

Effect of Cr_2O_3 addition on microstructural evolution and mechanical properties of Al_2O_3

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Abstract

The effects of chromia (Cr_2O_3) additions on the microstructural evolution and the mechanical properties of alumina (Al_2O_3) were investigated. When small amounts ($< 5 \text{ mol}\%$) of Cr_2O_3 were added in samples hot pressed at 1500°C , the grain size distribution became bimodal; large platelike grains were dispersed in a relatively small grained matrix. The large grains were composed of a core region that is free of Cr and a surrounding shell region rich in Cr. The interface between the core and the shell was composed of misfit dislocations. The high diffusion rate of Cr ions through the surface of alumina was attributed to this microstructural evolution. The mechanical properties of the specimens were strongly influenced by this microstructural change. The fracture toughness and the flaw tolerance (R-curve behavior) of Al_2O_3 were improved markedly by the formation of the large platelike grains. The hardness and the elastic modulus also increased, however, the fracture strength decreased by the addition of Cr_2O_3 . © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3 ; Cr_2O_3 ; Fracture toughness; Microstructure-final; Strength

1. Introduction

Alumina (Al_2O_3) is one of the most widely used ceramic materials because of its excellent physical and thermomechanical properties.¹ The role of microstructure on the mechanical properties of Al_2O_3 is now well established. Like most other ceramics, the strength of Al_2O_3 is determined by a critical flaw in the material which is commonly proportional to the size of the grains. Therefore, the strength is high when the microstructure of the Al_2O_3 is fine and homogeneous. In this case, however, the fracture toughness of the material is generally low.^{2,3} The fracture toughness of ceramic materials, including Al_2O_3 , increases when large elongated or platelike grains are randomly dispersed in a fine-grained matrix. During the fracture process, these large grains resist crack propagation effectively, like whiskers or platelets in composite materials.^{4–7}

There have been many studies aimed at controlling the microstructure of Al_2O_3 . Among those, the effects of sintering aids on the densification behavior and on the

microstructural evolution have been most thoroughly investigated.^{8–11} It is well known that small amounts of magnesia (MgO) suppress abnormal grain growth of Al_2O_3 during sintering, making the microstructure fine and homogeneous.^{12–14} Conversely, without MgO, abnormal grain growth generally occurs during the sintering of Al_2O_3 . Recently, much progress has been made to design the microstructure of Al_2O_3 by inducing the abnormal growth of grains in a controlled manner.^{15,16}

Despite some controversies in detail, it is generally agreed that the presence of second phases at the grain boundary (either intentionally added or not) is a necessary condition for the abnormal growth of Al_2O_3 grains.^{12–17} Therefore, the microstructure of Al_2O_3 has often been controlled by the addition of second phases, such as TiO_2 , MnO_2 or combination of SiO_2 and other oxides (Na_2O , CaO , SrO , and BaO).^{11,15,16} Addition of glass or in situ formation of aluminates was also found to be effective in controlling the microstructure of the Al_2O_3 .^{5–7} When a small amount ($\sim 1 \text{ wt}\%$) of calcium aluminosilicate glass was added, the Al_2O_3 had a bimodal grain size distribution with large elongated grains dispersed among fine matrix grains. The flaw tolerance of the specimens with bimodal size distribution was

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higher than that of the specimens with equiaxed grains.^{5,6} The formation of large aluminate platelets in Al_2O_3 grains was reported to increase the fracture toughness by about 50%.⁷ However, a large quantity of aluminates or the presence of glassy phases at the grain boundary might deteriorate the high-temperature mechanical properties and other unique physical properties of Al_2O_3 .

Chromia (Cr_2O_3) has long been used to improve the physical properties of Al_2O_3 .^{18–21} Different from the other additives mentioned above, Cr_2O_3 forms a solid solution with Al_2O_3 over the full range of compositions. The addition of Cr_2O_3 was found to increase the hardness, tensile strength, and thermal shock resistance of Al_2O_3 . Even though not thoroughly investigated yet, the improvements are believed to be closely related to the changes in microstructure. Rapid migration of the grain boundaries due to the coherency strain energy was proposed to be a possible reason for the changes in microstructure.^{22,23} However, the relationship between the microstructure and the mechanical properties was not systematically investigated, probably because of the difficulties in obtaining fully dense bodies. When the Cr_2O_3 is added, the sinterability of Al_2O_3 decreased markedly due either to the evaporation of the Cr-containing species or to the change in the sintering mechanism.^{24,25}

In the present study, we investigated the microstructural evolution and the effects of microstructure on the mechanical properties of Al_2O_3 containing Cr_2O_3 up to 10 mol%. To obtain bodies with full density, hot pressing technique was employed using relatively large starting powders. The microstructural and compositional evolution of the specimens containing different amounts of Cr_2O_3 was monitored. Mechanical properties, such as flexural strength, fracture toughness, hardness, elastic modulus, and R-curve behavior, were measured and related to the variations in the microstructure.

2. Experimental procedure

Commercially available Al_2O_3 (99.9%, ALM 43, Sumitomo, Tokyo, Japan) and Cr_2O_3 (99%, Junsei Chemical, Tokyo, Japan) were used as starting powders. The average particle size of the Al_2O_3 was about 3 μm and the major impurities were Na_2O (0.03 %), SiO_2 (0.05%), and Fe_2O_3 (0.01 %). Up to 10 mol% of Cr_2O_3 ($\sim 1 \mu\text{m}$) was added to the Al_2O_3 and ball milled for 12 h using distilled water and alumina balls as media. After drying and sieving, the mixtures were hot pressed with an applied pressure of 40 MPa in a vacuum at 1500°C for various periods of time.

The microstructure of the specimens was observed by SEM after thermal or chemical etching of the polished surface. Grain size distributions were measured using an

image analyzer. The composition and the morphology of individual grains were observed with a STEM (CM 20, Philips, Netherlands) equipped with energy dispersive X-ray spectroscopy.

Specimens for mechanical tests were cut from the hot-pressed disks and machined into a bar shape with dimensions of $3 \times 4 \times 25 \text{ mm}$. All the specimens were ground with a diamond wheel and polished with diamond slurries down to 1 μm . Edges of all the specimens were beveled to minimize the effect of stress concentration due to machining flaws. The strength was measured using a four-point bending configuration with a cross-head speed of 0.5 mm/min, and inner and outer spans of 10 and 20 mm, respectively. The fracture toughness was measured by the indentation-strength method. After indenting on the tensile surface with an applied load of 196 N, fracture strength was measured with the four-point bending configuration mentioned above. The equation of Chantikul et al.²⁶ was used to calculate the fracture toughness. The hardness and the elastic modulus of the specimens were measured with a micro-indentor with an applied load of 200 g and by the sonic resonance method,²⁷ respectively. For the flaw tolerance (R-curve behavior) characterization, indentation loads of between 9.8 and 196 N were employed. The relationship between the indentation load and the strength after indentation was used to estimate the R-curve behavior of the specimens.²⁸ At least 5 specimens were tested for each set of experimental conditions.

3. Results and discussion

The microstructure of Al_2O_3 specimens hot pressed at 1500°C for 1 h was changed significantly by addition of Cr_2O_3 . The microstructures of the specimens (perpendicular to hot pressing direction) containing different amounts of Cr_2O_3 are shown in Fig. 1(A)–(D). All the specimens had higher than 98.0% of theoretical density. The microstructure of the pure Al_2O_3 indicates that all the grains have angular shape, as shown in Fig. 1(A), implying the presence of liquid phase at the grain boundary.^{8,29–31} When 2 mol% Cr_2O_3 was added and processed under the same conditions, the size of grains became larger and very large grains up to 30 μm were formed, Fig. 1(B). As the amount of Cr_2O_3 was increased to 5 mol%, the size of matrix grains grew even larger, while that of abnormally large grains became smaller, as seen in Fig. 1(C). With further addition of Cr_2O_3 to 10 mol%, the abnormally large grains were not detected as shown in Fig. 1(D).

From these micrographs, the size distributions of the grains were measured on the basis of areal fraction and are shown in Figs. 2(A)–(D). The grain sizes of the undoped specimen followed a log-normal distribution frequently observed in other Al_2O_3 specimens.¹³ When 2

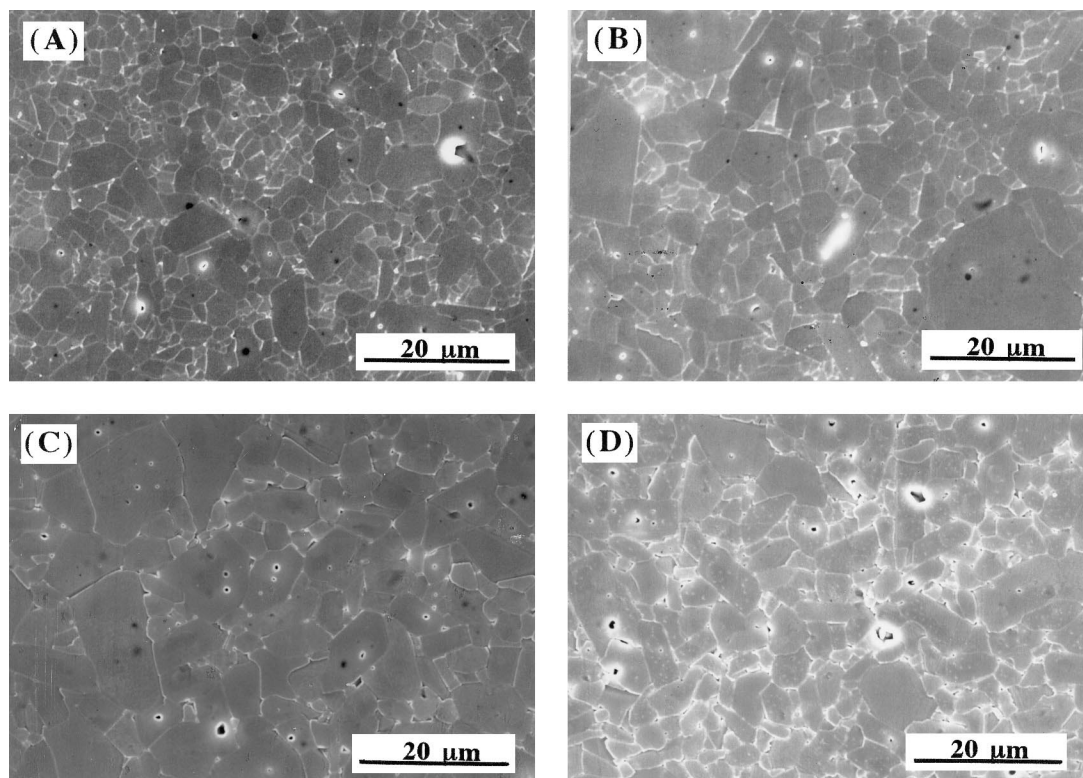


Fig. 1. Morphologies of Al_2O_3 specimens hot pressed at 1500°C for 1 h containing (A) 0 mol%, (B) 2 mol%, (C) 5 mol%, and (D) 10 mol% of Cr_2O_3 .

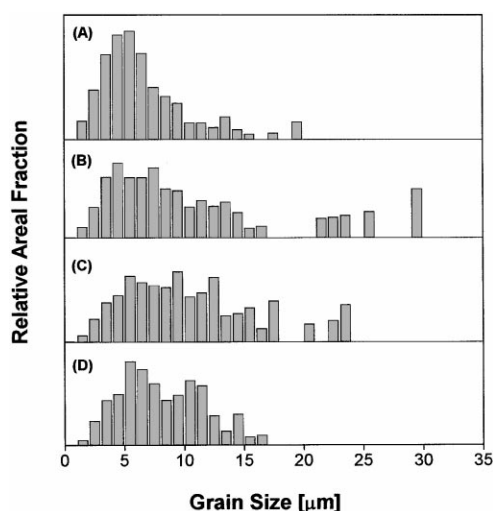


Fig. 2. Grain size distribution of Al_2O_3 specimens hot pressed at 1500°C for 1 h containing (A) 0 mol%, (B) 2 mol%, (C) 5 mol%, and (D) 10 mol% of Cr_2O_3 .

mol% Cr_2O_3 was added, the grains had a bimodal size distribution as shown in Fig. 2(B). In addition, the average size of matrix grains also increased compared to the undoped specimen. As the amount of Cr_2O_3 was increased to 5 mol%, the grains still exhibited a bimodal size distribution. However, the size of the abnormally large grains was diminished a little and the size distribution of the matrix grains became even wider [Fig. 2

(C)]. When the amount of Cr_2O_3 addition was increased to 10 mol%, the abnormally large grains were not formed as can be confirmed in Fig. 2(D).

The grains, especially the abnormally large grains, had an anisotropic morphology with respect to the hot pressing direction. A polished cross-section parallel to the hot pressing direction of a specimen containing 2 mol% Cr_2O_3 , shown in Fig. 3(A), suggests that the large grains have a platelike morphology. The grains were aligned perpendicular to the hot pressing direction. Another interesting feature of the microstructure is that the grains are composed of two regions of core and shell, as indicated by arrows in Fig. 3(A). The interface between the core and the shell regions was parallel to the boundary of the grains. Such an interface was also seen in a TEM micrograph, in Fig. 3(B). Analyses on the electron diffraction patterns showed that the flat plane in Fig. 3(B) is (0001) plane as expected.^{8,10}

The formation of the large grains is believed to be related to the increased growth rate of Al_2O_3 grains caused by the Cr ions. The diffusion coefficient of Cr through the surface of Al_2O_3 is several orders of magnitude higher than that through the bulk.^{32,33} Therefore, the surface of Al_2O_3 grain adjacent to Cr_2O_3 becomes rich with Cr ion at an early stage of sintering. Those grains rich with Cr ion are deemed to have grown faster than other grains because of the coherency strain energy at the grain boundary.^{22,23} Energy dispersive spectroscopy

(EDS) analyses actually illustrated that the shell region was rich in Cr while the core region was completely free of it. The interface between the core and the shell region was composed of misfit dislocations as illustrated in Fig. 3(C). These microstructural and compositional observations indicate that the large platelike grains were formed by the presence of heterogeneously distributed

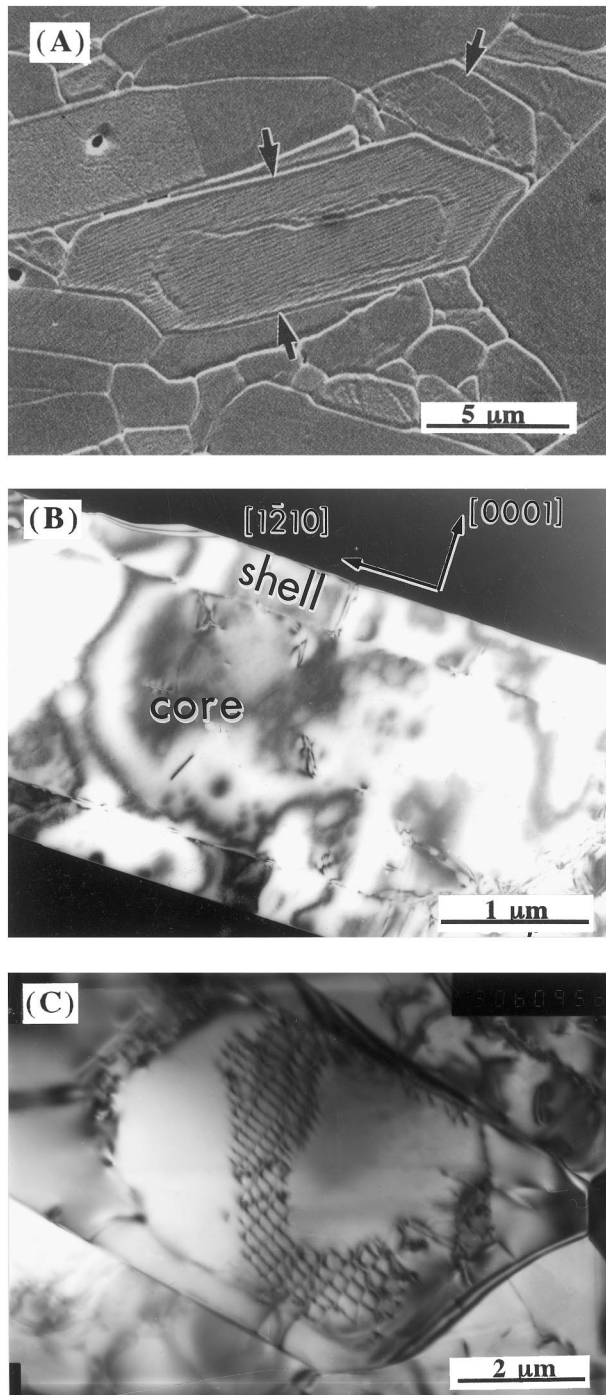


Fig. 3. Morphology of abnormally large grains; (A) parallel to the hot pressing direction, (B) TEM micrograph showing the interface between the core and the shell regions, and (C) TEM micrograph showing misfit dislocations at the interface.

Cr_2O_3 . Therefore, when a small amount (≤ 5 mol%) of Cr_2O_3 was added, only a small fraction of grains grew rapidly to become platelike grains, resulting in the bimodal grain size distribution. On the other hand, when a large amount of Cr_2O_3 was added, all the grains grow rapidly to become relatively large.

These microstructural evolutions had significant effects on the mechanical properties of the Al_2O_3 . The strength and the fracture toughness of the specimens with different amounts of Cr_2O_3 are shown in Fig. 4. The strength decreased by the addition of Cr_2O_3 , apparently due to the increase in grain size.² However, the fracture toughness increased when 2–3 mol% Cr_2O_3 was added. The fracture toughness of Al_2O_3 has been previously observed to increase when the average grain size became larger.³ The formation of large elongated or platelike grains was also reported to increase the fracture toughness of the material.^{5–7} In both cases, the bridging of the propagating cracks by the large grains was responsible for those increases.^{34–37} In the present experiment, the average grain size increased and the large platelike grains were formed at the same time when 2–3 mol% Cr_2O_3 was added. Therefore, both the platelike grains and the matrix grains might have played a major role in increasing the fracture toughness. However, when 5 mol% Cr_2O_3 was added, the fracture toughness decreased to the level of the undoped specimen,

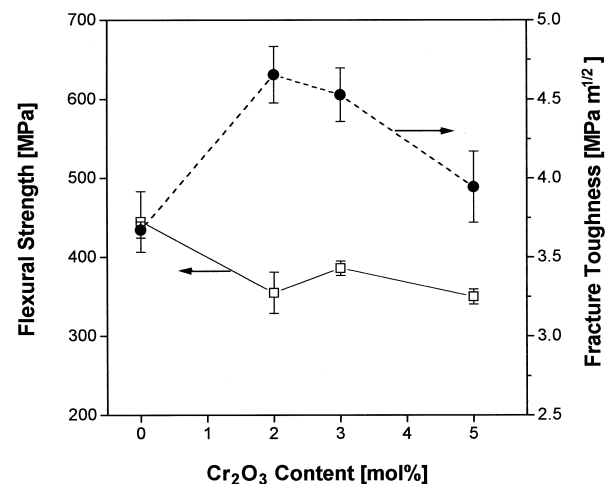


Fig. 4. Strength and fracture toughness of the Al_2O_3 specimens with different amounts of Cr_2O_3 .

Table 1

Summary of mechanical properties of Al_2O_3 contain different amount of Cr_2O_3

Cr_2O_3 contents	K_{IC} ($\text{MPa m}^{1/2}$)	MOR (MPa)	E (GPa)	Hv (kg/mm^2)
0 mol%	3.7 ± 0.05	445 ± 39	407 ± 2	1681 ± 20
2 mol%	4.7 ± 0.18	355 ± 26	411 ± 4	1738 ± 26
3 mol%	4.5 ± 0.17	386 ± 10	412 ± 4	1714 ± 35
5 mol%	3.9 ± 0.22	350 ± 10	402 ± 3	1653 ± 37

in spite of the increase in the average size of the matrix grains [Fig. 2 (C)]. The increase in fracture toughness, therefore, is mainly attributable to the formation of the large platelike grains. Other mechanical properties, hardness and elastic modulus, of the specimens are listed in Table 1. The hardness and the elastic modulus were also improved when 2–3 mol% Cr_2O_3 was added as was the case of fracture toughness.

The flaw tolerance (R-curve behavior) was estimated from the relationship between the indentation load and the strength after indentation as shown in Fig. 5. The slope of the undoped Al_2O_3 was slightly lower than $-1/3$ (-0.298), implying a weak rising R-curve behavior of the material.^{26,28} Crack bridging by the matrix grains is apparently one of the main causes for this behavior.^{34,35} When 2 mol% Cr_2O_3 was added, the slope became much flatter to -0.243 , indicating additional interactions of the crack with the large platelike grains. On the other hand, the slope of the specimen containing 5 mol% Cr_2O_3 was about the same as that of the undoped specimen.

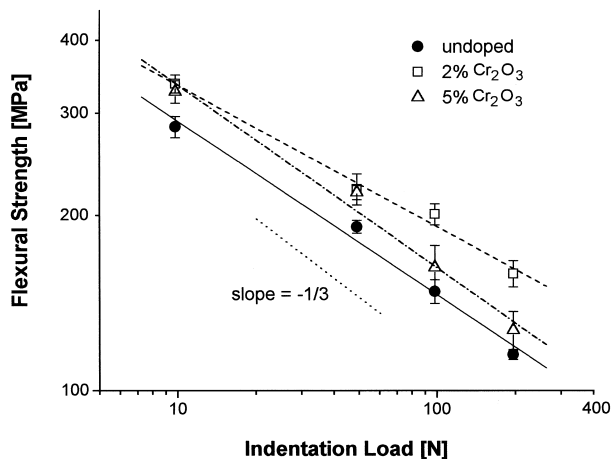


Fig. 5. Relationship between the indentation load and the indentation strength, showing flaw tolerance of the Al_2O_3 specimens containing different amounts of Cr_2O_3 .

The cause for the variations in the R-curve behavior is well illustrated by the crack paths generated by the indentation on the specimens as shown in Fig. 6(A)–(B). Even for the undoped Al_2O_3 , the crack path was not straight because of the crack interactions, such as crack deflection and crack bridging, with the matrix grains [Fig. 6(A)], leading to the rising R-curve behavior. The crack interaction became more intense when the large platelike grains had been formed by the addition of 2 mol% Cr_2O_3 , as shown in Fig. 6(B). These crack paths support that the increase in the fracture toughness is mainly due to the crack bridging by the platelike grains. Fracture surface of the specimen containing 2 mol% Cr_2O_3 is shown in Fig. 7. This micrograph illustrates that the fracture proceeded mostly by intergranular fracture and that the large platelike grains were pulled out during the fracture process. These micrographs support that the improvements in the fracture toughness and the flaw tolerance of Al_2O_3 by the addition of 2–3 mol% Cr_2O_3 are mainly due to the crack interactions with the large platelike grains.

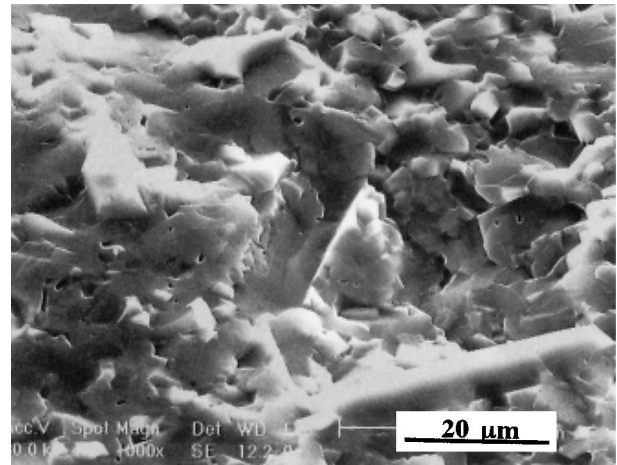


Fig. 7. Fracture surface of the Al_2O_3 specimen containing 2 mol% Cr_2O_3 .

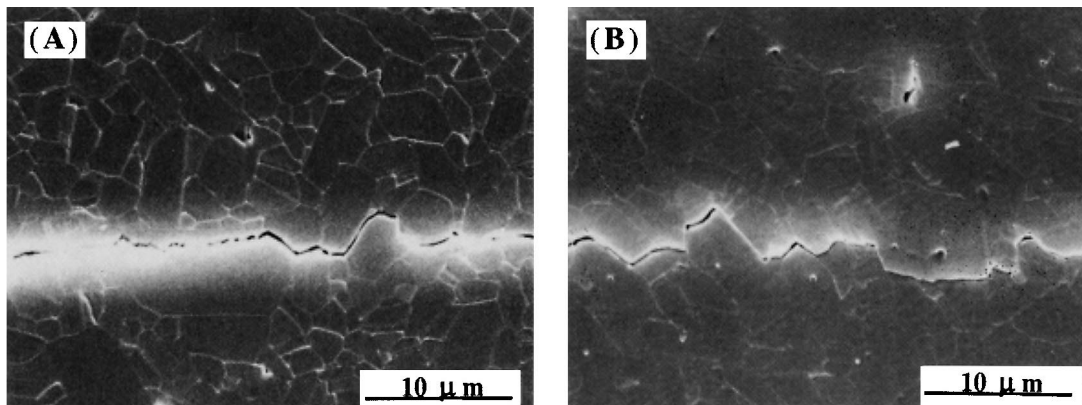


Fig. 6. Crack paths generated by indentation; (A) undoped Al_2O_3 and (B) Al_2O_3 with 2 mol% Cr_2O_3 .

4. Summary and conclusions

The effects of Cr_2O_3 addition on the microstructural evolution and the mechanical properties of Al_2O_3 were investigated. When a small amount of Cr_2O_3 (~ 2 mol%) was added, the grains became larger and bimodal in size distribution. The large grains had platelike shape and were composed of a core region that is free of Cr and a surrounding shell region rich in Cr. The interface between the core and the shell was associated with misfit dislocations. The high diffusion rate of Cr ions through the surface of Al_2O_3 was attributed to this microstructural evolution. The fracture toughness and the flaw tolerance of Al_2O_3 were improved remarkably by the addition of small amounts (~ 2 mol%) of Cr_2O_3 . Crack bridging by the large platelike grains was the main cause for the improvements. The hardness and the elastic modulus also increased, however, the fracture strength decreased by the Cr_2O_3 additions.

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