

An allotropic transformation induced by mechanical alloying

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This study concerns a hitherto unknown bcc→fcc allotropic transformation in Nb induced by the mechanical alloying of Nb₈₀Al₂₀. This metastable transformation is preceded by a gradual increase in the lattice parameter of bcc-Nb. The stored excess energy in nanocrystalline bcc-Nb may be responsible for the bcc→fcc phase transition. © 1999 American Institute of Physics. [S0021-8979(99)03622-1]

Mechanical alloying (MA) is a well-known route of synthesizing nanocrystalline aluminides with a metastable microstructure and composition.¹ Recently, a number of investigations concerning the MA of elemental powders of Nb and Al to produce Nb₃Al has been reported.²⁻⁵ However, attempts to synthesize Nb₃Al by MA have mostly remained unsuccessful. Instead, it is reported that the MA of Nb₇₅Al₂₅ yields a fcc phase which could be NbN.⁴ In this connection, the present investigation is aimed at determining the origin of the said fcc phase and provide a thermodynamic analysis in support of the concerned experimental results.

Elemental blend of Nb and Al powders (>99.5 wt % pure) of about 50 μm size having a nominal composition of Nb₈₀Al₂₀ was milled in a FRITSCH P5 planetary ball mill using hardened chrome steel (HS) media (vials and balls) with a ball to powder weight ratio of 10:1. A similar milling exercise was also carried out in HS and tungsten carbide (WC) media for an elemental Nb powder. Samples collected at different stages of milling were examined by x-ray diffraction (XRD) analysis using Co K_α radiation. Average grain size (d_c) was determined from the peak broadening analysis using the Scherrer equation⁶ after elimination of the strain effect by Lorentzian curve fitting⁷ and the instrumental effect by comparing the relevant peaks with those from a standard sample annealed in vacuum at 600 °C for 2 h.

Figure 1(a) shows a series of XRD patterns obtained from the Nb₈₀Al₂₀ samples collected at different stages of ball milling. In addition, the diffractograph obtained by the isothermal annealing of a 40 h ball milled sample at 900 °C for 2 h under vacuum has also been appended. The α-Fe peaks in Fig. 1(a) may arise due to Fe contamination from the milling media. It is interesting to note that the Nb peaks [say, (110)_{Nb}] undergo a continuous shift towards the lower Bragg angles (2θ) as time (t) increases. Furthermore, the (110)_{Nb} peak reveals a pronounced broadening with increase in t up to 30 h, beyond which (e.g., after 40 h) the XRD patterns can be indexed as due to a fcc phase having a lattice parameter (a) of 0.441 nm. Taking the insignificant difference between the atomic radii of Nb (0.28637 nm) and Al (0.28636 nm) into account,⁶ the considerable shift in the (110)_{Nb} peak position in Fig. 1(a) (say, at 30 h) cannot be

attributed to the solid-state dissolution of Al into Nb. Moreover, a careful deconvolution of the broad (110)_{Nb} peak suggests that the latter may arise due to overlapping of bcc-(110)_{Nb}, fcc-(111)_{Nb}, and fcc-(200)_{Nb} peaks [Fig. 1(b)]. Peng, Suryanarayana, and Froes⁴ have earlier suggested that the unusually broad (110)_{Nb} peak may arise due to an amorphous phase which subsequently transforms into (111) and (200) peaks of fcc-NbN. A carefully conducted quantitative chemical analysis of the milled products in the present study by the micro-Kjeldahl method⁸ reveals that the nitrogen content (possibly dissolved during milling) in the milled powder is only 0.11 wt %. Thus, according to the Nb-N phase diagram,⁹ the possibility of NbN being the principal constituent of the milled product is ruled out. Furthermore, it is interesting to note that the XRD pattern obtained from the isothermally annealed (at 900 °C) milled product reveals the presence of a sharp (110)_{Nb} superlattice peak indicating that the fcc phase undergoes thermally activated ordering into a cubic phase during isothermal annealing [Fig. 1(a)]. This ordering, if the fcc phase were NbN, would not have occurred.⁹

In order to acquire a better understanding of the bcc→fcc phase transition in the Nb₈₀Al₂₀ milled product, an elemental Nb powder was subjected to ball milling in HS and WC media under similar conditions as that adopted for the MA of Nb₈₀Al₂₀. Figure 2 shows the XRD line profiles for elemental Nb obtained after 2, 20, 30, and 40 h of milling in HS and 20, 30, and 40 h of milling in WC media. It may be noted that the (110)_{Nb} peaks of both elemental Nb (Fig. 2) and Nb₈₀Al₂₀ [Fig. 1(a)] record a similar shift towards lower 2θ value after say, 20 h of milling. Therefore, it is substantiated that the observed peak shift is due to expansion in a of Nb rather than that arising out of dissolution of Al in Nb. Moreover, the emergence of the fcc phase in elemental Nb both in HS and WC media and Nb₈₀Al₂₀ composition in HS media after 40 h of milling rules out the possibility of any contribution of Fe in formation of the fcc phase.

A possible explanation for the expansion of a with decreasing d_c as observed in bcc-Nb in the course of milling may be put forward by taking the negative hydrostatic pressure (P_h) developed in the grain boundary of the nanocrystalline materials as a function the excess free volume (ΔV_F) into account.^{10,11} As per definition, the bulk modulus (B) is expressed as: $B = -V(dP/dV)$,¹⁰ where P and V are the

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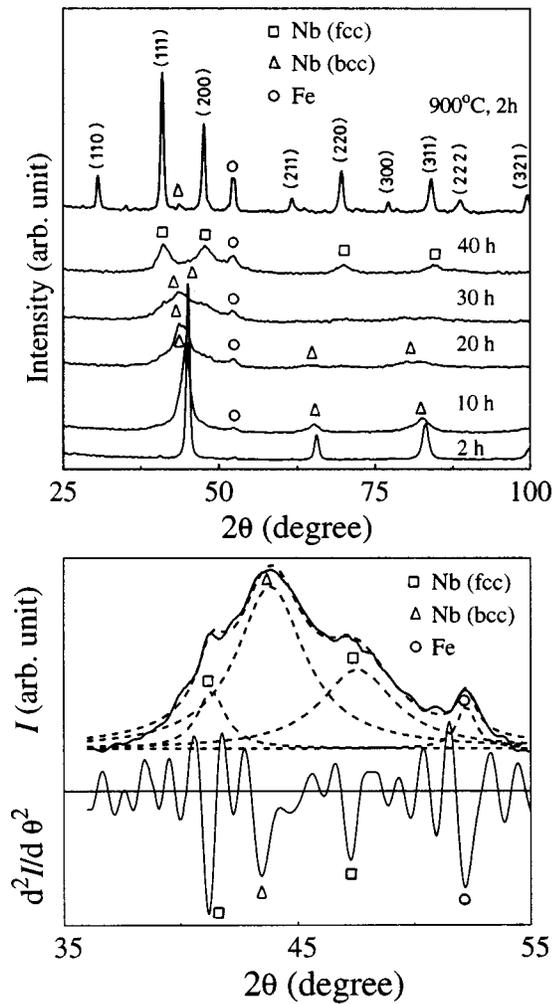


FIG. 1. (a) XRD patterns of ball milled Nb₈₀Al₂₀ samples at different t , and (b) deconvolution of $2\theta=35^\circ-45^\circ$ region of the XRD pattern for $t=30$ h into four constituent peaks.

pressure and volume, respectively. Assuming uniform dilation of the crystal due to the variation of P or more precisely, P_h at its boundary from the equilibrium value ($P_h=0$) in coarse-grained polycrystals to a given level (P_s) in the nanocrystalline state such that $-P_h$ equals P_s , a corresponding change in V from its initial (V_i) to final (V_f) value yields from the definition of B : $\ln(V_i/V_f)=(P_s/B)$. Substituting $V_i=a^3$ and $V_f=a_f^3$ (where, a_f is the final value of a), the latter equation may be expressed as: $(a_f/a)^3=\exp(P_s/B)$. Since $(P_s/B)<1$, the higher order terms in the expansion for the right-hand side of this equation may be neglected and accordingly, the fractional change in a may be obtained as

$$[(a_f - a)/a] = [1 + (P_s/B)]^{1/3} - 1. \quad (1)$$

Earlier, several attempts have been made to explain the genesis of a number of novel properties of nanocrystalline materials in terms of ΔV_F .^{10,12,13} However, a quantitative correlation is not yet available that can estimate ΔV_F as a function of d_c . Aaron and Bolling¹⁴ have mentioned earlier that a high angle grain boundary may be visualized as a liquid slab constrained between two walls signifying one less degree of constraint of atomic migration along the boundary

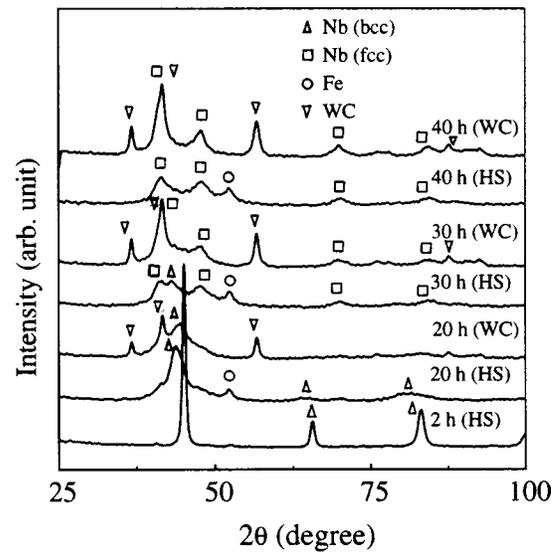


FIG. 2. XRD patterns of elemental Nb milled in HS and WC media for different time (t).

plane than that inside the bulk crystal. In accordance with this,¹⁴ some recent studies have observed that grain boundaries in nanocrystalline materials exhibit virtually a complete lack of long range structural periodicity parallel to the boundary plane.¹⁵ Therefore, some excess surface area, and hence, some excess volume per atom may be available in the grain boundary of a given thickness ($\Delta=1$ nm) in comparison to that in the bulk. Thus, the fractional excess area available in the grain boundary plane (located at $(d_c/2+\Delta/4)$ from the center of a spherical grain) than that in the bulk for the same number of atoms may account for ΔV_F as follows:

$$\Delta V_F = [(d_c + \Delta/2)^2 - d_c^2]/d_c^2. \quad (2)$$

Furthermore, it may be noted that Fecht,¹⁰ Wolf *et al.*,¹⁶ and Wang *et al.*¹⁷ have earlier indicated that the thermodynamic instability of grain boundary in nanocrystals coincides typically with $\Delta V_F=0.44$ ¹⁰ and $d_c=1.5-2$ nm,^{16,17} respectively. In the present study, Eq. (2) yields $\Delta V_F=0.44$ at $d_c=2.5$ nm, which is in reasonable agreement with the earlier results.^{10,16,17} Thus, Eq. (2) allows one to correlate ΔV_F with d_c . Figure 3 shows the variation of d_c for bcc- and fcc-Nb as a function of t . The minimum value of d_c obtained for bcc-Nb (6.6 nm) corresponds to a value of $\Delta V_F=0.16$ [from Eq. (2)], which yields a value of $-P_h=P_s=20$ GPa for Nb calculated as per Ref. 10. Substituting this value of P_s and

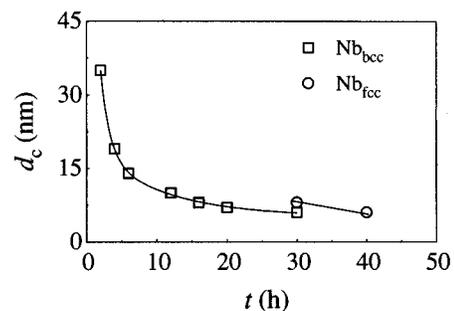


FIG. 3. Variation of d_c with t for bcc-Nb and fcc-Nb.

taking $B = 173$ GPa for Nb,¹¹ Eq. (1) yields a 3.7% expansion in a . It may be noted that the degree of lattice expansion calculated from the shift in the $(110)_{\text{Nb}}$ peak position of Nb [Fig. 1(a)] is $[(3.43 - 3.3)/3.3] = 4\%$. Thus, the experimental value of lattice expansion (=4%) of bcc-Nb due to ball milling agrees well with that (=3.7%) predicted by Eq. (1). Such an increase in a indicates an increase in the volume per atom (V_a) in bcc-Nb. Thus, the combined effect of decrease in d_c and increase in V_a suggests an increase in free energy of the crystallite according to the Gibbs–Thompson equation: $\Delta G = 2\gamma V_m/r$, where ΔG is the free energy of the crystallite of radius r with interfacial energy γ and molar volume V_m . This may energetically favor an allotropic transformation of bcc-Nb to fcc-Nb. Moreover, it may be mentioned that the increase in free energy as per the Gibbs–Thompson equation may be attributed to the increase in elastic energy of the bcc-Nb crystal due to the expansion in volume under the influence of P_s (i.e., $P_s \Delta V_a = 4.35 \times 10^{-20}$ J/atom), which is of the same order of magnitude as that for the theoretically predicted change of bcc-Nb to fcc-Nb ($= 1.46 \times 10^{-20}$ J/atom).¹⁸

Therefore, it may be concluded that the fcc phase appearing in the final milled product both in pure Nb and $\text{Nb}_{80}\text{Al}_{20}$ is an allotropic state of Nb rather than the single phase NbN. In this regard, it may be mentioned that the possibility of the bcc→fcc allotropic transformation in Nb induced by ball milling is in agreement with the earlier results concerning allotropic change of elemental Co¹⁹ and Ti–Al alloy²⁰ effected by similar milling routines.

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