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Aligned *in situ* growth of the fibrous Ni-Nb_2O_5 composite by preferential internal oxidation of amorphous Nb_2Ni_3

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Isothermal oxidation in air of amorphous Nb_2Ni_3 results in Ni–Nb_2O_5 composite aligned perpendicular to the surface of the sample. The process is controlled by oxygen diffusion through the Nb_2O_5 fibres or along the Ni–Nb_2O_5 interface.

1. Introduction

Interest in composite materials arises from the fact that their properties can be essentially different from those of the constituent phases [1–8]. *In situ* growth of oriented composite materials has been intensively studied during the last decade [9, 11], especially the eutectic solidification of binary [9–11] or polynary [12] melts, where a liquid, by unidirectional solidification in a positive (normal) temperature gradient, decomposes into aligned crystalline phases. Solid single phases can also be used as starting materials. Three cases can be distinguished: (i) the solid state disproportionation of supersaturated solid crystalline solutions [13], (ii) the solid state disproportionation of a eutectoid metallic [13–17] or oxidic [18] phase in a positive temperature gradient, and (iii) the solid state disproportionation of an amorphous or a vitreous phase in a negative temperature gradient (up-gradient) [19, 20].

Finally, aligned composite growth can be induced by isothermal reaction of an ambient with a crystalline solid solution [21, 22] or with a crystalline compound [23]. Though in principle the ambient can be any reactive component in the solid, liquid, or gaseous state, the reported experiments generally concern oxygen in the gaseous state that preferentially oxidizes one of the components of the solid solution or the compound. The volume fractions of the resulting oxide phases are limited by the maximum solubility when applying crystalline solid solutions, and by the width of the existence region in the case of compounds. However, the volume fraction of the resulting oxide phase can be greatly enhanced or varied, independent of mutual solubility or existence region, by using a metastable amorphous solid solution as a starting material. This is the subject of the present paper. The Nb–Ni system has been chosen as an example. At 600° C the solubility of Ni in Nb is about 1 at.%, and the solubility of Nb in Ni is about 6 at.% [24]. The system Nb–Ni exhibits the compounds $NbNi_3$ and NbNi and a eutectic at 40 at.% Nb and 1175° C. Amorphous Nb_xNi_{1-x} can be obtained by splat-quenching with $0.23 < x < 0.50$ [25]. The stable oxides of Nb are NbO, NbO_2 and Nb_2O_5, and of Ni, only NiO [24]. The compound Nb_2O_5 exhibits at 600° C an existence region of about 1 at.%.

2. Experimental

A splat-quench apparatus as described elsewhere [26] was used to produce the amorphous Nb_2Ni_3. About 1 g of the alloy was heated in a graphite crucible by a molybdenum induction furnace at about 1300° C, in an oxygen-free argon atmosphere. Subsequently the molten droplet was splat-quenched through an orifice of 0.1 cm diameter on a water-cooled copper substrate, by breaking a mylar foil of 80 μm thickness, which resulted in a shock wave of 60 atm. The purity of the starting material was 99.99%. According to X-ray analysis the resulting splats were amorphous; electron diffraction patterns of the thinnest parts of the splats showed diffuse rings, which are also characteristic of the amorphous state.

Amorphous Nb_2Ni_3 splats (typically 1 cm long, 0.2 cm wide and 50 μm thick) were isothermally

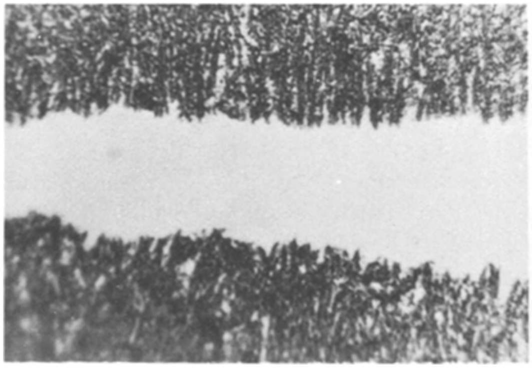

Figure 1 Partial preferential internal oxidation at 600° C of amorphous Nb_2Ni_3. The aligned dark fibrous structure consists of crystalline Nb_2O_5 (× 1300).

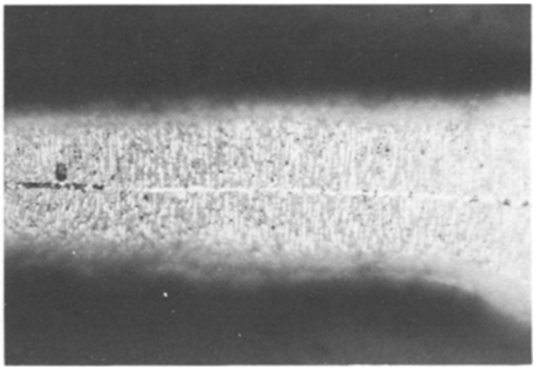

Figure 2 Complete preferential internal oxidation of Nb_2Ni_3 sample at 850° C (× 500).

heated in air at temperatures ranging from 500 to 650° C, for periods ranging from several hours to 15 min. Above 650° C the amorphous material crystallizes within 15 min. Typical results are shown in Figs. 1 and 2.

Fig. 1 shows the case where the reaction has only partially taken place, so that besides the oxidized structure there is still amorphous material present. The reaction front, i.e. the tangent along the tips of the fibres, was flat. The main reaction appeared to be

$$Nb_2Ni_3(\text{amorph}) + 2.5O_2(\text{gas}) \rightarrow 3Ni(\text{cryst}) + Nb_2O_5(\text{cryst})$$

According to X-ray analysis and electron microprobe analyses the Ni–Nb_2O_5 composite consisted of fibres of crystalline Nb_2O_5 (δ-modification, hexagonal with the *c*-axis perpendicular to the growth direction) in a polycrystalline Ni matrix. Lower oxides of Nb could not be detected. A thin (few microns) NiO layer was formed at the surface of the splat during oxidation. A few weak X-ray diffraction lines could not be interpreted. Fig. 2 shows the cross-section of a splat where the preferential internal oxidation reaction has been completed.

The volume increase on oxidation of Nb to Nb_2O_5 was by a factor of ~3, which implies that the volume of the resulting composite was about twice as large as the volume of the starting sample, i.e. a mean linear expansion of 25% occurs during oxidation. The Ni–Nb_2O_5 composite contains 75 vol % Nb_2O_5.

At a given temperature the penetration depth, ζ, of the Nb_2O_5 fibres was observed to increase with the square root of the annealing time (Fig. 3), and at a given time to increase exponentially with the annealing temperature (Fig. 4). Above 650° C the internal oxidation occurred via an intermediate

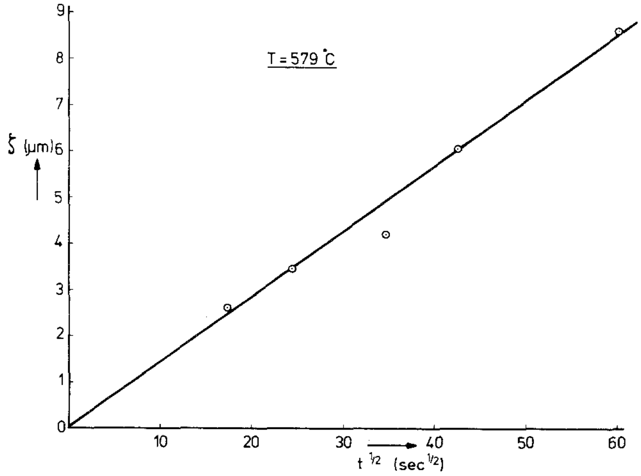

Figure 3 The penetration depth ζ of the Nb_2O_5 fibres as a function of time *t* at 579° C.

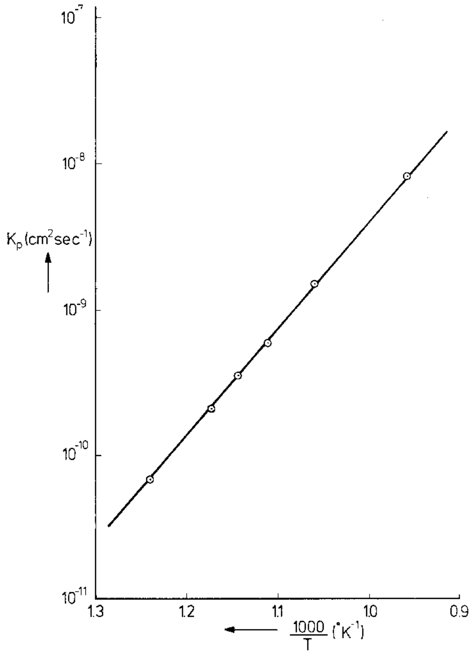

Figure 4 The oxidation rate constant, $K_p = \zeta^2/t$, of the Nb_2O_5 fibres as a function of temperature T.

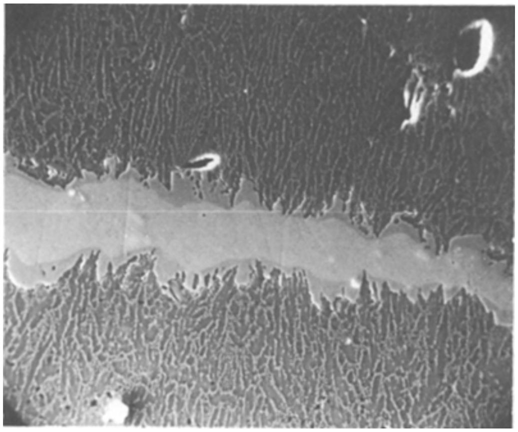

Figure 5 Partial preferential internal oxidation of a Nb_2Ni_3 sample at 750° C. Between oxidized and unoxidized material an intermediate layer of $NbNi_3$ (dark grey region) is visible. Secondary electron image (× 600).

layer of $NbNi_3$ surrounding the Nb_2O_5 tips (Fig. 5).

An Nb concentration profile was measured over the cross-section of a sample, completely oxidized at 750° C, and showed a dip over 6 μm in the middle of the sample, where the two growing fronts meet each other, with a minimum of 20 at. % Nb. The total width of the sample was about 120 μm.

3. Discussion

The flatness of the reaction front (Figs. 1 and 2) is due to the fact that the diffusion path of the oxygen is longer for protruding fibres, which reduces the rate of oxygen supply and hence the growth rate. From the fact that preferential internal oxidation occurs in amorphous Nb_2Ni_3 it follows that the affinity of oxygen for Nb is greater than for Ni, and that oxygen diffuses more rapidly than niobium [22]. The results given in Fig. 4 show that the composite growth behaviour is not noticeably affected by the crystallization of the amorphous material above 650° C, and the same may be assumed for the underlying diffusion processes. In principle, these involve both the diffusion of oxygen from the surface to the interior of the sample and the diffusion of niobium in the reverse direction. The fact that the completely oxidized sample, mentioned above, showed a 6 μm dip in the Nb concentration with a minimum of 20 at. % Nb in the middle of the sample indicates that the enrichment of the Nb_2O_5 due to the Nb diffusion is of the order of 1%. It is assumed that the oxidation reaction takes place only and completely at a sharp boundary plane between the internally oxidized and the remaining part of the specimen, and that the oxygen is taken up rapidly from the oxidizing atmosphere, so that the surface concentration is practically equal to the solubility C_O.

Further assuming

$$C_O D_O \gg C_{Nb} D_{Nb}, \qquad (1)$$

whilst

$$C_O \ll C_{Nb}, \qquad (2)$$

it follows that [22]

$$\frac{C_{ox}}{C_{Nb}} = 1 + \frac{nC_{Nb}D_{Nb}}{C_O D_O}, \qquad (3)$$

where n is the half the valency of Nb, D_{Nb} and D_O are the diffusion coefficients of Nb and O, C_O is the solubility of oxygen (atomic fraction), or the concentration difference of oxygen between the surface of the sample and the tips of the Nb_2O_5 fibres, C_{Nb} is the initial concentration of Nb (at. fract.) and C_{ox} is the concentration of Nb_2O_5, i.e. the concentration of Nb atoms (at. fract.) being oxidized to Nb_2O_5. The second term at the right-hand side corresponds to the amount of Nb missing behind the boundary [22]. With $C_{ox}/C_{Nb} = 1.01$

(see above), $n = \frac{1}{2}$, $C_O = 0.01$[*] and $C_{Nb} = 0.40$ it follows from Equation 3 that

$$D_{Nb} = 10^{-4} D_O. \qquad (4)$$

The inequalities 1 and 2 being well fulfilled, it follows from Equation 4 that the niobium diffusion is negligible compared with the oxygen diffusion, and will therefore be disregarded in the following.

In principle the oxygen diffusion can take place through the Ni matrix, and, because the Nb_2O_5 fibres are uninterrupted, through the Nb_2O_5 fibres and/or along the Ni–Nb_2O_5 interface. From the data in Figs. 3 and 4 the rate constant, $K_p = \zeta^2/t$, and the growth rate, $R(t)$, can be calculated

$$K_p = 0.15 \times 10^{-7400/T} \text{ cm}^2 \text{ sec}^{-1} \qquad (5)$$

and

$$R(t) = 0.19 \times 10^{-3700/T} t^{-1/2} \text{ cm sec}^{-1} \qquad (6)$$

From Ficks first law it follows that

$$Q \mathrm{d}\zeta = D_O \frac{C_O}{\zeta} \mathrm{d}t \qquad (7)$$

where Q is the atom fraction of O in Nb_2O_5. In Equation 7 the oxygen gradient has been taken to be C_O/ζ, which is a good approximation, because D_{Nb} is much smaller than D_O and C_O is much smaller than C_{Nb} [21]. Substituting of $K_p = \zeta^2/t$ and subsequent integration of Equation 7 give:

$$C_O D_O = \tfrac{1}{2} Q K_p \qquad (8)$$

Insertion of Equation 5, with $Q = 0.7$ gives

$$C_O D_O = 0.05 \times 10^{-7400/T} \text{ cm}^2 \text{ sec}^{-1}. \qquad (9)$$

For the diffusion of O in Ni it has been reported that [22, 28]

$$(C_O D_O)_{Ni} = 10^3 \times 10^{-17490/T} \text{ cm}^2 \text{ sec}^{-1}, \qquad (10)$$

i.e. between 500 and 800° C $(C_O D_O)_{Ni}$ is a factor of 10^8, i.e. 5×10^4 lower than the corresponding values given by Equation 9, while the activation energies in Equations 9 and 10 differ more than a factor of 2. Therefore it is concluded that the oxygen transport does not take place through the Ni matrix, but through the Nb_2O_5 fibres and/or along the Nb_2O_5–Ni interface.

The fact that no lower oxides of Nb are detectable may indicate that they are not present, because the nucleation of NbO and NbO_2 at, or in front of, the Nb_2O_5 tips is hampered, or it may mean that their amount is very small because the concentration profile of the oxygen in front of the Nb_2O_5 tips is very steep.

4. Conclusions

(1) Aligned composite films can be grown by subjecting an amorphous sample, the composition of which can be varied over a wide range, to a preferential internal reaction with atoms that are stored in the ambient of the sample.

(2) Preferential internal oxidation of amorphous Nb_2Ni_3 gives a composite consisting of a crystalline Ni matrix with 75 vol% crystalline Nb_2O_5 fibres of about 0.5 μm diameter. These fibres are aligned perpendicular to the surface.

(3) The growth of the Nb_2O_5 fibres occurs by virtue of the supply of oxygen diffusing from the surface to the interior of the sample through the Nb_2O_5 fibres or along the Nb_2O_5–Ni interface.

(4) The growth rate is inversely proportional to the square root of time and an exponential function of temperature.

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[*] In general $0 < C_O < 1$. At 600° C the value of C_O for Ni is about 0.001 [24] and for Nb_2O_5 may be estimated to be of the order of 0.01 [27].

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