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Cold-worked and hydrogen charged NbHf as studied by TDPAC and positron lifetime measurements

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Abstract. Time differential perturbed angular correlation (TDPAC) and positron life-time measurements on cold-worked and hydrogen charged NbHf indicate a strong binding of hydrogen decorated vacancy clusters with Hf impurities. Both TDPAC and positron lifetime results are mutually consistent on this aspect. Transformation of H-vacancy clusters into H-bubbles is indicated by the positron lifetime behaviour at annealing temperatures beyond 900 K. Impurity effects like oxygen pickup and coating of voids cannot be ruled out at elevated temperatures.

Keywords. TDPAC; positron lifetime; hydrogen-vacancy complex; defect recovery.

1. Introduction

BCC metals are of technological importance in fusion reactor environments where a detailed knowledge of the property changes due to lattice damage is crucial. Resistivity measurements have been reported on quenched, electron and proton irradiated samples of W, Nb, Mo and Ta (Rasch *et al* 1980; Schwirtlinch and Schultz 1980a,b; Frank 1981; Tietze *et al* 1982; Schultz 1987; Sengupta *et al* 1987). Positron lifetime and annihilation lineshape measurements have also been reported in low temperature electron and neutron irradiated pure Nb by Hautojarvi *et al* (1983) to study the recovery of vacancy-type defects in the presence of hydrogen. Isochronal resistivity recovery of pure Nb subjected to electron irradiation at 8 K indicates the migration of monovacancies at around 220 K (Petzold and Schultz 1987). In addition, the role of various impurities such as H, O, N, Pt, Hf and Zr in binding the defects produced due to electron irradiation are also discussed (Petzold and Schultz 1987). Presence of small traces of hydrogen in Nb is observed to shift stage III to about 350 K. The over sized impurity such as Hf is observed to shift the stage III in Nb to higher temperatures (Petzold and Schultz 1987).

The trapping of defects by In and Rh impurities has been reported in Nb by ^{111}Cd and ^{100}Rh TDPAC measurements (Sielemann *et al* 1981; Vianden and Winand 1981). ^{181}Ta TDPAC measurements have been reported on proton implanted Nb where, the trapping of hydrogen decorated vacancies by Hf impurities has been observed (Vianden and Winand 1981; Roitzheim *et al* 1989). Recent measurements on proton implanted NbHf with probe atoms introduced in the sample by alloying indicate the formation of H–V complexes associated with probe atoms (Govindaraj and Gopinathan 1997).

While defect properties in bcc transition metals have been studied extensively, there exists somewhat a scarce data on defect studies in group V transition metals like Nb. These metals dissolve large concentrations of interstitial atoms like hydrogen, oxygen etc. It is therefore important to study defect–impurity interactions and their influence on defect recovery in Nb. It is also interesting to study the important role of hydrogen impurities in the stability of three-dimensional vacancy clusters in Nb. With these objectives, combined studies of TDPAC and positron lifetime measurements have been attempted in cold-worked and hydrogen charged NbHf.

2. Experimental

Nb of 99·999% purity and Hf of 99·8% purity with 1 wt% of the latter have been alloyed using the arc furnace. The sample was subjected to a prolonged annealing at 1200 K for homogenization. The samples of dimensions 1 cm × 0·1 cm × 0·024 cm and 1 cm × 1 cm × 0·024 cm were prepared for TDPAC and positron lifetime measurements, respectively. Data analysis of the time dependent anisotropy spectrum for ^{181}Ta in the reference NbHf indicates the absence of any quadrupole component. The fitted $R(t)$ spectrum and its Fourier transform $P(\omega)$ are shown in figure 1, which shows the absence of any periodic pattern. This indicates that all the probe nuclei experience a zero quadrupole frequency and therefore are defect free and substitutional in bcc Nb matrix. A significant damping of the anisotropy

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spectrum as shown in figure 1 implies the presence of some impurity atoms like oxygen in the sample. It is known that Nb is susceptible to absorbing impurities like O. Positron lifetime measurements on the reference sample indicate the annihilation of positrons with a unique lifetime of 120 ps. This coincides with that of the defect free bulk lifetime of positrons in the Nb matrix as reported in the literature (Hautojarvi *et al* 1983).

The samples were 50% cold-worked and TDPAC measurement carried out in the cold-worked condition. The cold-rolled samples meant for TDPAC and positron lifetime measurements were electrolytically charged with hydrogen using water as an electrolytic medium. The charging was carried out for 3 h at a current of 25 mA. TDPAC and positron lifetime measurements were carried out on the respective samples. Subsequent measurements were carried out on these samples following the isochronal annealing treatments.

3. Results and discussion

TDPAC measurement on the cold-worked sample indicates that $0{\cdot}85 \pm 0{\cdot}04$ fraction of probe nuclei experiences a zero quadrupole frequency and the remaining fraction experiences the following quadrupole interaction parameters viz. $\nu_Q = 325 \pm 12$ MHz, $\eta = 0{\cdot}16 \pm 0{\cdot}04$ and $\delta = 0{\cdot}28 \pm 0{\cdot}06$. The corresponding fitted $R(t)$ spectrum and its Fourier transform $P(\omega)$ are shown in figure 2. The Fourier transform of the spectra indicates the occurrence of the fundamental component of the quadrupole frequency at 325 MHz. The quadrupole parameters of probe nuclei in the cold-worked sample are not observed in the reference sample, indicating the association of cold-work induced defects with probe nuclei. Positron lifetime measurement on the cold-worked sample indicates that in addition to a dislocation component, a lifetime component exists whose value is larger than that of mono-vacancy in Nb. On the basis of the results of TDPAC and positron lifetime measurements in the cold-worked sample, the defect component, as observed in the TDPAC measurement, can be attributed to probe nuclei trapping vacancy clusters. Also the probe nuclei bound to dislocations in general, might result in non-unique quadrupole frequencies which rules out dislocations being responsible for the observed frequency of 325 MHz.

Isochronal annealing measurements carried out in a cold-worked pure Nb sample by Tanigawa *et al* (1982) using positron lifetime spectroscopy indicate the onset of increase of the mean lifetime at 620 K which reaches a maximum at 773 K. This stage is attributed to vacancy migration and clustering in the cold-worked pure Nb sample. Therefore, the occurrence of vacancy clusters at room temperature in the as cold-worked NbHf sample in the present measurement, is understood to be due to the athermal trapping of vacancies by Hf impurities. Such an athermal trapping of vacancies by impurities is possible due to the interaction between dislocations and probe atoms (Collins *et al* 1981).

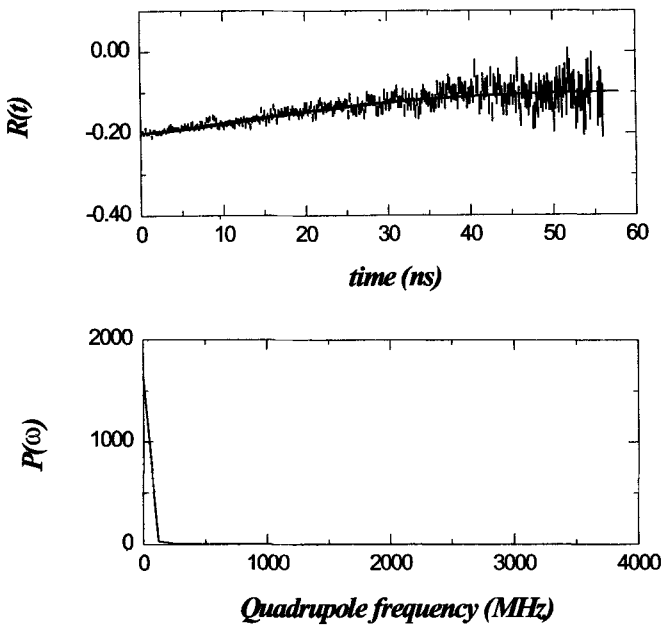

Figure 1. The experimental $R(t)$ vs t spectra at room temperature and its Fourier transformed spectra in the reference NbHf sample. The continuous curve in $R(t)$ is the one calculated using the fitted values of the parameters.

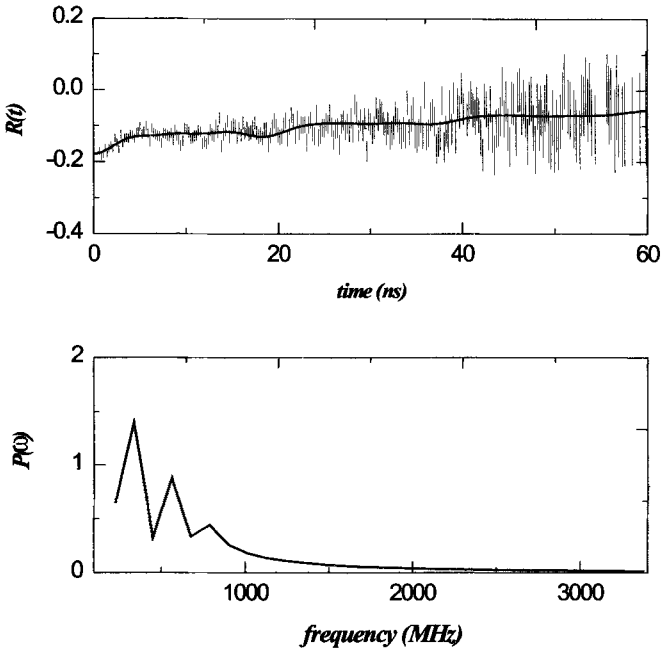

Figure 2. The experimental $R(t)$ vs t spectra at room temperature and its Fourier transformed spectra in the cold-worked NbHf sample. The continuous curve in $R(t)$ is the one calculated using the fitted values of the parameters.

3.1 *Effect of hydrogen on defect recovery in NbHf*

Results of analysis of TDPAC measurement on the cold-worked and hydrogen charged sample indicate the presence of the following hyperfine interaction parameters as experienced by probe nuclei viz. $f_1 = 0{\cdot}07 \pm 0{\cdot}04$, $\nu_{Q1} = 619 \pm 5$ MHz, $\delta_1 = 0{\cdot}26 \pm 0{\cdot}04$, $\eta_1 = 0{\cdot}68 \pm 0{\cdot}08$; $f_2 = 0{\cdot}09 \pm 0{\cdot}01$, $\nu_{Q2} = 649 \pm 5$ MHz, $\delta_2 = 0{\cdot}16 \pm 0{\cdot}08$ and $\eta_2 = 0{\cdot}46 \pm 0{\cdot}12$. The fitted anisotropy spectra for a few annealing treatments are shown in figure 3. The observation of two defect associated fractions of probe nuclei in cold-worked and hydrogen charged sample is in contrast to that in the earlier discussed cold-worked sample, where only a single defect associated quadrupole frequency was observed. The variations of hyperfine interaction parameters associated with the fractions f_1 and f_2 of the probe nuclei are shown in figures 4 and 5. The measurement on the cold-worked and hydrogen charged sample following the annealing treatment at 323 K indicates sharp changes in the hyperfine interaction parameters viz. $f_1 = 0{\cdot}1 \pm 0{\cdot}02$, $\nu_{Q1} = 320 \pm 6$ MHz, $\delta_1 = 0{\cdot}33 \pm 0{\cdot}04$, $\eta_1 = 0{\cdot}32 \pm 0{\cdot}12$, $f_2 = 0{\cdot}08 \pm 0{\cdot}01$, $\nu_{Q2} = 858 \pm 5$ MHz, $\delta_2 = 0{\cdot}12 \pm 0{\cdot}02$ and $\eta_2 = 0{\cdot}48 \pm 0{\cdot}08$ [cf. figure 5]. Beyond 323 K, the hyperfine interaction parameters viz. ν_{Q1} and η_1 remain almost constant and this behaviour persists up to 773 K. The fraction f_1 shows a maximum around 373 K beyond which it decreases to a steady value. There is a slight decrease in the value of ν_{Q1} from 332 ± 6 MHz to 274 ± 3 MHz at the end of the isochronal annealing treatment of the sample at 1273 K. As regards the second fraction associated with the probe nuclei, a clear stage is seen in figure 5 at 323 K, where ν_{Q2} as well as f_2 increases sharply.

The value of ν_{Q2} remains almost constant in the long annealing interval of 323–1023 K. The value of f_2 decreases slowly with annealing temperature and reaches zero following the annealing treatment at 1073 K. The value of η_2 shows a variation between 303–473 K and remains nearly constant thereafter.

In the as-charged state of the sample, the fraction f_1 associated with ν_{Q1} has a higher asymmetry parameter η_1 as compared to η_2 corresponding to the fraction f_2. But, the respective quadrupole frequencies associated with the two fractions are only slightly different as discussed earlier. This would suggest that both the types of defects corresponding to ν_{Q1} and ν_{Q2} must be associated with hydrogen in different configurations. The defect corresponding to the fraction f_1 is identified with hydrogen–vacancy complex while that associated with f_2 is identified with hydrogen decorated vacancy clusters. The sharp decrease of ν_{Q1} from 619 MHz to 320 MHz around 323 K indicates dissociation of H–V complexes

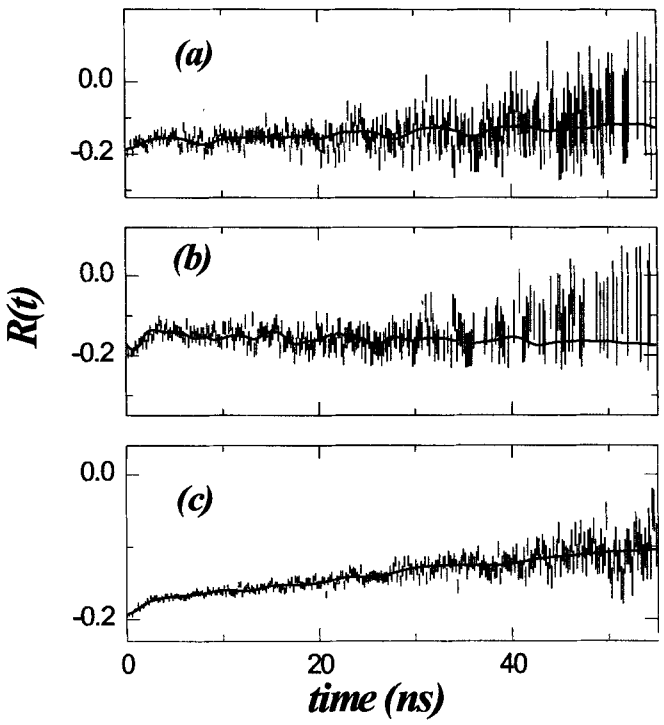

Figure 3. The experimental $R(t)$ vs t spectra at room temperature for the sample isochronally annealed at temperatures given below: (a) 473 K, (b) 773 K and (c) 1273 K.

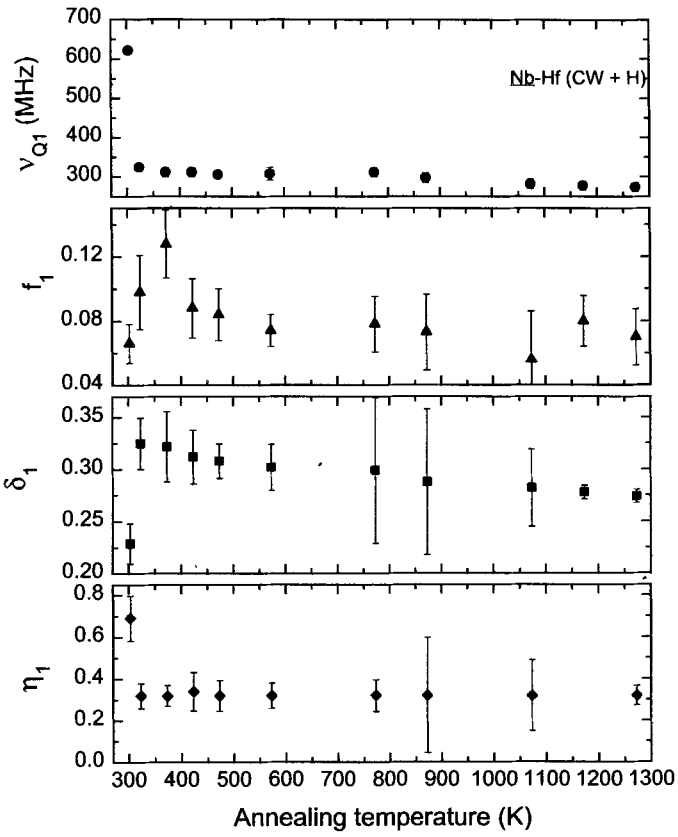

Figure 4. Variation of hyperfine interaction parameters viz. ν_{Q1}, f_1, δ_1 and η_1 with annealing temperature.

which is in agreement with the earlier reported positron results (Hautojarvi *et al* 1983) and resistivity results (Petzold and Schultz 1987) in Nb. The vacancies so released from the dissociating hydrogen–vacancy pairs are mobile and stabilize vacancy clusters. This is in accordance with the observed decrease of ν_{Q1} and increase of f_1 around 373 K. It may be noted that in the hydrogen charged sample, the value of ν_{Q1} associated with the fraction f_1 beyond 323 K is the same as the value of the frequency observed in the cold-worked sample without hydrogen (discussed earlier). This provides additional support for identifying the defect associated with f_1 as vacancy clusters subsequent to the dissociation of H–V complexes. Hydrogen release from the H–V complexes goes to decorate further the cluster associated with the fraction f_2. The resulting effect of multiple hydrogen decoration of vacancy clusters explains the increase of ν_{Q2} and f_2 between 400 and 900 K (cf. figure 5) and indicates the stability of small vacancy clusters (Hf–V_m) and small hydrogen decorated vacancy clusters (Hf–V_m–H_n), respectively in NbHf. In this temperature range the comparison of asymmetry parameters η_1 and η_2 would suggest that hydrogen decorated vacancy cluster has a more asymmetric configuration as compared to that of hydrogen free vacancy clusters.

At elevated temperatures (between 900 and 1273 K), the value of ν_{Q1} decreases from 320 MHz to 274 MHz. This value is close to the quadrupole frequency associated with Hf impurity trapping an interstitial oxygen (Wrede *et al* 1986). Hence, the observed frequency of ν_{Q1} at elevated temperatures may be attributed to the formation of oxygen mediated defect complexes at Hf sites. At these temperatures dissociation of vacancy clusters also takes place.

The results of positron lifetime measurements on the 50% cold-worked and hydrogen charged sample are shown in figure 6. In the as-charged state of the sample, two lifetime parameters are resolved as $\tau_1 = 160 \pm 4$ ps, $\tau_2 = 260 \pm 5$ ps and $I_2 = 15 \pm 3$. The observed τ_1 is close to the value reported for H–V complex in Nb (Hautojarvi *et al* 1983). However, in addition to H–V complexes in the sample, dislocations (both undecorated and H-decorated) are also present. Therefore, the observed τ_1 of 85% intensity may be attributed to the combined contributions from positron trapping at H–V complexes and dislocations. Since these lifetimes are very close, it is not possible to resolve them and delineate their contributions. It is for the same reason that the early annealing stage seen earlier in TDPAC corresponding to the dissociation of H–V complexes is not resolved in

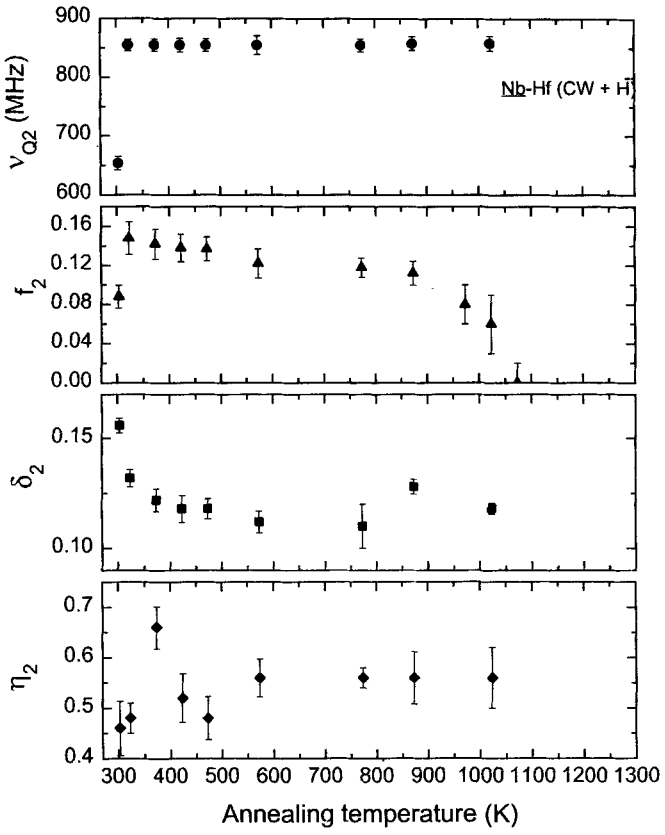

Figure 5. Variation of hyperfine interaction parameters viz. ν_{Q2}, f_2, δ_2 and η_2 with annealing temperature.

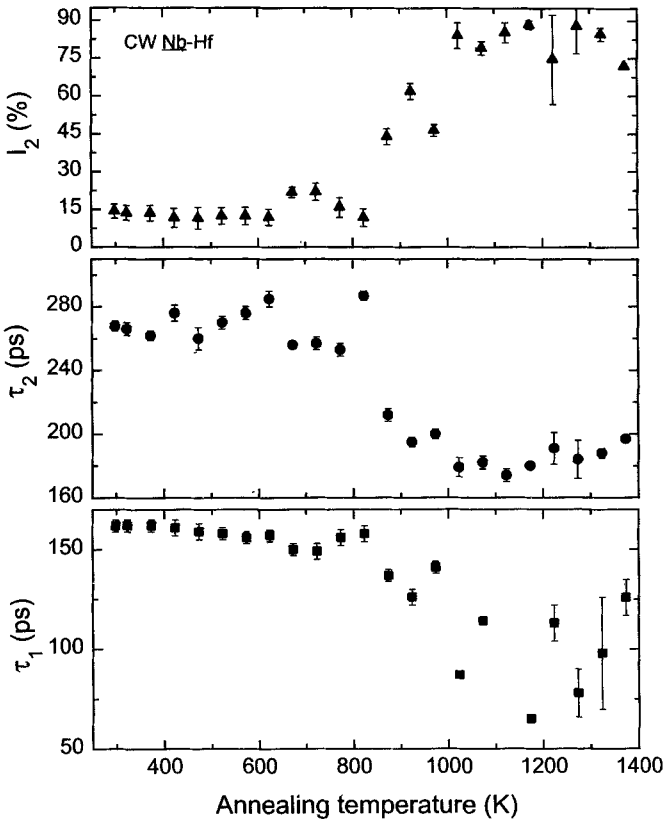

Figure 6. Variation of the resolved positron lifetime parameters with annealing temperature in the cold-worked and hydrogen charged NbHf sample.

lifetime measurements. The longer lifetime τ_2 of 260 ps, which is higher than that of monovacancy in Nb (Hautojarvi *et al* 1983), is explained as due to H-decorated vacancy clusters. Figure 6 shows that the resolved lifetime parameters τ_1, τ_2 and I_2 remain nearly constant in the annealing interval up to 800 K. This indicates stability of dislocations and H-decorated vacancy clusters. The latter, as seen from the positron results, is consistent with the earlier discussed TDPAC results.

For annealing temperatures beyond 823 K, there is a sharp decrease in τ_1 as well as in τ_2, while I_2 shows a marked increase. Both τ_2 and I_2 tend to level off at temperatures beyond 1173 K. The stage seen in τ_1 may be ascribed to partial dislocation recovery in NbHf while the stage corresponding to τ_2 (and I_2) may be explained by the transformation of H–vacancy clusters into stable H-bubbles. The reduction in τ_2 may be understood as due to increased hydrogen density in the bubble. The supply of hydrogen from the decorated dislocations which are annealing in this temperature range, as well as vacancy supply from the dissociating vacancy clusters (hydrogen free) contribute to this process. As more and more bubbles get stabilized, the consequent increase in their number density leads to enhanced trapping rate as seen from the behaviour of I_2. However, the observed six-fold increase in I_2 might suggest that some additional process is also contributing to the effect. It is earlier reported (Hautojarvi *et al* 1983) that high temperature defect recovery in Nb is affected by interstitial impurities like O, the concentration of which can increase during treatment at elevated temperatures. Such an oxygen pick-up and consequent coating of voids might lead to the observed reduction in lifetime. Such an oxygen mediated process cannot be ruled out at elevated temperatures, considering the fact that because of close lifetimes, it is difficult to distinguish between H-bubbles and O-coated voids. It may be recalled from the earlier discussion that TDPAC results on ν_{Q1} at elevated temperatures are suggestive of oxygen mediated defect process. The observation that H-bubbles as seen by positron lifetime measurements, are not detected by TDPAC (fraction f_2 reaching zero at elevated temperatures) can be based on the reasoning that extended defects like large sized bubbles are not trapped by Hf due to the short range nature of the probe–defect interactions.

4. Conclusions

TDPAC results on cold-worked and hydrogen charged NbHf indicate a strong binding of hydrogen decorated vacancy clusters with Hf impurities. Positron lifetime results on the same system show that H plays an important role in stabilizing vacancy clusters in NbHf. Positron lifetime behaviour at annealing temperatures beyond 900 K indicates the transformation of H-vacancy clusters into H-bubbles. Impurity effects like oxygen pickup and coating of voids become important to be considered at elevated annealing temperatures of the sample.

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