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The effect of cold working on Hf solute clusters in CuHf as studied by time differential perturbed angular correlation (TDPAC) and positron lifetime measurements

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Abstract. The presence of Hf solute clusters in a Cu matrix has been identified by time differential perturbed angular correlation (TDPAC) studies and further confirmed by energy-dispersive x-ray analysis. Cold working of the **Cu**Hf sample results in a strain at the Hf solute clusters as deduced from the TDPAC. Annealing treatments of the sample lead to the restoration of the strain-free nature of the solute clusters. A defect associated with a 0.06 fraction of probe nuclei which is stable up to 925 K is interpreted as a faulted dislocation loop. Positron lifetime measurements on the cold-worked sample indicate the presence of a single lifetime component which is interpreted as due to the annihilation of positrons predominantly at dislocations, faulted dislocation loops and in addition at misfit dislocations at the interface between the Hf solute clusters and the matrix.

1. Introduction

The understanding of the interaction between solute atoms and defects is of technological importance [1]. Clusters of solute atoms might bind defects more strongly than the isolated solute atoms, if the interaction between the defect concerned and a solute atom is attractive [2]. The interaction of solute atoms with defects critically depends upon the means of defect production, as the latter dictates the various kinds of defect that are formed.

The hyperfine interaction of impurities with their surroundings (i.e. the interaction between the nuclear moments of the impurities and electromagnetic fields at their sites [3]) provides a powerful method for studying the behaviour of defect–impurity interactions in metals [4]. The hyperfine-interaction-induced perturbation of angular correlation (PAC) of γ-rays emitted in cascade, by suitable radioactive probe atoms in the sample, has been established as a powerful technique for studying defects in solids [5]. The experimental hyperfine interaction parameters enable us to identify the defects that are bound to probe nuclei and their geometry. Many results have been reported on the interaction between the solute clusters and defects in materials using TDPAC [6, 7]. By means of TDPAC it is possible to determine the geometry of the solute clusters and their interaction with possible nearby defects and their evolution with the annealing treatments [8].

Positron annihilation spectroscopy has also been used for studying the interaction between defects and solute clusters in materials [9]. If the solute cluster is coherent (i.e. characterized by the absence of defects such as misfit dislocations at the interface between the matrix and the solute cluster), and if the positrons do not bind to the solute-atom clusters, then the positrons will mostly annihilate in the bulk of the sample. If the solute clusters are incoherent, then

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positrons may annihilate at misfit dislocations at the interface between the matrix and incoherent precipitates.

TDPAC and positron lifetime measurements on helium-implanted **Cu**Hf [10] indicate a strong binding of helium–vacancy complexes and vacancy clusters by Hf solute clusters. The present work examines:

(1) The effect of cold working on the Hf solute clusters in **Cu**Hf sample as reflected by the hyperfine interaction parameters deduced from TDPAC measurements and the positron lifetime parameters.
(2) The effect of isochronal annealing treatments on the coherency of the solute clusters.
(3) The cold-working-induced defects and their stability.

2. Experimental details

An alloy of Cu (99.8% purity) with 1 wt% Hf has been prepared by arc melting in a helium atmosphere and homogenized by prolonged annealing. **Cu**Hf samples of dimensions 10 mm $\times$ 2 mm $\times$ 200 μm and 10 mm $\times$ 10 mm $\times$ 200 μm were drawn from the melt and annealed at 1123 K for six hours to get the reference samples for TDPAC and positron lifetime measurements respectively.

The positron lifetime measurements were done using a fast–fast coincidence spectrometer with a time resolution of 240 ps (FWHM). The positron lifetime spectrum consists of a sum of exponential decay components, corresponding to different annihilation modes convoluted with the instrumental resolution [11]. The decay components include the annihilation of positrons in bulk, and open-volume defects that are present in the sample and the source material. The instrumental resolution as well as source contribution are evaluated by fitting the measured spectrum in a reference sample of known lifetime using the program RESOLUTION [12]. Knowing the instrumental resolution and source annihilation parameters, as evaluated from the RESOLUTION fit, the analysis of the actual lifetime spectrum of the sample under study is carried out to unfold the different lifetime components using a non-linear least-squares fitting program POSITRONFIT [12].

Samples for TDPAC measurements were thermal neutron irradiated at CIRUS reactor, Bhabha Atomic Research Centre, Bombay, to a fluence of 2×10^{22} n m^{-2}, to produce ^{181}Ta probe nuclei by the reaction

$$^{180}\mathrm{Hf}(\mathrm{n}, \gamma)^{181}\mathrm{Hf} \xrightarrow{\beta^-} {}^{181}\mathrm{Ta}.$$

The TDPAC of the 133–482 keV γ–γ cascade of ^{181}Ta was measured by a three-detector twin fast–slow coincidence set-up using NaI(Tl) detectors. The prompt time resolution of the set-up measured with a ^{60}Co source was 2.2 ns FWHM when gated for the above cascade of ^{181}Ta [13]. The details of the data acquisition and how to obtain the normalized anisotropy function $R(t)$ are given in [13, 14].

The normalized anisotropy $R(t)$ spectra were least-squares fitted to the function [14]

$$R(t) = A_2 \sum_{i=0}^{n} f_i G_2^i(t). \tag{1}$$

The value of n is determined by the number of resolved frequency components in the Fourier spectra of the $R(t)$ spectrum. The function $G_2^i(t)$ is given by

$$G_2^i(t) = \sum_{m=0}^{3} a_m^i \exp[-\delta_i k_m(\eta_i)\omega_{Qi} t] \cos[k_m(\eta_i)\omega_{Qi} t] \tag{2}$$

where

$$\sum_{i=0}^{n} f_i = 1$$

$$k_0 = 0 \qquad k_1(\eta_i) + k_2(\eta_i) = k_3(\eta_i)$$

$$\sum_{m=0}^{3} a_m^i(\eta_i) = 1.$$

The spin value of the isomeric state of ^{181}Ta is 5/2, leading to

$$\nu_{Qi} = eQV_{zz}^i/h = 10\omega_{Qi}/3\pi \tag{3}$$

where V_{zz} is the principal component of the electric field gradient (EFG) tensor. When the EFG is not axially symmetric, the asymmetry parameter

$$\eta = (V_{xx} - V_{yy})/V_{zz} \qquad (|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|)$$

is extracted from the fit of the measured $R(t)$ to equation (2). The values of k_m depend on η. Therefore the EFG tensor is completely determined by the frequency ν_Q and the asymmetry parameter η. A non-vanishing value of δ (i.e. the width of the Lorentzian distribution of the quadrupole frequency) implies either a significant concentration of defects and/or impurities in the material under study, or a disordered arrangement of atoms in the probe surroundings.

In the cases of the probe nuclei occupying a non-cubic and axially charge-symmetric environment in a polycrystalline sample or the probe atoms being associated with solute clusters having a non-cubic and axially charge-symmetric environment (i.e. coherent solute clusters), the value of the asymmetry parameter will be zero which will result in $k_m(\eta = 0) = m$. For these cases the values of a_0, a_1, a_2 and a_3 are 1/5, 13/35, 10/35 and 5/35 respectively with a_1:a_2:a_3 $\approx$ 3:2:1. If there is a selective orientation of the solute clusters associated with the probe atoms, then the value of the ratio a_1:a_2:a_3 will be very different from 3:2:1 [15, 16].

TDPAC and positron lifetime measurements were carried out at room temperature on the reference and 50% cold-worked **Cu**Hf samples. Subsequently room temperature measurements were carried out on the cold-worked samples as a function of isochronal temperature (323–1073 K). The annealing time at each temperature was 30 min.

3. Results and discussion

Analysis of a TDPAC spectrum for the reference sample indicates that a fraction 0.12 ± 0.02 of probe nuclei experience a quadrupole frequency of 290 ± 4 MHz with $\eta \approx 0.12 \pm 0.02$. The remaining fraction of probe nuclei experience a quadrupole frequency of 0 MHz implying that these occupy substitutional sites in the fcc matrix and that the local environment is defect free. The defect-associated fraction are identified as due to probe atoms associated with Hf solute clusters, as the corresponding quadrupole interaction parameters match those encountered by the probe nuclei in the Hf hcp matrix as reported [17]. The fitted TDPAC spectrum and the Fourier-transformed spectrum are shown in figure 1. Some solute clusters as observed by TEM were confirmed to be due to hafnium by EDAX measurements. On comparison of the EDAX spectra corresponding to the matrix (figure 2 (top panel)) (solute cluster-free zone) and the solute cluster-rich zone (figure 2 (bottom panel)) it is seen that the peaks corresponding to Hf are predominant in the latter case. This implies that the observed solute cluster is that of Hf.

A **Cu**Hf sample of 200 μm thickness was rolled to half of its thickness at 303 K. In the cold-worked sample it is observed that a 0.83 ± 0.02 fraction of probe atoms (f_0) are substitutional and are characterized by the defect-free microscopic environment. About 0.11 ± 0.02

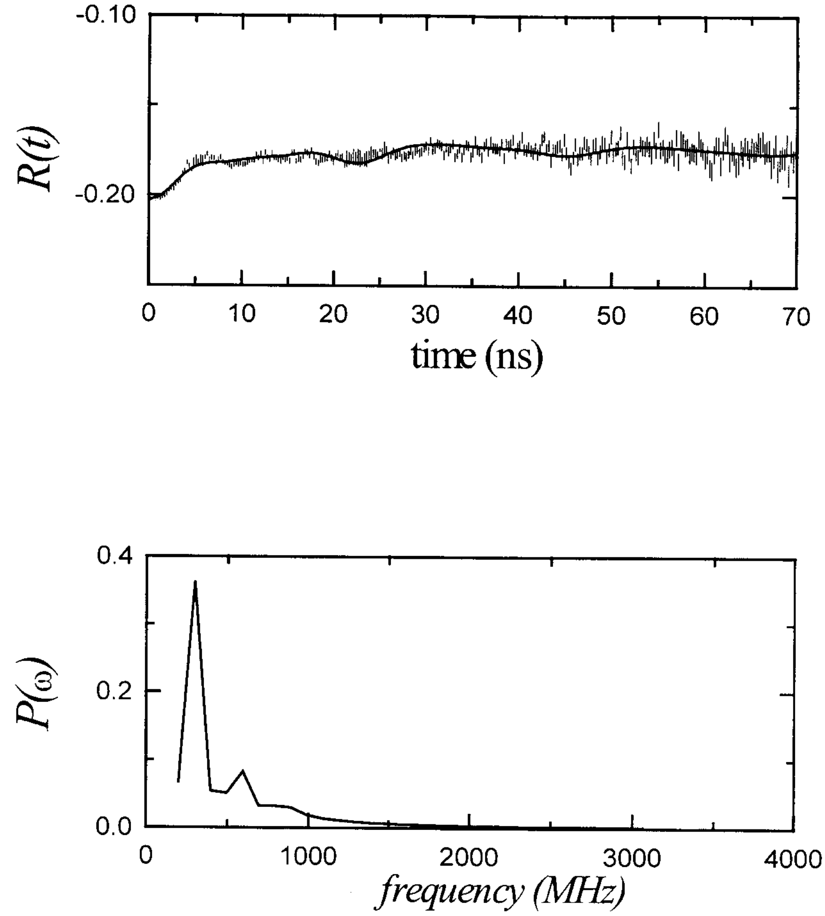

Figure 1. The experimental $R(t)$ versus t spectra at room temperature and the Fourier-transformed spectra for the as-n-irradiated sample (reference). The continuous curve for $R(t)$ is the one calculated using the fitted values of the parameters.

of the probe atoms (f_1) experience a quadrupole frequency (ν_{Q1}) of 290 ± 4 MHz with $\eta_1 = 0.12 \pm 0.02$, indicating that the quadrupole parameters as encountered by the probe atoms associated with Hf solute clusters remain almost the same as those of the reference sample. As far as this component is concerned however, the difference between these results and those for the reference sample is shown up as the variation in the amplitudes of the quadrupole frequency components as shown in figure 3(a). This is due to a preferential orientation of the solute clusters brought out by the cold working of the sample. The remaining fraction (f_2) 0.06 ± 0.01 of probe atoms experience a quadrupole frequency (ν_{Q2}) of 870 ± 22 MHz with an asymmetry parameter $\eta_2 = 0.14 \pm 0.04$. Identification of the cold-work-induced defect associated with this fraction of probe nuclei is made in the next paragraph.

The TDPAC spectra along with their Fourier transforms for a few annealing temperatures are given in figure 3. The analysis of the TDPAC data indicates that the values of ν_{Q1} and f_1 do not vary with annealing temperature. Only the value of η_1 corresponding to the probe atoms associated with Hf solute clusters changes with annealing treatment of the cold-worked sample as shown in figure 4. The change of η_1 is due to the strain produced at the interface, causing a

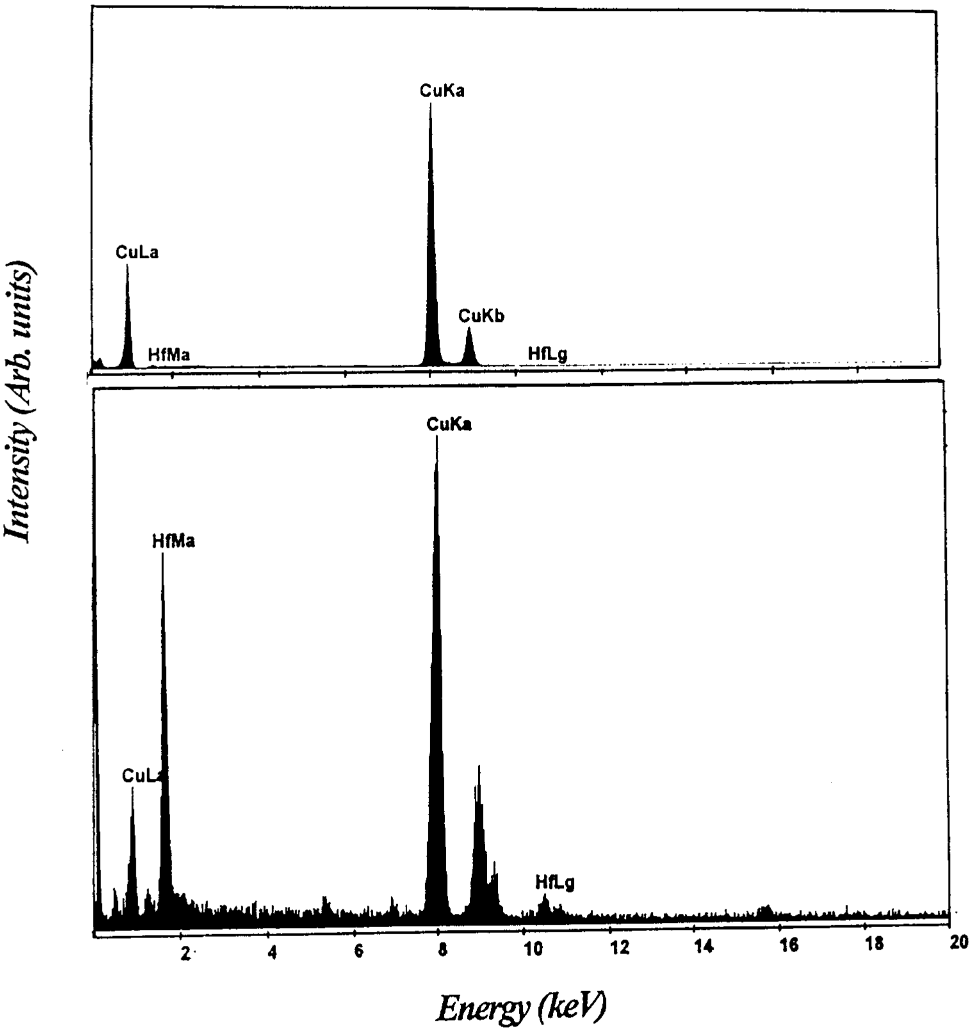

Figure 2. Energy-dispersive x-ray analysis (EDAX) spectra (top panel) for the matrix and (bottom panel) for the solute cluster-rich zone of the matrix.

slight change in the microscopic structure of the solute-atom clusters. A slight increase in the value of η_1 for annealing treatments up to 373 K is due to the increase in strain brought about by the effective interaction between dislocations and the solute clusters. The dislocation motion as impeded by the solute atoms is manifested as a constant value of η_1 for annealing temperatures between 373 and 423 K. The decrease in η_1 for annealing temperature beyond 473 K is due to the relieving of the strain and restoration of microscopic structure similar to that for the hcp lattice at the Hf solute clusters. Even following the annealing treatment of the sample beyond 873 K which is above the recrystallization temperature of Cu, no change was observed in either the fraction (f_1) or quadrupole frequency (ν_{Q1}) as experienced by probe atoms associated with Hf solute clusters. TDPAC measurements following isochronal annealing treatments of the sample indicate that the quadrupole parameters as encountered by the fraction f_2 of probe atoms do not change for annealing treatments up to 925 K. Following the annealing treatment

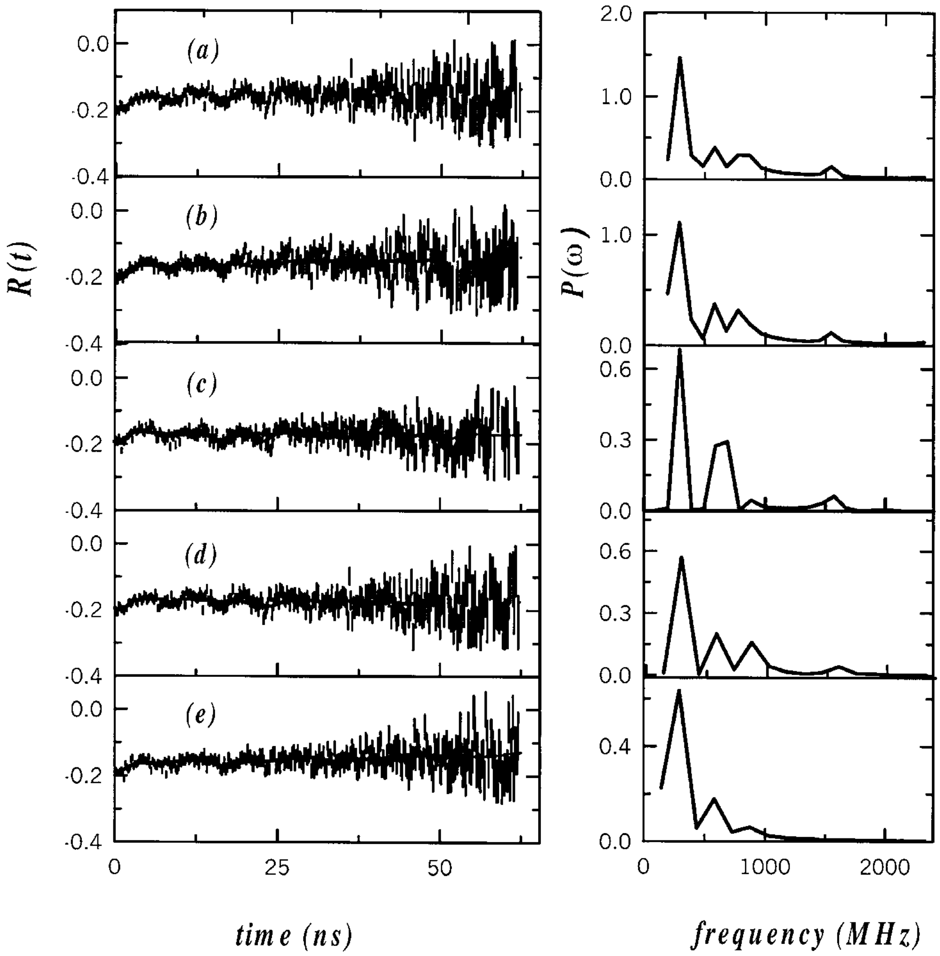

Figure 3. Time-dependent anisotropy spectra $R(t)$ for ^{181}Ta and the Fourier transform $P(\omega)$ for a cold-worked **Cu**Hf sample subjected to isochronal annealing treatment at various temperatures: (a) as cold worked; (b) annealed at 373 K; (c) annealed at 473 K; (d) annealed at 873 K; and (e) annealed at 973 K.

at 975 K, the value of f_2 becomes zero. On the basis of the high stability of the fraction f_2, the associated defect is plausibly interpreted as a faulted dislocation loop. Faulted dislocation loops are reported to be quite stable in cold-worked Cu [18] and Ti [15] samples, as found using TDPAC.

TDPAC measurements therefore indicate that the possible cold-work-induced defects are not so strongly trapped by the probe atoms as to have stable vacancy complexes in the presence of a significant concentration of dislocations in the cold-worked sample. But there exists a possibility for the occurrence of isolated vacancy clusters and other open-volume defects in the sample not associated with Hf atoms. To investigate this further, positron lifetime measurements have been carried out on a **Cu**Hf sample subjected to similar conditions.

Positron lifetime measurements on the reference sample show that all positrons annihilate with a mean lifetime of 120 ps, matching with the result reported for the bulk lifetime of positrons in Cu [19]. This further indicates that Hf solute clusters are coherent in the Cu

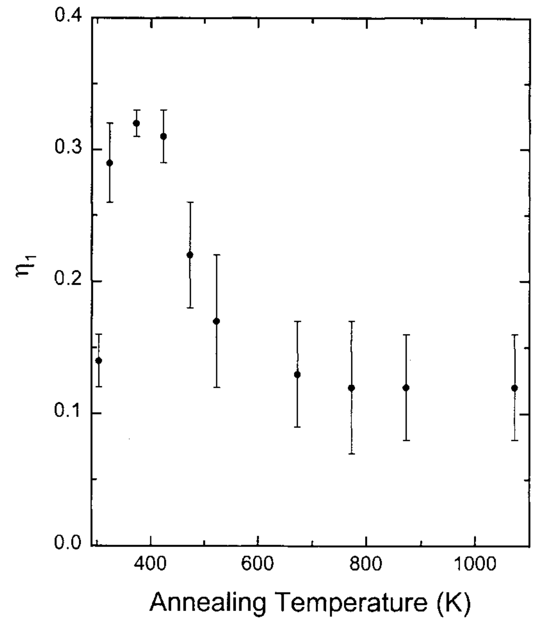

Figure 4. Variation of the asymmetry parameter η_1 as deduced from TDPAC measurements with annealing temperature.

matrix (i.e. the absence of misfit dislocations at the interface between the precipitate and the matrix) and that positrons do not have a positive affinity for annihilating at the coherent Hf solute clusters. This is based on the reasoning that no lifetime component could be observed close to 187 ps, which is equal to the value of the positron lifetime in a well annealed Hf metal [20]. The coherency of Hf solute clusters in the annealed reference sample is verified by the low value of the asymmetry parameter $\eta \approx 0.12$, as deduced from the TDPAC results discussed earlier.

Positron lifetime measurements on the cold-worked sample indicate the existence of a single component with a lifetime of 168 ± 2 ps considerably larger than the defect-free-bulk lifetime of positrons in Cu and smaller than that of the vacancy lifetime which is $\approx$175 ps. Therefore the observed lifetime of 168 ± 2 ps is explained as due to positrons annihilating at dislocations [21]. The variation of the positron lifetime τ with isochronal annealing temperature is shown in figure 5. It is observed that τ decreases monotonically with annealing temperature T_A, reaching a value of 124 ± 2 ps following the annealing treatment at 675 K and thereafter. This indicates the onset temperature of recrystallization of the sample.

The observed variation of the lifetime of the positrons is due to their annihilation at dislocations, faulted dislocation loops and also at the misfit dislocations present at the interface between the matrix and the Hf solute clusters. Figure 5 shows that at temperatures >675 K, there exists a saturation in the positron lifetime. This may be so because the nearly axially symmetric environment of the probe atoms associated with Hf solute clusters has been restored at these annealing temperatures. This can be seen from the saturation of η_1, the asymmetry parameter as encountered by TDPAC probe atoms associated with Hf solute clusters, for annealing treatments beyond 675 K as shown in figure 4. The contribution, due to the positron annihilation at the misfit dislocations at the interface between the Hf solute cluster and the matrix, is expected to be absent for annealing treatments beyond 675 K where the Hf solute

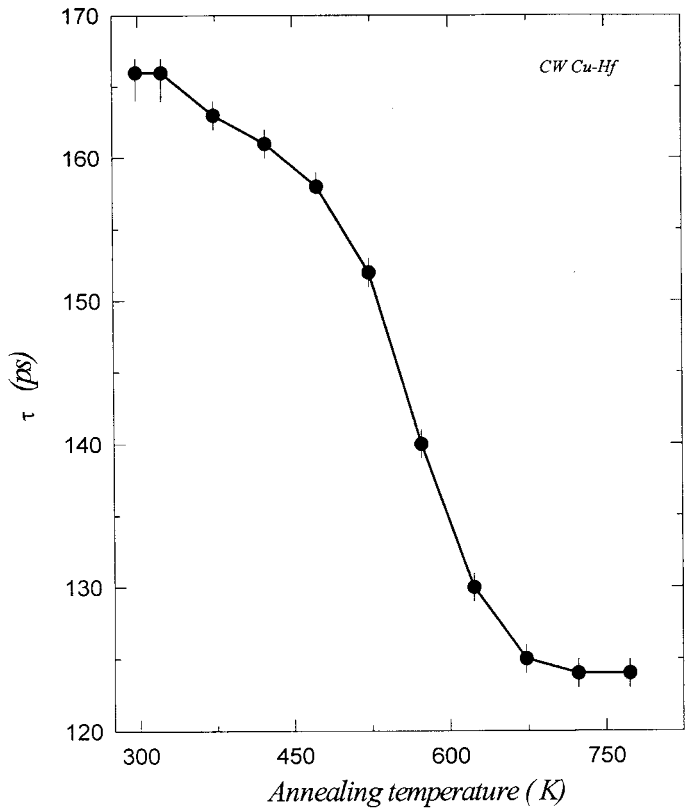

Figure 5. The variation of the mean positron lifetime τ with annealing temperature.

clusters are expected to become coherent as shown by TDPAC measurements. The variation of the positron lifetime beyond 675 K may indicate the annihilation of positrons at dislocations which are present in a smaller concentration than that in the as-cold-worked sample and at defects such as faulted dislocation loops. These annihilations are manifested as a slightly higher value of the positron lifetime than that for the well annealed reference sample as seen in figure 4 beyond 700 K. The results of positron lifetime measurements are also in agreement with those of TDPAC measurements indicating the existence of faulted dislocation loops to be associated with the fraction f_2 of Hf atoms, as the positron annihilates at the faulted dislocation loop with a lifetime almost equal to that of the dislocations.

On the basis of positron annihilation Doppler broadening measurements carried out on a cold-worked pure Cu sample, Mantl and Triftshauser [22] have inferred that vacancy clusters are not sufficiently stable to cause an observable effect in the presence of a dislocation density. On the basis of our results from TDPAC and positron lifetime measurements, it can be inferred that neither isolated Hf atoms nor the Hf-atom clusters bind vacancies strongly, leading to the formation of stable vacancy clusters in the cold-worked **Cu**Hf sample. This is in contrast to the results obtained on helium-implanted **Cu**Hf, where a strong binding of helium-associated vacancy complexes by hafnium solute clusters was deduced from TDPAC and positron lifetime measurements [10]. This may be understood as due to the effective interaction between vacancies and dislocations, leading to the loss of vacancies at these sinks in cold-worked **Cu**Hf.

4. Conclusions

Neither isolated nor clusters of Hf atoms bind vacancies to form stable vacancies/vacancy cluster complexes in cold-worked samples; this is deduced from TDPAC measurements. Cold working is observed to result in an axial asymmetry of Hf solute clusters as shown by TDPAC measurements, which is understood as due to the strain at the solute clusters due to the cold-working effects. Annealing beyond 675 K results in the restoration of the axially symmetric environment of the probe atoms associated with Hf solute clusters. A fraction of about 0.06 of the probe atoms are associated with dislocation loops and remain stable for annealing treatments up to 925 K. The vacancies do not survive in the cold-worked sample, as deduced from positron lifetime measurements. Vacancies are predominantly lost at dislocations. Positron lifetime measurements on cold-worked samples as functions of isochronal annealing temperature indicate dislocation recovery. Recrystallization of cold-worked **Cu**Hf is found to occur beyond 675 K, as shown by positron lifetime measurements.

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