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Positron annihilation in Zr-0·5 Nb alloy

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Abstract. The measurement of coincidence counting rate at the peak of the angular correlation curve shows a considerable difference between the recovery behaviour of cold-worked Zr-0·5 Nb alloy from that reported for pure zirconium. This difference in behaviour illustrates the point-defect activity during the course of isochronal annealing in this alloy. The recovery spectrum can be understood in terms of the vacancy-solute entrapment upto about 250°C. In the next stage the release and clustering effects of vacancies are indicated prior to their elimination. The study thus demonstrates the effect of alloying element on the defect mobility and associated point defect interactions in Zr.

Keywords. Positron annihilation; 2γ-angular correlation; cold-work recovery; dilute zirconium alloys.

1. Introduction

Positron annihilation spectroscopy (PAS) is a powerful nuclear technique for characterization of the defect microstructure in solids. For metals and alloys, the positron probe is very sensitive to changes in local electron density near the lattice defects, especially the vacancy type of structural imperfections. This selective nature of interaction makes it an important complementary and also a nondestructive research tool. It has helped in advancing the fundamental understanding of various metallurgical phenomena to a great advantage (Doyama 1984; Krishnan and Upadhyaya 1985). The mechanism of electron-positron annihilation and details of measurement techniques have been discussed by various authors (West 1973; Hautojarvi 1979; Upadhyaya 1985).

The present work is an investigation of the defect recovery behaviour of a dilute solid-solution composition of Zr-Nb system as studied by γ-γ angular correlation technique. These alloys are of interest in nuclear industry as cladding, coolant and pressure tube material. The thermomechanical processing parameters largely control the microstructural development and need to be studied in detail employing different techniques. Considering, for example, during thermal annealing of cold-worked metals the successive process steps recognised are recovery, recrystallization and grain-growth. These stages are conventionally followed in the form of changes observed in the average property parameters like hardness, resistivity etc. Supplementing these measurements with a defect-specific quantity like the positron annihilation parameter, greatly enhances the accuracy of the proposed annealing mechanism. The present results being on the latter aspect alone, demonstrate the mechanism of vacancy elimination in the presence of aliovalent impurity atoms in the lattice. A dilute solution composition was selected to prevent solute clustering effects.

2. Experimental

The alloy was prepared by melting together sponge purity Zr (purity better than 99·7%) and zone-refined niobium (nominal purity 99·95%) in an electric arc furnace under pure argon atmosphere. The alloy button thus produced was encapsulated in a silica tube (under a vacuum better than 10^{-4} torr) and given an homogenization treatment at 1000°C for 24 hr. It was then sealed in a copper tube and hot-rolled at 700°C down to about 1 mm thin plate form. Such plates were then subjected to crystallization annealing (600°C/48 hr) and finally cold-rolled to give a thickness reduction of about 30%.

Square cross-section (15 mm) samples were machined out of these strips for various isochronal annealing treatments upto a temperature of 350°C. A duration of 30 min was used at each annealing temperature (under argon atmosphere). Although the as machined samples were reasonably flat, an attempt to improve the surface finish by the usual metallographic techniques was found to change the results considerably. Therefore, before mounting onto the positron apparatus the only surface preparation process followed was by electro-polishing the samples in a dilute sulphuric acid bath and cleaning by rinsing in water and methanol.

The angular correlation was measured using a standard linear-slit configuration (Upadhyaya 1985). The angular resolution of the system was adjusted to be 1 mrad. The positron source used was ^{64}Cu of $\sim$1 Ci strength, prepared by irradiation in CIRUS reactor. The angular distribution spectrum ($N(\theta)$ vs θ) of coincidence counts was obtained for about 22 mrad across $\theta = 0$. A suitable data collection time at each angle was selected to achieve a good statistics and measurements were repeated 2 to 3 times for each sample. Data were normalized for equal area after the background and source decay corrections.

3. Results and discussion

Figure 1 shows the normalized peak value of 2γ-angular correlation curves of positron annihilation radiation in 30% cold-rolled Zr-0·5 Nb as a function of isochronal annealing temperature. A gradual fall in the peak count rate was observed upto 250°C and then a small increase in value in the range 250 to about 325°C. Above this temperature a further decreasing trend was observed. Positron experiments were not followed beyond 350°C annealing, in the recrystallization and grain-growth regime of the alloy.

Taking the Brandt and Paulin (1977) relationship, the energetic positron (E_β^{max}= 0·7 MeV) from ^{64}Cu source has a range of 58 μm in the Zr samples. Therefore the changes introduced in the annihilation events due to surface oxide contamination etc will be within the limits of experimental errors. However, substantial changes were observed on ground and polished samples, which was thus avoided for the entire set of measurements reported here. This can readily be ascribed to the sample being subjected to plastic deformation by mechanical polishing. This has been clearly demonstrated very recently (again by PAS-experiments) by Waber and Park (1986). Their positron lifetime results on mechanically polished single crystals of iron, enabled the mapping of dislocation-density profile. It showed that the abrasion damage extends to about 25 μm from the surface.

Cold work produces two types of lattice defects in metals; (i) point defects which

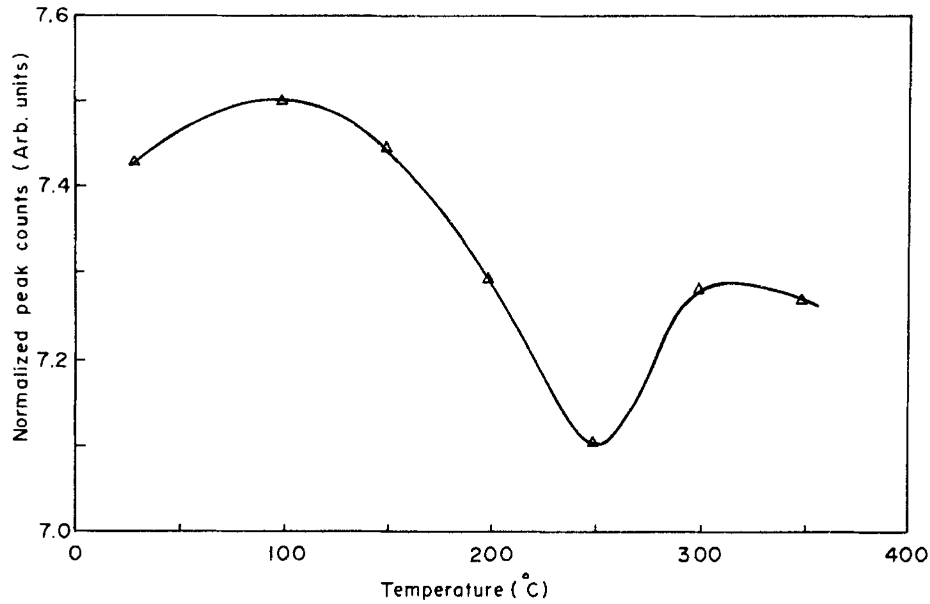

Figure 1. Coincidence counts at the peak of the angular correlation curve as a function of isochronal annealing temperature for Zr-0·5 alloy.

are mobile at temperatures close to room temperature (vacancies), and those are mobile at low temperatures (say interstitials) and (ii) dislocations which are randomly distributed initially, but get reorganized (during recovery temperature range) in arrays and later annihilate during recrystallization ($\simeq$0·2–0·5 Tm ranges). In the deformed lattice the region containing a point defect such as an isolated vacancy is deficient in ion core and hence deficient in higher energy core electrons. A positron trapped in the attractive potential of the vacancy has a higher probability of annihilation with lower momentum conduction electrons (Seeger 1976; Byrne 1980). This effect is revealed in the form of rise in the peak counting rate, $N(0)$ of 2γ-angular correlation events. Similarly, the vacancy agglomerates and dislocations etc are other effective positron traps. Any change, for instance, during annealing in the concentration and configuration of the defect species involved is thus monitored by the relative magnitude of the integral parameter $N(0)$.

Positron trapping by vacancies is strongly affected by the presence of impurities (which are also attracted into these defects forming various vacancy-impurity complexes). Results on several dilute alloy systems have shown that the specific trapping rate for vacancies is much reduced when bound to a higher valent impurity, e.g. Ge in Cu (Doyama *et al* 1974), Sn in Au (Shirai *et al* 1979) and In, Sb again in Cu (Bosse *et al* 1986) etc. Another special attribute of positron probe is to exhibit a higher degree of sensitivity for charge modification at individual lattice sites: such as for transition metal impurity atoms in Cu (Doyama *et al* 1973) or electron density variations due to 'charge transfer effects' in some binary alloys (Kubica *et al* 1975; Tsuchiya and Tamaki 1978).

The impurity size also influences the recovery of cold-rolled metals. As an example, for Ni the solutes which are largely oversized (like Sb, As and Pb) were found to induce a strong vacancy clustering effect whereas other solutes have a very weak or no effect for such defect agglomeration (Dlubek *et al* 1979; Brummer and Dlubek 1985). In the case of iron, the carbon impurity traps the vacancies and these carbon-vacancy pairs then dissociate at about 500 K. This acts as a source of free vacancies which then move and form clusters (Brandt and Dupasquier 1973). In general, the activation energy for diffusion of solute in dilute alloys seems to bear a direct dependence on the ratio of charge to size (e/a) parameter (Tiwari *et al* 1980).

The recovery behaviour of pure zirconium above room temperature was studied earlier by resistometry (Pande *et al* 1972) and by positron lifetime measurements (Tanigawa *et al* 1982). In either case, essentially a continuous decrease in resistivity or mean lifetime was observed, representing only the vacancy migration and recrystallization processes being operative. The electron irradiated α-Zr also showed a similar continuous recovery (Hood *et al* 1977), whereas for Zr-0·5 Nb alloy a multiple peak pattern was observed (Batra *et al* 1984).

In the present case, the initial rise can be understood to be associated with the onset of free vacancy migration (Hood *et al* 1984). After about 100°C stage we visualize a defect configuration of the type of single vacancy being trapped at Nb impurity atoms. Since Nb is an undersized atom, and has an excess positive charge (pentavalent) with the result that the migrating vacancy will have a greater probability for being trapped at it. Now, as mentioned above, the positrons will show a lower affinity for such a vacancy (bound to a higher valent impurity site). Thus, in contrast to pure zirconium, the Nb-bound vacancy in the alloy partially nullifies the charge imbalance and results in the depletion of the vacancy cause effect. With increasing temperature and up to 250°C, the steady decrease in the peak count rate merely signifies an increase in the concentration of such solute-decorated vacancies. The number of multiple defect aggregates is generally negligible in dilute alloys (Bosse *et al* 1986).

Concerning the rise in peak parameter above 250°C, it is likely to be due to the release of the solute-bound vacancies and their clustering effect. Moreover, these clusters become unstable and are eliminated on dissociation at about 325°C. Above this temperature the recovery spectrum follows the same pattern as for pure Zr. Thus the difference in behaviour is only with respect to the dip in the recovery curve (figure 1) at 250°C in Zr-0·5 Nb. This corresponds to the binding energy of impurity-vacancy complexes in the alloy. The detrapping mechanism suggested above 250°C is in conformity with the results on Zr-Sn system (Anand *et al* 1985). The temperature range of 500 K (for Zn-Sn) is also in fairly good agreement for the present alloy composition.

The present investigation shows that with the help of angular correlation measurements an explicit analysis of the processes occurring during the annealing of the point defects in metals is possible. Moreover, in the context of plastically defected metals the location of the recovery stages and their intensities essentially depend upon the degree of deformation and on the purity of the sample. Therefore in order to understand the detailed mechanism of recovery process, similar studies need to be extended to a series of other alloy systems as a function of cold-work parameter and also the solute parameters like its size, valency and concentration.

4. Conclusions

(i) Positron annihilation measurements have been utilized to monitor the isochronal recovery of Zr-0·5 Nb alloy specimens. Positron probe has a selective sensitivity

towards vacancy-like defects and vacancy-agglomerates. These experiments thus greatly help in resolving the recovery process by identifying the participating defect species.
(ii) In contrast to the continuous recovery spectrum reported for α-Zr, a distinctively two-stage process was indicated in the presence of Nb impurity. The mobile vacancies above 50°C get trapped by the solute atoms and remain bound upto about 250°C. The solute-vacancy binding energy being the controlling factor for the release of free vacancies, which, with increasing temperature migrate and form clusters.
(iii) The dissociation of these vacancy clusters is activated by thermal stimulation above 325°C. These are subsequently absorbed at dislocation sinks. Finally the stages of recrystallization and grain growth take over.

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