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Sintering of CuO investigated by positron lifetime spectroscopy

R. PAREJA, R. M. DE LA CRUZ
Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense, 28040 Madrid, Spain

L. DÍAZ
Instituto de Optica, CSIC, Serrano 121, 28007 Madrid, Spain

The sintering process of CuO under isochronal annealing has been investigated by positron lifetime spectroscopy. A long-lived component of 370 ± 20 psec, observed in as-pressed samples and samples annealed at $T \leqslant 900$ K, has been attributed to continuous channels along three-grain junctions. A short-lived component of about 224 psec is attributed to positron traps at two-grain interfaces. The annihilation parameters exhibit recovery stages which may be correlated with the stages of sintering. A drastic recovery, starting at 975 K, is correlated with the final stage of sintering. The results suggest a lifetime of approximately 147 psec for positrons in the bulk of CuO.

1. Introduction

At present, solid-state sintering is a crucial process in the production technique of many new materials such as polymers, refractory metals and alloys, ceramics and superconducting materials. By means of solid-state sintering, compacted powders become a dense polycrystalline material whose properties are determined by the final microstructure of the sintered material. The achievement of sintered materials with suitable properties requires a good understanding of the sintering process, as well as knowledge of the optimal sintering conditions for the material. Dilatometry, buoyancy, gas adsorption and quantitative microscopy have been the experimental techniques commonly used to investigate sintering in materials. These techniques have revealed the existence of three stages in a real sintering process [1]. Nevertheless, certain difficulties in interpretating the sintering kinetics can appear because of the coexistence of alternative sintering mechanisms and the overlapping of the sequential stages. Moreover, it seems that the sintering parameters given by the techniques mentioned, i.e. pore or neck size, shrinkage and specific surface, have certain limits in distinguishing the superimposed mechanisms.

Positron annihilation is a very sensitive technique to open volume defects in solids, so that it could be an alternative technique to investigate solid-state sintering. Positron lifetime experiments in nanocrystalline materials [2, 3] and ZnO [4], obtained from compacted powders, have recently been reported. These results have revealed the existence of positron trapping in the pores and microvoids of the compacted materials. In the present work the sintering of CuO under isochronal annealing is investigated by positron lifetime spectroscopy. Because CuO is an important constituent in the superconducting oxides and in other sintered materials, used as electrical contacts for special switches, cathodes and dielectrics, the present investigation could contribute to the knowledge of the sintering processes in these interesting materials.

2. Experimental procedure

The samples were prepared by compacting into discs analytical reagent grade CuO powder (Scharlau) under mechanical pressures between 0.7 and 1.0 GPa in a vacuum of 0.1 Pa. The powder grain size was previously homogenized by milling. A ^{22}NaCl positron source of $\simeq 0.5$ MBq, enclosed in a 0.4 mg cm^{-2} nickel foil, was sandwiched between two samples 0.6 mm thick obtained under identical conditions. Positron annihilation measurements were performed at room temperature using a fast–fast coincidence system having a resolution of 305 psec (FWHM). After measuring the as-pressed samples, they were isochronally annealed in air. The annealing experiments were made over a temperature range inside the CuO stable region in the phase diagram of the system Cu–O_2 [5], i.e. $T < 1300$ K, and for 30 min at each temperature.

The positron lifetime spectra were analysed in terms of two or three exponential decay components after substracting two source corrections.

3. Results and discussion

The as-pressed samples exhibited a two-component or three-component spectrum. It was observed that the appearance of a very weak long-lived component, with an intensity, I_3, of $\leqslant 0.3\%$ and a lifetime, τ_3, between 1.5 and 2.0 nsec, is related to the surface of the samples. This component is absent in as-pressed samples having very good surfaces. The subsequent anneals

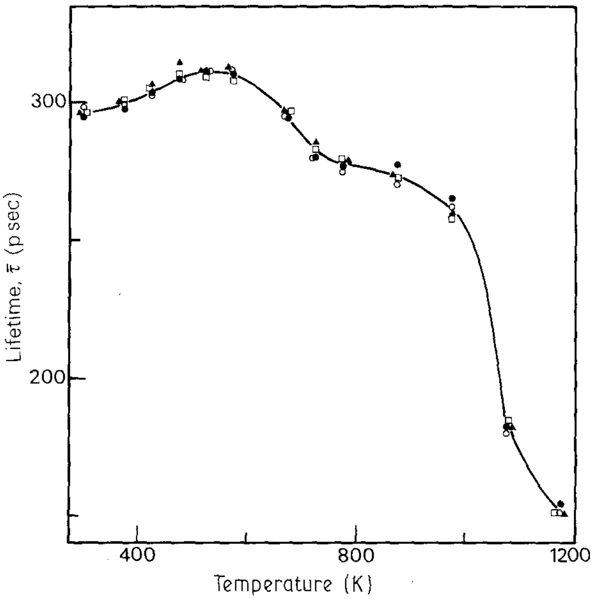

Figure 1 Mean positron lifetime plotted against annealing temperature for four pairs of CuO samples compacted at pressures in the range 0.7 to 1.0 GPa.

either induce the appearance of this long-lived component or alter slightly the τ_3 and I_3 values if this component was previously present. No annealing temperature dependence of τ_3 and I_3 is observed. Moreover, these parameters change, while the remainding annihilation parameters do not, when the experiments are repeated changing the position of the positron source on the sample surface. These facts suggest that this long-lived component has its origin in the sample surface and/or in the internal surfaces of very large cavities rather than in the bulk. Thus, this component will not be considered further here.

Fig. 1 shows the average positron lifetime, $\bar{\tau} = I_1\tau_1 + I_2\tau_2$, as a function of the annealing temperature for four pairs of samples compacted under different pressures. No differences in $\bar{\tau}$ and in its recovery curve, as well as in the remainding annihilation parameters, were found for these four pair of samples. All as-pressed samples exhibited a second component having a lifetime value τ_2 of 370 $\pm$ 20 psec and an intensity I_2 of 50 $\pm$ 3%. No meaningful changes in the τ_2 value were induced by the successive anneals at $T \leqslant 875$ K. The anneals at $T \geqslant 975$ K produced a continuous decrease in this long-lived component. The behaviour of τ_2 and I_2 for one pair of samples is shown in Fig. 2. Fig. 3 shows the τ_1 values of the short-lived component, obtained analysing the spectra for $T < 975$ K with the τ_2 value constrained to 370 psec, in four pairs of samples.

Figs 1 to 3 reveal a three-stage process in the sintering of CuO by isochronal annealing. Below 525 K a slight increase in $\bar{\tau}$ and I_2 is observed while τ_1 and τ_2 remain practically constant. Above 525 K two recovery stages are simultaneously observed in the $\bar{\tau}$ and τ_1 values. A first recovery occurs between 575 K and 900 K, and a very drastic second recovery above 975 K. During the first recovery stage, i.e. below ~ 900 K the τ_2 value is essentially constant as seen in Fig. 2, although the intensity I_2 decreases slightly between 575 and 725 K and then it remains constant in the interval 725 to 975 K. Above 975 K the drastic recovery in $\bar{\tau}$ and τ_1 is accompanied by a decrease in I_2 and τ_2. After annealing at 1175 K, I_2 decreases up to 2% or 3% and τ_2 results in a value between 260 and 305 depending on the pair of samples.

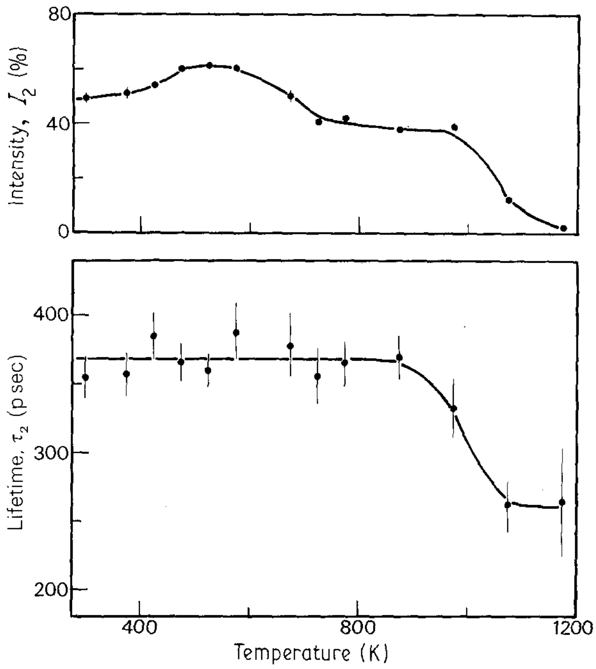

Figure 2 Intensity and lifetime of the long-lived component plotted against annealing temperature for a pair of CuO samples compacted at 0.7 GPa.

Although the observed annihilation spectra in these samples appear to be two-component, the simultaneous decrease in I_2 and τ_1 rules out the two-state trapping model in these samples. According to this model a decrease in I_2 is accompanied by an increase in the τ_1 value [6]. Therefore, the short-lived component cannot be exclusively attributed to positrons annihilated in the CuO bulk, i.e. in free states, but rather it is either due to trapped positrons or it is, at the most, a composed component due to free and trapped positrons.

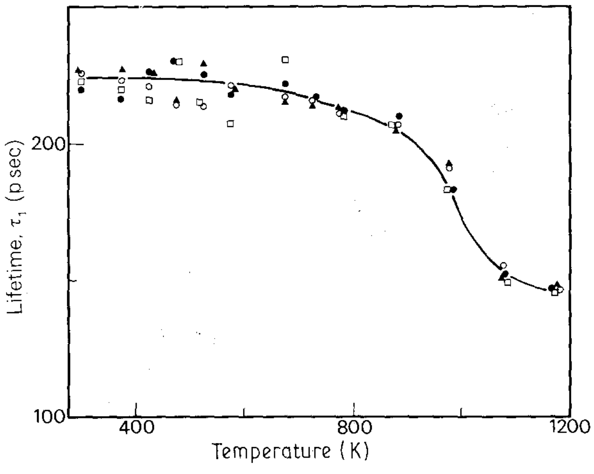

Figure 3 Lifetime of the short-lived component plotted against annealing temperature for four pairs of CuO samples compacted at pressures in the range 0.7 to 1.0 GPa.

In the light of the present results we would attribute tentatively the long-lived component of 370 ± 20 psec to positron annihilation at cylindrical pores or channels created along three-grain junctions. In nanocrystalline metals an intermediate lifetime component of values around 350 psec, has been attributed to positrons trapped in this type of pore and the short-lived component associated with trapping at vacancy-sized traps in the two-grain interfaces [2, 3]. τ_1 decreases from values of 224 ± 4 psec in as-pressed samples or samples annealed at $T \lesssim 525$ K, up to 147 ± 2 psec when the samples underwent annealing at 1175 K. This decrease in τ_1 is accompanied by an increase of its intensity, I_1 from 50 ± 2% up to 97% or 98%. This behaviour in τ_1 and I_1 suggests that the short-lived component is also due to trapped positrons, at least in the case of as-pressed samples and samples annealed at $T \lesssim 675$ K, i.e. in the temperature range where no significant changes in τ_1 are produced. According to the model proposed by Schaefer and Würschum for positrons in nanocrystalline metals [2], the traps responsible for this component may be small pores in the two-grain interfaces. Because the positron lifetime in the bulk of simple oxides like NiO, Al_2O_3 and MgO is in the range 110 to 175 psec [7] and a value of 174 psec has been proposed for Cu_2O [8], the value of about 147 psec obtained for τ_1 after annealing at 1175 K seems to be in the range of the values expected for the positron lifetime in the CuO bulk. Thus, it is reasonable to attribute the short-lived component in the spectra of the samples annealed at 1175 K to free positron annihilation in the bulk, while the long-lived component, having now a lifetime between 260 and 305 psec and an intensity of 2% to 3%, would be associated with positrons trapped in a kind of pore different from those responsible for the long-lived component of 370 psec observed after annealing at $T \leqslant 900$ K. So, during the recovery stage observed at $T > 900$ K, the major part of positron traps disappears although a small residue of traps is still present in the samples after annealing at 1175 K. Because the τ_1 value after this annealing is very probably a value close to the free positron lifetime in the CuO bulk, the short-lived component during this stage should be a composed component due to free and trapped positrons.

For a pair of samples sintered by isochronal annealing in the range 975 to 1375 K, the behaviour of the annihilation parameters is very similar to that observed in the case of samples isochronally annealed over the range 375 to 1175 K; Fig. 4 summarizes the results. A continuous decrease in $\bar{\tau}$ and I_2 is observed up to 1275 K. Annealing at 1375 K, i.e. in the Cu_2O stable region of the phase diagram, results in an increase in $\bar{\tau}$, τ_1 and I_2. This change in the behaviour of the annihilation parameters is undoubtedly due to Cu_2O and, perhaps, copper precipitation, as is revealed by the appearance of the samples after annealing at 1375 K. The long-lived component, which was about 370 psec after compacting, becomes a component with a 301 ± 16 psec lifetime after annealing at 975 K and remains essentially constant after subsequent anneals. Annealing at 1375 K does not induce a significant change in the τ_2 value but it produces a noticeable increase in the intensity I_2 which can be attributed to stoichiometric defects in the Cu_2O phase. A lifetime of about 320 psec has been attributed to positrons trapped at $V_{Cu}^- - V_O^+$ pairs in Cu_2O [8].

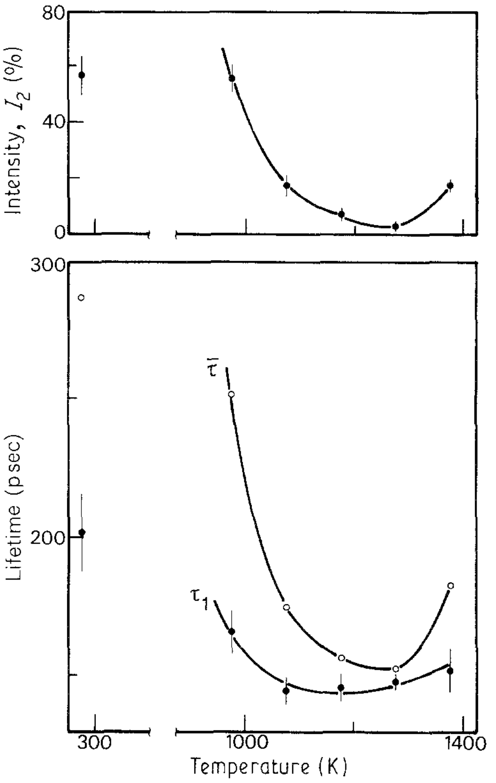

Figure 4 Positron annihilation parameters of a pair of CuO samples compacted at 0.9 GPa and sintered in the temperature range 975 to 1375 K.

The above facts support the idea that annealing at $T \gtrsim 975$ K removes the traps responsible for the lifetime component of 370 psec, i.e. the cylindrical pores or continuous channels along the three-grain junctions; at the same time new positron traps characterized by a lifetime between 260 and 305 psec appear and positron traps contributing to the short-lived component start to be annealed out. Furthermore, the recovery stage starting at 975 K clearly seems to coincide with the final stage of sintering in the samples.

The behaviour of the annihilation parameters during the final stage of sintering can be accounted for by the sequence of configurational changes in the pores during this stage [9, 10]. As is known, the final stage of sintering starts with the dissociation of the cylindrical pores along the three-grain junctions into isolated pores at these junctions. Afterwards, these isolated pores are detached from the junctions to a position on two-grain interfaces as a previous step for the complete separation of pores from these interfaces to the inner of the grains. The transformation of the long-lived component of 370 psec into another of 260 to 305 psec seems to be related to the transition from cylindrical pores into isolated pores at three-grain junctions and subsequent localization at two-grain interfaces. Because the pore separation from junctions on to two-grain interfaces is a process faster than the pore detachment from the two-grain interfaces [10] and the component of 260 to 305 psec is present through the final stage of sintering, the positron traps responsible for this lifetime component would probably be these new pores attached to two-grain interfaces. The decrease in its intensity I_2 may be either due to the pore shrinkage at two-grain interfaces or to the pore separation from these interfaces and subsequent shrinkage of the detached pores inside the grains. Because positron trapping would be expected in the detached pores inside the grains, the short-lived component would include a contribution from positrons annihilated in these pores in addition to the contribution due to positrons trapped in other two-grain interface defects, and/or free positrons in the bulk. The shrinkage of the detached pores inside the grains and annealing out of interfacial defects would produce the decrease in the τ_1 value and its approximation to the free positron lifetime in the CuO bulk.

An alternative attribution of the long-lived component of 260 to 305 psec to detached pores inside the grains could probably be excluded. The fast decrease of its intensity I_2, i.e. the fast disappearance of pores, upon annealing above 975 K, suggests that it is performed by a fast diffusion mechanism, such as a grain-boundary diffusion process. This supports the idea of pores attached to grain boundaries as the traps responsible for this long-lived component observed through the final stage of sintering. In the case of pores inside the grains, the shrinkage would be accomplished by lattice diffusion, a mechanism much slower than grain-boundary diffusion.

Following the above discussion about the final stage of sintering, the other stages observed in the recovery curve of the annihilation parameters can be interpreted in the following terms.

1. Below 525 K no changes in τ_1 and τ_2 and a slight increase in I_2 only suggest a rearrangement of the powder particles in this stage, creating more cylindrical pores or continuous channels along three-grain junctions; this rearrangement would be due to the thermal expansion induced by heating.
2. Between 575 and 900 K the recovery of $\bar{\tau}$ is due to a slight decrease in I_2 and a continuous reduction in the τ_1 value. No meaningful change in τ_2 accompanying a slight decrease in I_2 indicates no configurational change in the pores or channels along three-grain junctions but a reduction in the number of these pores. This behaviour can be explained by a new rearrangement of particles leading to the formation of two-grain interfaces accompanied by a reduction in the number of junctions, followed by the disappearance of a certain number of continuous channels. This is, in fact, the initial stage of sintering which is closely correlated to the temperature interval between 525 and 725 K. It should be noted that the τ_1 value scarcely changes in this temperature range. In the range 725 to 900 K, τ_1 decreases significantly, but τ_2 and I_2 remain constant. This behaviour of the annihilation parameters could be explained by a certain transformation in the two-grain interfaces which reduces the number of positron traps and does not alter significantly the configuration of pores along three-grain junctions. Such a transformation could be grain-boundary migration. This behaviour in the temperature range 725 to 900 K seems to correlate with an intermediate sintering stage preceding the final stage of sintering observed above 975 K.

4. Conclusions

The sintering process of CuO under isochronal annealing shows recovery stages in the positron annihilation parameters which appear to be correlated with the sintering stages. A long-lived component of about 370 psec, essentially constant after annealing at $T < 975$ K, has been attributed to positrons trapped in continuous channels along three-grain junctions. Annealing at 975 K induces a transformation in these positron traps and a reduction in their positron lifetime is observed. The onset of the final sintering is found at about 975 K. The earlier stages in the sintering process seem not to produce a meaningful change in the lifetime of the positron trapped in the pores along three-grain junctions. However, during these stages a continuous reduction in the lifetime of the short-lived component is observed. This decrease is attributed to the continuous disappearance of positron traps at two-grain interfaces induced by grain-boundary migration. The complete sintering of CuO appears to occur between 975 and 1275 K, approximately.

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