Ceramics International 23 (1997) 509–512

PII: S0272-8842(96)00062-4
0272-8842/97 $17.00+.00

The Effect of Chromium and Titanium Implantation on the Mechanical Properties of Polycrystalline Alumina: The Role of Residual Stress

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(Received 15 March 1996; accepted 8 May 1996)

Abstract: Mechanical properties of ion implanted ceramics are connected with the microstructure and the residual stresses introduced by implantation. In this work, studies on the implantation of chromium and titanium in alumina are reported. The residual surface compressive stress has been determined using an indentation technique, based on the method of Lawn and Fuller which deduces stress from the size of cracks around Vickers hardness indentation. The measurement of the mechanical properties, i.e. fracture toughness, in the treated surface, was undertaken using a Vickers indentation method. Finally, these implantations have been investigated by means of SEM and SIMS to study the eventual formation of chemical compounds in the implanted zone. For the two ions implantation, the increase of K_{1c} has been attributed to the compressive stresses. After heating, relaxation of residual stresses occurs in the two cases and TiO_2 formation in the case of titanium implantation. The oxide formation increases the fracture toughness by a compensation of the residual stresses relaxation. For chromium implantation the relaxation decreases the toughness. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Ion implantation in ceramics and insulating materials has been developed over the last few years. In the beginning, the studies focused on the nature of defects induced by implantation[1] and on phase transformations based on the reactivity of the chemical compounds induced in the uppermost layer by the ion beam. More recent studies have taken into account the damage and the residual stress induced by implantation, as well as the recovery processes afforded by thermal treatments which can explain their mechanical properties changes.[2]

The progressive damage of alumina in the implanted zone is attributed to an increase in concentration of the point and linear defects. A destruction of the crystalline order is often observed, due to an amorphization near the zone of maximum concentration of defects. This amorphization may occur at the surface if the fluence increases, which is easier with covalent than with ionically bonded ceramics. When the amorphization threshold is reached, a strong decrease of residual stress is observed, similar to the cases when these samples are subjected to heat treatments.[3]

An indentation technique described by Lawn and Fuller[4] was used to determine the residual stress in the implanted layers of the specimens. This technique involves careful measurements of the changes in the crack trace lengths of specimens between the implanted and un-implanted states. All the stresses are compressive in nature.[5]

The damage recovery process of alumina during the thermal treatment depends on the heating atmosphere. Under air or oxygen, the recovery begins at low temperature, irrespective of the implanted ions, initially at the aluminium sub-lattice, and subsequently at the oxygen sub-lattice.[1]

α-Al_2O_3, largely used in the ceramics industry, has been chosen in this work. α-Al_2O_3, a typical material containing both covalent and ionic bonds (ionicity $\approx 63\%$), which requires, to be amorphized, fluences higher than 10^{17} ions/cm^2 at room temperature and lower fluences at a temperature of 77 K.[6]

2 EXPERIMENTAL PROCEDURE

2.1 Sample preparation

Implantation studies were carried out on commercial polycrystalline α-Al_2O_3 (MATROC 995 F, purity 99.95% and grain size $< 3\,\mu m$). Samples were polished and annealed at 1200°C in air for 1 h to remove residual surface damage due to the mechanical polishing. Specimens were implanted at room temperature with 10^{17} ions/cm^2 at 110 keV with chromium and titanium ions. After implantation, thermal annealing treatments were performed in air for 1 h at 1200°C.

2.2 Fracture toughness

The Vickers indentation is particularly suitable to measure the toughness of brittle materials. Recently, Liang *et al.*[7] have proposed a unified formula which enables the determination of toughness in both cases of median or Palmqvist's cracks.

$$\frac{K_c\Phi}{Ha^{\frac{1}{2}}}\left(\frac{H}{E\Phi}\right)^{0.4}\alpha = \left(\frac{C}{a}\right)^{(C/18a)-1.51}$$

$$\alpha = 14\left[1 - 8\left(\frac{4\nu - 0.5}{1+\nu}\right)^4\right]$$

where K_c is the fracture toughness, H is the hardness of the material, ν is the Poisson's ratio, Φ is a constant close to 3, $2a$ is the indent diagonal, C is the length of the radial crack and E is the Young's modulus of the material.

The polycrystalline material used in this study is an industrial product and possesses a heterogeneous microstructure. This leads to a dispersion in the measured values of toughness. For this reason, the results showing a large deviation from the mean values are excluded in this study. The mean values derived give an indication of the changes to the material toughness.

2.3 Residual stress

Lawn and Fuller have recently suggested a relationship linking the modification of radial crack length to the level of stress σ_s in a surface layer of thickness d, taking into consideration the crack pattern produced by a standard "point" indenter, i.e. Vickers or Knoop.

Basically, the cracks have penny-like geometry, with their centres placed just at the contact point. They found the following relation:

$$1 - \left(\frac{C_o}{C}\right)^{\frac{3}{2}} = \frac{2\psi\sigma_s\sqrt{d}}{K_c}$$

where K_c is the substrate toughness, C_0 is the radial crack length at stress $\sigma_s = 0$, C is the crack length at stress σ_s, d is the thickness of the stressed layer and Ψ is a constant taken as unity (≈ 1) depending upon crack geometry. In the case where $C < C_0$, σ_s is negative, and the stresses are compressive.

Generally, implanted samples become amorphous and this leads to the enhancement of the toughness,[5] but the fluences used in this study are not sufficient to amorphize alumina. Hence, we should consider again the idea developed here that the toughness increase for the as-implanted samples is due to the compressive stresses induced by the implantation.

3 RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of fracture toughness with load for specimens implanted at room temperature with Ti^+ and Cr^+ (10^{17} ions/cm^2, 110 keV). Cracks occur only after a particular applied load. The fracture toughness values have been evaluated for different loads. Figure 3 shows residual stress vs load curves for the chromium and titanium implanted into alumina at room temperature. According to Burnett and Page,[2] the

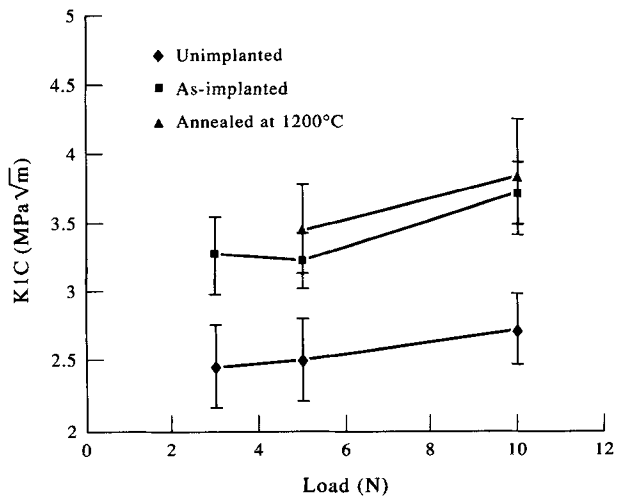

Fig. 1. Variation of fracture toughness with load of Al_2O_3 implanted with Ti^+ (10^{17} ions/cm$_2$, 110 keV).

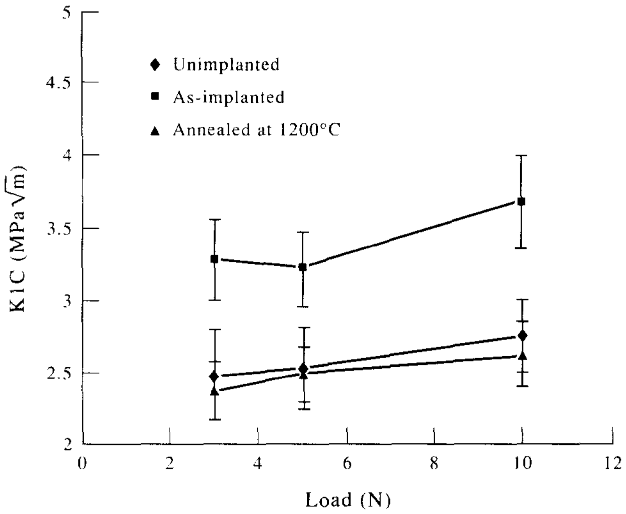

Fig. 2. Variation of fracture toughness with load of Al_2O_3 implanted with Cr^+ (10^{17}ions/cm_2, 110 keV).

residual stresses introduced in the implanted layer are compressive in nature. The results obtained with different indentation loads give slightly different values of stress. The method of Lawn and Fuller gives a lower value of stress than the method of Krefft and Eernisse.[8]

Figures 4 and 5 are SEM micrographs for alumina implanted with Ti^+ and Cr^+ (10^{17}ions/cm^2, 110 keV) and annealed at 1200°C. The formation of TiO_2 precipitate can be seen in the case of titanium implantation.[9]

Figures 6 and 7 show depth profiles for both titanium and chromium implantation and annealed at 1200°C.

The in-depth profile of Ti^+ is gaussian at room temperature. After annealing at 1200°C a displacement is observed on the profile, showing that a part of Ti has disappeared (Fig. 6). The migration of Ti to the surface induces an oxidation of this element at the surface, as shown in Fig. 4, in the form of titanium oxide precipitates.

The Cr distribution profile shows that Cr remains within the implanted layer and no temperature dependent effects are observed (Fig. 7),

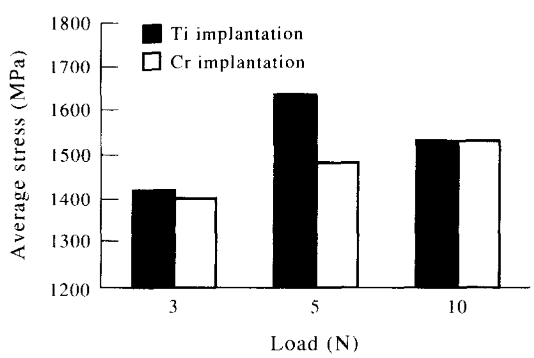

Fig. 3. Average residual surface stress with load for both titanium and chromium implantation. All stresses are compressive in nature.

Fig. 4. SEM micrograph of the implanted alumina (10^{17} Ti^+/cm^2, 110 keV) after thermal annealing in air at 1200°C.

and any chemical composite was created in the surface at 1200°C (Fig. 5).

The different variations of toughness can be explained as follows:

(a) (i) At room temperature: for the two ions used, the increase of toughness observed on the implanted samples which remain crystalline[10] could be attributed to the compressive stresses induced by implantation.
(b) (ii) At 1200°C: after the annealing temperature, two phenomena are induced simultaneously, namely stress relaxation and TiO_2 formation.
(c) — for Ti, the chemical compound formed during thermal treatments exhibits a higher toughness than alumina and contributes to an increase in the toughness.
(d) — for Cr, the toughness is restored to the original value without enhancement, because no new chemical compound is formed (Fig. 5).

Fig. 5. SEM micrograph of the implanted alumina (10^{17} Cr^+/cm^2, 110 keV) after thermal annealing in air at 1200°C.

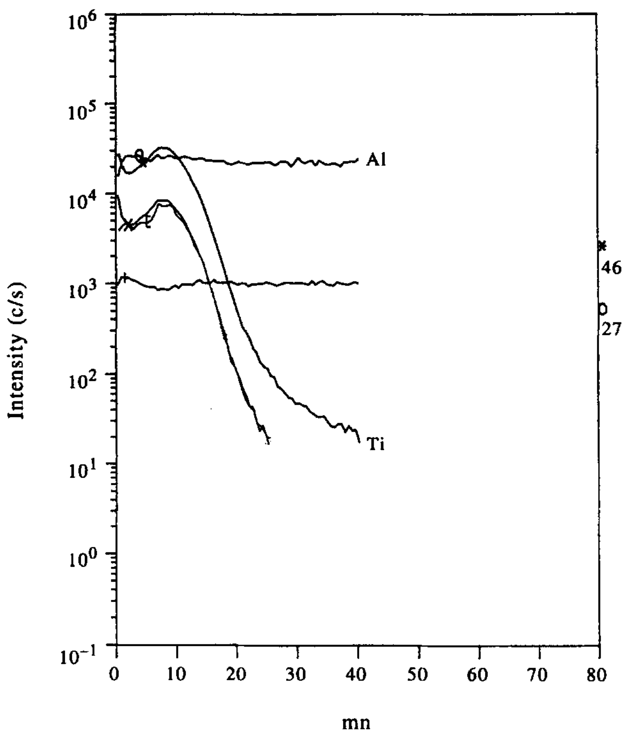

Fig. 6. In-depth profile of the titanium implanted into Al_2O_3 (10^{17} Ti^+/cm^2, 110 keV) and annealed in air at 1200°C.

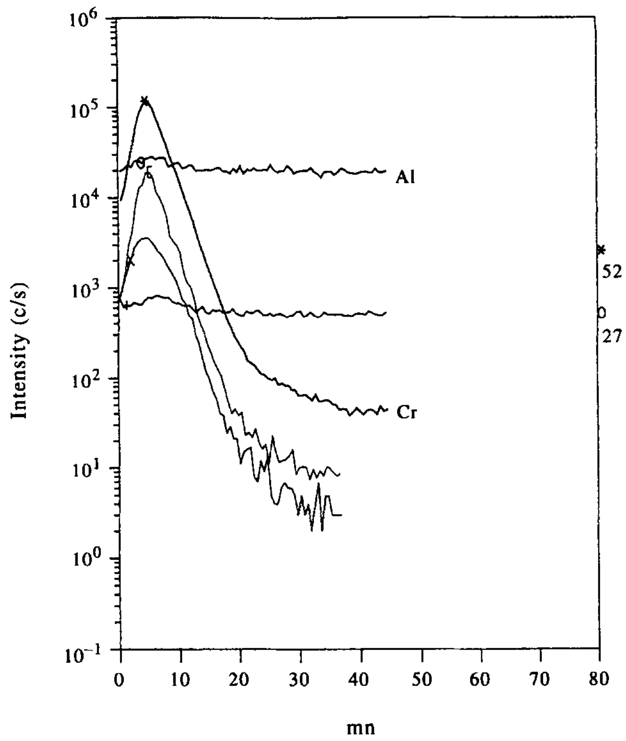

Fig. 7. In-depth profile of the chromium implanted into Al_2O_3 (10^{17} Cr^+/cm^2, 110 keV) and annealed in air at 1200°C.

4 CONCLUSION

The study has resulted in the following interesting observations:

- implantation induces surface stresses which are compressive in nature
- thermal annealing leads to relaxation of these stresses (oxides–oxides type) at the surface in the bulk on the implanted layer, depending on the nature of the ion used for bombardment.

To conclude, our studies have shown that ion implantation could be used to modify the mechanical properties, i.e. fracture toughness and surface morphology. However, it is also applicable to particular cases of ceramics to obtain interesting mechanical properties with or without heat treatment or in combination with very special and precise conditions of heat treatment to obtain desirable mechanical properties.

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