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Surface nitridation of Al_2O_3 based composite by N_2-HIP post-treatment

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Surface nitridation of Alumina based composites reinforced with silicon carbide particles and/or whiskers has been studied. The composites processed by hot-pressing were post-treated by HIP process at 1650–1750 °C under 150 MPa of nitrogen gas pressure. X-ray diffraction (XRD) analysis indicates that Alumina and silicon carbide on the surface of the composite are converted to aluminum nitride and silicon nitride, respectively, during the post-treatment. Examinations of surface nitrided layer by scanning electron microscopy (SEM) suggest that grain size can be significantly affected by post-treatment condition. Flexure tests indicate that strength increases significantly by the post-treatment. It is discussed that the improvement of mechanical properties included two parts: one came from the densification of sample, the other came from the surface nitrided layer. Specially, the residual compressive stress plays a key role on the improvement of the flexural strength.

1. Introduction

HIP (hot isostatic pressing) process was developed at first in the field of powder metallurgy. In the last decade, the running temperature of HIP equipment was increased significantly [1, 2] and could satisfy the sintering of ceramic materials such as silicon carbide. Compared with pressureless sintering, hot-press sintering and gas-pressure sintering [3–5], the high temperature and high isostatic gas pressure of HIP process contribute to densification and uniform microstructure of ceramic materials. The green bodies, however, have to be encapsulated with high melting point glass to get an effective gas pressure transfer during HIP sintering [6, 7]. Thus, only simple shape ceramic samples can be prepared by HIP process. Afterwards, a two-step process was applied to avoid the complex encapsulation process [8]. First, the green bodies were pre-sintered to get a low open porosities, then the pre-sintered samples were hot-isostatic-pressed to get further densification. By two-step HIP process, full densification and excellent performance were reached without encapsulation, too. Then, Jiang *et al.* [9, 10] put forward a "Reaction-HIP" process in which nitrogen gas was used as pressure transferring medium instead of argon gas. Under 150 MPa nitrogen gas presure at 1650–1750 °C, the surface of samples, such as SiC, reacted with nitrogen gas and formed a surface layer of different composition. On the other hand, the surface nitriding reaction contributes to healing the surface defects and improving the microstructure of surface layer [8]. All of these will improve the mechanical properties.

In the present study, hot pressed SiCp-Al_2O_3 and SiCp-SiCw-Al_2O_3 composites were fired by HIP with nitrogen gas as pressure transferring medium (N_2-HIP post-treatment). The microstructure, compositions and strength were measured by scanning electron microscopy (SEM), X-ray diffraction (XRD) and flexural test, respectively. The effect of the surface nitrided layer on mechanical properties was studied. The strengthening mechanism of N_2-HIP post-treatment was discussed in detailed.

2. Experimental

2.1. Raw materials

In present work, γ-Al_2O_3 powder was used. The average particle size of γ-Al_2O_3 was 0.3 μm. The reinforcement used in present work include two SiC powders and one SiC whiskers. The SiC powders had an average particle size of 45 nm (β type) and 0.9 μm (α type), respectively. The average aspect ratios of SiC whiskers produced with a average diameter of 1–3 μm by American Matrix Company (AM-SiCw) were adjusted to 10–15 by attrition-milling.

2.2. N_2-HIP post-treatment and characterization

The compositions of SiCp-Al_2O_3 and SiCp-SiCw-Al_2O_3 were listed in Table I. First, the composite mixtures were hot-pressed. The resulted relative densities were above 98% and open porosity below 1.0%. Then,

TABLE I Compositions and characters of SiCp-Al_2O_3 and SiCp-SiCw-Al_2O_3 composite mixtures

	SiC whisker		SiC powder		γ-Al_2O_3 powder	
Samples	Content (vol %)	Aspect ratio	Content (vol %)	Particle size (μm)	Content (vol %)	Particle size (μm)
ASP5	0	—	5	0.045	95	0.3
AM-ASS10	20	10–15	10	0.9	70	0.3

the hot-pressed samples were machined into standard flexural testing bars (3 × 4 × 36 mm^3). Part of the standard bars were bent to test the flexure strength, the other bars were fired 30–60 minutes by HIP process with filter paper packing to provide carbon source at 1650–1750 °C under 150 MPa nitrogen gas pressure. In order to confirm the advantage of "Reaction-HIP" process and identify the effect of surface nitriding reaction on the mechanical properties, half of the N_2-HIP post-treated specimens were carefully polished off a certain thickness about 50 μm to completely remove the surface nitrided layer. Then, the flexural strength of hot-pressed, polished and non-polished N_2-HIP post-treated specimens were tested.

The density and porosity were determined by water-displacement method. The compositions of surface layer and inside of N_2-HIP post-treated specimens were determined by measuring the X-ray diffraction of both polished and non-polished specimens. Scanning electron microscopy (SEM) was used to observe the microstructure of both the surface nitrided layer and the inside of the N_2-HIP post-treated specimens.

3. Results and discussions

3.1. Surface nitriding reaction

During N_2-HIP post-treatment, the nitriding reactions as following took place:

$$3SiC(s) + 2N_2(g) \rightarrow Si_3N_4(s) + 3C(s) \qquad (1)$$

$$Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2AlN(s) + 3CO(g) \qquad (2)$$

Equation 2 consisted of two steps [11]:

$$Al_2O_3(s) + 2C(s) \rightarrow Al_2O(g) + 2CO(g) \qquad (2.1)$$

$$Al_2O(g) + N_2(g) + C(s) \rightarrow 2AlN(s) + CO(g) \qquad (2.2)$$

or:

$$Al_2O(g) + N_2(g) + CO(g) \rightarrow 2AlN(s) + CO_2(g) \qquad (2.3)$$

In Equation 2, the C(s) come from the carbonized filter paper. Simultaneously, Equation 1 may provide some C(s), too. The nitriding reactions depended on the inword diffusion of N_2 and C(s) took place at first along with the open pores, surface flaws and grain boundary on the specimen surface. The reaction products AlN and Si_3N_4 deposited *in-situ* and grew gradually. Because of the difficulty of inword diffusion of N_2 and C(s), especially for C(s), only a thin nitridation layer formed. The grain size and microstructure of nitridation layer depended on N_2-HIP condition as discussed below.

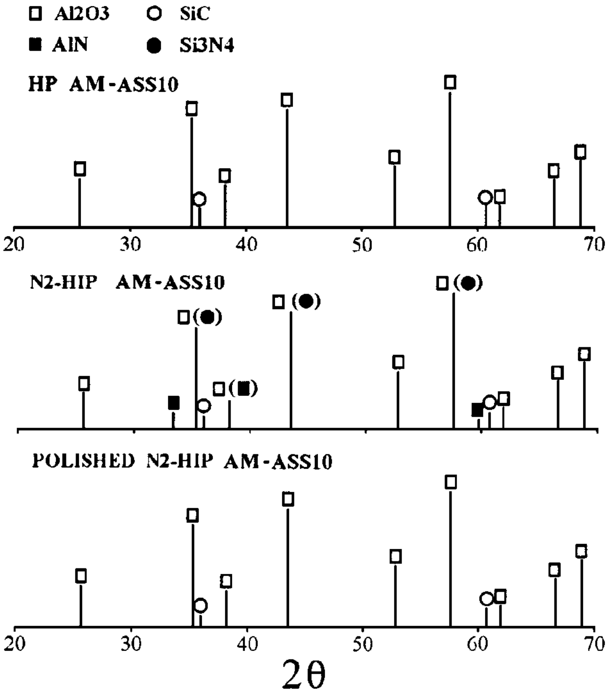

Figure 1 Surface XRD diagram of N_2-HIP post-treated AM-ASS10 composites, both AlN and Si_3N_4 were found on the surface nitrided layer.

3.2. Composition and microstructure of nitrided layer

Fig. 1 illustrates the XRD patterns. Peaks of Si_3N_4 and AlN with high relative intention are found for N_2-HIP post-treated specimen. After the surface reaction layer was removed about 50 μm by polishing, no diffraction peaks of Si_3N_4 and AlN are identified, which confirms that the four phases composition presents only in 50 μm depth.

In order to analyses the microstructure of N_2-HIP post-treated ASP5, a continuous SEM observation from edge to center of fracture surface was conducted step by step. Fig. 2 represents the SEM fracture morphology of ASP5 post-treated at 1750 °C for 60 minutes. In the depth range from 0 to 10 μm (Fig. 2A), no clear grain can be observed and fracture process is transgranular fracture, which demonstrates that the excessive firing temperature and holding time generate significant AlN grain growth besides complete transformation from Al_2O_3 to AlN in the very thin surface layer. With increase of depth, clear grain presents and grain size reduces. Fig. 2B represents microstructure from 50–63 μm depth. The grain size is similar with the central grain size. The fracture process, however, is mainly transgranular fracture different with intergranular fracture at center. The variation of fracture process indicates the strengthening of interface bonding which

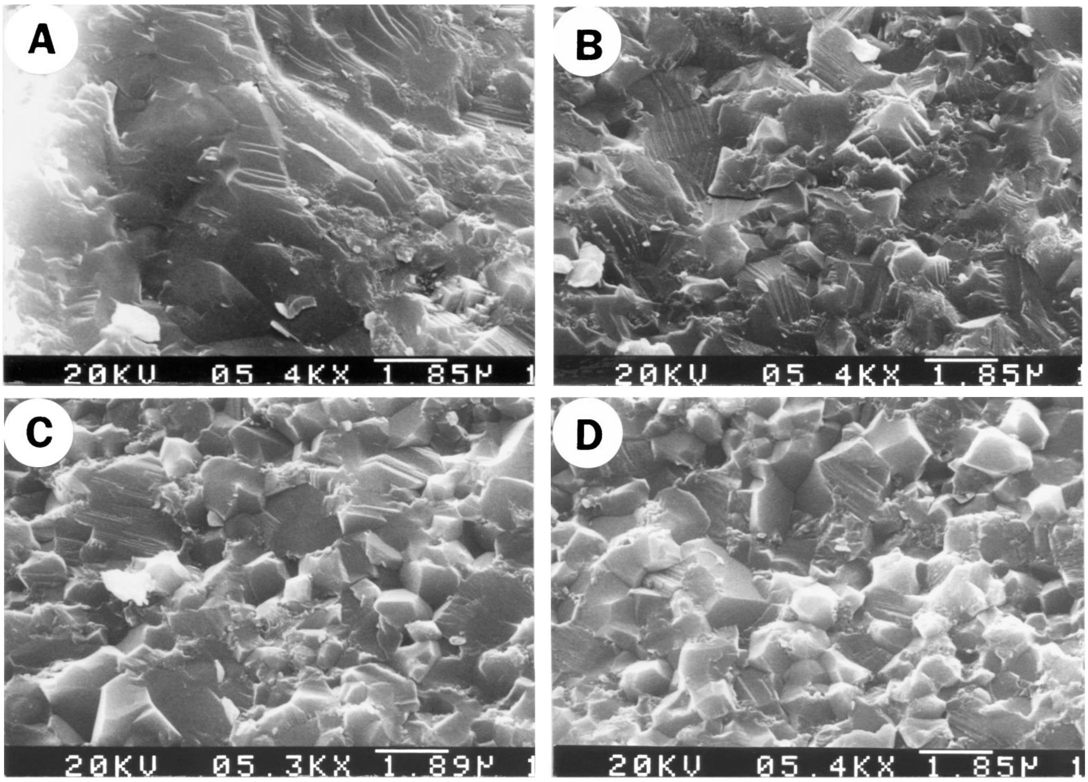

Figure 2 Continuous SEM fracture morphology of ASP5 from surface of nitridation layer to substrate, a lot of intergranular fracture was found. The depth from left to right was (A): 0–13 μm, (B): 50–73 μm, (C): 100–113 μm, (D) at center.

maybe result from interface chemical reaction due to slight diffusion of C(s) and N_2 or Al_2O(g) along with grain boundary. Fig. 2C shows that both the grain size and fracture process at the depth >100 are same as that at the center (Fig. 2D) of the sample. Taking account of the excessive firing at 1750 °C for 60 minutes, lower firing temperature (1650 °C) and shorter holding time (30 minutes) was selected for the N_2-HIP post-treatment of AM-ASS10. Compared with ASP5, SEM observation indicates that AM-ASS10 shows a different microstructure of surface nitrided layer as illustrated in Fig. 3A. The grain size of surface nitrided layer is only about 0.5 μm. It is much smaller than the original grain size ($\sim$2.0 μm) of hot pressed sample. Thus, a desirable microstructure of surface reaction layer can be controlled by adjusting the N_2-HIP post-treatment condition. In addition, SiC particles (0.9 μm, 10 wt %) and SiC whisker (20 wt %) may play an important role in restricting free grwoth of AlN grain. On the contrary, the low content (5 wt %) and small grain size (45 nm) of SiC particle could not prevent the AlN grain from free growth. Generally, a reduced grain size is in favor of the mechanical properties. For present work, firing at 1650 °C for 30 minutes is the optimum.

3.3. Densification during N_2-HIP post-treatment

The densities, open porosities and flexural strengths of hot-pressed (HP), polished (P-HIP) and non-polished

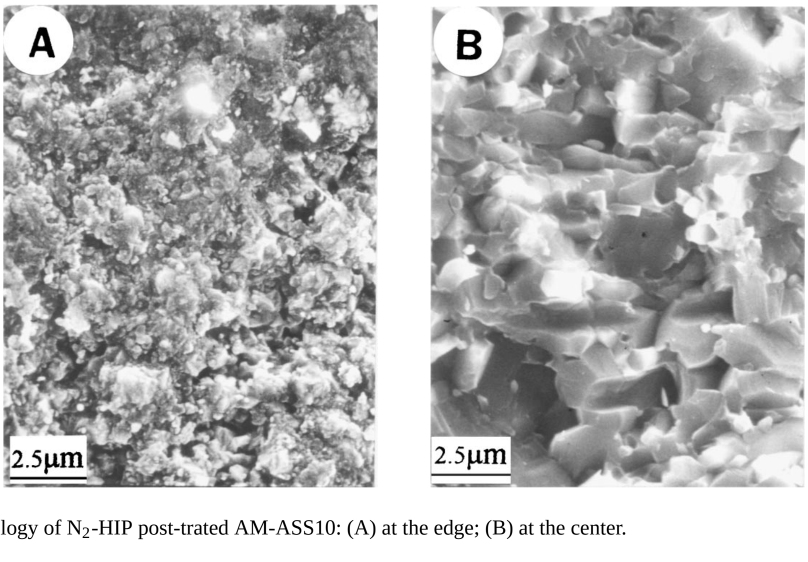

Figure 3 Fracture morphology of N_2-HIP post-trated AM-ASS10: (A) at the edge; (B) at the center.

TABLE II Properties of SiC-Al_2O_3 composites before or after N_2-HIP post-treatment

	Density (g/cm^3)			Open porosity (%)			Flexural strength (MPa)		
Samples	HP	HIP	P-HIP	HP	HIP	P-HIP	HP	HIP	P-HIP
ASP5[a]	3.86	3.90	3.92	0.65	0.53	0.08	460	895	570
AM-ASS10[b]	3.66	3.68	—	0.52	0.49	—	705	1033	—

[a] Condition of N_2-HIP: 1750 °C, 150 MPa, 60 minute.
[b] Condition of N_2-HIP: 1650 °C, 150 MPa, 30 minute.

TABLE III Volume expansions and the change of densities after nitridation

Composition (vol %)		Volume expansion (%)	Density (g/cm^3)	
SiC	Al_2O_3		Before nitridation	After nitridation
5	95	−1.3	3.923	3.213
30	70	3.6	3.735	3.553

(HIP) N_2-HIP post treated specimens are listed in Table II. The theoretical density of SiC, Si_3N_4, Al_2O_3 and AlN is 3.21, 3.19, 3.96 and 3.26 g/cm^3, respectively. According to theoretical density and Equations 1 and 2, the transformation from SiC into Si_3N_4 will generate a volume expansion of 17.4%. The transformation from Al_2O_3 into AlN, however, generate a slight volume shrinkage about 2.3%. In case of complete transformation from SiC and Al_2O_3 to Si_3N_4 and AlN, the resulted volume expansions and the densities of composities are listed in Table III.

Because of the theoretical density of Si_3N_4 and AlN are lower than SiC and Al_2O_3, the density of N_2-HIP post-treated specimen must lower than the original density whatever nitriding reaction extent. The measured densities in Table II, however, show that no density reduction but a slight density increase after N_2-HIP post-treatment. Moreover, the polished N_2-HIP specimens have a higher density than both hot-pressed and non-polished N_2-HIP post-treated specimens. Therefore, the original specimens must be densified during N_2-HIP post-treatment process, which also gave a resonable explanation for the improvement of flexural strength of polished N_2-HIP specimens comparing with hot-pressed specimens.

The difference of open porosities between hot-pressed and N_2-HIP post-treated (non-polished) specimens is very small. The open porosities of polished N_2-HIP specimens, however, are much lower than that of hot-pressed specimens. The reduction of open porosity of polished N_2-HIP samples coincides with the deduction of densification during N_2-HIP post-treatment process.

3.4. Flexural strength and strengthening mechanism of SiC-Al_2O_3 by N_2-HIP post-treatment

The tested results showed that the flexural strengths are improved significantly (Table II) by N_2-HIP post-treatment. After elaborately removing the surface nitride layer, the flexural strengths of ASP5 is just 570 MPa, much lower than 895 MPa of non-polished N_2-HIP post-treated specimens. However, it is still higher than the strength of 460 MPa of hot-pressed specimens. The differences of flexural strength between polished N_2-HIP post-treated specimens and hot-pressed specimens come from the further densification during HIP post-treatment. The differences between polished and non-polished N_2-HIP post-treated samples demonstrates that the surface nitrided layer resulted in the significant improvement of flexural strength.

Thermal residual compressive stress plays a important role to improve the flexural strength. As known, the thermal expansive coefficient of Al_2O_3 and SiC is 8.8×10^{-6}/°C, and 4.8×10^{-6}/°C, respectively, and it is only 3.3×10^{-6}/°C for Si_3N_4 and AlN. After N_2-HIP post-treatment, the surface layer consists of Si_3N_4, AlN, SiC and Al_2O_3, the mismatch of thermal expansion would caused great residual compressive stress on the surface layer when the specimens cooled from firing temperature to room temperature [12–15]. Assuming uniform temperature distribution, Timoshewko *et al.* [16] proposed Equation 3 as below to predict the maximum normal stress (σ_c) generated in a coating layer during cooling over the effective temperature difference ΔT:

$$\sigma_c = \left[\frac{E_c(\alpha_c - \alpha_s)\Delta T}{1 - \nu_c}\right] \Bigg/ \left[2\frac{h_c}{h_s}\frac{E_c}{E_s}\frac{(1 - \nu_s)}{(1 - \nu_c)} + 1\right] \tag{3}$$

Here, E, α and ν are young's modules, mean linear thermal expansion coefficient and Poisson's ratio, the subscript c and s refer to coating layer and substrate, respectively. h_c is the thickness of coating layer spread on both sides of a substrate of thickness h_s. For present work, $h_c \ll h_s$. So, σ_c becomes independent of the reaction layer thickness as Equation 4:

$$\sigma_c = \frac{E_c(\alpha_c - \alpha_s)\Delta T}{1 - \nu_c} \tag{4}$$

Using 250 MPa and 0.25 for E_c and ν_c (AlN). For a ΔT of 1000 °C [17], a maximum compressive surface stresses $\sigma_c \approx -2300$ MPa is calculated, it means that the surface nitride layer suffers a significant compressive stress from the substrate. As known, failure in fracture occurs at the surface in tension but can occur either from the center tensile stress or from surface compressive stresses [18]. According to stress concentration fracture analysis [18], in general, when the maximum stress in the vicinity of the crack tip $\sigma_m = \sigma_{th}$, failure takes place. Under compression, failure would be expected when the stress at the crack tip exceeds the theoretical strength and compressive stress; that is, when $\sigma_m = \sigma_{th} + \sigma_c$. Although the actual stress distribution may be altered by gradient compositional change and creep relaxation, the absence of the residual compressive stress would explain the substantial increase of strength.

Besides the residual compressive stresses, both surface nitriding reaction and HIP densification are in favor of strengthening. During nitriding reaction, the in-situ deposition of AlN at flows or open pores would contributed to healing surface flaws and very small open pores. Undoubtedly, which will improve the flexure strength. On the other hand, HIP densification leads to the increase of strength (Table II) as discussed above. Thus, the residual compressive stress, the HIP densification and the healing of surface defects were the main strengthening mechanisms.

4. Conclusions

Hot-pressed SiC-Al_2O_3 composite ceramics were post-treated by "Reaction-HIP" process. The grain size and microstructure of nitridation layer could be controlled by adjustment of N_2-HIP process condition. by N_2-HIP post-treatment, the flexural strengths were increased about 35–95%. The residual compressive stress, the HIP densification and the healing of surface defects were the main strengthening mechanisms.

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