NDE POSITRON STUDY OF Cu AND Cu-Al ALLOYS

THERMALLY CHARGED WITH HYDROGEN AND DEFORMED

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INTRODUCTION

Some aspects of the deformation of Cu, Cu-2 w/o Al, and Cu-4 w/o Al alloy samples after thermal charging with hydrogen at 1000°C and rapid quenching (to -150°C isopentane) were treated in an earlier publication [1]. Comparisons were made with samples treated as just described except for use of an Ar atmosphere at 1000°C. The main experimental measurements then as now were of the Doppler broadening of the positron annihilation spectrum and the microhardness. The deformation was imposed by a Brinell indentation of 500 kgf.

It has been known for some time that protons can screen defects such as quenched in vacancies and dislocations from detection by positrons. This is a consequence of the trapping of the proton at the defect which then repels a subsequently arriving positron. The latter particle is thereby not able to trap at the defect and later annihilate with an electron in the defect neighborhood and eventually it annihilates instead with an electron in a more perfect region. This type of behavior was documented earlier in steel by Alex et al. [2], in Ni by Kao et al. [3], in Cu by Panchanadeeswaran and Byrne [4], and for cathodic hydrogen charging of Cu and Cu-Al alloys by Kim and Byrne [5,6].

In the present paper we wish to present three new aspects of the deformation of thermally hydrogen-charged Cu and Cu-Al alloys, namely: a cross-correlation of the positron peak parameter and the hardness after rolling deformation; warming-experiments from 90°K to 300°K for various degrees of deformation; and R parameter analysis of deformation induced by indentation (in order to identify trapping mechanisms).

EXPERIMENTAL DETAILS

Thermal charging of hydrogen consisted of exposure at 1000°C in a hydrogen atmosphere for times between 1 and 4 hours followed by a rapid quench into -150°C isopentane as in the work of Wampler et al. [7] and using the same furnace as Panchanadeeswaran and Byrne [4]. An Ar atmosphere was used for control samples. The sample materials were either 90% cold-rolled Cu, Cu-1.8 w/o Al, or Cu-3.69 w/o Al (hereafter called Cu,Cu-2 Al and Cu-4 Al for convenience). Hardness measurements were done with a Vickers indenter
and a 25 gf load. Deformation was induced either by cold-rolling or by indentation with a 10-mm Brinell ball under a load of 500 kgf.

An intrinsic Ge gamma ray detector, multichannel analyzer, analog-to-digital converter, and an IBM PC XT computer were used to record and analyze the positron annihilation spectrum for each sample. Positrons were put into each sample from a radioactive source. Each such positron then thermalized and annihilated with some electron. Defects serve as trapping sites for positrons and trapped positrons usually annihilate with the lower-energy electrons in the region of such a defect trap. If the center of mass of the electron-positron pair were stationary at the time of annihilation, two γ-rays each of 511 keV energy would be emitted at 180° to one another, but, since the center of mass of the annihilating pair is not stationary, the γ-ray energies each suffer a Doppler shift from the 511 keV value. This shift is larger for annihilation with a more energetic core electron than for annihilation with a lower-energy conduction electron. Hence, for a positron trapped in a defect, a smaller Doppler shift is a consequence of the higher probability that a conduction electron is involved in such an ion-core-poor location. Smaller Doppler shifts lead to a sharper annihilation spectrum or to a higher value of P which is the ratio of the number of events in the central or peak region of the spectrum to the total number of events in the whole spectrum.

Warming experiments, during which the annihilation spectrum shape was measured between 90 and 300°K, were conducted in the same cryostat as described elsewhere [4] and used 68Ge as the positron source. Experiments involving measurements of the spectrum shape as a function of distance from a Brinell indentation or on cold-rolled samples used a 22Na positron source for convenience.

RESULTS AND DISCUSSION

Figure 1 is a plot of the Doppler peak parameter P (a ratio of the annihilation peak area to the total area of the spectrum) versus the Vickers hardness for Cu samples which were held one hour at 1000°C, furnace-cooled, and cold-rolled (Curve A), and for samples thermally hydrogen-charged at 1000°C for one hour, isopentane-quenched to -150°C, and then

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Doppler peak parameter (P) of Cu versus hardness after cold-rolling samples which had been held one hour at 1000°C in either Ar or H2, quenched to -150°C isopentane, and then cold-rolled.
cold-rolled (Curve B). Clearly the peak parameter for a given hardness is lower for the hydrogen-charged condition. We interpret this to mean that some of the defects present are being screened by hydrogen as has been reported earlier in similar situations [1-6]. If one considers the increase in hardness for a fixed increment in peak parameter, the increase is greater for the hydrogen-charged material; i.e., hydrogen in Cu causes hardening as well as work-hardening, unlike its effect in some other materials where dislocation mobility is increased by the presence of hydrogen as reported for example by Eastman et al. [8].

Similar experiments were performed on Cu-2 w/o Al and Cu-4 w/o Al and resulted in the data plotted in Figs. 2 and 3. One can see that the straight lines through the data points, for hydrogen and argon atmospheres,

![Figure 2](image-url)  
**Figure 2.** Doppler peak parameter (P) of Cu-2 w/o Al alloy versus hardness after cold-rolling samples which had been held one hour at 1000°C in either Ar or H₂, quenched to -150°C isopentane, and then cold-rolled.

![Figure 3](image-url)  
**Figure 3.** Doppler peak parameter (P) of Cu-4 w/o Al alloy versus hardness after cold-rolling samples which had been held one hour at 1000°C in either Ar or H₂, quenched to -150°C isopentane, and then cold-rolled.
become closer to one another as the percentage of Al increases in the alloys. As in Fig. 1, the hydrogen-charged sample has a lower peak parameter than the argon-annealed sample in each of Figs. 2 and 3. The progressively closer approach of the curves in Figs. 2 and 3 relative to those in Fig. 1 is attributed to the increasing lack of correlation between the locations of protons and positrons in the wide stacking faults of the alloys. The stacking-fault energy of Cu decreases very rapidly with Al additions as reported by Thornton et al. [9] and by Miller et al. [10]. It is also known that both positrons and protons are attracted to stacking faults. Since the distance between the fault bounding partial dislocations increases rapidly with Al content, it is clear that the proton-positron correlation should decrease, and hence the proton screening of the fault from detection by positrons also should decrease. The latter then allows the data curves in Figs. 2 and 3 to more closely approach one another. Some facts related to this concept are obtained from relaxation experiments in which the peak parameter \( P \) is measured as a function of time at room temperature after times of thermal charging of 1, 2, 3, and 4 hours. Pan and Byrne showed [1] that, for Cu samples thermally hydrogen-charged, quenched, held in liquid nitrogen, and finally aged at room temperature, a maximum lowering in \( P \) was produced by three hours of thermal charging at 1000°C. This screening effect was gradually lost at room temperature, presumably as the hydrogen left the defects it was screening. Similar findings were reported for cathodically charged Ni [3]. However, when the thermal charging-type experiment is done with Cu-2 w/o Al and Cu-4 w/o Al we find first that the level of \( P \) after complete relaxation in 4 hours at room temperature is at about \( P = 0.375 \) for both alloys, whereas it was at about \( P = 0.3735 \) for pure Cu; and second that the screening change is much smaller, i.e., it is only about \( \Delta P = 0.0005 \) for Cu-2 w/o Al and \( \Delta P = 0.0003 \) for Cu-4 w/o Cu relative to a \( \Delta P \) for pure Cu of 0.002. This behavior may be interpreted, as earlier, in terms of the hydrogen (proton form) and the positrons not correlating in position very often in the wider stacking-fault regions of the alloy samples. Another aspect of this behavior noted by Pan and Byrne [11] is that, in the Al-containing alloys, the Al\(^{+++}\) ions should strongly attract vacancies, resulting in protons avoiding vacancies and trapping instead at stacking faults where they may go relatively undetected by positrons.

The balance of this paper will be devoted to R parameter analysis of various deformation experiments of thermally charged samples. The R parameter comes from a reformulation [12] of a positron-trapping model of Connors and West [13]. The parameter R is defect-specific, independent of defect concentration, and hence changes only when the defect-positron-trapping mechanism changes. R can be defined by

\[
R = \left| \frac{I_v^f - I_v^f}{I_c^c - I_c^c} \right|
\]

in which \( I_v^f \) and \( I_c^f \) are the peak and wing parameters, respectively, for samples "free" of defects, and \( I_v \) and \( I_c \) are the peak and wing parameters respectively for samples intermediate in defect concentration between saturated and completely free. The symbols v and c refer to valence and core electrons, respectively, since the peak region of the Doppler spectrum is formed from annihilations with valence electrons and the wings of the spectrum come from annihilations with core electrons.

The first application of R parameter analysis here is to experiments in which the Doppler spectrum was observed with a positron line source as a function of distance from a Brinell indentation placed in samples either quenched from 1000°C hydrogen or 1000°C Ar. Figure 4 shows R versus distance from the center of a 500-kgf indentation in each of H\(_2\)- and Ar-treated samples of pure Cu. The curves are almost the same for H\(_2\) and Ar treat-
ments, which suggests that hydrogen dissolved in Cu has no effect on \( R \) and hence on the positron-trapping mechanism. At the center of the indentation, where sample dislocation density is the highest, the \( R \) value of 0.70 is quite close to the value of 0.65 reported by Mantl and Triftshäuser [14] for dislocation traps in Cu. The \( R \) value of 0.86 in the undamaged region at 6 mm from the indentation is in excellent agreement with the value of \( R = 0.85 \) [14] for vacancy clusters and vacancy loops. Thus independent of whether a sample is previously treated in Ar or \( H_2 \), Cu seems to trap positrons at dislocations in the deformed region and at vacancy loops or clusters in the undeformed region.

This is not the case in the Cu-Al alloys, i.e., Fig. 5 shows a slight gradual increase in \( R \) as a function of distance from deformed to undeformed
regions for the Cu-2 w/o Al alloy, and Fig. 6 shows a constant R value over the same distance for the Cu-4 w/o Al alloy. A slight change or no change in R both denote that the trapping mechanism is the same in both deformed and undeformed regions. We suggest that the common positron trap in both regions, in both alloys for both atmospheres, is the stacking fault, because in the Cu-Al alloys vacancies are attracted to $A^{+++}$ ions and so are not as available as in Cu in which vacancy clusters and dislocation loops tend to form. The presence of increasingly widely extended stacking faults (as the % Al increases) is the only defect common to all current situations which is capable of accounting for the R parameter results of Figs. 5 and 6. This defect is, relatively speaking, not the controlling one, however, in the pure Cu case.

![Figure 6](image1.png)

**Figure 6.** R parameter versus distance in mm from the center of a 500-kgf indentation in Cu-4 w/o Al alloy quenched from one hour at 1000°C in either Ar (Δ) or H$_2$ (○), quenched into -150°C isopentane and warmed to room temperature.

![Figure 7](image2.png)

**Figure 7.** R parameter for Cu versus time held at 1000°C in either Ar (Δ) or H$_2$ (○) prior to quenching.
If Cu is thermally treated for various times up to 60 minutes at 1000°C in either H₂ or Ar, quenching to -150°C followed by R parameter determination shows, in Fig. 7, only the R value corresponding to vacancy clusters or vacancy loops. These defects again seem to be dominant in Cu independent of whether Ar or H₂ is present at 1000°C.

In Fig. 8 one does see a drastic change in R and hence in trapping mechanism when the H₂ or Ar treatments are performed at a series of increasing temperatures. The cold-rolled value is shown at room temperature. No further change occurs until 500°C is exceeded because the vacancy supersaturation on quenching is insufficient to form clusters or loops at lower temperatures. But the R value becomes 0.825 at 750°C and 0.890 at 1000°C which suggests the dominance of vacancy clusters and loops in Cu samples quenched from temperatures above 500°C independent of treatment atmosphere.

CONCLUSIONS

Thermal charging of hydrogen into Cu followed by cold-rolling results in a linear dependence of Doppler peak parameter (P) on hardness. Similar treatments utilizing argon gas also result in a linear dependence of (P) on VHN; however, the latter data points always lie above the former hydrogen points for any given hardness. This is ascribed to proton screening of dislocations from positron detection in the case of the hydrogen-charged specimens.

Similar behavior to that described in the previous paragraph is observed for Cu-2 w/o Al and Cu-4 w/o Al alloys. An important exception, however, is that the separation of the linear hydrogen and argon data sets becomes smaller as Al content increases (or the stacking-fault energy decreases). This is ascribed to the decreasing amount of correlation between protons and positrons trapped in the progressively wider stacking faults as the w/o Al increases.

Measurements of the magnitude of the proton screening effect (ΔP) after quenching from a hydrogen atmosphere show that ΔP decreases from 0.002 to 0.0005 to 0.0003 for Cu, Cu-2 w/o Al, and Cu-4 w/o Al respectively. This is an example of the decreasing correlation of proton and positron locations as w/o Al increases, as mentioned in the previous paragraph.

Figure 8. R parameter for Cu versus temperature at which held in either Ar(△) or H₂(●) prior to quenching.
R parameter analysis of samples quenched from either Ar or H₂ at 1000°C and then indented show that R varies as a function of distance from the center of a 500-kgf indentation to undeformed material 6 to 7 mm removed from that center as follows: (1) For Cu, R changes from a value of 0.70 (close to the value of 0.65 for dislocations) at the center of the indentation to a value of 0.86 (close to the value of 0.85 for vacancy clusters or vacancy types of positron-trapping site in Cu) changes from dislocations in the deformed region to vacancy clusters and loops in the undeformed region. R values are independent of whether hydrogen or argon is used. (2) For Cu-2 w/o Al and Cu-4 w/o Al alloys, one finds a slowly changing R value and a constant R value, respectively, as a function of distance from the center of the indentation. Both behaviors suggest no change in trap type from deformed to undeformed regions. We suggest that the common trap in the alloys is the extended dislocation.

The R value for Cu remains at the cold-rolled value of 0.665 for either Ar or H₂ treatment at temperature of 500°C or less, becomes 0.825 for 750°C, and 0.89 for 1000°C treatments. It is suggested that this implies a change of trap site from the dislocation for quenching from temperatures below 500°C to the vacancy cluster or loop for quenches from 1000°C.

The R value of Cu after quenching does not change from a value of about 0.88 with treatment time at 1000°C (in either Ar or H₂) for times up to 60 minutes, i.e., the trap type remains in the vacancy cluster or loop.

REFERENCES