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Microstructure and mechanical properties of reaction hot pressed Al_xCo_y/Al_2O_3 composites

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Abstract

Al_2O_3/Al_xCo_y composites have been fabricated by reaction hot-pressing of milled powder mixtures containing Al, Co_2O_3 and Al_2O_3 at 1450 °C in Ar atmosphere under 30 MPa. The intermetallic/ceramic ratio of Al_2O_3/Al_xCo_y composites was adjusted by adding Al_2O_3 to the starting mixture. The effect of Al to Co_2O_3 ratio in the starting powders on phase development, microstructure and mechanical properties has been investigated. The fracture modes are different with the increase of the Al content. The metal oxide (Co_2O_3) was in situ reduced by Al to form Al_xCo_y aluminides, dispersed in the ceramic matrix. The improvements in bend and fracture strength can be attributed to the ductile failure of the fine Al_xCo_y particles. The maximum bending strength and fracture toughness were 513 MPa and 5.2 MPa $m^{1/2}$, respectively.

Keywords: B. Composites; C. Mechanical properties; D. Al_2O_3; In situ synthesis

1. Introduction

In the last decades, considerable efforts have been devoted to improve the mechanical properties of Al_2O_3 ceramics, especially their fracture toughness. By adding metallic reinforcements, such as Ni, Co, Cu, Al [1–5], the mechanical properties are significantly improved. However, the reinforcement approach is limited by the poor wetting of metallic melts on ceramics and the poor oxidation and corrosion resistance of metals. Intermetallic compounds obtained by in situ reaction synthesis may possibly overcome these shortcomings.

Among the reactive processing techniques, the thermite reaction synthesis is a low-cost and simple technology of in situ manufacturing of aluminide/alumina composites. The process involves the chemical reaction of raw materials, like aluminum and transition metal oxides (e.g. Fe_2O_3, TiO_2, NiO) to produce FeAl–Al_2O_3, Ti_3Al–Al_2O_3, NiAl–Al_2O_3 composites [6–9]. As a result, the fine and thermodyamically stable intermetallic reinforcements produced by in situ reaction have a stronger interfacial bond with the ceramic matrix. In the present work, the reaction process between Al and Co_2O_3 has been investigated. The reaction can be written as

$$Al + Co_2O_3 \rightarrow Al_xO_y + Al_2O_3 + \Delta H \quad (1)$$

where ΔH is the heat generated by the reaction. In order to control the reaction rate and maximum heat during reaction synthesis and adjust the content of aluminides, Al_2O_3 powders were added in the starting mixtures. Al_2O_3/Al_xCo_y composites with different x to y ratio have been prepared. The microstructural characteristics will be described in detail. Furthermore, we discuss the effects of the dispersion of Al_xO_y on the mechanical properties of Al_2O_3/Al_xCo_y composites at room temperature.

2. Experimental procedure

The processing route for Al_2O_3/Al_xCo_y composites is illustrated by the flow diagram in Fig. 1. Powder mixtures investigated consisting of Al (99.95%, 325 mesh), Co_2O_3 (99.52%, 1–5 μm) and γ-Al_2O_3 (99.98%, 0.35 μm) are summarized in Table 1. The powders were attrition milled for 8 h in ethanol–isopropanol (molar ratio at 1:4) using alumina balls, subsequently dried and passed through a 200

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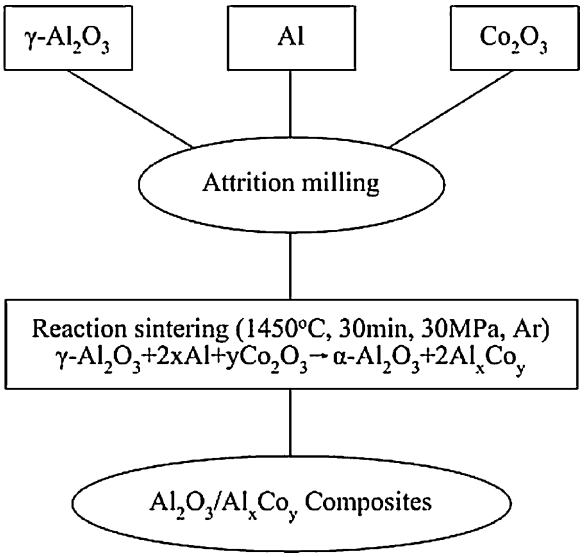

Fig. 1. Flow diagrams of the preparation Al_2O_3/Al_xCo_y composites processing route.

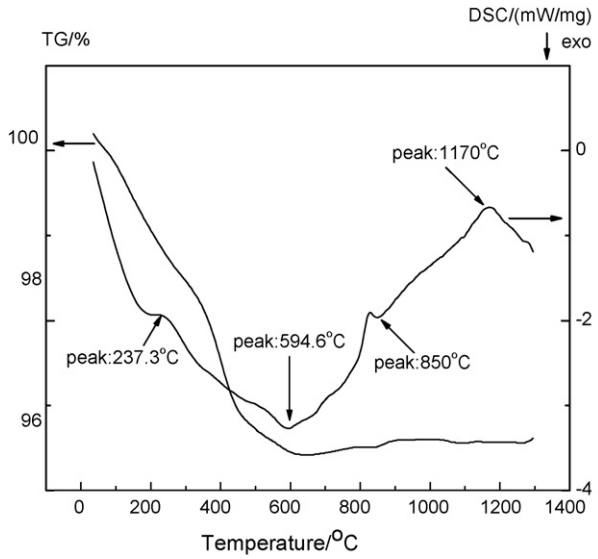

Fig. 2. TG-DSC micrograph of $Al_2O_3/Al–Co_2O_3$ composite powders.

mesh sieve. The powder mixtures were uniaxially hot pressed in a graphite die at 1450 °C by heating at 10 °C min^{-1}, under a pressure of 30 MPa, in Ar for 30 min.

Phase identification was determined by X-ray diffraction (XRD; Rigaku, Tokyo, Japan) in the 2θ range from 10° to 80° with Cu K_α radiation. Thermal analysis of the precursor was carried out from ambient temperature to 1300 °C by thermogravimetry (TG) and differential scanning calorimetry (DSC) (TG-DSC; Model STA 449C, Netzsch, Germany). The heating rate was 10 °C min^{-1}. The fracture surface morphology was observed by scanning electron microscopy (SEM; JSM-6700F, JEOL, Japan). The bend strength was measured using three-point bending test with a span length of 20 mm and a crosshead speed of 0.5 mm min. The fracture toughness of the composites was estimated by the Vickers indentation method under a load of 49 N.

3. Results and discussion

The reaction sequence of the Al, Co_2O_3 and γ-Al_2O_3 powder mixtures includes the aluminothermic reduction of the metal oxide as well as the formation of the corresponding aluminides. Additionally, Al_2O_3 is formed in situ as a product from the reaction between Co_2O_3 and Al. The TG-DSC results of the composite powder mixtures using a heating rate of 10 °C min^{-1} are shown in Fig. 2. Two exothermic and two endothermic peaks were observed in the DSC curves. The first weak endothermic peak at about 237.3 °C is believed to correspond to the desorption of the surface adsorbed water, while the second one (about 1170 °C) may possibly be related to the melting of Al_xCo_y. As discussed later, the first exothermic peak (about 594.6 °C) is most likely related to the aluminothermic reactions between Al and Co_2O_3, and the second (about 850 °C) to a reaction between nascent Co and excess Al to form Al_xO_y [5,10]. The reactions can be written as

$$2Al + Co_2O_3 \rightarrow 2Co + Al_2O_3 + \Delta H_1 \quad (2)$$

$$xAl + yCo \rightarrow Al_xO_y + \Delta H_2 \quad (3)$$

where ΔH_1 is the enthalpy of the aluminothermic reaction; ΔH_2 is the enthalpy of aluminide formation. The high enthalpy of the aluminothermic reaction (ΔH_1) can easily be controlled during the reaction synthesis by adding Al_2O_3 in the precursor powders.

Table 1
Starting powder compositions

Designation	Starting composition (mol)		
	Al	Co_2O_3	Al_2O_3
AC1	0.050	0.025	0.1379
AC2	0.075	0.025	0.1313
AC3	0.100	0.025	0.1237
AC4	0.150	0.025	0.1114

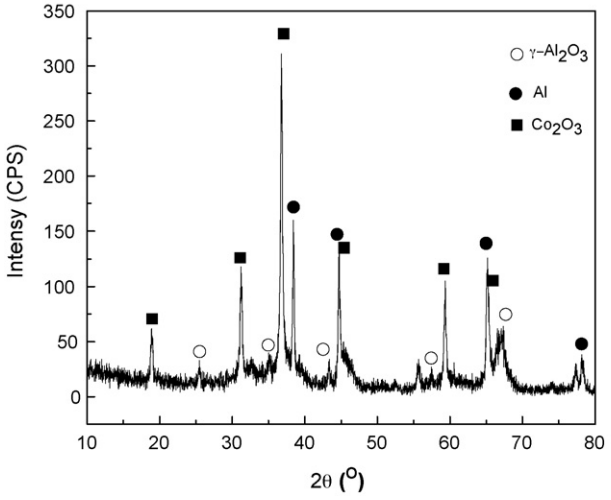

Fig. 3. The XRD patterns of the milled powders (8 h ethanol–isopropanol solution).

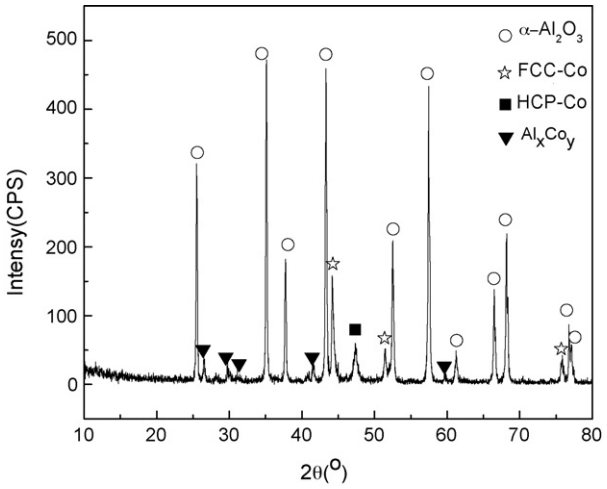

Fig. 4. The XRD patterns of Al_2O_3/Al_xCo_y composites (hot pressed, 1450 °C, 30 min, 30 MPa, in Ar).

The XRD pattern for the green powder mixtures and Al_2O_3/Al_xCo_y composite ceramics after hot-pressing are shown in Figs. 3 and 4, respectively. In Fig. 3, the XRD analysis indicates that there are no changes in the phase composition, which consists of Al, Co_2O_3 and γ-Al_2O_3 after milling. Fig. 4 shows that the specimens after reduction/hot processing at 1450 °C and 30 MPa for 1 h are mainly composed of α-Al_2O_3 and FCC-Co. Moreover, a small amount of HCP-Co and Al_xO_y is present.

SEM micrographs of the fracture surface of Al_2O_3/Al_xCo_y composites are shown in Fig. 5(a)–(d). The fracture phenomenology changes with the increase of Al-content. Fig. 5(a) shows the fracture surface to be mainly intergranular in the AC1 composite, because Al and Co_2O_3 are in stoichiometric proportion and the nascent Co particles are physico-chemically incompatible with the Al_2O_3 matrix. Intergranular and transgranular types coexist in the AC2 and AC3 composites, while transgranular is the main fracture mode, due to the strong interfacial bonding between the Al_2O_3 matrix and Al_xCo_y obtained by in situ reaction synthesis. Further, the intergranular fracture in AC4 composite is due to the relaxation of compressive thermal residual stresses and grain coarsening. The particle-size distribution of the Al_2O_3/Al_xCo_y composites appears very large, with maximum size of Al_2O_3 grains up to 5–6 μm. Combined with Fig. 2, the abnormal growth of the grains may result from the local overheating produced by the thermite reaction. However, in situ formed Al_2O_3 and Al_xCo_y from the reaction between the metal oxide and Al is relatively small.

Table 2
Mechanical properties of Al_2O_3/Al_xCo_y composites (hot pressed, 1450 °C, 30 min, 30 MPa, in Ar)

Designation	Bending strength (MPa)	Fracture toughness (MPa $m^{1/2}$)	HV
AC1	513 ± 18	4.5 ± 0.2	1432 ± 16
AC2	480 ± 21	4.2 ± 0.2	1418 ± 10
AC3	476 ± 34	4.8 ± 0.1	1338 ± 17
AC4	364 ± 23	5.2 ± 0.1	1264 ± 21

The mechanical properties of the Al_2O_3/Al_xCo_y composites summarized in Table 2 depend notably on the Al content in the starting powders. The bending strength decreases as the content of aluminum increases. In the present system, compressive thermal residual stresses induced by the thermal expansion coefficient mismatch between the matrix Al_2O_3 grains and the

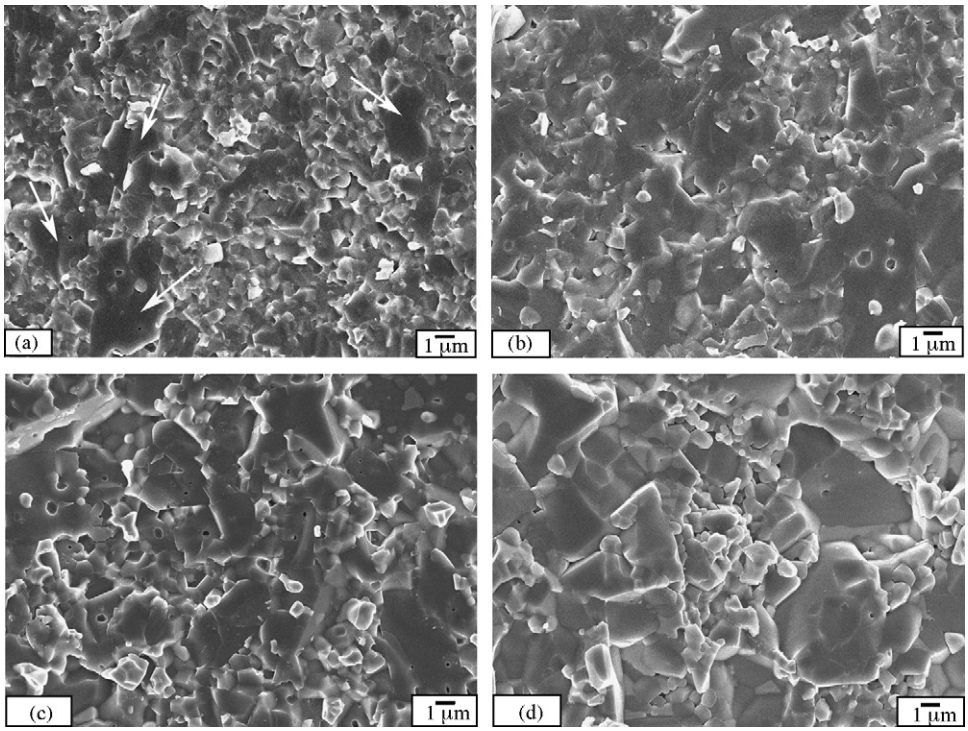

Fig. 5. SEM micrographs of the fracture surface for Al_2O_3/Al_xCo_y composites (hot pressed, 1450 °C, 30 min, 30 MPa, Ar): (a) AC1, (b) AC2, (c) AC3 and (d) AC4. The arrows indicate the positions of transgranular type of the samples.

dispersed Al_xCo_y are a primary factor for the bending strength of the composites. On the other hand, the reinforcement phases produced by the in situ reaction are thermodynamically compatible with the matrix [11–13], so the strong interfacial bond is also beneficial to the bending strength. However, the increase of the content of the plastic phase Al and the intermetallic phase will decrease the bending strength of Al_2O_3/Al_xCo_y composites and plays a dominant role. The synergy of these factors determines bending strength. The room-temperature Vicker's hardness of Al_2O_3/Al_xCo_y composites decreases as the Al-content increases as shown in Table 2. The observed hardness variations with increasing Al-content coincide with the hardness changes that are calculated by the composite rule [14]. The fracture toughness first decreases slightly by increasing Al-content from AC1 to AC2, then increases noticeably. The relaxation of thermal residual stress decreases the fracture toughness, whereas the increase of fracture toughness at high Al-content seems to be attributed to the increase of the plastic metal and intermetallic phases. In conclusion, the cooperative action of the compressive thermal residual stresses and the content of the metal and intermetallic phases determine the fracture toughness of Al_2O_3/Al_xCo_y composites.

4. Conclusions

It has been shown that Al_2O_3/Al_xCo_y composites can be prepared by in situ displacement reaction between Al and Co_2O_3. Al_2O_3/Al_xCo_y composites were obtained by hot-pressing at 1450 °C in Ar atmosphere under 30 MPa. The composites were found to have a wide grain size distribution. The fracture morphology shows transgranular fracture as the main fracture mode, indicating a strong interfacial bond between Al_2O_3 and Al_xO_y. The maximum bending strength and fracture toughness achieved were 513 MPa and 5.2 MPa $m^{1/2}$, respectively.

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