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The Evolution of Defects in Deformed Cu-Ni-Si Alloys during Isochronal Annealing Studied by Positron Annihilation *

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The effect of isochronal annealing on the deformation-induced defects in pure Cu and Cu-Ni-Si alloys is studied by positron annihilation spectroscopy. For the cold-rolled Cu, annealing up to 900°C causes a gradual recovery of the deformation-induced defects and monotonous decrease of the hardness. This indicates that its hardening is mainly related with defects such as dislocations. However, for the hot-rolled and quenched Cu-Ni-Si alloy, although there is a partial recovery of defects after annealing below 500°C, formation of additional defects is observed after annealing above 500°C. The hardness of Cu-Ni-Si alloy has a maximum value after annealing at 500°C, which suggests that the hardening of Cu-Ni-Si alloy is not due to defects, but primarily due to the precipitation formed during annealing. Further annealing of the Cu-Ni-Si alloy above 500°C results in over-aging effect and the precipitates lose coherence with the host matrix, which leads to positron trapping by vacancy clusters in the incoherent interface region.

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Cu-based alloys are widely used in electronic fields, such as in the framework of IC and connectors,[1–4] due to their high performances of mechanical strength and electrical conductivity. Among them, Cu-Ni-Si alloy has attracted much attention because of its super-high strength and high conductivity. It represents a sort of precipitation hardened alloy, in which the high strength is caused by nanometer precipitates formed in the alloy during aging.[5–8]

It has been reported that a pre-deformation treatment such as cold-rolling of the Cu-based alloy before aging will shorten the peak-aging time when the maximum strength occurs.[7,8] This is believed to be due to deformation-induced defects. A large number of dislocations and vacancies can be formed by deformation, and these defects will expedite formation of the nano-precipitates. Therefore, a detailed study of the deformation-induced defects and especially their thermal evolution will be helpful for understanding the hardening processes of Cu-based alloy.

Positron annihilation spectroscopy (PAS) is a well-developed non-destructive technique with a high sensitivity to open-volume defects, e.g., vacancies, dislocations and vacancy clusters.[9] It is a good probe of atomic-scaled microstructures in metals and alloys.[10–13] In this Letter, we study the effect of isochronal annealing on the deformation induced defects in both pure Cu and Cu-Ni-Si alloy using positron annihilation spectroscopy. The change of hardness for these samples during annealing at different temperatures is also measured. The microstructural mechanism underlying the hardening process of pure Cu and Cu-Ni-Si alloy is tentatively discussed.

The pure Cu sample (purity >99.99%) is commercially available oxygen-free electronic grade C10100 sheet nominally 6 mm in thickness. It is cold-rolled with 60% reduction in thickness. The Cu-Ni-Si alloys were prepared using high-purity copper together with Ni and Si in a medium-frequency coreless induction furnace, and a 35-mm-thick ingot was cast in an iron mold under N_2 atmosphere. The compositions of the as-cast alloys are Cu-1.5Ni-0.34Si (wt%). The ingot was hot-rolled to 2 mm in thickness after homogenization at 920℃ for 4 h. The finishing temperature was controlled at 650 ± 50℃ and then the alloy was quenched by cold water. Both the pure Cu and the Cu-Ni-Si alloy were isochronally annealed for 60 min up to 900℃ under an argon atmosphere.

Positron lifetime spectra are collected using a fast-fast coincidence spectrometer with a time resolution of 210 ps. Each spectrum contains more than 10^6 counts and at least two spectra are accumulated for each sample in order to ensure reproducibility of the data. Coincidence Doppler broadening (CDB) spectra were measured simultaneously with total counts of about 4×10^6 for each spectrum. The CDB spectrum was characterized by the line shape parameter (S) which is defined as the ratio of the total counts in the low momentum ($|P_L| \leq 0.68$ keV) region to the total region of the 511 keV annihilation peak. Hardness measure-

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ments are performed using a Vickers hardness tester (HXD-1000TMB, Shanghai Taiming Optical Instrument Co., Ltd., China) with applied a load of 1000 g for 10 s. For each sample, more than ten readings are taken at different positions on the sample, and the standard deviations are estimated. All the measurements were taken at room temperature.

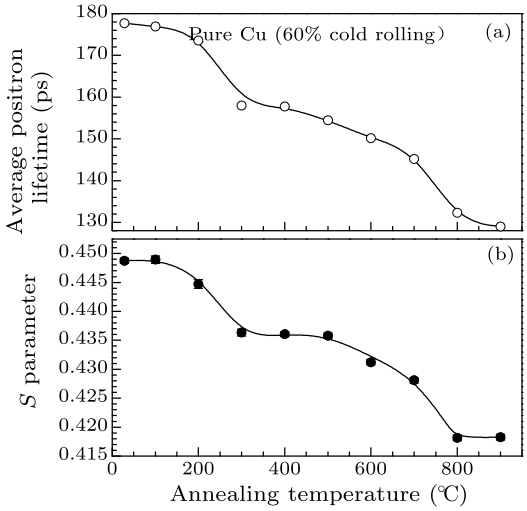


Fig. 1. Average positron lifetime and the Doppler broadening S parameter for cold-rolled pure Cu as a function of the annealing temperature.

All the lifetime spectra are fitted to two components using the PATFIT program.[14] In pure Cu the second component τ_2 is about 200 ps, which might be a mixture of positron lifetime in dislocations, monovacancies, and vacancy clusters. The reported positron bulk lifetime for Cu from the literature varies from 103 ps to 122 ps, and the trapped positron lifetime in single vacancy is around 179–182 ps, in dislocation around 170–182 ps, and in vacancy cluster 220–350 ps.[10,15–17] This indicates that in the 60% cold-rolled Cu, most of the positrons probably annihilate in dislocations and mono-vacancies, and some others are trapped by vacancy clusters which are the agglomeration of deformation induced vacancies. There have been numerous reports about the introduction of dislocation and vacancies during deformation such as rolling in metals and alloys.[18–21]

After annealing the cold-rolled Cu, the positron lifetime shows significant changes. However, decomposition of the lifetime spectra becomes unstable. Thus we rely on the average positron lifetime τ_m. Figure 1 shows τ_m and Doppler broadening S parameter as a function of annealing temperature. Variations of the two parameters have almost the same trend, which can be divided into four stages. In the first stage, where the annealing temperature is below 200℃, there are no distinct changes in τ_m and S parameter. It can be inferred that the deformation induced defects remain stable at 200℃. After annealing in the second stage (200–300℃), there is a pronounced drop in τ_m from 174 ps to 158 ps. The S parameter also decreases from about 0.445 to about 0.436. This may be attributed to the rapid recovery of defects; especially dislocations and monovacancies. These defects can be recovered more easily than vacancy clusters.[15,22] Accompanied by the recovery of defects, recrystallization and disappearance of sub-grain boundary also occurs.

In the third annealing stage, i.e., 300–700℃, both τ_m and S show a slight decrease. Since most of the dislocations or monovacancies are annealed at 200–300℃, the prevailing defects are vacancy clusters in this stage, which have higher thermal stability. The slow grain growth in this stage might be the reason for the decrease of positron lifetime. After further annealing at 700–900℃ (the fourth stage), the vacancy clusters begin to recover, which leads to the fast decrease of τ_m and S parameter. This indicates rapid grain growth and complete recrystallization. However, even after annealing at temperatures as high as 900℃, the positron lifetime is still higher than the bulk lifetime in Cu. This indicates that there are some residual defects that cannot be annealed out; possibly stable defect-solute complexes.

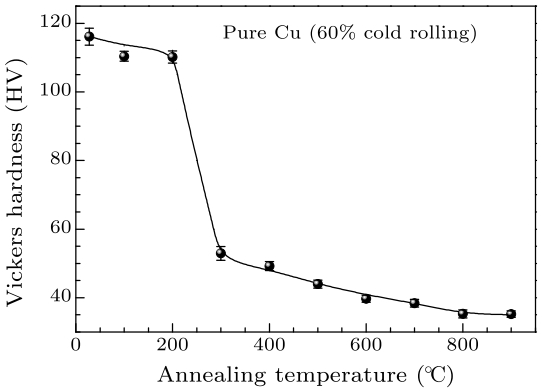


Fig. 2. Variation of the Vickers hardness for cold-rolled purity Cu as a function of the annealing temperature.

Figure 2 shows the Vickers hardness (in HV) of cold-rolled Cu as a function of annealing temperature. Its annealing behavior shows good correspondence to the recovery of defects reflected in Fig. 1. After annealing below 200℃, the Vickers hardness shows very slight decrease from 116 HV to 110 HV. After annealing at 200–300℃, it decreases significantly from 110 HV to 53 HV by a factor of nearly 50%. After that, the hardness shows a slight and continuous decrease up to the annealing temperature of 900℃. Considering the results of positron annihilation shown in Fig. 1, it can be determined that the hardening of cold rolled pure Cu is mainly due to defects, especially dislocations introduced by deformation.

As for the Cu-Ni Si alloy, significantly different annealing behavior of the defects was found in comparison with that of pure Cu. The dependence of average

positron τ_m, defect-related lifetime τ_2 and the Doppler broadening S parameter on the annealing temperature for Cu-Ni-Si alloy is presented in Figs. 3 and 4. Before annealing, τ_m is about 188 ps, and τ_2 is found to be about 245 ps. In analogy to the pure Cu, τ_2 is probably the average lifetime for positrons trapped in dislocations, monovacancies, and vacancy clusters. Since the defect lifetime is much higher than that for monovacancies, it may contain a large number of vacancy clusters.

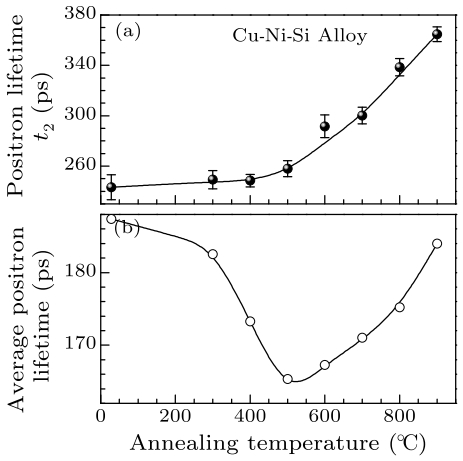


Fig. 3. Average positron lifetime and the defect related positron lifetime τ_2 for Cu-Ni-Si alloy as a function of the annealing temperature.

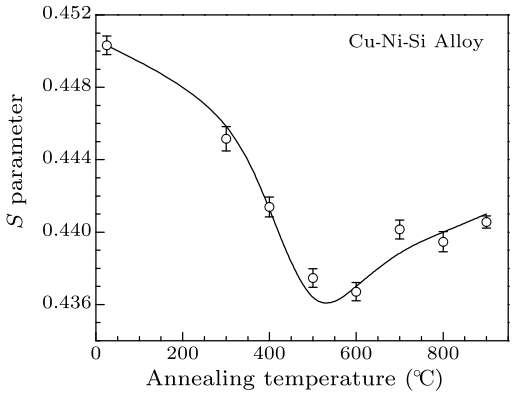


Fig. 4. Doppler broadening S parameter for Cu-Ni-Si alloy as a function of the annealing temperature.

Three annealing stages can be distinguished from Figs. 3 and 4 for Cu-Ni-Si alloy. In the first stage from room temperature to 300℃, no obvious changes in τ_2, τ_m, and S parameter are detected, suggesting that defects remain basically stable in Cu-Ni Si alloy up to 300℃. From 300℃ to 500℃ is the second annealing stage. A rapid decrease in τ_m and S parameter and an indistinct change in τ_2 can be seen in this stage. This is due to the recovery of defects such as dislocations and monovacancies, and possibly partial recovery of some vacancy clusters. In the third annealing stage from 500℃ to 900℃, it is interesting to note that there is a significant increase in τ_m and S parameter, which increases from 165 ps to 184 ps and from 0.435 to 0.441, respectively. The defect lifetime τ_2 also increases significantly from about 255 ps to about 365 ps. This indicates obviously formation of new defects in the sample, which are mainly large vacancy clusters.

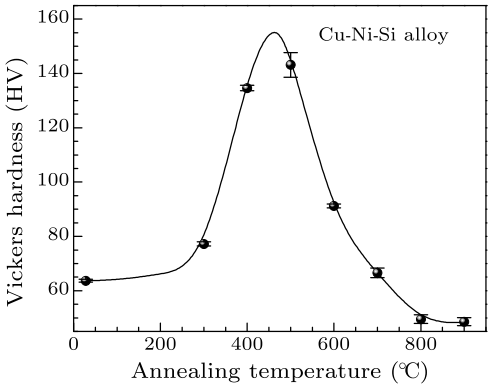


Fig. 5. Variation of the Vickers hardness for Cu-Ni-Si alloy as a function of the annealing temperature.

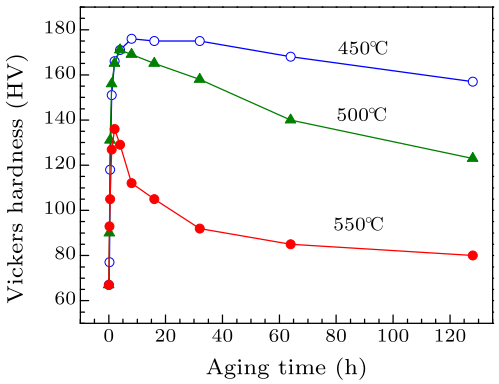


Fig. 6. Dependence of the Vickers hardness for Cu-Ni-Si alloy on the aging temperature.

Figure 5 shows the Vickers hardness of Cu-Ni-Si alloy as a function of the annealing temperature. For this sample, the change of Vickers hardness is no longer in accordance with the variation of positron annihilation parameters as it is in pure Cu. In the first annealing stage below 300℃, the hardness shows a very slight increase, and after annealing in the second stage (300–500℃), it increases drastically from 77 HV to 143 HV, while the defects show fast recovery in this stage as indicated by positron annihilation measurements. After annealing above 500 ℃, the hardness of Cu-Ni-Si alloy begins to decrease, and after annealing at 800–900℃, it decreases to even lower than the value before annealing. The inconsistency between Vickers hardness and defects suggests that increase of Vickers hardness in Cu-Ni-Si alloy during annealing is not due to defects, but is mostly related to precipitation. This is a common phenomenon observed in many alloys.

It has been reported by Toman *et al.*[1] and Lock-

yer *et al.*[5,6] that the precipitate responsible for the strengthening effect in Cu-Ni-Si system alloy is δ-Ni_2Si. These precipitates grow into nanoclusters and impede the movement of dislocations, which makes the alloy difficult to slip, and lead to the hardening of alloy. A detailed aging experiment on this Cu-Ni-Si alloy was also performed at three different temperatures ranging from 450℃ to 550℃. According to the aging curves as shown in Fig. 6, during aging at 450℃ a maximum Vickers hardness was reached at an aging time of 8 h, while it needs 4 h at 500℃ and only 2 h at 550℃ to reach the maximum Vickers hardness. Compared with these aging curves, it suggests that after annealing the alloy at 500℃ for 1 h, the Vickers hardness reaches nearly the maximum value, which corresponds to the peak-aging effect.

The CDB technique may provide some hints about the precipitation of solute atoms during annealing process. However we can not find a clear signal of Ni elements in the CDB curve. There are two possible reasons. First, according to the theoretical calculation, the positron affinity to Ni is lower than that of Cu,[23] which leads to a weaker competition of Ni compared with Cu. Second, the momentum distributions of core electrons for Ni and Cu are very close to each other,[24,25] therefore even if positrons are trapped by Ni clusters, their momentum distribution is indistinguishable from that of elemental Cu.

As for the decrease of hardness of Cu-Ni-Si alloy after annealing above 500℃, it might be due to the further growth of precipitate size, which finally leads to the loss of coherence with the host matrix, causing the significant decrease of hardness. The formation of incoherent precipitates produces distortion around the crystal lattice. The interface region between the precipitates and the host lattice loses the long-range order and may contain a large number of vacancy clusters or voids. The positrons are therefore trapped by the vacancy clusters within the distortion region, which leads to the significant increase of τ_m and τ_2.

In summary, we have found that in cold-rolled pure Cu, the decrease of hardness after annealing shows consistency with the recovery of defects, indicating that its hardening is closely related to deformation-induced defects such as dislocations. While for the Cu-Ni-Si alloys, annealing behavior of the hardness is against the recovery of defects. This suggests that its hardening is primarily due to the precipitation of solute atoms instead of defects. Further annealing above 500℃ causes a decrease of the hardness, which could be attributed to the coarsening of precipitates.

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