Polymorphic transformation and lattice expansion in nanocrystalline niobium revealed by positron annihilation at grain boundaries

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Abstract

Positron lifetimes in nanocrystalline niobium were measured over the grain size range from 35 nm down to 5 nm. Two lifetimes were obtained indicating distinct annihilation sites at the grain surfaces and in the intercrystalline region. X-ray diffraction studies had indicated a bcc to fcc transformation and a concomitant lattice expansion. Positron lifetimes drastically varied below a grain size of 10 nm, coinciding with a sharp increase in the excess free volume of atoms at the grain boundaries as revealed in a model analysis. Doppler broadening measurements also indicated a redistribution of electron momentum, implying a restructuring of the grain surfaces. The occurrence of bcc to fcc transformation is also observed in binary Nb–Al and ternary Al–Nb–Cu alloys. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Investigations into the origin of the improved physical properties of nanoscale materials often are focussed on to the structure of the grain boundaries and interfaces [1,2]. This is justified in the context of the majority of atoms lying on the grain boundaries. However, there is a need to pay some attention to the physical and thermodynamical stability of the grains and boundaries at extremely low grain sizes. This became evident when we recently worked on nanocrystalline elemental niobium as well as binary Nb–Al and ternary Al–Nb–Cu alloys, which pointed towards the need to look at these aspects in a more rigorous way and the present paper briefly discusses the details of our work.

2. Experimental

Elemental niobium (Nb) powder of a mean particle size of 50 μm was milled in a Fritsch P5 planetary ball mill at 300 rpm using hardened steel vials and balls. A number of samples were prepared by milling for different intervals of time and were examined by X-ray diffraction using a Philips PW 1710 diffractometer.

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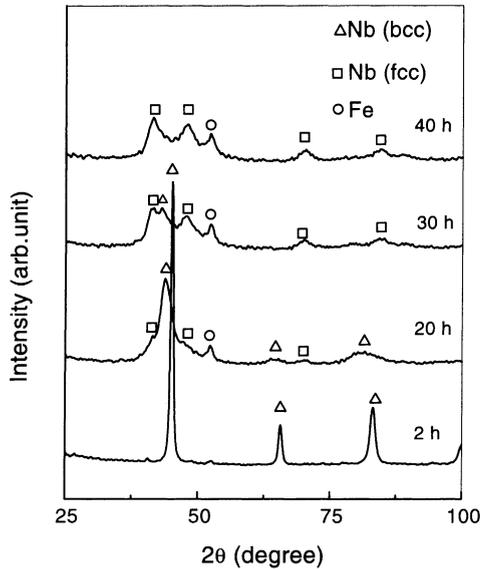imanna@metal.iitkgp.ernet.in (I. Manna).

Fig. 1. X-ray diffraction patterns of nanocrystalline Nb after different hours of ball-milling.

A few illustrative patterns are shown in Fig. 1. The average grain size was determined from the peak broadening analysis using Scherrer equation [3]. Positron annihilation studies were conducted using a ^{22}Na source ($\sim$1.5 μCi) kept immersed in the powder. The positron lifetime spectra were recorded using a gamma ray coincidence spectrometer with a prompt time resolution (FWHM) $\sim$240 ps. The spectra were then analysed using the computer programs RESOLUTION and POSITRONFIT [4]. An HPGe detector with a resolution of 1.14 keV at 514 keV (^{85}Sr) was used for Doppler broadening measurements.

3. Results and conclusions

From the positron lifetime spectra, three separate components τ_1, τ_2, and τ_3 (with relative intensities I_1, I_2 and I_3) were obtained. The longest one $\tau_3 = 2.8$ ns (with $I_3 < 1\%$) is attributed to the formation and annihilation of orthopositronium atoms in the intercrystalline region and is not considered in further discussion. The other two lifetimes in order of their increasing numerical values are expected to originate from the trapping and eventual annihilation of positrons in the vacancy-type defects on the grain

boundaries and in the intercrystalline region [5]. Various reasons can be quoted to substantiate the rationality behind this attribution. The most convincing among them is that the values of τ_1 in all the samples were significantly higher than that for bulk Nb ($=138$ ps) and for the smallest open-volume defect in a crystalline solid, i.e. a monovacancy, in which the trapped positron should live for 200 ps before annihilation [6]. It should be pointed out that positrons get rapidly thermalised on entering the grain and the average thermal diffusion length ($\sim$100 nm) is higher than the grain sizes used in this work. Invariably all the positrons will then annihilate either at the grain boundaries or in the intercrystalline region. A characteristic line shape parameter S is derived from the Doppler broadened spectra to reflect any qualitative changes in the electron momentum distribution when the grain size is varied [5]. The parameter is generally defined as the ratio of the counts integrated under a central segment of the spectrum spreading over $\pm$600 eV to the total counts under the full spectrum (from 503.3 to 518.7 keV).

Fig. 2 shows the variation of this parameter as well as that of the mean positron lifetime τ_m with grain size. τ_m is defined as $(\tau_1 I_1 + \tau_2 I_2)/(I_1 + I_2)$ and is reliable enough to indicate the qualitative variation of the
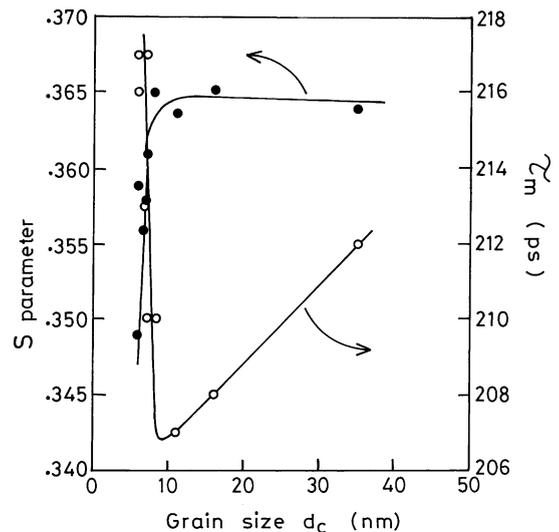

Fig. 2. The variation of the S parameter (closed circles) and the mean positron lifetime τ_m (open circles) with grain size in nanocrystalline Nb.

electronic environment around the positron trapping centres. It is remarkable that both these quantities drastically changed when the size of the grains is decreased below about 10 nm. The positron lifetime in fact is a decreasing function of the density of electrons n_e at the site of annihilation, as given by the well-known Dirac equation

$$\tau = (\xi \pi r_0^2 c n_e)^{-1} \tag{1}$$

where r_0 stands for the classical electron radius and c is the velocity of light. ξ accounts for the local enhancement in the density of electrons due to the Coulomb interaction with the positron. The significant increase in the positron lifetime would therefore imply a characteristic increase of open volume ("excess free volume", as referred hereafter) at the grain boundaries or surfaces. We have earlier modeled this in terms of the fractional excess surface area of the grain boundary plane located at a radius $(d_c + \Delta/2)/2$ from the centre of a grain with diameter d_c [5]. Here Δ ($=1$ nm) is the thickness of the interfacial region shared by two adjacent grains [7]. The assumption thus leads to an equation for the excess free volume of the atoms at the grain boundaries as

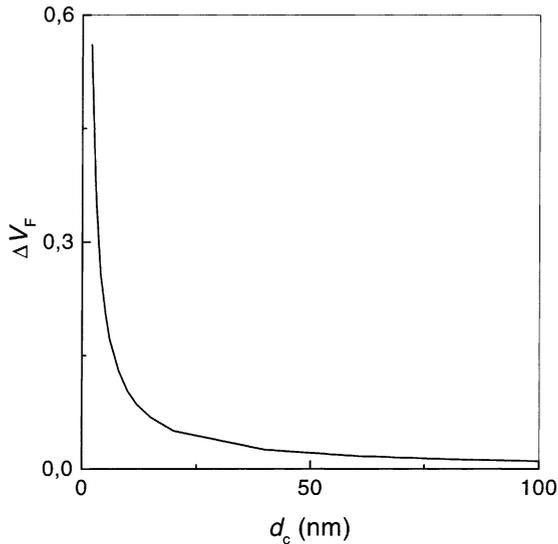$$\Delta V_F = \frac{(d_c + \Delta/2)^2 - d_c^2}{d_c^2} \tag{2}$$

Fig. 3. The variation of the excess free volume ΔV_F of the atoms at the grain boundaries vs. the grain size d_c.

The variation of ΔV_F versus d_c, as shown in Fig. 3, then clearly indicates the genuineness of the increase in positron lifetime below a grain size of 10 nm. Conversely that the experimental observation is consistent with the ΔV_F versus d_c variation further gives credence to the model employed for its estimation.

It should be mentioned that the assignment of a direct correlation of the increase in ΔV_F with the observed increase in positron lifetime here is not straightforward since the sites of annihilation are on the grain boundaries. In bulk Nb, for example, an increase of about 10 ps in the lifetime of positrons trapped in defects (as is the case when the grain size decreases from 10 to 6.5 nm) would mean about 30% increase in the radius of a vacancy-type defect [6]. This, in turn, implies a 2.2 times increase in the defect volume and significantly is in agreement with almost an equal increase in ΔV_F in the same region of grain size reduction (Fig. 3). However, any such quantitative extrapolation of the actual size of the defects on the grain boundaries from the measured positron lifetime will be unrealistic until the actual atomic arrangement on the grain boundaries is clearly understood. Our arguments are therefore restricted to qualitative aspects only.

It should, however, be noted that the S parameter is drastically reduced in the region below the size of 10 nm, despite the enhancement in the excess free volume at the grain boundaries. This makes it necessary to turn back our attention to Fig. 1 again where elemental Nb is shown to transform from the bcc phase to an fcc structure after increasing hours of ball-milling (or decreasing grain size). Further the grain lattice expands with decreasing grain size, as indicated by the shifting of the peaks to lower diffraction angles (2θ). The lattice parameter for the fcc structure obtained finally was found as 0.428 nm and is large compared to 0.343 nm of the starting bcc phase. This in fact results in nearly a 6% increase in the volume per atom and practically nullifies the otherwise expected increase in packing fraction from 68% (bcc) to 74% (fcc). Here we note that the transformation from the bcc phase to fcc one brings from the interior of the grain one atom per face of the unit cells forming the outermost atomic layer. The positrons trapped at the grain boundaries will therefore locally encounter a situation identical to a transforming lattice with increased number (from 4 to 6)
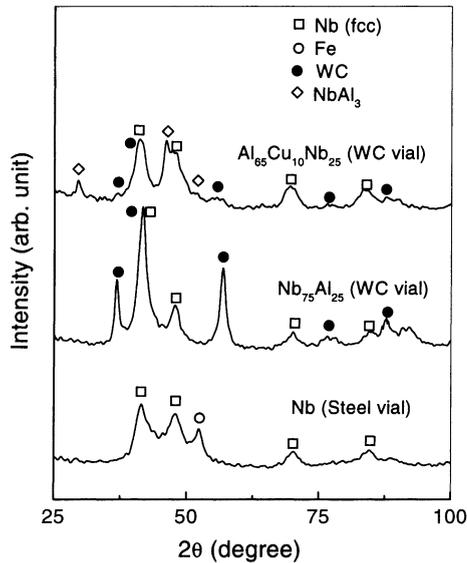
Fig. 4. X-ray diffraction patterns of nanocrystalline elemental Nb, binary Nb–Al and ternary Al–Nb–Cu alloys.

of nearest-neighbour atoms with nearly unaltered distance (0.297 nm in bcc and 0.303 nm in fcc phases). The resulting redistribution of the average electron momenta causes the sharp fall in S at extremely low grain sizes (Fig. 2).

What essentially serves as the real genesis of such a transformation now needs to be debated in detail, as identical observations have been made recently in binary and ternary systems with Nb as a constituent. Fig. 4 presents the recent X-ray diffraction patterns obtained for $Nb_{75}Al_{25}$ and $Al_{65}Cu_{10}Nb_{25}$ where the appearance of the fcc phase similar to that of elemental Nb becomes evident despite the change in the medium of ball-milling (vials of WC instead of hardened steel) and the presence of other alloying element(s). This overrules the earlier prediction that the fcc phase could be the nitride of Nb formed due to the contamination from the milling medium [8]. Moreover, the coexistence of the fcc Nb and $NbAl_3$ in the case of the Al–Nb–Cu system further confirms that the transformation is governed by thermodynamic factors related to the evolution of the individual phases, rather than the influence of any kind of impurity.

Recently we had used the isothermal equation of state, proposed by Fecht [9], for a grain boundary to calculate the negative hydrostatic pressure originating

due to the excess free volume of atoms and obtained a value of about 20 GPa for the smallest grain size of 6 nm used in the present work [5]. Significantly this pressure corresponded to a lattice expansion of 3.7% and is almost in agreement with what was estimated as 4% from Fig. 1. The amount of energy involved in such expansion (0.27 eV per atom [2]) is also in excess to that predicted to be necessary for the bcc to fcc transformation of Nb (0.09 eV per atom) [10]. Further the combined effect of a decreasing grain size and an expanding lattice would suggest an increase in free energy of the grain according to the Gibbs–Thomson equation $\Delta G = 4\gamma V_m d_c^{-1}$ where γ is the interfacial energy and V_m is the molar volume. Such an increase in free energy would then be countered by the system (the nanocrystalline grain in this case) through such processes that would restore the original energy state and the transformation to a new structural orientation is one such possibility. The fcc phase that we observed in this case thus enables the grain to regain its stability against a rapidly softening boundary. It should be stated that the unhindered lattice softening would ultimately lead to a near-collapse of the mechanical and thermodynamical stability of the grains, as predicted by others in earlier studies [11,12]. Fecht's prediction of a lower size limit of $\Delta V_F = 0.44$ (or $d_c = 2.5$ nm from Eq. (2)) further corroborates these convictions [9].

Before concluding this paper, we like to point out the reason for not observing the discretisation of quantum energy levels that one would anticipate to occur in such grain size regimes. The theory of Wood and Ashcroft [13] would imply a grain size as low as 1.9 nm (bcc) or 2.0 nm (fcc) for such effects to occur at room temperature [5]. Needless to say, both these sizes are below the limit of stability of the grains ($d_c = 2.5$ nm) pointed out by Fecht [9]. It needs to be mentioned that such a possibility of quantum size effects might exist for grains of size about 5 nm at temperatures below 20 K.

Acknowledgements

References

[1] H.-E. Schaefer, R. Wurschum, R. Birringer, H. Gleiter, Phys. Rev. B38 (1988) 9545.

[2] P.P. Chatterjee, S.K. Pabi, I. Manna, J. Appl. Phys. 86 (1999) 5912.

[3] B.D. Cullity, Elements of X-ray Diffraction, Addison Wesley, Reading, MA, 1978, p. 102 and p. 356.

[4] P. Kirkegaard, M. Eldrup, O.E. Mogensen, N.J. Pedersen, Comput. Phys. Commun. 23 (1981) 307.

[5] P.P. Chattopadhyay, P.M.G. Nambissan, S.K. Pabi, I. Manna, Phys. Rev. B 63 (2001) 54107.

[6] P. Hautojarvi, H. Huomo, P. Saariaho, A. Vehanen, J. Yli-Kaupilla, J. Phys. F: Met. Phys. 13 (1983) 1415.

[7] R.W. Siegel, in: R.W. Cahn, P. Haasen, E.J. Kramer (Eds.), Processing of Metals and Alloys, Material Science and Technology, Vol. 15, VCH, Weinheim, 1991, p. 583.

[8] Z. Peng, C. Suryanarayana, F.H. Froes, Metall. Mater. Trans. A 27 (1996) 41.

[9] H.J. Fecht, Acta Metall. Mater. 38 (1990) 1927.

[10] L. Kaufman, in: P. Rudmann, J. Stringer, R.I. Jaffe (Eds.), Phase Stability of Metals and Alloys, McGraw-Hill, London, 1966, p. 125.

[11] D. Wolf, J. Wang, S.R. Phillpot, H. Gleiter, Phys. Rev. Lett. 74 (1995) 4686.

[12] J. Wang, D. Wolf, S.R. Phillpot, H. Gleiter, Philos. Mag. A 73 (1996) 517.

[13] D.M. Wood, N.W. Ashcroft, Phys. Rev. B 25 (1982) 6255.