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Effect of heating rate on grain morphology of *in situ* reinforced reaction bonded aluminium niobate-based composites

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Reaction-bonded aluminium niobate-based composites with tailored microstructures were fabricated through controlled nucleation and growth of $AlNbO_4$ needle-like grains. Using heating rates of 0.5 to $>160\,^{\circ}C\ min^{-1}$, the effects of heat-up period on microstructure development, and the volume content, grain-size distribution as well as aspect ratio of $AlNbO_4$ grains has been investigated. The morphology of the final microstructure is principally determined by the grain growth during heat-up. Equiaxed to elongated grains were obtained by using different heating rates and thermal ageing at 1320 °C in air. SEM observations revealed that increasing the heating rate promotes the development of large and homogeneously distributed needle-like grains. The results presented show that tailoring of final $AlNbO_4$ microstructures become possible by the control of heating rate.

1. Introduction

In situ toughened materials containing high-aspect-ratio phases have attracted considerable attention over the past two decades owing to their improved mechanical properties at room and elevated temperatures [1–7]. These self-reinforced materials inherently possess a bimodal microstructure, where large elongated grains have developed within a small-grained matrix. In order to optimize mechanical properties, self-reinforced materials should exhibit microstructures containing a considerable amount of elongated grains homogeneously distributed in a fine-grained matrix.

In order to obtain *in situ* toughened materials with a desired bi-modal microstructure, several approaches have been used. "*In situ* microstructures" have been tailored through addition of sintering additives [8–11], sintering conditions [12–15] and by controlling nucleation and growth of needle-like grains by seeding [16–18].

The formation of duplex microstructures containing $AlNbO_4$ needle-like grains with high aspect ratio and basic rules to tailor the microstructure of *in situ* reinforced niobium-modified reaction-bonded aluminium oxide (Nb–RBAO), have been reported previously [19, 20]. The morphology of $AlNbO_4$ grains could be readily changed (from equiaxed to needle-like) by modifying the processing conditions. In a previous paper [21] it was indicated that heating rates can be used to produce improved microstructures.

The present work describes the results of a study aimed at understanding the effect of heating rates on the microstructure development of Nb–RBAO and on needle-like $AlNbO_4$ grain morphologies.

2. Experimental procedure

Reaction-bonded aluminium niobate composites containing 89.6 vol % $AlNbO_4$, 5.8 vol % $Nb_2Zr_6O_{17}$, and 4.6 vol % α-Al_2O_3 were prepared from attrition-milled powder mixtures containing 39.3 vol % Al, 15.4 vol % Nb, 37.7 vol % Nb_2O_5 and 7.6 vol % $Nb_2Zr_6O_{17}$ as described elsewhere [21]. In order to induce the formation of needle-like grains, CaO was added by infiltrating the samples with 0.13 M $Ca(NO_3)_2$ solution and subsequent sintering at 1320 °C. Microstructure development was investigated using constant heating rates of 0.5–15 $^{\circ}C\ min^{-1}$. To obtain the highest possible heating rate, samples were introduced rapidly into a furnace preheated to the sintering temperature (denoted rapid heating). Assuming that the samples reach a maximum temperature after 8 min, the effective heating rate is $>60\,^{\circ}C\ min^{-1}$.

Phase composition was characterized by X-ray diffractometry (XRD) of powdered and bulk samples. Microstructural evolution was followed by firing the samples with hold times ranging from 15 min to 12 h and cooling to room temperature. Samples for microstructural characterization were polished to 1 μm finish, and thermally etched at 1260 °C for 15 min. The microstructure was observed using scanning electron microscopy (SEM) and field-emission gun-type microscopy (Jeol JSM 6320 FK, Tokyo, Japan). To characterize quantitatively the microstructure of specimens, needle-like grain diameters, d, and lengths, l, of two-dimensionally exposed grains were measured using SEM equipped with an imaging analysis software (AnalySIS 2.0—Soft-Imaging Software GmbH, Germany). The aspect ratios were calculated from individual two-dimensional measurements.

3. Results and discussion

XRD patterns of sintered and thermally aged samples are comparable and can be ascribed to $AlNbO_4$, $Nb_2Zr_6O_{17}$, and α-Al_2O_3. Fig. 1a–e show the microstructure of composites for different heating conditions after thermal ageing for 12 h at 1320 °C (see also Table I). A heating rate of 0.5 °C min^{-1} causes only slight growth of grains with equiaxed shape. At heating rates $>$0.5 °C min^{-1}, the shape of some $AlNbO_4$ grains is distinctively different, developing a needle-like morphology during thermal ageing. The size of $AlNbO_4$ grains increases from $<$1 μm for 0.5 °C min^{-1} to lengths of $>$20 μm for 15 °C min^{-1}, whereas almost no matrix grain growth takes place. The average grain length of the materials processed by rapid heating was not significantly different. The standard deviation shows that the homogeneity of the microstructure improves with increasing heating rate. At low concentrations of needle-like grains, growth occurs readily by Ostwald ripening; however, if the number of large grains is further increased, the growth in the length direction is reduced due to steric hindrance.

It was found that needle-like grains grow from niobium-poor grains that are substantially larger than the average grain size. Needle-like grains grow of an anisotropic rate of growth in the [1 0 0] and [0 1 0] crystallographic directions [22]. As shown in Fig. 2, evidence of needle-like grain formation from

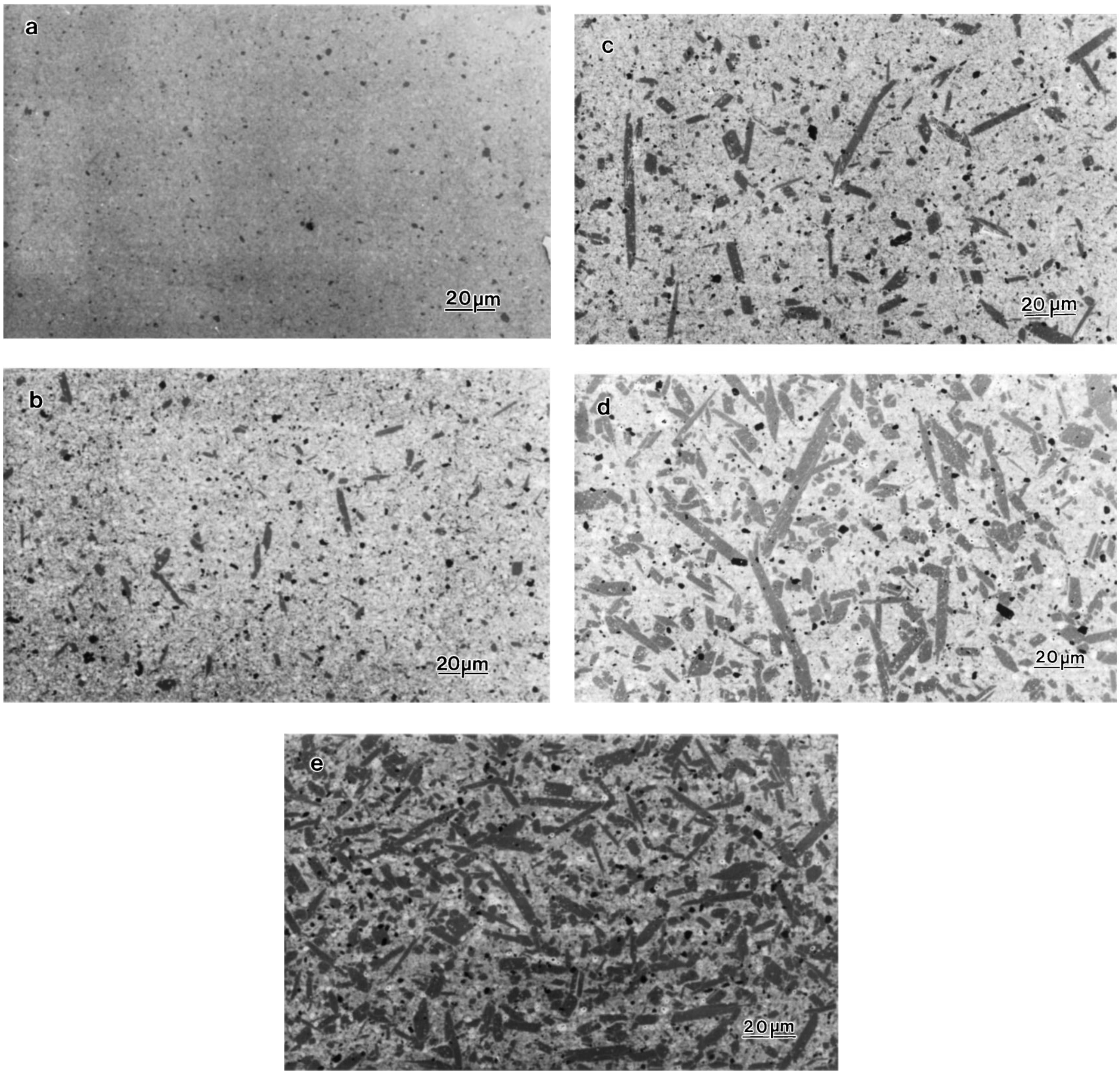

Figure 1 Scanning electron micrograph of polished and etched surface of $AlNbO_4$ composite sintered at 1320 °C for 12 h at constant heating rates of (a) 0.5 °C min^{-1}, (b) 3 °C min^{-1}, (c) 8 °C min^{-1} and (d) 15 °C min^{-1} and (e) rapidly heated.

TABLE I Mean values of volume content, average size, standard deviation of length and aspect ratio of needle-like grains in $AlNbO_4$ composites sintered at 1320 °C for 12 h using different heating rates

Heating rate (°C min^{-1})	Volume content of needle-like grains (%)	Average length (μm)	Standard deviation deviation (%)	Aspect ratio
0.5	—	—	—	—
3	8	6	40	4.6
8	12	14.1	62	5
15	29	17.7	68	8
>160	33	18	42	7

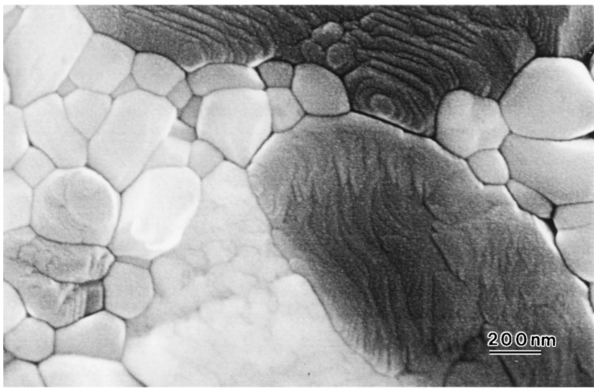

Figure 2 Scanning electron micrograph of a polished and etched surface of $AlNbO_4$ composite sintered at 1320 °C for 15 min at constant heating rates of 15 °C min^{-1} showing growth of $AlNbO_4$ needle-like grains via screw dislocation motion.

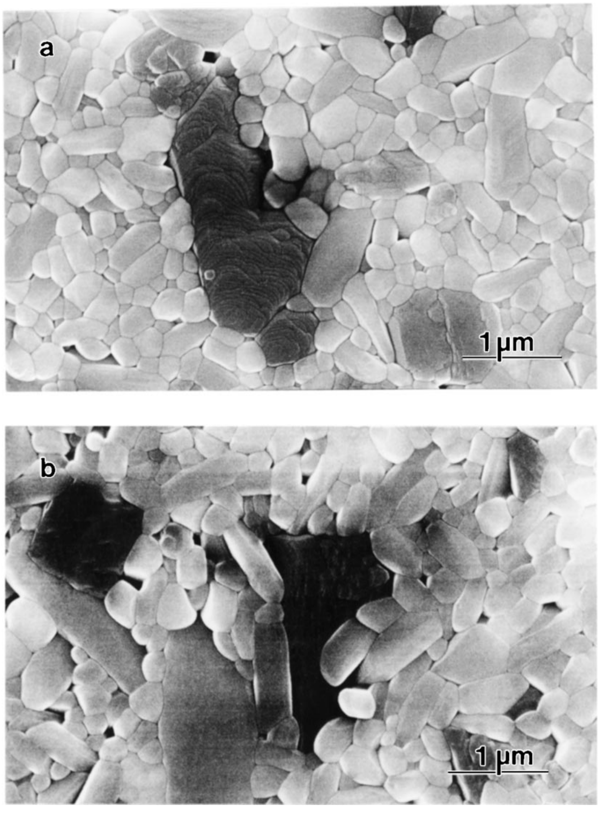

Figure 3 Scanning electron micrograph showing microstructure around niobium-poor grains after sintering for 15 min at 1320 °C using constant heating rates of (a) 0.5 °C min^{-1} and (b)15 °C min-1.

niobium-poor grains in the early stage is indicated by the typical step contrast for crystal growth along screw dislocations (e.g. SiC). The formation of elongated $AlNbO_4$ grains strongly depends on the microstructure around the niobium-poor grains developed during heating. A slow heating rate (0.5 °C min^{-1}) (Fig. 3a) caused a preferential disappearance of the smaller grains around niobium-poor grains, forming strongly faceted grains. The abnormal grain growth observed around niobium-poor grains is stimulated by the presence of Nb_2O_5 and CaO which form a low-melting point eutectic [23] and the long period of time necessary to heat up. The observed restructuring around the niobium-poor grains delay or inhibit additional grain growth during thermal ageing and therefore an evolution toward a more homogeneous and finer-grained distribution is favoured. As shown in Fig. 3b (heating rate of 15 °C min^{-1}), after relatively rapid heating the niobium-poor grains are surrounded by fine-equiaxed grains, which enables the grain to grow to the observed high aspect ratio by incorporation of the surrounding smaller grains during ageing.

4. Conclusions

1. The heating rate influences the microstructural evolution of Nb–RBAO microstructure. Slow heating rate favour homogeneous and fine-grained microstructures. Increasing the heating rate promotes the development of large needle-like grains.

2. The morphology of the final Nb–RBAO microstructure is principally determined by the grain growth during heating. The formation of elongated $AlNbO_4$ grains strongly depends on the grain morphology around niobium-poor grains in the early stage of sintering.

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