Powder processing of ductile-phase-toughened Nb–Nb₃Al in situ composites

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Abstract

Model high temperature Nb–Nb₃Al in-situ intermetallic matrix composites have been successfully fabricated using powder metallurgy and arc-melting techniques. Vacuum hot pressing of elemental Nb and Al powders, mixed in the ratio Nb–6wt.%Al and synthesized at 1200 °C, yielded a dual-phase microstructure consisting of equiaxed islands of ductile Nb particles in a brittle Nb₃Al matrix. Subsequent thermal treatment at 1800 °C for 24 h resulted in an alternative composite microstructure with the Nb present in a lamellar morphology following a peritectic transformation, similar to structures obtained via arc-melting and thermal treatment procedures. The precipitation of ductile Nb phase following thermal aging was found to nucleate heterogeneously at grain boundaries and to progress along specific growth directions, resulting in a uniform and fine distribution of filamentary Nb within the Nb₃Al matrix. Both equiaxed and lamellar Nb–Nb₃Al composite microstructures show improved fracture toughness of about 6 MPa m¹/² compared with unreinforced Nb₃Al (about 1 MPa m¹/²), principally because of crack bridging and crack reactivation effects induced by the presence of the ductile Nb phase.

1. Introduction

Niobium-aluminide-based intermetallic alloys have recently been the subject of much research aimed at designing new structural materials for use at high temperatures in advanced aerospace propulsion systems [1–3]. Specifically, the goal is to develop materials for structural applications above service temperatures of 1100 °C, and as high as 1650 °C, beyond the usable range of directionally solidified single-crystal and oxide-dispersion-strengthened nickel-based superalloys, at present used in gas turbine engines. Since, the efficiency and total thrust of a jet engine are a direct function of the peak temperature of the working fluid and current operating limits are set by thermal constraints on materials, the next generation of high performance engines will require markedly stiffer materials operating at higher stresses and much higher temperatures. Materials systems for these applications include other ordered intermetallics, and ceramics and their composites, all of which suffer from problems of low ductility and toughness.

Niobium aluminate alloys are preferred over many refractory-metal compounds because of their lower density. Among the various Nb aluminides, namely Nb₃Al, Nb₃Al and NbAl₁ (Fig. 1), the higher melting temperature and better creep resistance of Nb₃Al makes it the most promising [1, 2]. Like most intermetallics, Nb₃Al has a low symmetry, complex (Al₅) crystal structure (Fig. 2), with a melting point of 2060 °C and a density of 7.29 g cm⁻³. However, the complex structure is simultaneously responsible for its high temperature strength and extreme susceptibility to brittle fracture at room temperature. Recent efforts have therefore been aimed at enhancing the ambient temperature ductility and fracture properties of Nb₃Al alloys.

One approach to improving the toughness of brittle intermetallics such as Nb₃Al is to fabricate an Nb₃Al composite by incorporating a refractory ductile metal phase in the microstructure; the principle here is to induce ductile-phase toughening, primarily by impeding crack advance via ductile–ligament bridging in the crack wake [4]. Such composites can be processed either by utilizing in-situ phase transformations in the alloy system through arc melting and thermomechanical treatments [5, 6], or by artificially hybridizing the microstructure with ductile phases [7–10]. As shown in Fig. 1, Nb₃Al is formed by a peritectic reaction at 2060 °C [11] with uniquely sloping phase boundaries such that the Nb-rich solid solution (Nb₃Al) overlaps the intermetallic at high temperatures; this aspect of the phase formation provides a mechanism for the in-situ precipitation of duplex microstructures of Nb₃Al composites with excess Nb₃Al as the ductile reinforcement phase. Previous studies have shown this to be a sluggish
transformation, such that Nb₃Al can be retained at room temperature with only a moderate degree of undercooling [11-13]; further thermal treatment is necessary to precipitate the ordered second phase. The precipitation is reported to occur through a massive transformation, resulting in a highly uniform and fine distribution of a filamentary Nb within a non-contiguous Nb₃Al matrix [11].

The purpose of this paper is to examine alternative processing routes, specifically based on powder metallurgy (P/M) and reactive sintering techniques, for fabricating dual-phase Nb–Nb₃Al composite microstructures with improved ambient-temperature toughness induced by ductile-phase-bridging mechanisms; the microstructures and properties are compared with those obtained using arc-melting techniques.

2. Experimental procedures

2.1. Powder processing of Nb–Nb₃Al microstructures

Commercially pure Nb powder (1–10 μm size) was obtained from Cerac, Inc., Milwaukee, WI; atomized Al powder (about 3 μm size) was obtained from Valimet, Inc., Stockton, CA. The powders were mixed in the ratio of Nb–6wt.%Al (Nb–18at.%Al), prior to ball milling for 20 min at room temperature. The mixed powder was then synthesized by heating in vacuo to 1400 °C at a rate of 20 °C min⁻¹ to initiate the reaction

\[
\text{Nb} + 3\text{Al} \rightarrow \text{Nb₃Al}
\]

The powders were held at 1400 °C for 1 h and stored in an argon atmosphere to prevent oxidation; the sintering sequence was repeated to ensure complete synthesis of Nb₃Al from the elemental Nb and Al powders.

Subsequently the synthesized Nb₃Al powder was compacted using a graphite die of 38 mm diameter and hot pressed in vacuo by simultaneously increasing the pressure and temperature to 36 MPa and 1650 °C respectively, holding for 10 min and then cooling to room temperature. Several samples were fabricated in a single operation by separating the powders by graphite spacers, coated with a boron nitride lubricant to prevent welding between graphite and the synthesized Nb–Al powder. The resulting samples obtained
from hot pressing about 25 g of synthesized powder were disks, about 38 mm in diameter and about 2.5 mm thick, which were readily amenable for fracture mechanics testing.

2.2. Ar melting of Nb–Nb$_2$Al microstructures

Alloys were also prepared by arc melting rods of Nb and Al in a water-cooled copper hearth under an inert atmosphere in the ratio of Nb–7wt.%Al (Nb–20at.%Al). The higher Al content was necessary to compensate for Al vaporization losses during processing; the final composition was determined to be Nb–5wt.%Al from energy-dispersive X-ray spectroscopy (EDS) measurements. However, arc melting results in a sample in the form of a button which is difficult to machine to the final form of a mechanical test specimen for fracture and fatigue testing.

2.3. Thermal treatment of Nb–Nb$_2$Al microstructures

To develop a composite microstructure with a lamellar Nb morphology, vacuum hot-pressed (P/M processed) Nb–Nb$_2$Al composites were thermally aged for 1, 4, and 24 h, at 1800 °C in an inert environment, and cooled at 15 °C min$^{-1}$ to room temperature. The samples were additionally annealed at 1450 °C for 24 h to reduce internal stresses and to consolidate the lamellar microstructure. Similarly, the Nb lamellae in arc-melted samples were slightly coarsened by thermal exposures at 1450 °C for up to 24 h.

2.4. Preparation of monolithic Nb$_2$Al

Pure (unreinforced) Nb$_2$Al was prepared by mixing and ar: melting Nb and Al rods in the ratio Nb–9wt.%Al (Nb–25at.%Al); volatilization after flipping and remelting the sample four times resulted in samples of composition Nb–7wt.%Al, assessed using EDS methods. The samples contained several cracks from rapid quenching in the water-cooled hearth of the furnace. These were later ball milled for 2 h to fine Nb$_2$Al powder, before vacuum hot pressing at 1500 °C for 15 min at a pressure of 36 MPa. The final samples were in the form of discs, about 38 mm in diameter and about 2.5 mm thick.

2.5. Microstructural characterization and fracture testing

Sections of all samples were metallographically polished, etched using a solution of 10 ml of HNO$_3$, 10 ml of HF, and 30 ml of lactic acid, and examined using optical and scanning electron microscopy. Specimens for transmission electron microscopy (TEM) were prepared by ion milling thin disks, 3 mm in diameter, that were thinned by prior mechanical grinding and polishing. X-ray diffraction (XRD) studies were performed on all alloys to identify the phases present in the different microstructures; the final compositions were estimated using EDS.

The fracture toughnesses $K_{IC}$ for Nb$_2$Al, Nb and the various Nb–Nb$_2$Al composites were evaluated by monotonic loading fatigue-precracked disk-shaped compact tension specimens 25 mm wide and 2.5 mm thick to failure, according to procedures detailed in ASTM Standard E-399-90 [14]. Additional tests on selected microstructures were performed using the Vickers diamond indenter at loads between 10 and 15 kg to initiate cracking. The flexure properties of the materials were determined using beams 4 mm square and 12 mm long loaded in four-point bending.

3. Results and discussion

3.1. Microstructures

3.1.1. Powder processed Nb–Nb$_2$Al

The composite Nb–Nb$_2$Al microstructure obtained through P/M processing i.e. by vacuum hot pressing the synthesized Nb–6wt.%Al powders at 1650 °C, is shown in Fig. 3(a). The duplex microstructure consists predominantly of approximately 5 μm-sized equiaxed islands of Nb$_{38}$ (light phase) dispersed as a secondary phase in an Nb$_2$Al matrix, as expected from the Nb–Al phase diagram (Fig. 1); the volume fraction of the ductile Nb$_{38}$ phase is estimated to be about 40 vol.%. The corresponding XRD pattern, shown in Fig. 4(a), also reveals intensity peaks characteristic of Nb$_2$Al and Nb. Although several peaks of Nb, Nb$_2$Al and Nb$_{38}$ phases can overlap, the presence of Nb and Nb$_2$Al can be unambiguously identified from the diffracted intensities of Nb$_2$Al (2θ = 64.7°) and Nb (112) (2θ = 69.8°). However, similar to previous studies [11, 12], it may be noted that the Nb$_2$Al peaks are displaced slightly to the left of actual stoichiometry (Nb–25at.%Al), while the Nb peaks are shifted to the right of the intensity peaks expected for pure Nb. This indicates the presence of Nb in the form of Nb$_{38}$ phase with a slightly reduced lattice parameter ($a_{Nb} = 3.275$ Å vs. 3.305 Å for pure Nb) accounting for the peak shift toward higher 2θ values. Similarly, Nb$_2$Al has a smaller lattice parameter, presumably owing to a lower Al content than expected from stoichiometry. EDS analyses also confirm these notions; the Nb$_2$Al matrix is found to be Nb–23at.%Al with the secondary Nb$_{38}$ phase containing about 12.5 at.% Al, close to the solubility limit of Al in Nb at the elevated temperature.

Small amounts of elemental Al and Nb were also present owing to incomplete synthesis of the Nb and Al powders; these are seen as minute dark and light particles in Fig. 3(a). Minor traces of Nb$_2$Al and NbAl,
were also present because of the localized nature of the synthesis. Although the hot pressing of synthesized Nb$_5$Al powder resulted in sufficiently dense samples, some porosity is still apparent (Fig. 3a); the densification, however, is far greater than that achieved through simple hot pressing of elemental (unsynthesized) Nb and Al powders [15].

3.1.2. Influence of thermal treatment

A typical microstructure, obtained after heat treating the as hot-pressed (equiaxed) Nb–6wt.%Nb$_5$Al alloy at 1800°C for 24 h, is illustrated in Fig. 3(b); the corresponding XRD pattern is shown in Fig. 4(b). Both Nb$_5$Al and Nb phases are clearly evident although the ductile-Nb-phase morphology is clearly altered owing to the peritectic transformation; the structure now contains lamellae of Nb$_5$Al with a stringy Nb$_{ss}$ phase between them. The Nb$_{ss}$ phase is rather fine, on the order of a few microns in thickness, and distributed uniformly throughout the matrix. At lower aging times of 1 and 4 h, however, the duplex Nb–Nb$_5$Al structure is not fully developed and the alloy retains Nb$_{ss}$ with fine substructural features indicative of the early stages of transformation.

The decomposition of Nb$_{ss}$ → Nb + Nb$_5$Al through the peritectic reaction is seen to nucleate heterogeneously at prior Nb$_{ss}$ grain boundaries and to extend into the grain interior (Figs. 5 and 6). Analysis of TEM selected-area diffraction patterns reveals that the lamellar growth of Nb–Nb$_5$Al colonies occurs along the Nb$_{ss}$[110] and Nb$_5$Al[211] direction (see also ref. 16), although previous studies have suggested a different growth direction for Nb$_5$Al [17]. The lamellae then fuse into small elongated grains with a 5–8° misorientation between them (Fig. 6(c)). A high density of dislocations and bend contours is observed within the Nb$_{ss}$ and the ordered Nb$_5$Al phases respectively (Figs. 6(b) and 6(c)); this is presumably related to the strains associated with the peritectic transformation and mismatch in thermal expansion properties. In fact,
previous work [18, 19] on A15 compounds has shown that, since Nb₃Al has a substantial mismatch with the parent Nb₃Sn, the initial precipitates are likely to be under considerable strain. Alternatively, compressive and tensile strains can be set up from lattice movement associated with the different diffusivities of Nb and Al. Such internal strain may, however, be relieved partially by the preferential nucleation of the Nb₃Al along grain boundaries and/or matrix dislocations.

3.1.0. Arc-melted Nb–Nb₃Al

The microstructure of the arc-melted Nb–7wt.%Al rods (Fig. 7(a)) also reveals the presence of Nb₃Sn dendrites at room temperature. The retention of the Nb solid solution at room temperature can be explained by following the solidification sequence of a molten Nb–5wt.%Al (Nb–15at.%Al) alloy (after accounting for volatilization losses of about 2 wt.% Al during arc melting). As the alloy cools, the first phase to appear is the Nb solid solution with a composition Nb–5at.%Al. The Nb₃Sn grows dendritically with successive layers solidifying at compositions determined by the local temperature and the Nb₃Sn solidus. As the remaining liquid becomes rich in Al, the Nb₃Al phase can precipitate surrounding Nb₃Sn dendrites. Incomplete diffusion in the Nb₃Sn solid and/or across the Nb₃Al phase (owing to fast cooling rates achieved in the water-cooled copper hearth) effectively prevents the peritectic reaction. Dendritic solidification, with no diffusion in the solid, can lead to the formation of small amounts of Nb₃Al and NbAl₃ around the Nb₃Sn dendrites; this is revealed as preferential etching due to the entrapped phases between the dendrites (Fig. 7(a)).

Subsequent heat treatment at 1450°C for 24 h resulted in the precipitation of the ordered Nb₃Al phase; the duplex structure features a uniform and fine distribution of a filamentary niobium within a non-contiguous Nb₃Al matrix (Fig. 7(b)) similar to those
3.2. Mechanical properties

The mechanical properties of the Nb–Nb₆Al composites were distinctly superior to those of unreinforced Nb₆Al, displaying a significantly higher toughness at roughly comparable strength levels (Table 1). The unreinforced Nb₆Al material was found to have a high hardness but a very low fracture toughness \( (K_{IC} \approx 1.1 \text{ MPa m}^{1/2}) \), with an estimated yield strength (based on one third of the Vickers hardness [20]) of 274 MPa and a flexure strength of 212 MPa. In comparison, the equiaxed Nb–Nb₆Al composite showed a lower hardness but displayed a sixfold increase in toughness \( (K_{IC} \approx 6.5 \text{ MPa m}^{1/2}) \) and a flexure strength of 460 MPa, over twice that of pure Nb₆Al.

However, thermal treatments at 1800 °C lead to reductions in hardness (and strength) consistent with the fact that the microstructures are primarily hardened by the Nb₆ phase to the slow kinetics of Nb₆Al precipitation, especially in the 1 and 4 h aged conditions. Correspondingly, indentation toughness results suggest values in excess of 10 MPa m\(^{1/2}\) (Table 1), as no cracks were observed at the corners of the indentation for loads of up to 14.5 kgf. With prolonged aging for 24 h, the Nb–6wt.%Al alloy regains its hardness concurrent with the precipitation of Nb₆Al. Although this lamellar microstructure also exhibits an increase in toughness \( (K_{IC} \approx 5.5 \text{ MPa m}^{1/2}) \), it is slightly lower than for the equiaxed microstructure; the yield and flexure strengths are also slightly reduced. Both composite microstructures display improved fatigue properties compared with monolithic Nb₆Al [21].

The fivefold to sixfold increase in toughness shown by the in-situ Nb–Nb₆Al composites compared with monolithic Nb₆Al can be attributed primarily to the role of ductile Nb₆ phase bridging of the crack, and to a lesser extent plastic deformation in the ductile phase. This is clearly evident by the presence of uncracked Nb₆ particles in the crack wake (Fig. 8(a) and 8(b)), which subsequently fail by ductile microvoid nucleation and growth mechanisms (Fig. 8(c)). This aspect is critical for the successful fabrication of Nb–Nb₆Al in-situ composites, since the ductility of Nb can be significantly degraded by contamination from interstitial impurities such as oxygen and hydrogen [22, 23].

The contribution to the toughening of Nb₆Al from the Nb₆ phase arises from resultant tractions bridging the two crack surfaces, thereby partially shielding the crack tip from remotely applied loads. Other mechanisms such as crack deflection, crack trapping, crack renucleation, multiple matrix cracking and decohesion along the Nb–matrix interfaces can further enhance this effect. At steady state, where the bridging zone length is at a maximum, governed by ductile ligament rupture at a critical displacement \( u^* \), the extent of toughening due to bridging can be estimated using

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3.1.4. Unreinforced Nb₆Al

Microstructures for monolithic Nb₆Al were relatively featureless, exhibiting a grain structure with an average size of about 50 µm. Higher magnifications reveal the presence of small Nb dendrites and some porosity (less than 2%) at certain locations in the sample; precipitation of large second-phase particles, as in the hot-pressed or thermally treated condition, was not apparent.
simple models [4, 8] in terms of the area fraction \( f \) of ductile ligaments intersecting the crack path, their uniaxial yield strength \( \sigma_y \) and a representative cross-sectional radius \( t \). These yield expressions for the composite toughness \( K_c \) of the form

\[
K_c = (K'_{c}^{2} + Ef \sigma_y)\chi^{1/2}
\]

where \( K'_{c} \) can be taken as the toughness of the Nb₃Al matrix, \( E \) is Young's modulus, and \( \chi \) is a dimensionless representation of work of rupture [4, 8] for the specific composite. \( \chi \) can vary between 0.5 and 8 depending upon the degree of interface debonding and constitutive properties of the reinforcement phase [4, 7, 8]. This formulation is applicable only under small-scale bridging conditions, where the bridging zone size is small compared with the crack length and specimen dimensions. For the equixed Nb–Nb₃Al composite, taking the area fraction of ductile Nb phase intersected by the crack path as \( f = 0.27 \) (since only two thirds of the 40 vol.% Nb particles interact with the crack), yield strength for Nb \( \sigma_y = 90 \) MPa, the composite modulus \( E = 123 \) GPa, \( K_c = 1 \) MPa m\(^{1/2} \), the Nb particle size \( t = 5 \) \( \mu \)m and \( \chi_{Nb} = 2.7 \) (assuming a well-bonded Nb–Nb₃Al interface [8]), the predicted composite toughness from eqn. (1) is 6.5 MPa m\(^{1/2} \), in good agreement with the experimental result. Using similar values for the lamellar Nb–Nb₃Al composite, where \( t \approx 1 \) \( \mu \)m and \( f = 0.4 \), eqn. (1) yields a composite toughness of about 4 MPa m\(^{1/2} \), which is somewhat lower than that observed experimentally.

4. Concluding remarks

It has been demonstrated that ductile-phase-toughened Nb–Nb₃Al intermetallic matrix composites can be successfully processed using P/M techniques, specifically by hot pressing the reaction-synthesized Nb and Al powders mixed in the ratio Nb–6wt.%Al. Utilizing the peritectic reaction in the phase diagram, the Nb morphology can be modified by thermo-mechanical treatments to fabricate a lamellar Nb–Nb₃Al composite microstructure, similar to those obtained by arc melting procedures. The P/M route is particularly advantageous over the arc-melting practice since it yields specimens with near-net shape that are readily amenable for mechanical property characterization or actual use as structural components with minimal machining.

The resulting Nb₆₋₆Nb₃Al composites show nearly a sixfold increase in fracture toughness (\( K_c \approx 6 \) MPa m\(^{1/2} \)) at comparable strength levels, compared with monolithic Nb₃Al (\( K_c \approx 1 \) MPa m\(^{1/2} \)). Such toughening is primarily attributed to crack bridging by uncracked Nb particles in the crack wake, with additional beneficial effects from plastic deformation within the Nb phase, crack deflection and renucleation, and multiple (coplanar) cracking in the matrix. Despite the marked improvement in toughness, compared with Nb₃Al, the Nb–6wt.%Al alloy with duplex Nb–Nb₃Al microstructures, the absolute fracture toughness is still relatively low for it to be used as a structural material. Specifically, the fine micron-sized Nb particles in the present microstructures limit the formation of a significant bridging zone. In this regard, future developments toward achieving coarse microstructures, via solid state reactions or lamination with characteristic dimensions of the Nb phase on the order of 50–500 \( \mu \)m, are expected to be promising.

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