

Alumina- γ -Aluminum Oxynitride Composites from Alumina Nitrided by Ammonia

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Abstract

By reaction between transition (γ) aluminas from boehmite and ammonia ($T \approx 1000$ – 1100°C), up to 1% wt nitrogen can be fixed in the form of a γ -aluminum oxynitride layer on γ - Al_2O_3 surface grains. This layer delays the polymorphic transformation of γ - into α - Al_2O_3 . For higher nitrogen contents, aluminum nitride appears. An application can be the preparation of partially nitrided Al_2O_3 powder in γ -AlON and/or AlN, that can lead to γ -AlON single phase or Al_2O_3 - γ -AlON composites. Such composites, obtained by γ - Al_2O_3 partially nitrided in AlON, present γ -AlON along grain boundaries; that microstructure is efficient in increasing the composite wear resistance.

Durch die Reaktion von γ - Al_2O_3 (Boehmit) mit Ammoniak bei 1000°C – 1100°C kann in einer oberflächennahen Schicht der γ - Al_2O_3 Körner bis zu 1 Gew.% Stickstoff in Form von γ -AlON aufgenommen werden. Diese Schicht verzögert die polymorphe Umwandlung von γ - Al_2O_3 in α - Al_2O_3 . Bei höheren Stickstoffgehalten bildet sich AlN. Eine Anwendung dieses Verhaltens bietet sich in der Herstellung teilweise nitridierten Al_2O_3 -Pulvers, entweder in γ -AlON und/oder AlN Modifikation, das zu einphasigem γ -AlON oder Al_2O_3 - γ -AlON Verbundwerkstoffen führen könnte. Derartige Verbundwerkstoffe, die aus γ - Al_2O_3 -Pulvern mit oberflächlicher AlON-Schicht gewonnen wurden, bestehen entlang der Korngrenzen aus γ -AlON. Dieses Gefüge

führt zu einer Verbesserung des Verschleißverhaltens des Verbundwerkstoffs.

L'action de l'ammoniac sur des aluminas de transition (principalement γ , à partir de boehmite, $T \approx 1000$ – 1100°C), permet de fixer jusqu'à 1 pds% d'azote, sous la forme d'une couche d'oxynitride d'aluminium en surface de grains de Al_2O_3 γ . Cette couche retarde la transformation de l'alumine γ en alumine α . Pour des teneurs en azote supérieures, le nitrure d'aluminium apparaît. Ce procédé permet de préparer des poudres d'alumine partiellement nitrurées en γ -AlON et/ou AlN, pouvant conduire à du γ -AlON monophasé ou à des composites Al_2O_3 - γ -AlON. Dans les composites obtenus à partir d'aluminas γ nitrurées en γ -AlON, la répartition le long des joints de grains de la phase γ -AlON est bénéfique aux propriétés de frottement du matériau.

1 Introduction

The alumina- γ -aluminum oxynitride composite (Al_2O_3 - γ -AlON: ALUMINALON¹, is constituted by an alumina matrix in which γ -AlON grains are dispersed. The Al_2O_3 - γ -AlON composites exhibit interesting properties:² for example, wear resistance (principally against steel under high loads); their mechanical properties, which are almost the same as alumina's at room temperature, are maintained at high temperatures (neutral atmosphere, $T < 1400^\circ\text{C}$).

Aluminum oxynitride powders are not yet available, so the Al_2O_3 - γ -AlON composites are obtained

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by reaction sintering of alumina–aluminum nitride powder mixtures ($T > 1600^\circ\text{C}$ ³). Recently, a new nitridation process, the action of ammonia on alumina at $T = 1200^\circ\text{C}$, has been developed to obtain a pure and reactive AlN.⁴

The present work deals with the possibility of synthesizing γ -aluminum oxynitride in the same way. Then, different nitrided aluminas are hot-pressed to obtain the Al_2O_3 - γ -AlON composites, whose mechanical properties are compared.

2 Phenomenological Study of Nitridation⁵

Boehmite (AlOOH , PSB 160, Martins Werk–Lonza, Bergheim, FRG) was chosen as the starting powder, because it presents a high specific area and changes into γ -alumina above 500°C (γ - Al_2O_3 presents the same spinel structure as γ -AlON).

2.1 Action of ammonia on γ - Al_2O_3

To point out the action of ammonia on boehmite, the effect of two different treatments are compared: the powder was heated at 1030°C for 16 h, under argon or ammonia. When treated under neutral gas, the boehmite changes according to the polymorphic transformations; at the end of the step, θ - and α -aluminas are present (Fig. 1(a)).

When treated under ammonia, the powder contains 1.14 wt% of nitrogen, as determined by the Kjeldahl method. It shows a very different powder X-ray pattern (Fig. 1(b)), similar to that of a poorly crystallized γ -alumina, with some small peaks of δ - and θ -alumina, without any α -phase. That shows that the polymorphic transformation is slowed down in an ammonia atmosphere.

It is shown here that ammonia stabilizes the γ -alumina spinel structure, and that nitrogen is introduced into the structure.

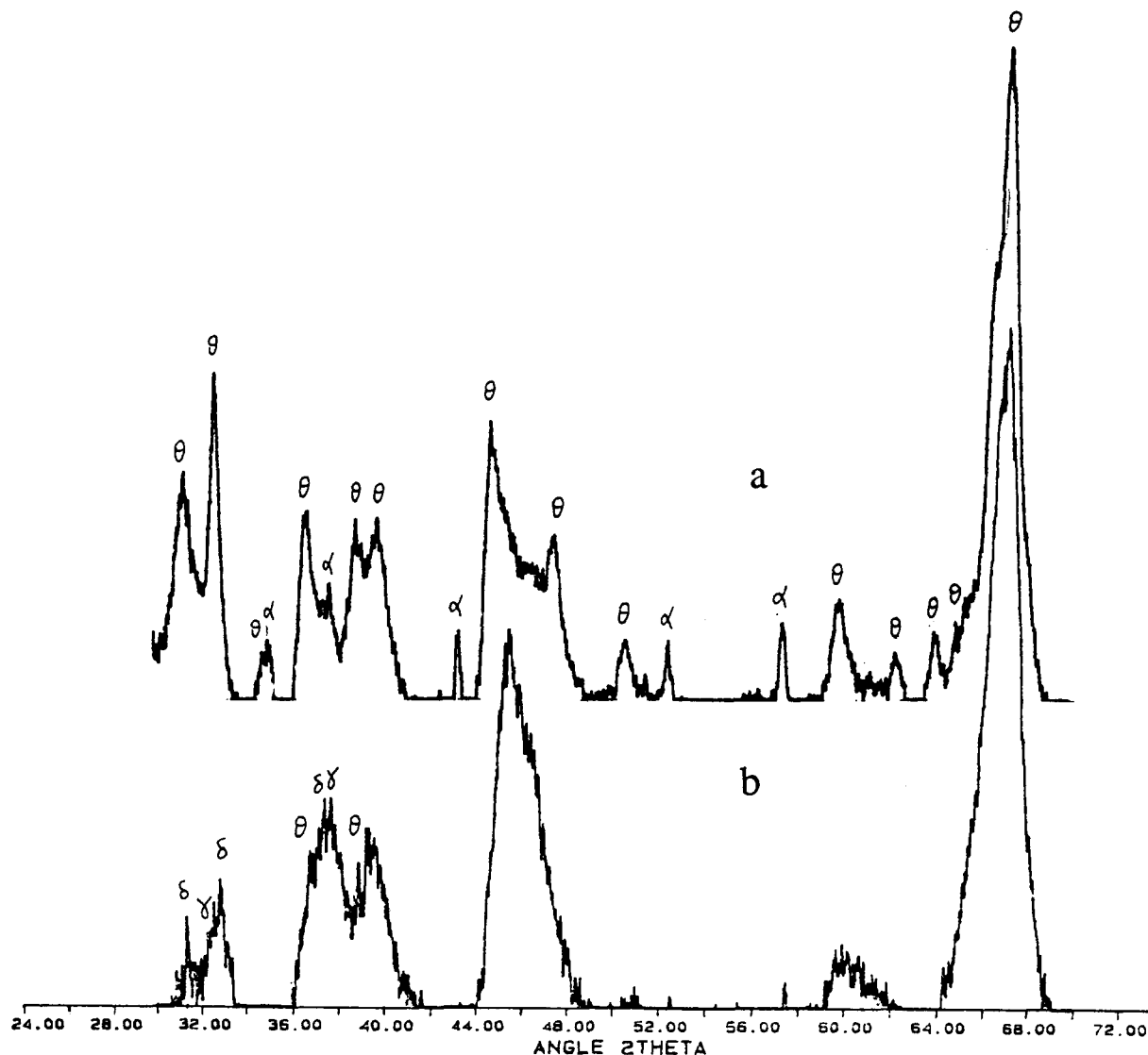


Fig. 1. XRD patterns of powders treated during 16 h at 1050°C , showing polymorphic forms of alumina: γ , spinel; δ , tetragonal; θ , monoclinic; α , hexagonal; a, under Ar; b, under NH_3 .

2.2 Characterization of the stabilized spinel phase

The nitrated powders were characterized by different methods to determine if the stabilized spinel is similar to the aluminum oxynitride obtained at high temperature ($> 1600^\circ\text{C}$)³. Boehmite was nitrated at 1100°C for 20 h, under a NH_3 flow of 90 liters/h. The nitrated powder shows an X-ray pattern of γ -alumina with traces of $\alpha\text{-Al}_2\text{O}_3$ (no AlN is detected by XRD) and contains 0.96 wt% of nitrogen.

2.2.1 Annealing

The nitrated powder was annealed under nitrogen at about 1400°C . This treatment does not affect the nitrogen content.

Figure 2 shows the evolution of the powder components (intensity of the main peak of a phase divided by the sum of the main peak intensity of each phase) versus the annealing duration: the spinel phase ratio decreases, and α -alumina and aluminum nitride appear. The γ -phase completely disappears after 4 h, even though it only requires 0.5 h to transform boehmite into α -alumina.

2.2.2 Spectroscopy

Different powders were studied by both IR and ESCA spectroscopy. The absorption spectrum of the nitrated powder (Fig. 3) resembles that of γ -alumina, and no absorption band belonging to aluminum nitride or γ -aluminum oxynitride are detected on it. ESCA analyses point out the existence of γ -aluminum oxynitride in the nitrated powder: the bond energy of the nitrogen 1s electrons ($395.3 < E < 395.7 \text{ eV}$) is nearer to that of AlON ($395.5 < E < 395.7 \text{ eV}$) than to that of AlN (396.4 eV).

2.2.3 Oxidation

The nitrated powder was oxidized in air as the temperature was increased up to 1500°C (temperature increase rate = $10^\circ\text{C}/\text{min}$).

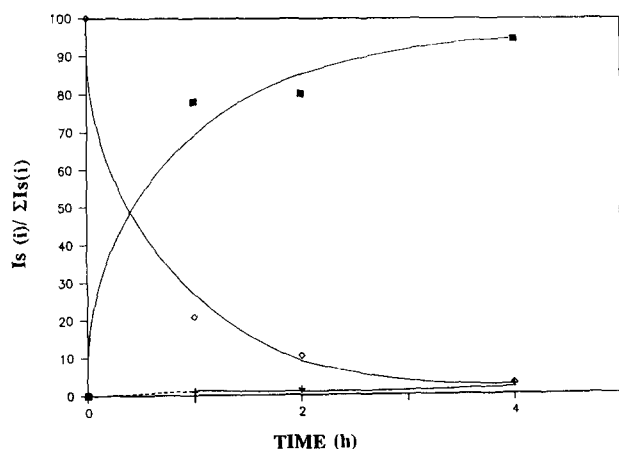


Fig. 2. Evolution of the nitrated powder after annealing treatments. ■, Al_2O_3 ; +, AlN; ◇, spinel.

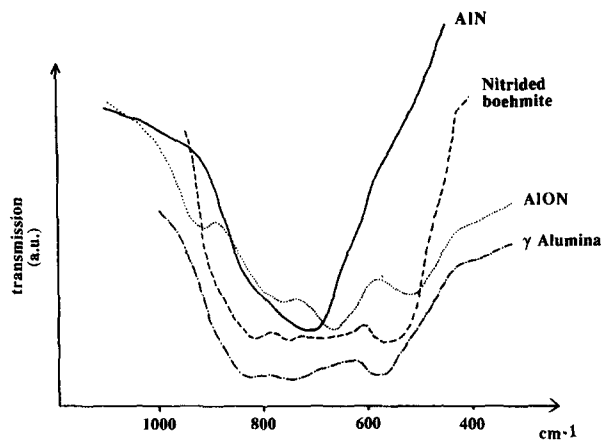


Fig. 3. Infra-red spectra.

The thermograph (Fig. 4) is characteristic of the γ -aluminum oxynitride oxidation.⁶ First, it oxidizes with a weight gain into γ -alumina, which contains atomic nitrogen (N^0), then nitrogen is eliminated with a weight loss, while γ -alumina changes into α -alumina.

2.2.4 TEM study

The boehmite and the nitrated powder are both very thin acicular particles (Fig. 5), which means that nitridation does not change the grain morphology. The grains are about a few nanometers thick, the nitrated powder grains being slightly thicker than those of boehmite.

2.3 Conclusion

The various analytical methods allow it to be concluded that γ -aluminum oxynitride is formed by reacting ammonia with γ -alumina, but only on the surface of the grains whose cores are γ -alumina.

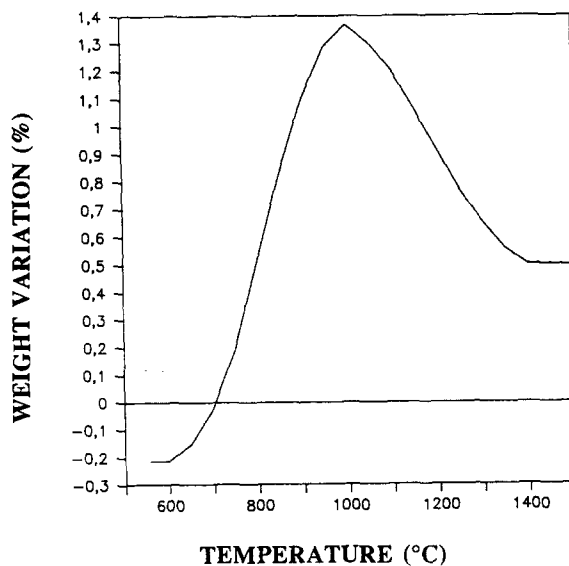
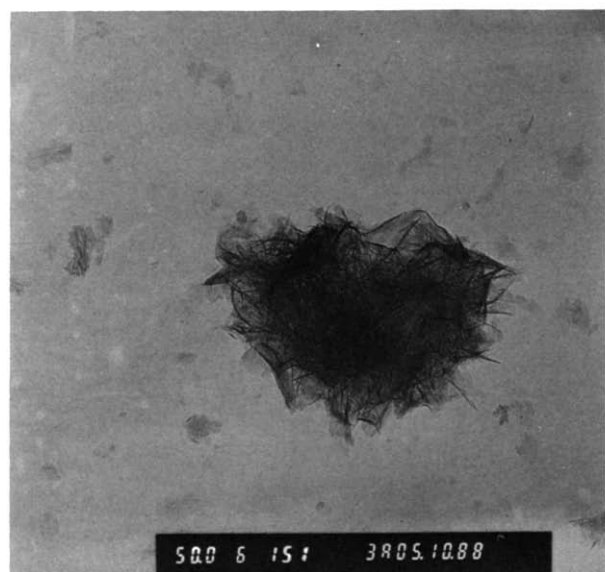
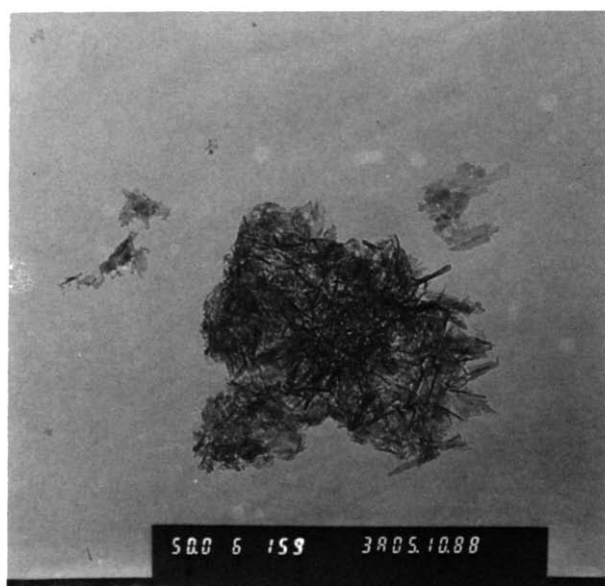


Fig. 4. Thermogravimetric study of the nitrated powder oxidation.



(a)



(b)

Fig. 5. TEM observations of the powders: (a) initial boehmite; (b) boehmite nitrided at 1050°C for 16 h.

This explains the apparent contradictory results of the two spectroscopic analyses: on the one hand, IR spectroscopy is a volume analysis that permits detection of only the most important phase (γ - Al_2O_3) in the nitrided powder. On the other hand, ESCA analysis, that only concerns grains surfaces, permits observation of the AlON. This surface layer stabilizes the spinel structure and the morphology of the γ -alumina grains, but this phase is metastable and decomposes into α -alumina and aluminum nitride during prolonged annealing at 1400°C under neutral gas. When nitrogen leaves the spinel phase to form aluminum nitride, the spinel phase is no longer stabilized and transforms into α -alumina.

The nitridation reaction can be described as follows. At about 500°C, the boehmite dehydrates and transforms to γ -alumina. Hydroxyl group elimination gives unsaturated aluminum atoms which act as Lewis acid groups. On these sites, ammonia molecules could be adsorbed by interacting with the free electrons of the nitrogen.

Extrapolating the thermodynamic results of Simpson,⁷ compounds like $\text{Al}_2\text{O}_{2.5}\text{NH}_3$, and hence Al-N bonds, could be formed at the γ -alumina surface grains. The hydrogen atoms of the ammonia molecules should be eliminated, forming water with adjoining oxygen atoms or hydroxyl groups. Then, γ -aluminum oxynitride is formed on the surface of γ -alumina grains.

Other nitridation reactions at higher temperature and soaking times show that only 1–1.5 wt% of nitrogen can be fixed by a powder with a spinel-like structure. Beyond this limit aluminum nitride is formed, then nitrided powders are mixtures of γ -alumina, γ -AlON and AlN (sometimes α - Al_2O_3).

3 Elaboration of Ceramics from Different Nitrided Powders⁸

The applications of the boehmite nitridation by ammonia are the elaboration of different powders containing γ -aluminum oxynitride:

- (a) A very pure (carbonless) single-phase γ -aluminum oxynitride is produced in two steps:⁹
 - Nitridation at about 1100°C, that leads to mixtures of γ - Al_2O_3 , γ -AlON and some AlN;
 - annealing at about 1700°C under neutral gas. If the powder is compacted after the first step, a fully dense γ -AlON piece can be obtained by pressureless sintering at 1700°C.
- (b) A partially nitrided alumina containing 1 wt% nitrogen ($\approx \gamma$ - $\text{Al}_2\text{O}_3 + \gamma$ -AlON) which can be used to prepare Al_2O_3 - γ -AlON composites without any mixing step.

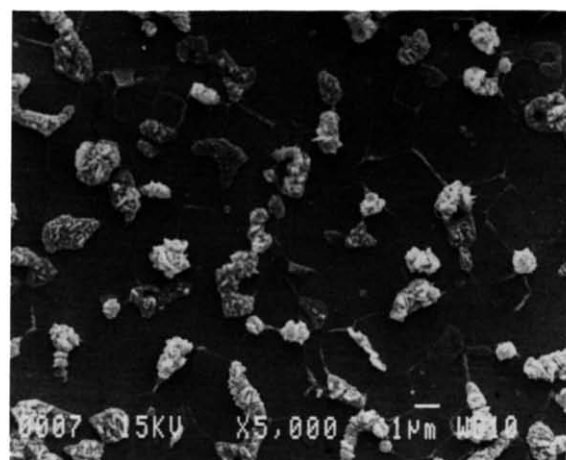
Considering these possibilities, three types of Al_2O_3 - γ -AlON composites are compared:

- Composite A, from Al_2O_3 and AlN mixtures (AlN from Ref. 4).
- Composite B, from AlN partially nitrided alumina (cf. (b)) containing $\approx 1\%$ wt N.
- Composite C, from Al_2O_3 and γ -AlON (cf. (a)⁹) mixtures.

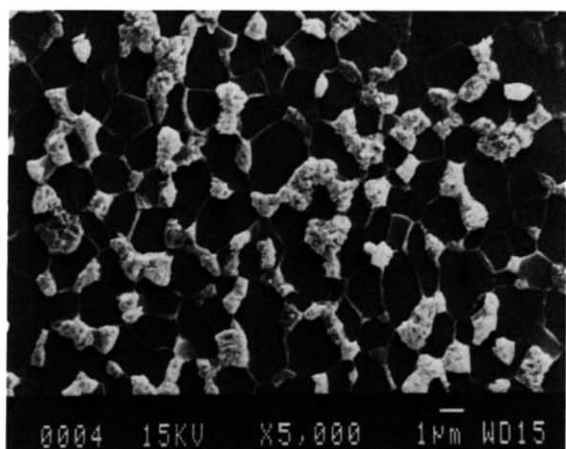
These composites were hot-pressed (1650°C, 30 min, 40 MPa) under nitrogen (relative densities higher than 99%). They contained about 20 vol.% γ -AlON after sintering.

3.1 Microstructures

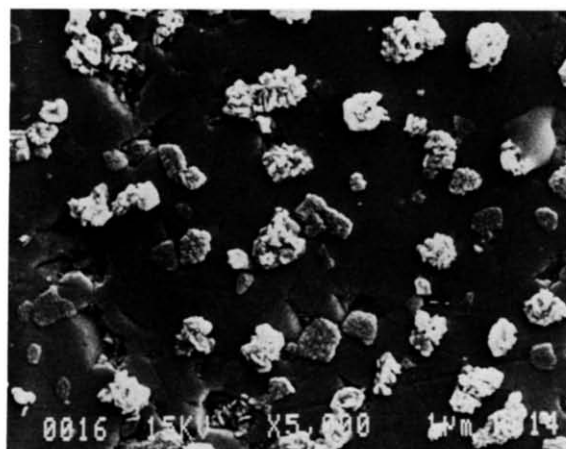
As shown on Fig. 6, the composite aspects depend on the starting powders or mixtures, but the three look homogeneous. Alumina (dark grey) grain size is low



(a)



(b)



(c)

Fig. 6. Microstructures (SEM) of Al_2O_3 - γ -AlON composites.

($\approx 2 \mu\text{m}$) in the three cases (A, B, C) in relation to the fine dispersion that inhibits the alumina grain coarsening during sintering. In spite of its low initial specific area ($2 \text{ m}^2/\text{g}$), due to the annealing treatment at 1700°C, it is interesting to mix pure γ -AlON with alumina. The γ -AlON powder is easily milled during the mixing by ball-milling. The γ -AlON (light grey) presents two kinds of forms:

- γ -AlON grains similar to Al_2O_3 grains.
- An intergranulate structure along alumina grain boundaries.

In the composite B (from Al_2O_3 partially nitrated in γ -AlON), the second kind of morphology is developed. In contrast, the composite C ($\text{Al}_2\text{O}_3 + \gamma$ -AlON mixtures) presents no γ -AlON along boundaries. The composite A is an intermediate. The specific microstructure for the composite B can be correlated with the high homogeneity of the γ -oxynitride in the initial powder due to the nitridation process.

3.2 Mechanical properties

Table 1 shows the composites' mechanical properties: flexural strength by three-point bending tests, toughness by flexion bending tests of SENB specimens, microhardness by Vickers indentation under 10N. They are nearly the same for the three composites.

3.3 Wear resistance

The wear resistance was evaluated by friction tests of plane composite samples against a rotating steel (52100) ring in water under a load of 700N.

Figure 7 shows the evolution of the wear volume for the three composites. The nitrated powder (B) leads to a slightly better wear resistance than the others. The presence of γ -AlON in an intergranular structure seems to be efficient, perhaps by its contribution to the third body formation that delays the composite degradation.

4 Conclusion

Ammonia reacts ($T \approx 1000$ – 1100°C) on fine transition alumina powders (from boehmite), and some

Table 1. Mechanical properties of the Al_2O_3 - γ -AlON composites obtained through three different routes

Samples	Flexural strength (σ_f MPa)	Toughness (K_{Ic} : $\text{MPa}\sqrt{\text{m}}$)	Hardness (Hv: GPa)
A	660 ± 60	3.85 ± 0.25	20.9 ± 1.3
B	640 ± 60	3.65 ± 0.03	19.8 ± 0.2
C	700 ± 80	—	20.3 ± 1.8

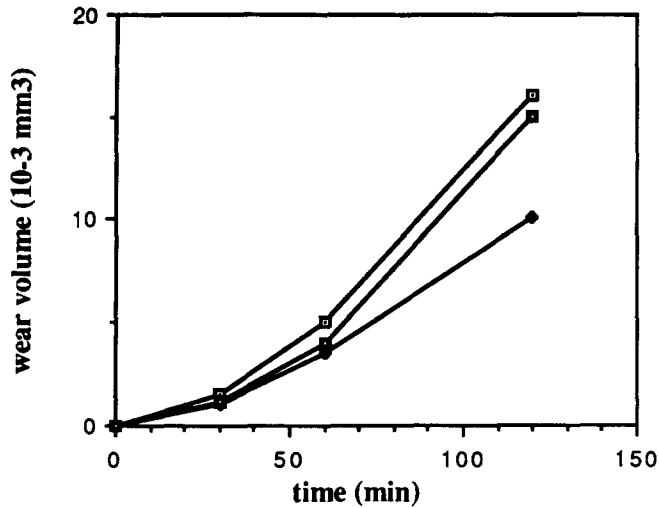


Fig. 7. Al₂O₃-γ-AlON wear resistance. □, A; ◆, B; ■, C.

γ-aluminum oxynitride is formed at γ-alumina grains surface. This was determined by different analyses: infra-red spectrometry, ESCA, transmission electron microscopy, oxidation and annealing.

Depending on the nitridation conditions, it is possible to get partially nitrided alumina powders containing γ-AlON, with or without AlN. Using this process pure γ-AlON (powder or dense materials) or Al₂O₃-γ-AlON composites can be obtained.

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