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Synthesis of Al_2O_3 matrix composites by reactive infiltration

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Reactive infiltration of a NiO-base blended powder with molten aluminium was attempted at 1673 K in order to obtain Al_2O_3 matrix composites containing a dispersion of Al_3Ni, AlNi and/or $AlNi_3$. The NiO powder was barely infiltrated by the molten aluminium after a 3600 s holding time at 1673 K. A continuous layer of Al_2O_3 was observed to exist at the infiltration front, which prevented any further infiltration. TiB_2 particles were added to the NiO powder in order to absorb the heat of reaction between NiO and aluminium. When the TiB_2 particle content in the [NiO + TiB_2] powder blend was greater than 20 vol %, spontaneous infiltration occurred completely. Thus, it was shown that the addition of the TiB_2 particles assisted in the spontaneous infiltration. The specimens produced by the *in situ* reaction consisted of Al_2O_3, TiB_2 and Al_3Ni. Al_3Ni was mainly located between the TiB_2 and Al_2O_3. The effect of the TiB_2 addition on the infiltration kinetics was to decrease the maximum attainable temperature caused by the exothermic reaction. This in turn prevented the formation of a continuous Al_2O_3 film at the infiltration front. This resulted in the production of pathways for the infiltration of the molten aluminium and made possible the complete infiltration.

1. Introduction

The infiltration of a ceramic preform with molten aluminium has been used to fabricate aluminium matrix composites [1, 2]. Generally, non-reactive metal/ceramic systems have been used in this infiltration technique to prevent the degradation of the ceramic phase. Materials obtained using this process basically consist of a continuous metal matrix and discontinuously dispersed ceramic particles, i.e., metal matrix composites. Reactive systems have begun to be introduced into the infiltration process [3, 4]. Since the ceramics or intermetallics are synthesized *in situ*, this process can provide a continuous ceramic or intermetallic matrix, i.e., ceramic or intermetallic matrix composites [5]. This is one of the outstanding features of this technique in that a bulk ceramic can be synthesized at relatively lower temperatures in a short time. Another advantage is that the highly reactive combination of a ceramic with a molten metal is in many cases wettable [6, 7], which enables a spontaneous infiltration.

In this work, nickel oxide (NiO) and aluminium were used as the starting materials, and the spontaneous infiltration of NiO-base blended powder with molten aluminium was attempted. As a result of the reaction between aluminium and NiO shown below;

$$3NiO + 2Al \rightarrow Al_2O_3 + 3Ni \qquad (1)$$

aluminium oxide (Al_2O_3) and nickel are produced. In reactive synthesis, the processing temperature tends to affect the microstructure of the synthesized specimen [6], and it should be noted that a sharp increase in the temperature due to the exothermic nature of the reaction is expected in this experiment. In order to absorb the heat of reaction and thus control the increase in the temperature caused by the exothermic reaction, titanium diboride (TiB_2) particles were blended with the NiO powder. Since TiB_2 is stable in molten aluminium, it has no influence on the *in situ* reaction shown in Equation 1.

The aim of this work is to synthesize Al_2O_3 matrix composites via the infiltration process, and to this end the reactive infiltration of a [NiO + TiB_2] powder blend with molten aluminium is dealt with in this paper. We particularly focus on (i) investigation of the effect of the TiB_2 addition on the infiltration kinetics and (ii) observation of the composite microstructure.

2. Experimental procedure

2.1. Infiltration process

The starting materials used in this work are NiO particles (99%, 44–105 μm), TiB_2 particles (99.5%, under 44 μm) and an aluminium ingot (99.99%). The TiB_2 particles were blended with the NiO particles at various fractions between 0–60 vol %. A schematic illustration of the experimental setup for the spontaneous infiltration is shown in Fig. 1. As is shown in Fig. 1, the loose [NiO + TiB_2] powder blend (3.0 g) is placed at the bottom of the Al_2O_3 crucible. The aluminium ingot (8.0 g) was then placed on the powder blend. The specimen was heated up to 1673 K in a nitrogen atmosphere and held for 3600 s to induce the spontaneous infiltration. After the holding period

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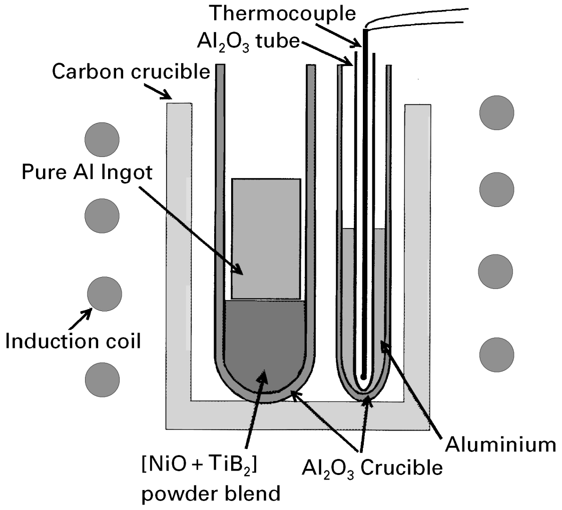

Figure 1 A schematic illustration of the experimental setup.

of 3600 s, the specimen was cooled in the furnace and removed from the crucible. The vertical cross-section was observed and analysed by scanning electron microscopy (SEM), an electron microprobe analyser (EMA) and X-ray diffraction (XRD) techniques.

2.2 Differential thermal analysis

Aluminium powders were mixed with the NiO powder at a molar ratio of 2:3 (Al:NiO). The powder blend was consolidated by applying a pressure of 1000 MPa and a piece of the compact was probed using differential thermal analysis (DTA). The analysis was conducted in an argon atmosphere at a heating rate of 10 K min^{-1}.

3. Results and discussions

3.1. Reaction products and a macroscopic view of a specimen

An optical micrograph of the vertical cross-section is shown in Fig. 2 for the specimen with a TiB_2 content of 25 vol %. The lower part of the photograph shows a composite whilst the upper part is residual aluminium that did not infiltrate into the $[NiO + TiB_2]$ powder blend. Since the shape of the specimen is similar to that of the Al_2O_3 crucible, complete infiltration has apparently occurred. The X-ray diffraction pattern of this specimen is shown in Fig. 3. The X-ray peaks of Al_2O_3 were observed at the appropriate angular positions, whereas those of NiO were rarely detected. This observation supports the hypothesis that the reaction shown as Equation 1 occurs at the applied processing conditions. The nickel produced in this reaction immediately reacts with the aluminium to produce Al_3Ni. A few peaks corresponding to aluminium were still observed in the X-ray diffraction pattern indicating the presence of a minute quantity of aluminium in the composite.

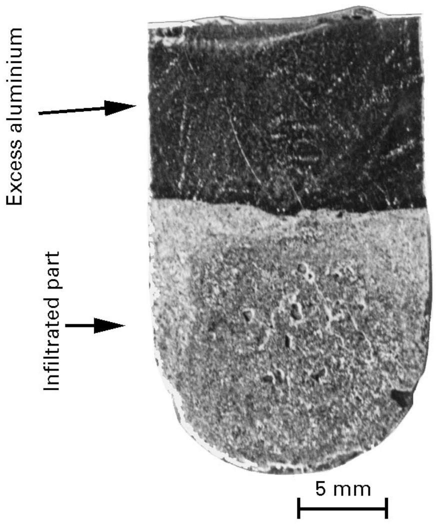

Figure 2 Optical micrograph of the cross-section for the specimen with 25 vol % TiB_2 in the powder blend.

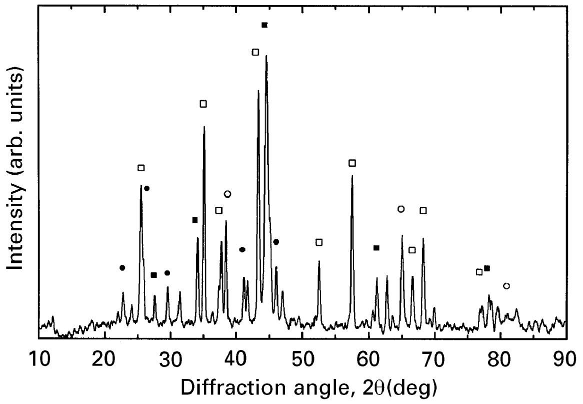

Figure 3 The X-ray diffraction pattern of the $[NiO + TiB_2]$/pure Al system fabricated by the spontaneous infiltration. Key: (○) Al; (□) Al_2O_3; (●) Al_3Ni and (■) TiB_2.

3.2. Effect of the TiB_2 content on the infiltration kinetics

As previously stated, the TiB_2 particles absorb the excess energy produced in the reaction between the NiO and aluminium, which makes it possible to control the temperature increase caused by the exothermic reaction. The infiltrated ratio (infiltrated depth / total depth of the powder blend) is shown in Fig. 4 as a function of the TiB_2 content in the $[NiO + TiB_2]$ powder blend. The infiltration barely occurred at TiB_2 contents in the range of 0–15 vol %. However, complete infiltration was achieved when the TiB_2 content was greater than a threshold value of 15–20 vol %. The following two points can be inferred from these results: (i) the TiB_2 particles in the powder phase assist with the infiltration, and (ii) the change between non-infiltration to complete-infiltration occurs abruptly.

3.3. Microscopic observations

Vertical cross-sections of the infiltrated region were observed by SEM for specimens with TiB_2 contents of of 5 and 25 vol % (Fig. 5 (a and b), respectively). A continuous layer of Al_2O_3 can be clearly identified in Fig. 5a. This continuous nearly-monolithic Al_2O_3 is

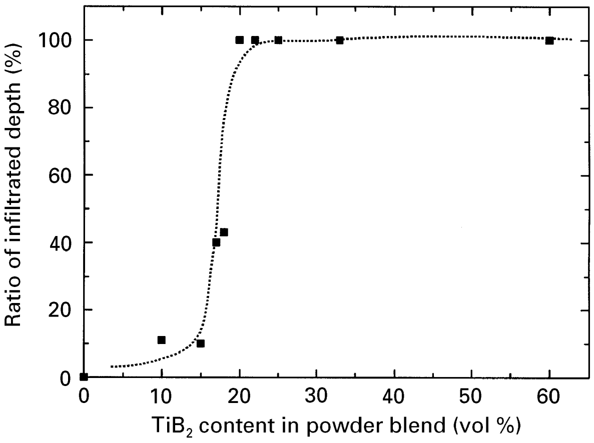

Figure 4 Ratio of the infiltrated depth as a function of the TiB_2 content in the powder blend.

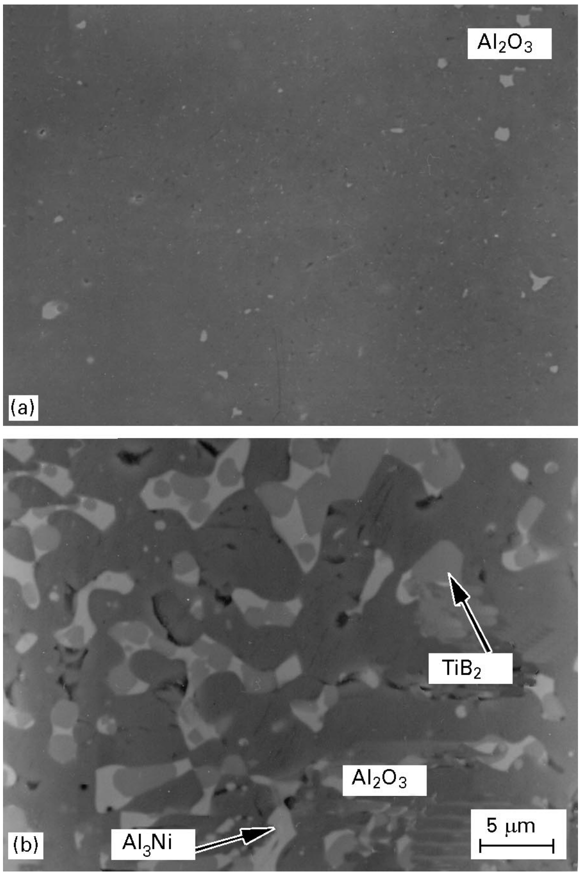

Figure 5 Scanning electron micrographs for specimens with (a) 5 vol % and (b) 25 vol % TiB_2 in the powder blend.

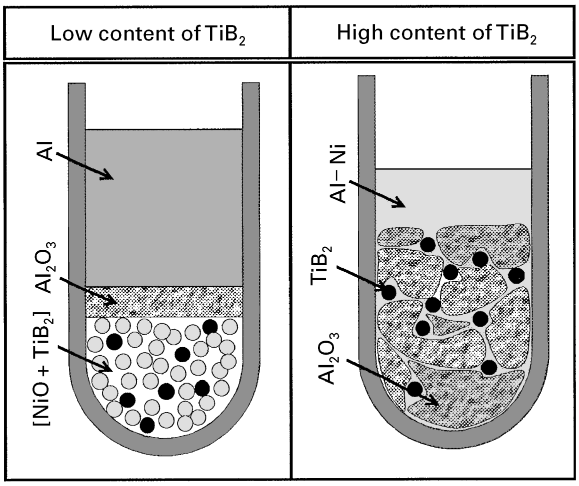

Figure 6 Schematic illustration of cross-sections for the non-infiltrated specimen and the completely-infiltrated specimen.

normally produced through a melting–solidification processing of Al_2O_3, and thus it infers that the increase in the temperature caused by the exothermic reaction exceeded the melting point of Al_2O_3. The TiB_2 particles and nickel were segregated from molten Al_2O_3, and after the solidification of the Al_2O_3, no further infiltration was allowed.

Unlike the microstructure shown in Fig. 5a, the Al_2O_3 formed *in situ* did not have the form of a continuous film at TiB_2 contents of 25 vol % (Fig. 5b). The TiB_2 particles were embedded into the Al_2O_3 matrix and Al_3Ni was observed to form at gaps between the TiB_2 and Al_2O_3. According to the Al–Ni phase diagram [7], the decomposition temperature of Al_3Ni is 1127 K, whereas the processing temperature employed here was 1673 K. Hence, Al_3Ni was a liquid during the holding process and the gaps between the TiB_2 particles and the *in situ* formed Al_2O_3 could be the infiltration pathway.

Since the TiB_2 particles added to the powder phase act as an absorber of the heat of reaction between the NiO and aluminium, the adiabatic temperature of the system decreases with an increase in the TiB_2 content. Consequently, the formation of molten Al_2O_3 could be prevented by the addition of more than 20 vol % of TiB_2 to the powder blend. From these observations it can be concluded that the addition of TiB_2 (i) decreases the adiabatic temperature of the system, which prevents the Al_2O_3 from melting and forming a continuous layer and (ii) helps produce the route for the infiltration (Fig. 6).

3.4. Differential thermal analysis

A differential thermal analysis of an [NiO + Al] powder compact was conducted in order to identify the initiation temperature of the *in situ* reaction. The DTA profile shown in Fig. 7 revealed one sharp exothermic peak at around 930 K, which is near the melting point of aluminium. No endothermic peak indicating the fusion of aluminium was detected. The reaction between the NiO and aluminium, therefore, occurs on the melting of the aluminium. From the DTA result, it is apparent that, during the infiltration process, the *in situ* reaction takes place when molten aluminium and NiO come into contact at the infiltration front.

3.5. Calculation of the adiabatic temperature

According to the XRD analysis and the SEM observations, the system changes through the reaction as follows.

before infiltration: $3NiO + 11Al + xTiB_2$

after infiltration: $Al_2O_3 + 3Al_3Ni + xTiB_2$

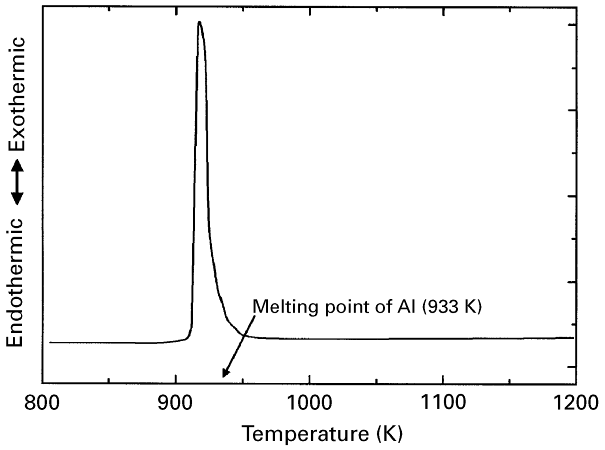

Figure 7 Differential thermal analysis curve obtained from the [NiO + Al] powder compact. The mixture has a mole ratio of Al:NiO of 2:3.

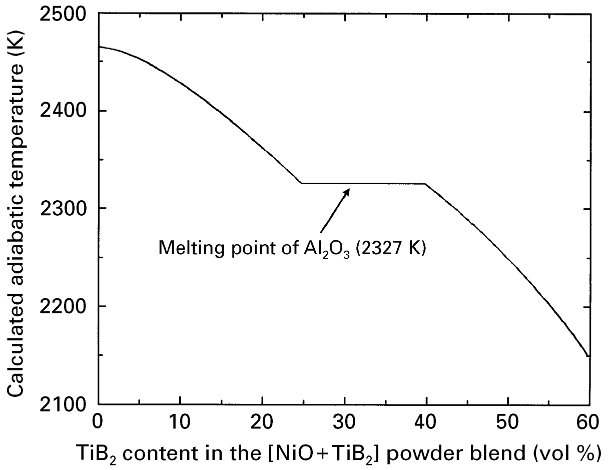

Figure 8 Calculated adiabatic temperature of the system as a function of the TiB_2 content in the [NiO + TiB_2] powder blend.

where x denotes the amount of TiB_2 added to the powder phase. The adiabatic temperature (T_1), of this reaction can be calculated by the following equation:

$$\Delta H_{f,Al_2O_3} + \int_{T_0}^{T_m,Al_2O_3} C_{P,Al_2O_3}\,dT + V_m \Delta H_{m,Al_2O_3} + \int_{T_m,Al_2O_3}^{T_1} C_{P,Al_2O_3}\,dT + 3\int_{T_0}^{T_1} (3C_{P,Ni} + 9C_{P,Al} + xC_{P,TiB_2})\,dT = 0 \quad (2)$$

where ΔH_f is the heat of formation, T_m is the melting point, V_m is the mole fraction of molten Al_2O_3 at its melting point, C_p is the heat capacity and ΔH_m is a latent heat of fusion. On the basis of the DTA result shown in Fig. 7, an initial temperature (T_0) of 933 K (the melting point of aluminium) was used in the calculation. Then, the adiabatic temperature of the system was calculated as a function of the content of TiB_2 in the [NiO + TiB_2] powder blend (Fig. 8). The adiabatic temperature shows a con-stant decrease with increasing the TiB_2 content until it reaches a plateau at the melting point of Al_2O_3. The transfer of Al_2O_3 from a liquid phase to a solid phase was calculated to begin at 25 vol % TiB_2. The minimum TiB_2 content to induce the spontaneous infiltration was then estimated to be in the range of 25–40 vol %, although the practical minimum TiB_2 content required for the infiltration was 15–20 vol %. This means that the calculated adiabatic temperature was higher than the maximum temperature attained in the experiment. An adiabatic system was assumed for the calculation, however this assumption may not be valid in practice and the dissipation of heat should be taken into account. Nevertheless, this calculation does reproduce the fundamental trend of the shift from non-infiltration to fully-infiltrated with an increase in the TiB_2 content.

4. Conclusions

Spontaneous infiltration of the [NiO + TiB_2] powder blend with molten aluminium to obtain Al_2O_3 matrix composites was attempted at 1673 K. The results obtained in this experiment were:

(1) The addition of TiB_2 particles assisted the spontaneous infiltration when the content of TiB_2 particles in the [NiO + TiB_2] powder blend was more than 20 vol %, whereas the infiltration hardly occurred at TiB_2 contents less than 15 vol %.

(2) The specimens mainly consisted of continuous Al_2O_3, TiB_2 particles and Al_3Ni after the *in situ* reaction. Gaps between the TiB_2 and Al_2O_3 were filled by the Al_3Ni.

(3) The reaction between NiO and aluminium is initiated at the melting point of the aluminium.

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