to Cu with more than 50wt.%Zn (Ref 13).

The microstructures of cast Cu at 473, 673, 873, and 1073 K are shown in Fig. 1(a)-II, 2(a)-I, 2(a)-II, and 3(a), respectively. It appears that pure cast Cu exhibits recrystallization and grain growth with the increase in annealing temperature.

For Cu-5wt.%Al, rearrangement of the α solid solution at 473 K (Fig. 1b-II), elongated grains at 673 K (Fig. 2b-I), more equiaxed grains at 873 K (Fig. 2b-II), and the formation of subgrains from the α solid solution (oriented in one direction) at 1073 K.

For Cu-10wt.%Al, the basket weave structure observed at RT is replaced by an acicular martensitic structure at 473 K (Fig. 1c-II), which is similar to the microstructure of Ni-Al bronze with 9-11% Al, quenched from 1130 K (Ref 14). After annealing at 673 and 873 K, a homogeneous basket weave structure develops. The microstructure after annealing at 1073 K shows some disturbance in the basket weave (Fig. 3c).

Cu-20wt.%Al exhibits a single elongated directional γ_2 structure after annealing at 473 K (Fig. 1d-II). However, after annealing at 673 K, the elongated γ_2 grains lose their directionality. Subgrains can be seen after annealing at 1073 K (Fig. 3d).

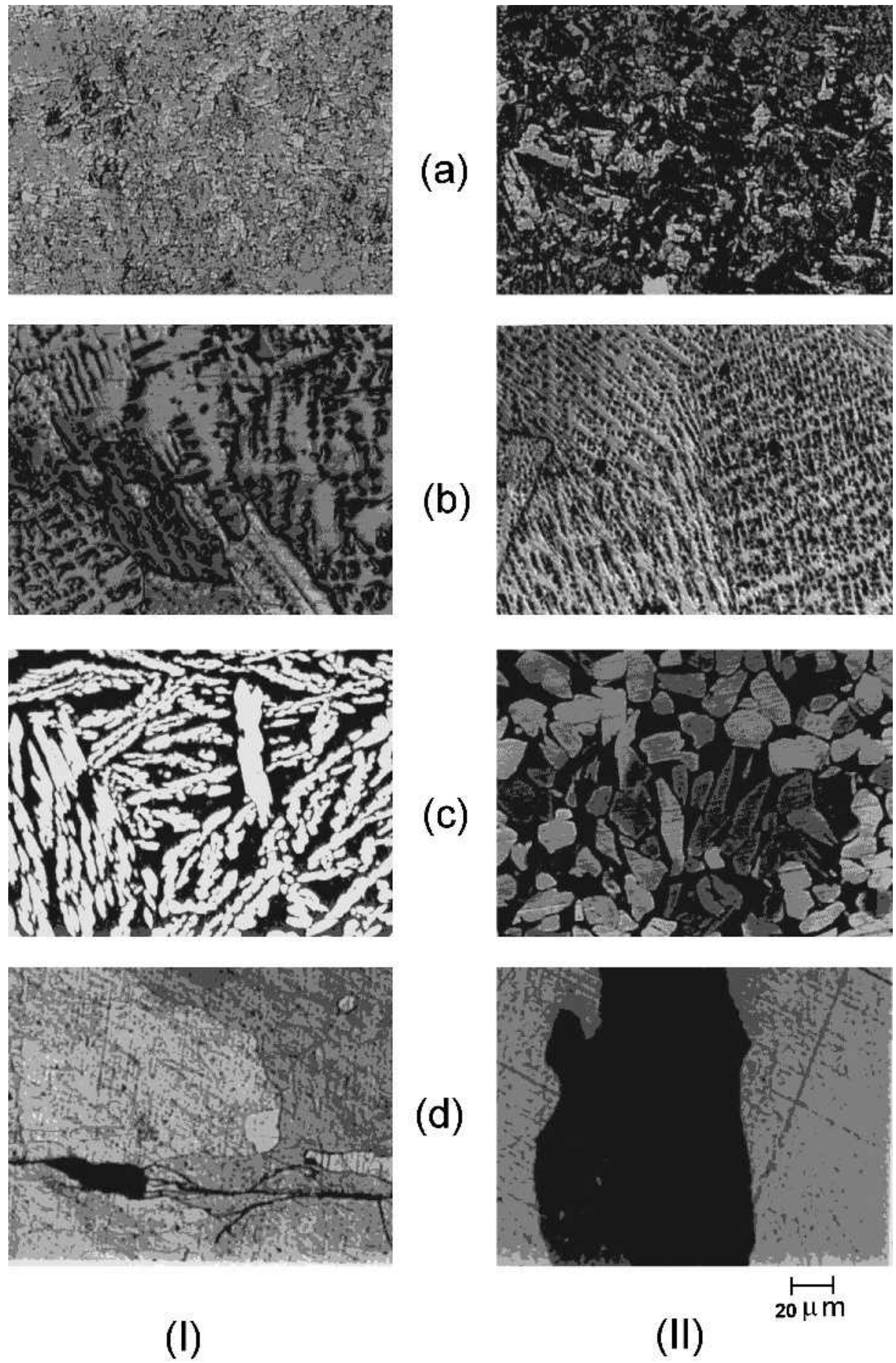

Fig. 1 Microstructure for cast Cu and Cu-Al alloys at (I) RT (II) 473 K: (a) cast-Cu, (b) Cu-5wt.%Al, (c) Cu-10wt.%Al, and (d) Cu-20wt.%Al

3.2 Microhardness (H_v) and PAL Measurements

Figure 4 shows the relationship between the average lifetime (τ_{av}) and microhardness (H_v) for cast Cu and Cu-Al after isochronal annealing. For cast Cu, the behavior of H_v and τ_{av} is the same after annealing, i.e., a slight decrease followed by gradual decrease, and finally saturation at higher temperatures. This is similar to previous results (Ref 15, 16). However, for the Cu-Al alloys, the behavior of τ_{av} with temperature is completely different than that of H_v, which is similar to that observed in 60/40 Cu-Zn (Ref 15). It should be noted that H_v generally increases with increasing Al content; whereas τ_{av} for Cu-5wt.%Al and Cu-10wt.%Al is lower than that of cast Cu (except at 673 K) and higher for Cu-20wt.%Al.

The behavior of Cu-Al alloys as a function of annealing temperature can be divided into three stages. In the first stage (RT-573 K), τ_{av} and H_v for Cu-5wt.%Al show a gradual

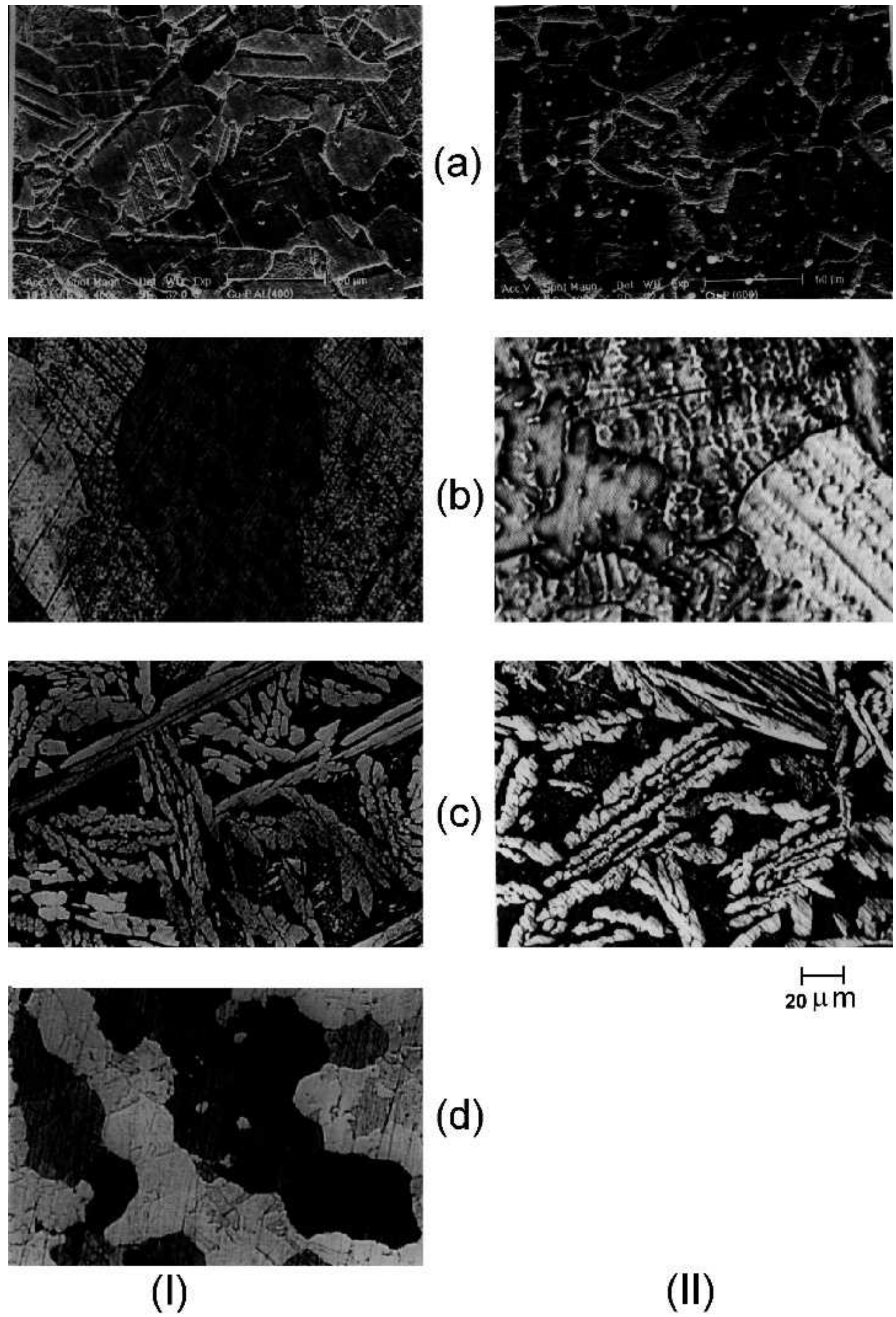

Fig. 2 Microstructure for cast Cu and Cu-Al alloys at (I) 673K (II) 873 K: (a) cast-Cu, (b) Cu-5wt.%Al, (c) Cu-10wt.%Al, and (d) Cu-20wt.%Al

decrease, whereas for Cu-10wt.%Al and for Cu-20wt.%Al, a decrease of τ_{av} occurs and H_v increases.

In the second stage (573-873 K), a decrease of both τ_{av} and H_v is observed for Cu-20wt.%Al. For Cu-10wt.%Al, an increase of τ_{av} and H_v is followed by a decrease. However, Cu-5wt.%Al shows a saturation of H_v and a large increase of τ_{av} at 673 K followed by a drastic decrease.

In the third stage (823-1173 K), a tendency to a slight change of H_v is observed for all alloys, and τ_{av} shows an increase for Cu-20wt.%Al and a decrease for Cu-5wt.%Al and Cu-10wt.%Al.

4. Discussion

The mechanical properties of Al bronze depend mainly on the Al content (Ref 2). Alloys with up to 8wt.%Al have a ductile single-phase structure. As the Al content increases between 8 wt.% and 10 wt.%, a second phase forms in the microstructure, strengthening the alloy. Alloys with Al contents above 10 wt.% have even greater strength and hardness. Moreover, H_v of the Cu-Al alloys in this study remains higher than cast Cu even after annealing at the elevated temperatures. The increase of H_v ob-

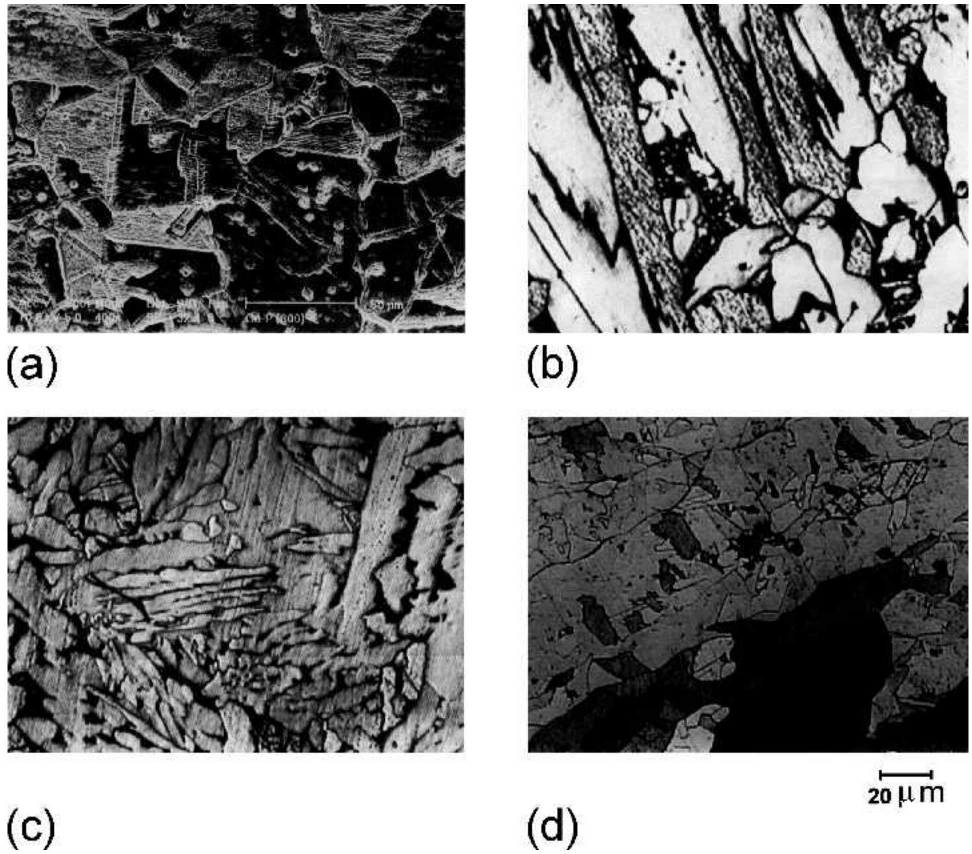

Fig. 3 Microstructure for cast Cu and Cu-Al alloys at 1073 K: (a) cast-Cu, (b) Cu-5wt.%Al, (c) Cu-10wt.%Al, and (d) Cu-20wt.%Al

served in Cu-20wt.%Al is attributed to the presence of γ_2 phase (Ref 2).

The three stages observed for cast Cu are recovery, partial recrystallization, and complete recrystallization. In this case, τ_{av} and H_v show the same trend with annealing temperature. The same behavior was observed before for pure deformed Cu (Ref 16). It was observed that τ_{av} of cast Cu is higher than that of Cu-5wt.%Al and Cu-10wt.%Al, except after annealing at 673 K (τ_{av} for Cu-10wt.%Al is comparable with cast Cu and is very high, reaching ~247 ps for Cu-5wt.%Al). It is well known that the reduction in electron density, which accompanies the increase in the size of defects, leads to an increase in the lifetime of the trapped positrons (Ref 5, 9). It was also found previously for Cu that τ_{av} = 350 ps at 723 K, or above, and is characteristic for three-dimensional (3D) vacancy agglomerates, i.e., cavities such as small voids (~10-15 vacancies) (Ref 7, 17). For Cu-5wt.%Al, referring to the microstructure after annealing at 673 K (Fig. 2b-I), maximum disorder accompanied by elongated grains is observed. It was also previously found that elongated grains exhibited higher lifetimes (Ref 6).

The behavior of τ_{av} with annealing temperature is completely different than that of H_v for the cast Cu-Al alloys. This is expected because when the microstructure becomes more complex, the hardness depends on the Al content and measures only the surface properly. However, the lifetime is sensitive to bulk material defects like grain boundaries, cavities precipitates, and phase transformation, which are considered 3D defects (Ref 17).

In the first stage, a gradual decrease of τ_{av} is observed for Cu-5wt.%Al and Cu-10wt.%Al. Conversely, a drastic decrease in τ_{av}, followed by saturation, is noted for Cu-20wt.%Al. The hardness of Cu-10wt.%Al and Cu-20wt.%Al shows anneal hardening, whereas Cu-5wt.%Al exhibits anneal softening. This phenomenon has been observed before in cast Cu-Al alloys (Ref 17).

The second stage may be attributed to partial recrystallization ending with complete recrystallization for Cu-10wt.%Al and Cu-20wt.%Al. Complete recrystallization is observed in this stage for Cu-5wt.%Al.

In the third stage, Cu-5wt.%Al and Cu-10wt.%Al show complete recrystallization. This is indicated by a decrease of both H_v and τ_{av}. For Cu-20wt.%Al, it is interesting to note that an increase in τ_{av} is observed, which may be caused by the formation of subgrain boundaries (Fig. 3d).

For this study, the presence of a volume fraction of 3D defects (i.e., grain boundaries, cavities, precipitates, phase transformation, etc.) was assumed to be responsible for the higher lifetimes observed in these materials, where several types of defects exist.

Xiong et al. (Ref 10) suggested that the trapping of a positron in 3D defects (volume fraction) can be expressed through α, where $\alpha = (\lambda_1 - \Gamma)/(\lambda_1 - \lambda_2)$. Therefore, the fraction of positrons in the free state is equal to $(1 - \alpha)$. The detrapping rate can be neglected, and hence, the mean disappearance rate (Ref 10, 11) of positron in a sample can be expressed as:

$$\Gamma = I_1\lambda_1 + I_2\lambda_2 \qquad \text{(Eq 5)}$$

where

$\lambda_1 = 1/\tau_1$ and $\lambda_2 = 1/\tau_2$

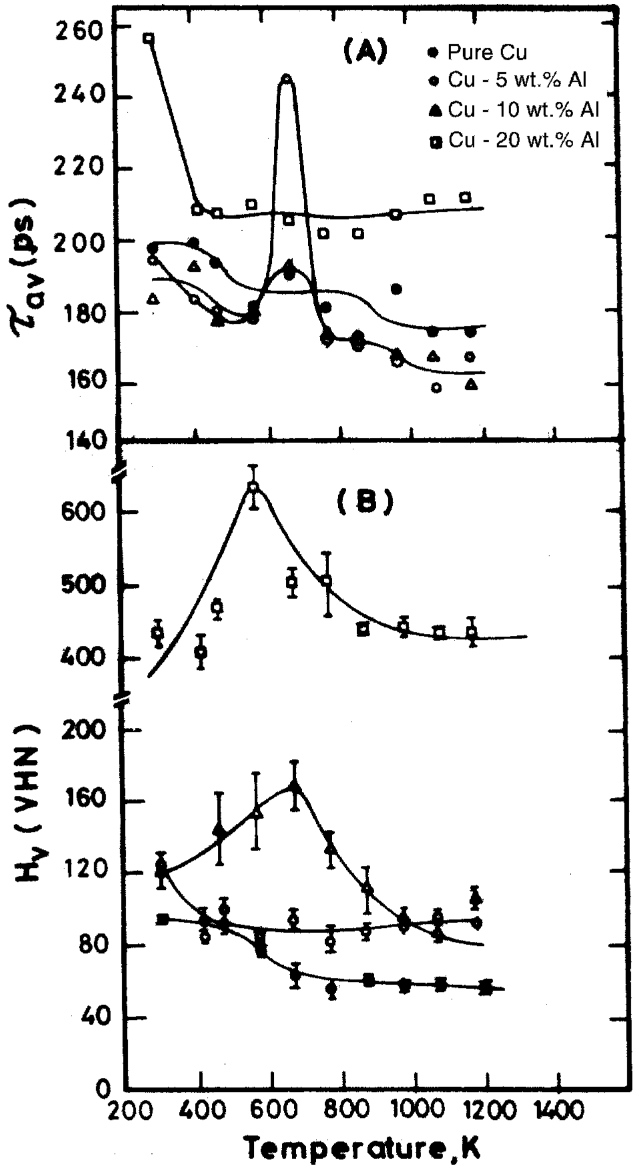

Fig. 4 Relationship between the isochronal annealing with (a) τ_{av} and (b) H_v for cast Cu and Cu-Al alloys

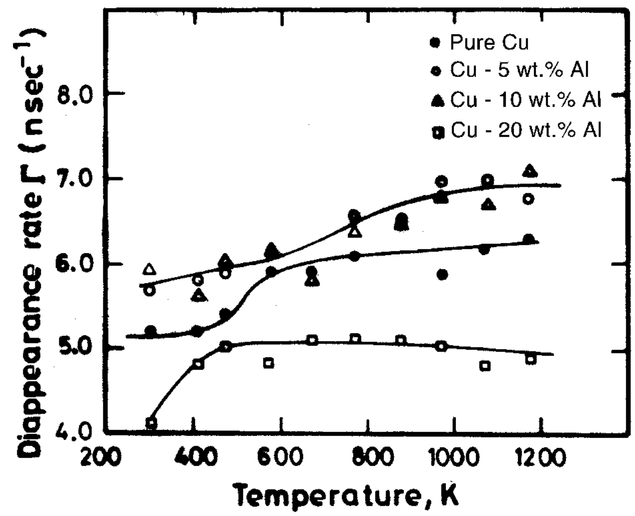

Fig. 5 Relationship between the annealing temperature and the mean disappearance rate Γ for cast Cu and Cu-Al alloys

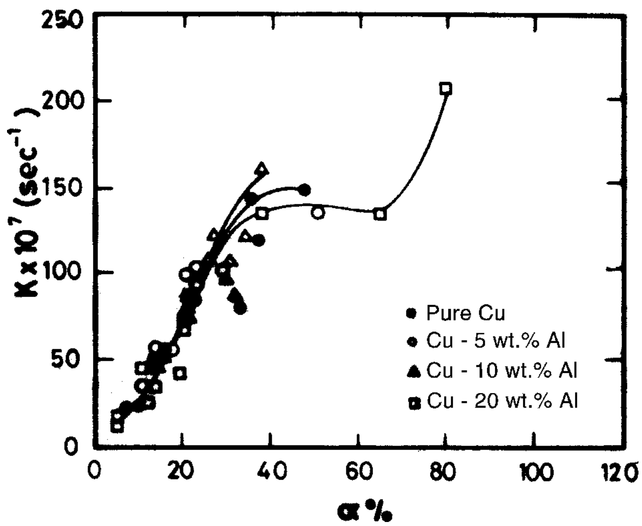

Fig. 6 Relationship between the fractional volume (α%) with the trapping rate (k) for cast Cu and Cu-Al alloys

Figure 5 clarifies this relation with respect to the annealing temperature for Cu and Al-bronze. For Cu-20wt.%Al, the plateau for the disappearance rate begins at a low temperature (~473 K), which reflects the high stability of the microstructure (largest grain size), as in Fig. 1, 2, and 3. For Cu, the plateau for the disappearance rate is delayed to 573 K (i.e., the beginning of recrystallization) due to the stability of the microstructure after this point. For the two other alloys, Cu-5wt.%Al and Cu-10wt.%Al, the distribution of grain size is unstable; therefore, the disappearance rate increases for both, which gives a retarded saturation that begins at ~973 K. Figure 6 shows the relationship between the fractional volume percent (α) with the trapping rate (k). The behavior of Cu-20wt.%Al shows an increased in α with respect to the other samples (i.e., Cu, Cu-5wt.%Al, and Cu-10wt.%Al). The maximum value of α for these three samples varies between 38% and 51%. This value is extended to 80% for Cu-20wt.%Al and is expected due to the increase in grain size and complexity of the microstructure.

5. Conclusions

The results of the above investigations can be summarized as follows:

- The microhardness of the Cu-Al alloys increases with increasing Al content, and it remains high relative to cast Cu even after elevated temperature annealing.
- The behavior of H_v and τ_{av} with temperature shows three stages for both cast Cu and Cu-Al alloys: For cast Cu, H_v, and τ_{av} show positive correlation with annealing temperature, i.e., a slight decrease followed by a gradual decrease, then saturation is observed at high annealing temperatures. These stages are attributed to recovery, partial recrystallization, and then complete recrystallization, respectively, which has been confirmed by previous results.
- The variation of τ_{av} and H_v with annealing temperature for cast Cu-Al alloys is not the same due to the fact that the

microstructure is more complex than cast Cu. The presence of Al leads to more defects, such as grain boundaries, transformed phases, cavities, etc., a reflection of PALS being more sensitive for the bulk, whereas microhardness is more surface sensitive.

- τ_{av} is a maximum at 673 K for Cu-5wt.%Al due to maximum disordering and elongated grains.
- The analysis of positron lifetime indicates the existence of 3D defects in addition to one-dimensional defects, so modification of the simple trapping model is needed when considering inhomogeneous trapping.
- The present work demonstrates that PALS can provide valuable information about the microstructure of simple materials and is sensitive to defects from monovacancies up to cavities that are not easily detected by the traditional methods.

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