Effects of oxide distributed in grain boundaries on microstructure stability of nanocrystalline metals

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Abstract. Nanocrystalline copper and zinc prepared by high-pressure compaction method have been studied by positron lifetime spectroscopy associated with X-ray diffraction. For nanocrystalline Cu, mean grain sizes of the samples decrease after being annealed at 900 °C and increase during aging at 180 °C, revealing that the atoms exchange between the two regions. The positron lifetime results indicate that the vacancy clusters formed in the annealing process are unstable and decomposed at the aging time below 6 hours. In addition, the partially oxidized surfaces of the nanoparticles hinder the grain growth during the ageing at 180 °C, and the vacancy clusters inside the disorder regions which are related to Cu₂O need longer aging time to decompose. In the case of nanocrystalline Zn, the open volume defect (not larger than divacancy) is dominant according to the high relative intensity for the short positron lifetime (τ₁). The oxide (ZnO) inside the grain boundaries has been found having an effect to hinder the decrease of average positron lifetime (τᵥ) during the annealing, which probably indicates that the oxide stabilizes the microstructure of the grain boundaries. For both nanocrystalline copper and zinc, the oxides in grain boundaries enhance the thermal stability of the microstructure, in spite of their different crystal structures. This effect is very important for the nanocrystalline materials using as radiation resistant materials.

1. Introduction
Some computer simulations have been performed on nanocrystalline materials recently which reveal the self-healing ability of these materials for the radiation damage [1, 2]. These materials are highly promising for the use in the future nuclear reactors. When nanocrystalline materials are irradiated by particles, the grain boundaries play a key role which can serve as effective sinks for radiation-induced defects such as interstitials and vacancies. Moreover, these interstitials then are emitted to annihilation vacancies in the crystallites. Hence the stability of the microstructure is essential for the nanomaterials keeping the radiation resistance, especially at the elevated temperature.

Positron annihilation technique can sensitively detect open volume defects in materials, and gives detailed information about the defects, such as, types and concentrations of defects, and the chemical identity of the elements surrounding the defects. Many positron annihilation measurements have performed on nanocrystalline materials to investigate defects associated with the extraordinary structure of the grain boundaries in nanocrystalline materials [3-5]. However, interpretation of the positron lifetime results has to be different because of the obviously different structure of nanocrystalline materials prepared by different techniques.

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In this work, positron lifetime spectroscopy associated with X-ray diffraction is used to study the microstructure of two typical nanocrystalline metals, Cu and Zn. The emphasis is to investigate the effects of oxide in grain boundaries on the microstructure thermal stability of nanocrystalline metals.

2. Experimental

Samples were prepared by high-pressure compaction method. Cu nanoparticles for samples A and B were produced by flow-levitation (FL) method [6] and chemical vapor deposition (CVD) [7], respectively. Zn nanoparticles for samples C and D were prepared by wire explosion method [8]. The mean grain size for all as-prepared samples is about 55 nm obtained by XRD. Sample B was compacted in air. Nanoparticles for sample D were oxidized in air at 100 °C for 100 minutes. These treatments were to increase the oxide in grain boundaries of samples B and D.

In order to reduce the gas impurities and the residual porosity, the samples A and B were annealed at 900 °C for 30 minutes under the argon atmosphere before ageing experiment. The ageing experiment was performed at 180 °C for aging time from 1 to 108 hours in a vacuum furnace. Isochronal annealing of sample C and D was performed in the Ar gas atmosphere from the temperature of 50 to 410 °C for 30 minutes at each temperature point. After each ageing or annealing, the samples were cooled slowly to room temperature.

Before positron lifetime and XRD measurements, the samples were polished with emery paper (800 mesh) to remove the possible surface oxide. X-ray diffraction measurements were performed on a BRUKER AXS D8 ADVANCE X-ray diffractometer using Cu Kα radiation. A digital positron lifetime spectrometer (for details see [9]) with a time resolution of about 240 ps was used to perform the lifetime measurements at room temperature. The positron source employed was ²²NaCl encapsulated with Ti foil, which is sandwiched by two identical samples under investigation.

3. Results and discussion

3.1. Nanocrystalline Cu

The mean grain size (obtained by XRD) versus ageing time is shown in figure 1. What is surprising is the decrease in the mean grain size of both samples after the annealing at 900 °C. The grain size obtained using XRD profile analysis is the ordered region size. After annealing the ordered regions decrease because the atoms in the edge of the ordered regions are activated thermally and move to the disordered regions. We also can see from figure 1 that the mean grain size of sample B increases slowly compared to that of sample A. Sample B was prepared in air, so the surface oxidation of nanoparticles could be expected [10]. This oxide (Cu₂O) (confirmed by XRD) distributed in the grain boundaries of the sample retard the increase of the mean grain size in the sample.

![Figure 1](image1.png)

**Figure 1.** Mean grain sizes of samples A and B as a function of aging time at 180 °C. The ageing time ‘0’ means as-annealed.

![Figure 2](image2.png)

**Figure 2.** Average lifetimes for annealed samples A and B as a function of ageing time at 180 °C.
The spectra of nanocrystalline Cu samples were decomposed into three components \( \tau_1, \tau_2 \), and \( \tau_3 \), with relative intensities \( I_1 \), \( I_2 \), and \( I_3 \). The lifetimes \( \tau_1 \) and \( \tau_2 \) are roughly 130 ps and 310 ps, respectively. The lifetime \( \tau_3 \) is from positron annihilation in vacancy defect containing about ten monovacancies[11]. The longest lifetime \( \tau_3 \) is between 1 and 2 ns. Detailed discussions on these components can be found in [10]. We here present the positron average lifetime \( \tau_{av} = \frac{\Sigma \tau_i I_i}{\Sigma I_i} \) for a description of changes that occur during the ageing. From figure 2 we can see that the ageing behavior of average lifetime \( \tau_{av} \) for annealed samples A and B is similar at the intervals of about 0-10 h and 70-108 h. In the former interval the average lifetimes decrease to their minimum values for samples A and B and in the latter interval increase slowly to their maximum values. Furthermore, the average lifetime for both samples may reach their saturation values when the ageing time is beyond 108 h, and then the microstructure of the samples would be in a stabilization state. The obvious difference in the ageing behavior of \( \tau_{av} \) is at the mediate interval of the ageing time, where the average lifetime for sample A slightly reduces but for sample B increases in general. This difference may be caused by the partial surface oxidization of nanoparticles for sample B. The oxide impedes the decomposition of the vacancy clusters distributed in grain boundaries and causes the continuous increase in the size of the vacancy clusters. When the vacancy clusters become large enough, they become unstable and then might collapse. This deduction is supported by the changes of the lifetime \( \tau_2 \) (not shown here).

3.2. Nanocrystalline Zn

For sample C, the lifetime components \( \tau_1 \) and \( \tau_2 \) with their relative intensities \( I_1 \) and \( I_2 \) as a function of annealing temperature are presented in figure 3. The longest lifetime component \( \tau_3 \) (about several nanoseconds) is not discussed because of their really small intensity (below 0.5%). The lifetime \( \tau_2 \) is attributed to positron annihilation at the large vacancy clusters containing dozens of monovacancies. Because the lifetimes of monovacancy and divacancy in bulk Zn are about 220 ps and 260 ps [12, 13] respectively, the lifetime \( \tau_1 \) for as-prepared sample C is an effective lifetime containing contributions from the positrons trapped both at defects containing one or two monovacancies and in disorder regions which will give a lifetime a little smaller than that of monovacancy [14].

**Figure 3.** Positron lifetimes and their relative intensities for sample C with different annealing temperatures.

**Figure 4.** Positron lifetimes and their relative intensities for sample D with different annealing temperatures.

In order to clearly observe the influence of the oxide in grain boundaries on the thermal stability of the microstructure, sample D is annealed for comparison. The positron lifetime result for sample D is presented in figure 4. From this figure we can see that the lifetimes \( \tau_1 \) and \( \tau_2 \) both increase at the beginning of the annealing, which is due to the release of the stress induced in the compacting process.
After the temperature reaches 100 °C the lifetime $\tau_2$ is almost unchanged, indicating that the size of vacancy cluster changes very little. The lifetime $\tau_1$ declines very slowly above 50 °C. The recovery process of the open volume defects is suppressed. It is noteworthy that the relative intensities $I_1$ and $I_2$ are almost unchanged after the annealing temperature reaches 50 °C, which is very different to sample C. In the case of sample C, the intensity $I_2$ increases fast from 10% to 30% in the interval of 50-200 °C, and then changes slight. For sample D, above 50 °C the intensities $I_1$ and $I_2$ are almost unchanged and there is only a slow decrease of the lifetime $\tau_1$. Hence, we conclude that the oxide in grain boundaries have an active effect on the stability of the defect structure. If we consider the disordered regions in grain boundaries to be a kind of defect, the stability of the defect structure suggests the stability of the microstructure of grain boundaries. The typical positron diffusion length in crystal is about 100 nm. When grain size is larger than the diffusion length, positron may annihilate in the free state which will contribute a short lifetime component (about 160 ps) [15]. The lifetime $\tau_1$ does not below 220 ps during the whole annealing process probably indicating that the mean grain size of the sample is still below about 100 nm. This observation probably suggests that the oxide in grain boundaries suppress the grain growth.

4. Conclusions
Positron annihilation spectroscopy and XRD were used for investigating the influences of the oxide in grain boundaries on the microstructure thermal stability of nanocrystalline Cu and Zn prepared by compacting very small crystallites. For nanocrystalline Cu, the decrease of mean grain sizes after annealing at 900 °C and increase during ageing at 180 °C is observed by XRD. However, the increase of the grain size of the sample with oxide in grain boundaries is apparently slow. According to the positron lifetime results the vacancy clusters related to Cu$_2$O need a longer aging time to decompose during the ageing process at 180 °C. For nanocrystalline Zn, the experiment results indicate that small open volume defects are dominant in the grain boundaries. The oxide in grain boundaries stabilizes the microstructure of the nanocrystalline Zn sample under the heat treatment. Although copper and zinc have different crystal structures, which are face-centred-cubic (fcc) and hexagonal-close-packed (hcp) respectively, oxides distributed in their grain boundaries have a similar effect to enhance thermal stability of the microstructure. However other properties may be degraded due to the oxides.

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References
[1] Bai X -M, Voter A F, Hoagland R G, Nastasi M, Uberuaga B P 2010 Science 327 1631.
[2] Ackland G 2010 Science 327 1587.
[3] Jakub Čížek, Ivan Procházka, Miroslav Cieslar et al 2002 Phys. Rev. B 65 094106
[4] Würschum R, Scheytt M, and Schaefer H -E 1987 Phys. Stat. Sol. A 102 119
[5] Schaefer H -E, Würschum R, Birringer R, and Gleiter H 1988 Phys. Rev. B 38 9545
[6] Li C-M, Lei H, Tang Y-J, Luo J-S, Liu W and Chen Z-M 2004 Nanotechnology 15 1866
[7] Swihart M T 2003Curr. Opinion in Colloid and Interface Sci. 8 127
[8] Wang Q, Yang H B, Shi J L and Zou G T 2001 Mater. Sci. Eng. A 307 190
[9] Li H, Shao Y D, Zhou K, Pang J B, Wang Z 2011 Nucl. Instrum. Meth. A 625 29
[10] Zhou K, Li H, Pang J B, Wang Z 2011 Physica B 406 760
[11] Ohkubo H, Tang Z, Nagai Y et al 2003Mater. Sci. Eng. A 350 95
[12] Hidalgo C and Diego N de 1986 Appl. Phys. A 40 25
[13] Campillo J M, Plazaola F and Diego N de 2000 J. Phys.: Condens. Matter 12 9715
[14] Sui M L, Lu K, Deng W, Xiong L Y, Patu S and He Y Z 1991 Phys. Rev. B 44 (1991) 6466
[15] Zhou K, Li H, Pang J B, Wang Z 2012 Physica B 407 1219