Possibility of enhanced strength and self-recovery of surface damages of ceramics composites under oxidative conditions

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Abstract

Oxidation of NiAl/α-Al$_2$O$_3$ composites provides the metamorphic surface layers consisting of boundary NiAl$_2$O$_4$ and Al$_2$O$_3$ grains with compressive stress. Strengthening and toughening from 515 MPa and 4 MPa m$^{1/2}$ (sintered) to ~655 MPa and ~6 MPa m$^{1/2}$ (oxidized) are enabled by a controlled development of the metamorphic layers at 1200–1300 °C. The reactivity of an oxidation product, NiO, with the matrix-Al$_2$O$_3$ and the rapid diffusion along the grain boundary repairs the damages on surfaces by filling and re-bonding the defects and cracks. The oxidation further progresses via the repaired defects to develop the metamorphic layers supporting them to enhance the recovery of the strength. The degraded strength of the material with defects, 150 MPa, is recovered to 531 MPa by the reparation against the limited recovery to 343 MPa by a thermal healing in Ar.
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1. Introduction

Chemical reactions such as nitridation and oxidation providing volume expansion are applicable to generate compressive surface stress for the improvement of mechanical properties of ceramics,[1–3] as well as the thermal shrinkage mismatch during cooling from the sintering temperatures for trilayer composites.[4,5] The authors have demonstrated the toughening of oxidized NiAl/α-Al$_2$O$_3$ composites, where the oxidation of NiAl forming NiAl$_2$O$_4$ induces the volume expansion providing the compressive stress attaining to -128 MPa.[1] The peculiarity of this process are the following reactions developing metamorphic layers by the diffusion of NiO along the grain boundary.[1,2]

$$2NiAl + 5/2O_2 = NiAl_2O_4 + NiO \qquad (1)$$

$$NiO + Al_2O_3 \,(grainboundary) = NiAl_2O_4 \qquad (2)$$
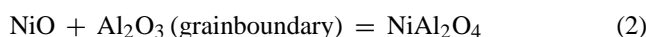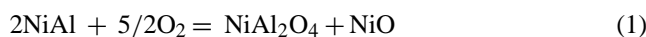
The resulting boundary network of NiAl$_2$O$_4$ in metamorphic layers efficiently converts the volume expansion to compressive stress to improve the fracture toughness from 4 MPa m$^{1/2}$ (as-sintered) to 6–8 MPa m$^{1/2}$ (oxidized).[1]

The reactivity of an oxidation product, NiO, with the matrix-Al$_2$O$_3$ through the rapid diffusion along the grain boundary strongly suggests the reparation of damages on surfaces by filling and re-bonding the micro-defects and micro-cracks.[1,2] The compressive surface stress would enhance the recovery of mechanical properties by supporting the repaired defects. Although the reparation is limited for the surface micro-damages and the response of chemical reactions is insufficient to the drastic failure with the rapid propagation of the cracks, it should be an alternative way to improve the reliability and to expand the of materials life of ceramics, because even the drastic fracture frequently occurs after certain concentrations of micro-defects on surfaces.

However, in the previous paper,[2] the strength was degraded for the material oxidized at 1400 °C, where the delamination of the oxidized layers was estimated as the reason for the degradation.[2] Then, in the present paper,

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the oxidation conditions contributing to toughening and strengthening have initially been studied. Then, the possibility of reparation is investigated for 10 %-NiAl/Al$_2$O$_3$ materials after introducing an artificial defect by a Vickers method.

2. Experimental

Precursors for 10 vol.%-NiAl/α-Al$_2$O$_3$ powder were synthesized by pouring a water/methanol solution (1:1) of NiCl$_2$ and AlCl$_3$ to the precipitant solution dispersing a fine α-Al$_2$O$_3$ powder (Taimei Chem.) for matrix at 70 °C. The amounts of the precipitants, C$_6$H$_5$COONH$_4$, N$_2$H$_5$Cl, and CH$_3$COONH$_4$ were the twice the stoichiometric requirement. The precipitate mixture, [Ni(N$_2$H$_4$)$_2$–Al] (C$_6$H$_5$COO)$_{3.7}$(OH)$_{1.7}$ + [α-Al$_2$O$_3$]$_{powder}$, was filtered and washed by the solvent. The dried precursor was thermally decomposed to Ni + amorphous-Al$_2$O$_3$ + C + [α-Al$_2$O$_3$]$_{powder}$ at 550 °C and converted to NiAl/α-Al$_2$O$_3$ at 1300 °C in Ar. The residual carbon was removed by a heat-treatment at 600 °C in air. The detail of the preparation process of the powder is described elsewhere.[1,6,7] The synthesized powder was press-formed to rectangular bars (5 mm × 5 mm × 22 mm), CIP-ed at 150 MPa, and sintered at 1600 °C for 2 h in Ar. The sintered materials were ground to test bars with the size of 3 mm × 3.5 mm × 17 mm, polished by 1 μm diamond- and 0.06 μm SiO$_2$-abrasives, and chamfered. The oxidation was performed at 1200–1400 °C in air. The bending strength (σ_f), Vickers hardness (H_V) and effective fracture toughness ($K_{C\text{-eff}}$) were measured. For the reparation test, an artificial defect was introduced on the center of the 3.5 mm-width surface by a Vickers indentation method. Reparation was examined at an oxidation condition of 1250 °C for 10 h in air. Two reference materials, annealed specimens in Ar at 1250 °C for 10 h and ground-off specimens in which the defect layer was removed to the depth of 500 μm, were prepared. The bending strength of the defected, repaired, annealed and ground-off specimens was compared.

The sintered density was measured by an Archimedes method. The degree of surface oxidation (ξ) was represented by $\left(1 - I_{oxd}^N / I_{sint}^N\right)$, where I_{oxd}^N and I_{sint}^N were the integrated X-ray diffraction intensity (Cu Kα radiation, 40 kV, 20 mA) of the (1 1 0) reflection of NiAl for the oxidized and sintered materials, respectively. The thickness of the metamorphic layers (δ) was measured on the SEM images of the fracture surface. The coverage of the surface (Ω) by the oxidation product was evaluated by analyzing the SEM images of the surfaces. The compressive stress (σ_R) of the matrix alumina was determined by an X-ray method using Fe Kα radiation (40 kV, 36 mA, exposure: 600 s, collimator: Ø 0.8 mm). The three-point bending test was conducted at a span of 10 mm and a crosshead speed of 0.5 mm min^{-1}. Vickers test was performed at a load of 196 N. The fracture toughness was calculated by Evans equation using the crack length deter-

mined by analyzing the SEM images at the magnification of ×150.

3. Results and discussion

3.1. Oxidation and formation of metamorphic layers

The oxidation of NiAl dispersed in the composites started above 900 °C. Almost complete oxidation to the depth of several μm (the penetration depth of the X-ray) was observed at 1400 °C for 5 h. Fig. 1 illustrates the temperature dependence of the degree of oxidation (ξ) in Arrhenius-style plots, where the determined ξ values are the averages in the thin surface within the depth of the penetration depth of X-ray. The oxidation slowly progressed below 1200 °C. Above this temperature, ξ increased almost in proportion to the reciprocal temperature at every oxidation time. The discontinuous dependence of ξ on reciprocal temperature indicated the change in the mechanism controlling the oxidation kinetics. The reaction-controlled formation of NiAl$_2$O$_4$ was properly assumed for the extremely low degree of oxidation at 1000 °C, because of the limited oxidation of NiAl powders up to 1050 °C.[2] The immediate oxidation of NiAl above 1200 °C indicated the diffusion-controlled mechanism.[2]

Fig. 2 shows the surface morphology of sintered and oxidized composites with the cracks propagated from the indentations. The dispersed NiAl grains with the size ranging 0.5–4.5 μm were observed for the sintered materials. Additionally, many NiAl grains smaller than 0.5 μm were observed in the high-magnification images. The NiAl grains larger than 2 μm were the result of conjugation. The grain size of the matrix-Al$_2$O$_3$ was 0.8–3 μm. Even at the same ξ, the morphology of the oxidized surface was different. At low temperatures, the network structures along the boundary of
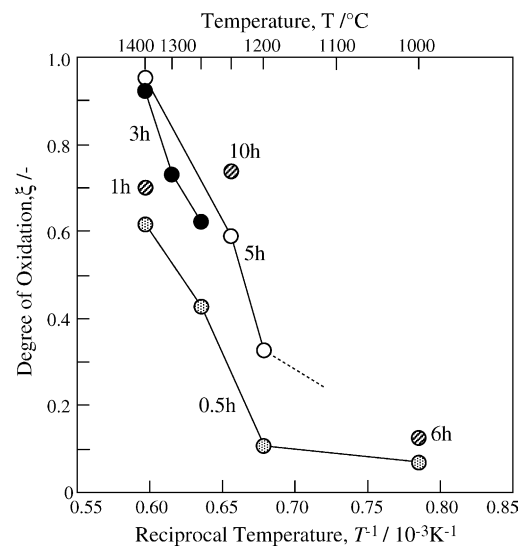

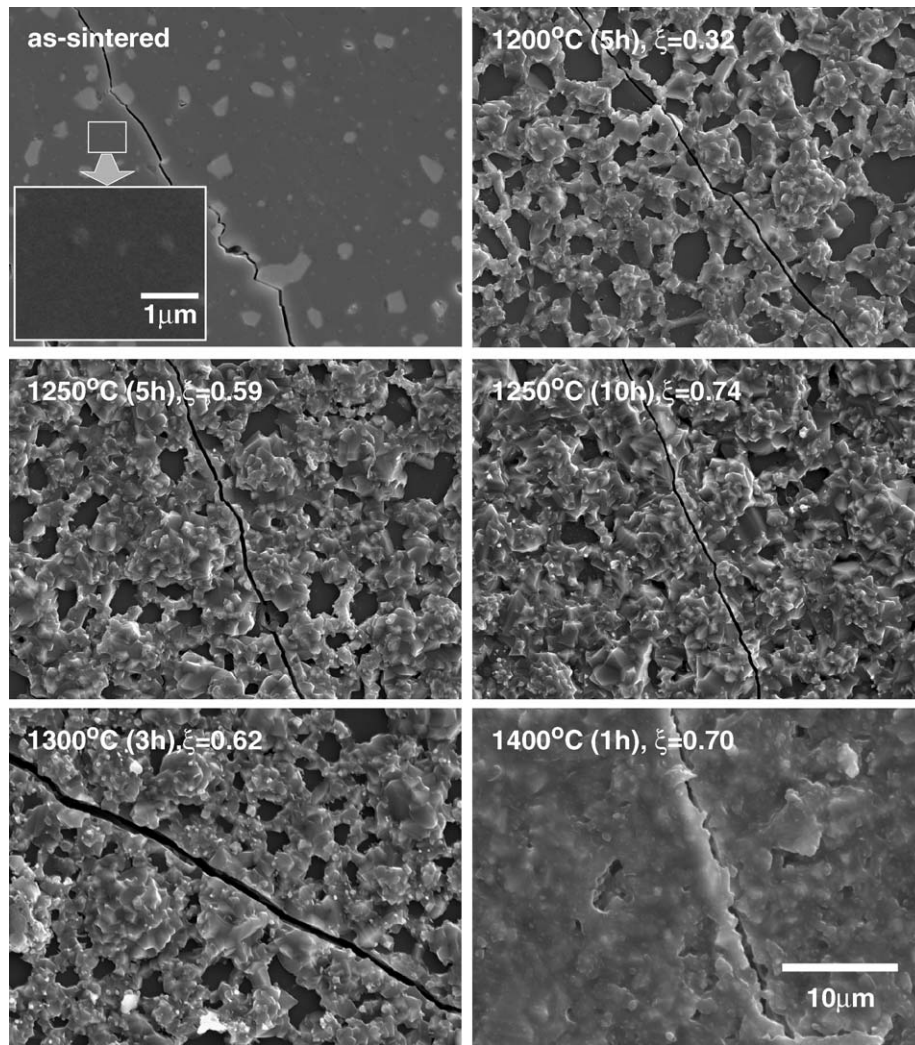Fig. 1. Temperature dependence of oxidation of NiAl in Al$_2$O$_3$-matrix composites.

Fig. 2. Surface morphology of sintered and oxidized materials.

the matrix-Al_2O_3 were dominant. At the high temperature, film structure was observed. The surface diffusion took place markedly at 1400 °C contrary to the dominant boundary diffusion at 1200–1300 °C.

Inside the surface developments, metamorphic layers were observed. Fig. 3 shows the diagonally cut image (left) and the expanded views at every depth from the surface. The top surface of the material oxidized at 1400 °C was completely covered by the $NiAl_2O_4$ film. At the depth of 10 and 20 μm, networks of $NiAl_2O_4$ (gray image) along the boundary of matrix were developed. At 40 μm, dispersed NiAl grains were observed.

Fig. 4 displays the thickness of the metamorphic layer (δ) and the coverage of the surface (Ω). The thickness and coverage increased with the progress in oxidation. However, the dependences of δ and Ω on ξ below 1250 °C were different from those at 1400 °C, despite ξ increased in accordance with the diffusion-controlled formation of $NiAl_2O_4$. The balanced increase in δ and Ω at 1200–1250 °C indicated the uniform development of the metamorphic lay-

ers. Contrary, the development of metamorphic layers at 1400 °C progressed after the almost complete coverage of the surface, because of the dominant surface diffusion at 1400 °C.

The growth of the surface films is promoted by the removal of NiO formed according to reaction (1) from the inner parts to the surface at 1400 °C. The diffusion of NiO toward the surface disturbs the development of the metamorphic layers in reaction (2). Then, it is considered that the high compressive stress due to the large volume expansion is restricted inside the thin metamorphic layers to increase the interfacial stress degrading the strength. On the other hand, in the temperature range from 1100 to 1300 °C, the enhanced strength of the oxidized materials is expected because of the thick metamorphic layers without removal of the oxidation products to the surface and the layer interface with the gradient on the degree of oxidation. The later peculiarity estimated from the above discussion was supported by X-ray diffractometry of the samples after removing the 40 μm metamorphic layers; both NiAl and $NiAl_2O_4$ were detected together for the material oxidized
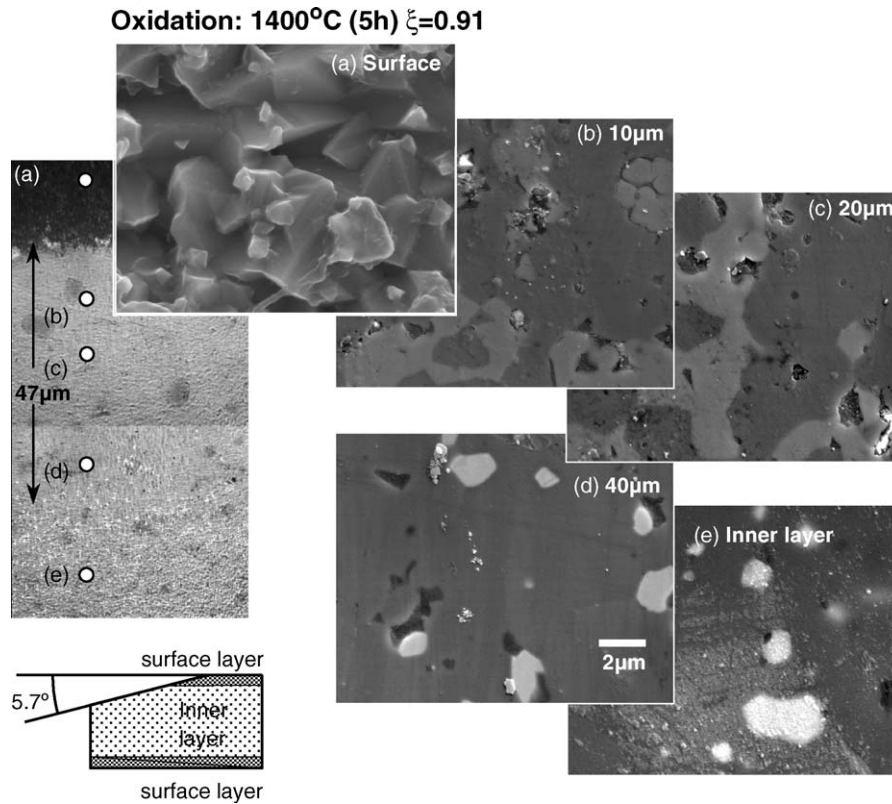
Fig. 3. Diagonally cut-off image of metamorphic layer (left) and morphology inside it.

at 1250 °C for 5 h ($\xi = 0.74$, $\delta = 43$ μm), while only $NiAl_2O_4$ was observed at 1400 °C for 3 h ($\xi = 0.85$, $\delta = 42$ μm).

3.2. Mechanical properties of oxidized composites

Fig. 5 shows the effect of the compressive stress (σ_R) to toughening. The compressive stress evidently contributed to toughening. The effective fracture toughness (K_{C-eff}) at

the temperatures showing the balanced increase in δ and Ω was closely related to σ_R (<1300 °C). However, K_{C-eff} above 1350 °C deviated. At 1400 °C, the thin metamorphic layer inefficiently repressed the crack propagation despite the high σ_R in the short oxidation time (1 h). Then the inevitably low K_{C-eff} was determined. The prolonged oxidation (3 and 5 h) promoted both the developments of thick metamorphic layers
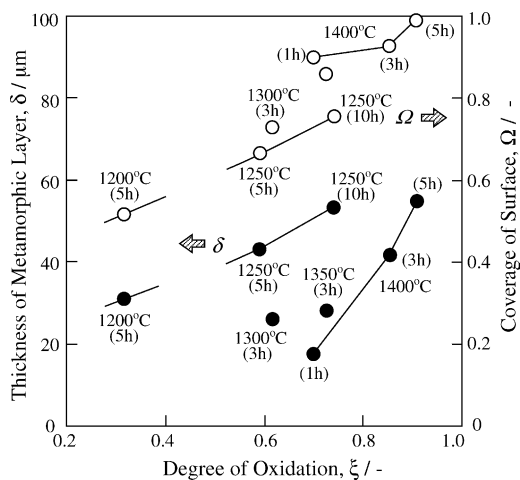

Fig. 4. Development of metamorphic layers and surface coverage the progress in oxidation.
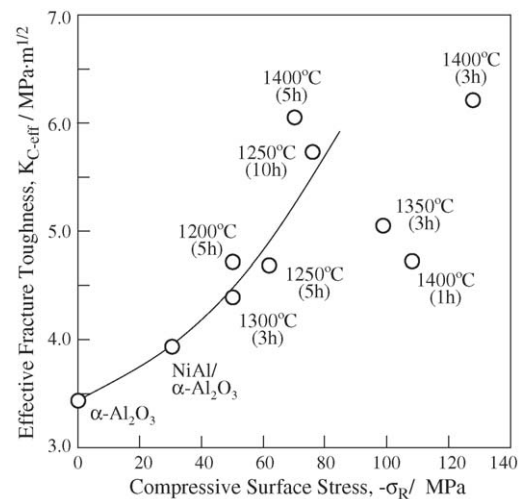

Fig. 5. Contribution of compressive stress in metamorphic layers to fracture toughness.

and surface films. The increased δ resulted in the higher $K_{C\text{-eff}}$ values, but σ_R for the material covered by the $NiAl_2O_4$ film completely (5 h) became irregularly low. The growth of thick films on the surface concealed the compressive layers making the determination of σ_R difficult under the shallow penetration of X-ray. The compressive stress was not generated in the surface films grown on the surface vertically.

To evaluate the contribution of the compressive metamorphic layers qualitatively, $K_{C\text{-eff}}$ and the bending strength (σ_f, average of four to six specimens) are plotted against the product, $V\xi\delta d^{-1}$, where V and d are the volume content of NiAl and the thickness of specimens, respectively. The parameter, $V\xi\delta d^{-1}$, represents the integrated compressive stress in the metamorphic layers. The ratio, δ/d, is used according to the following relation (3) of σ_R with δ/d.

$$\sigma_R = \left[\frac{E\Delta\beta}{1-\nu}\right]\frac{\delta}{d} \tag{3}$$

In Eq. (3), E is the elastic modulus, $\Delta\beta$ the linear expansion, and ν the Poisson's ratio. Fig. 6 indicates the linear relation between $K_{C\text{-eff}}$ and the product, $V\xi\delta d^{-1}$. The least-square fitting provided the following contribution of the product.

$$K_{C\text{-eff}} = (1.34 \times 10^3)(V\xi\delta d^{-1}) + (4.01) \tag{4}$$

When assuming the complete oxidation of 10 vol.%-$NiAl/Al_2O_3$ ($\xi = 1.0$) and estimating δ as 80 μm at the temperature range of balanced increase in δ and Ω (<125 0°C) in Fig. 4, $K_{C\text{-eff}}$ for 3 mm-thick specimens was calculated as 7.59 MPa m$^{1/2}$ by Eq. (4). By the similar calculations, the thickness required to exceed 10 MPa m$^{1/2}$ in $K_{C\text{-eff}}$ was 134 μm for 10 vol.%- and 67 μm for 20 vol.%-NiAl materials. It seems to be possible to materialize these requirements.

The strength also increased with the increase in the product. However, it was terminated at 1.3×10^{-3} in $V\xi\delta d^{-1}$ (1250 °C, 10 h) and turns to the marked decrease
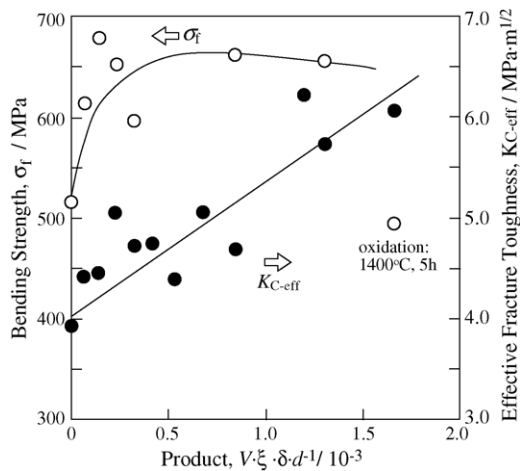

Fig. 6. Strength and toughness as a function of the product of NiAl content (V), degree of oxidation (x), layer thickness (d) divided by the thickness of specimens (d).
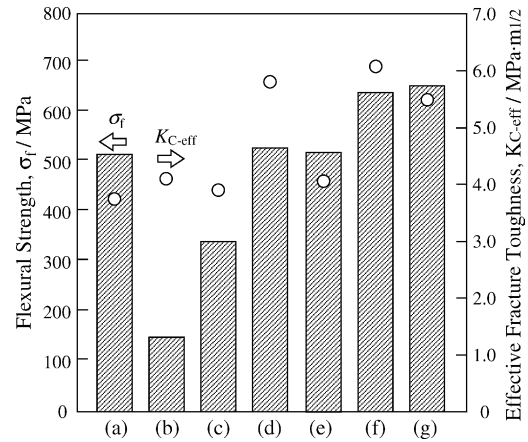

Fig. 7. Reparation of strength under oxidation: (a) without defect, (b) defected, (c) annealed, (d) repaired, (e) removal of defect, (f) oxidized without defect, and (g) oxidized after removal.

at 1.7×10^{-3} (1400 °C, 5 h). This should be caused by the increased interfacial stress. As a conclusion, the bending strength exceeding 650 MPa and the fracture toughness larger than 6 MPa m$^{1/2}$ are simultaneously obtainable by the oxidation treatment of 10 vol.%-$NiAl/Al_2O_3$ composites at the temperature range from 1100 to 1300 °C. The Vickers hardness (H_V) of 14 GPa for sintered composites increased to 16–17 GPa after oxidation, but the clear relation with σ_R was not obtained.

3.3. Reparability of the composites

For the reparation test, one Vickers indentation and derived cracks were introduced for the polished specimens. The oxidation for reparation was conducted at the adequate temperature to strengthening, 1250 °C (10 h). The toughness ($K_{C\text{-eff}}$) and strength (σ_f) of the non-defected (a), defected (b), annealed (c), repaired (d) and removed-off specimens (e) were presented in Fig. 7. The σ_f and $K_{C\text{-eff}}$ for the oxidized materials without defects (f) and after the defect-removal (g) are also shown for comparison. The toughness values were unchanged by annealing (1250 °C, 10 h) and the removal of 500 μm-surface. The strength degraded to 150 MPa by the introduction of medial crack with the radius of 187 μm. Marked recovery of σ_f (531 MPa) exceeding the original one (515 MPa) was attained by the reparation, while only the limited recovery of σ_f (343 MPa) was obtained by the annealing in Ar at the same temperature.

By applying the average crack length introduced ($c = 187$ μm) and σ_f and $K_{C\text{-eff}}$ determined for the defected material, the constant χ in Eq. (5) was obtained to be 1.96. This was inconsistent for the median cracks on the surface.

$$\sigma_f = (1/\chi)k_{C\text{-eff}}c^{-1/2} \tag{5}$$

The size of fracture origin (c) calculated by Eq. (5) was 15 μm for the starting composite, 32 μm for the annealed material, and 30 μm for the repaired material. The artificial cracks were

healed under annealing in Ar. However, there was no significant difference in c for the annealed and repaired materials despite the considerable improvement of σ_f for the repaired material. One possible explanation for this is the combination of the compressive stress increasing $K_{C\text{-eff}}$ and the thermal healing of the defect in the similar degree to the annealed material. The shrinkage of c to the size (30 μm) smaller than δ (52 μm) for the oxidized material also supposed this possibility, but the difference in σ_f between the annealed and repaired materials, 198 MPa, evidently larger than the compressive stress, 76 MPa.

Another possibility is suggested in Fig. 8 showing the fracture surface. The Vickers indentation observed on the fracture
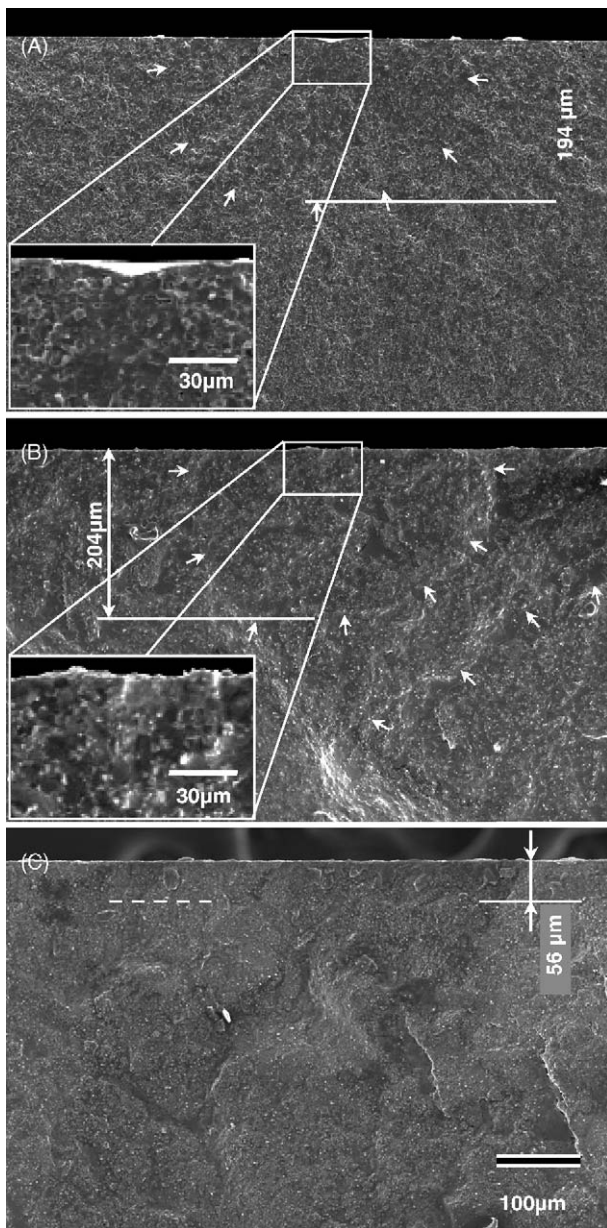

Fig. 8. Fracture surface of (A) defected, (B) repaired and (C) oxidized materials.

surface of the defected material (A) was disappeared after the reparation treatment (B). It was filled by the reaction product completely. In contrast, the median crack with the size of 194 μm in the defected material (A) was not disappeared so much as indicated the enhanced morphology after the reparation (B, 204 μm). Metamorphic layer showing flat fracture surface was developed surrounding the re-bonded crack (B) as well as on the surface of the oxidized non-defected material (C). The transgranular fracture of the matrix-Al_2O_3 grains typical of the metamorphic layers was observed inside and outside the repaired crack. The filling of the indentation, the oxidation broadened into the whole area of the initial crack, and the development of the metamorphic layer surrounding the repaired crack meant the dominant re-bonding of the cracks by the oxidation reactions rather than the thermal healing. Such re-bonding of the cracks is also described by Chu et al. for SiC and Si_3N_4.[8] In the present study, the compressive stress supporting the repaired defects contributes to enhance the recovery of strength. It is considered that the oxidation reaction faster than the healing and providing the enhanced recovery of the strength can contribute to the improvement the reliability and the expansion of materials life.

4. Conclusion

Oxidation of NiAl/α-Al_2O_3 composites provides the metamorphic surface layers consisting of boundary $NiAl_2O_4$ and Al_2O_3 grains with compressive stress. Strength and toughness of the starting 10 vol.%-NiAl/Al_2O_3 composites, 515 MPa and 4 MPa m$^{1/2}$ are improved to ~655 MPa and ~6 MPa m$^{1/2}$ after the controlled oxidation at 1200–1300 °C. The toughness is increased in proportion to the product of the degree of oxidation and the thickness of the metamorphic layers divided by the thickness of specimens for a certain content of NiAl. The reactivity of an oxidation product, NiO, with the matrix-Al_2O_3 and the rapid diffusion along with the grain boundary repairs the damages on surfaces by filling and re-bonding the defects and cracks with the reaction product, $NiAl_2O_4$. The oxidation further progresses via the repaired defects to develop the metamorphic layers supporting them. The compressive surface stress enhances the recovery of strength. The degraded strength of the defected material, 150 MPa, is recovered to 531 MPa by the reparation, while only a limited recovery to 343 MPa is attained by a thermal healing in Ar.

Acknowledgements

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