Journal of the European Ceramic Society 20 (2000) 1765–1769

Sintering behaviour of alumina–niobium carbide composites

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Received 14 September 1999; received in revised form 9 February 2000; accepted 15 February 2000

Abstract

Ceramic cutting tools have been developed as a technological alternative to cemented carbides in order to improve cutting speeds and productivity. Al_2O_3 reinforced with refractory carbides improve fracture toughness and hardness to values appropriate for cutting applications. Al_2O_3–NbC composites were either pressureless sintered or hot-pressed without sintering additives. NbC contents ranged from 5 to 30 wt%. Particle dispersion limited the grain growth of Al_2O_3 as a result of the pinning effect. Pressureless sintering resulted in hardness values of approximately 13 GPa and fracture toughness around 3.6 MPa $m^{1/2}$. Hot-pressing improved both hardness and fracture toughness of the material to 19.7 GPa and 4.5 MPa $m^{1/2}$, respectively. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Composites; Cutting tools; Hardness; NbC; Sintering

1. Introduction

Structural ceramics are characterised by high hot-hardness and superior chemical stability. Nevertheless, their brittle nature restrains their use as cutting tools to a present 5% of a consolidated market dominated by high-speed steels (AISI class T and M), and cemented carbides (Co-WC).[1] The growing interest in ceramics for cutting tools is justified from both an economical and technological perspective. Wear consists basically in a systemic phenomenon, which implies that each class of wear-resistant materials may find use in different applications, according to the counterpart of the tribological couple. Ceramics resist higher temperatures than metals without deforming. This allows tools to cut at faster speeds and deeper depths, resulting in increased removal rates and, consequently, cost efficient machining.[2] Recent developments in cutting tool ceramic materials include escalating improvements on the strength, fracture toughness, and wear-resistance of Al_2O_3 and Si_3N_4. Albeit its high-strength and thermal-shock resistance, Si_3N_4 has proven effective only for machining a limited number of materials, including cast irons and nickel-based alloys.[3] Furthermore, machining with Si_3N_4 usually requires the use of coolants, which represent three times the current cost of cutting. On the other hand, Al_2O_3-based ceramic composites do not require cutting fluids yielding both economic and environmental benefits.[1]

The development of new Al_2O_3-based composites has been accompanied by a significant improvement in properties. This increases the range of applications for such materials as cutting tools, from widely used steels and cast irons to very hard steels and superalloys for the aerospace industry.[2] Aspects such as processing and microstructure have been extensively investigated. Fracture toughness, strength, hardness, and wear resistance have been particularly improved by the dispersion of hard carbide particles, such as TiC,[4–7] WC,[8] and NbC.[9,10] Moreover, the presence of dispersed particles can produce a pinning effect[11] and inhibit the grain growth of the matrix, which further contributes to the final performance of the composite.

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0955-2219/00/$ - see front matter
PII: S0955-2219(00)00060-1

NbC depicts a series of attractive properties as Al_2O_3 reinforcement, including high melting point (3600°C) and high hardness (<2000 kg/mm^2). Al_2O_3 and NbC also are thermo-mechanically compatible, since their Young modulus (390 and 340 GPa, respectively) and thermal expansion coefficient (6.7×10^{-6} and $6–9\times10^{-6}$ K^{-1}, respectively) are closely matched. This reduces the formation and development of thermo-mechanical residual stresses upon sintering of the composite and at service conditions, under fast cutting speeds. The presence of residual stresses is particularly detrimental to brittle materials since they result in the formation of cracks and corresponding loss of mechanical strength. Moreover, sintering without additives requires rather high temperatures which enhances the formation of thermal cracks. Brazil holds the main world niobium reserves, concentrated in its high-grade ore deposits,[12] making the use of this metal strategic particularly in components of high aggregated value. In this scenario, the objective of the present study is to investigate the sintering behaviour, pinning effect of the dispersed particles on matrix grain growth, and the resulting properties of NbC-reinforced Al_2O_3-composites. Both pressureless and hot-pressed specimens have been processed and characterised.

2. Experimental procedure

The starting powders consisted of Alumina APC-2011 SG (Alcoa, Brazil), D50 = 2.3 μm, surface area 1.5 m^2/g; and NbC (Hermann Starck, Berlin, Germany), D50 = 2.3 μm. Al_2O_3 and NbC were dry-mixed during 4 h in a planetary ball milling containing Al_2O_3 grinding media. Compositions containing 5, 10, 20 and 30 wt% NbC were prepared. Subsequently, powders compacts were uniaxially pressed into pellets of 8 mm in diameter under 100 MPa. Next, specimens were pressureless sintered under flowing argon either at 1650°C/30 min or 1800°C/15 min in a graphite-resistance-heated furnace. The heating and cooling rates were set to 20°C/min. Second series of samples was hot-pressed at 1650°C/30 min in flowing argon. The density of sintered specimens were measured by the Archimedes method.

Microstructural characterisation was carried out on specimens polished with diamond paste to a 1 μm finish, and thermally etched under vacuum at 1500°C/30 min. Grain size distributions were estimated by scanning electron microscopy and image analysis using the IMAGE-C computer program (INTRONIC, Germany). The identification of crystalline phases was carried out by X-ray diffraction. The parameters related to the intended application for the composites were gathered by the indentation method. Vicker's microhardness (H_V) and fracture toughness (K_{IC}) were evaluated by measuring the lengths of the cracks and the diagonal impressed by a Vickers indenter applying loads that varied from 30 to 100 N during 15 s. Loads varied according to the carbide content of the test specimen, aiming at the minimum necessary to produce radial cracks without ramification. Further details on the method used for fracture toughness evaluation can be found elsewhere.[13]

3. Results and discussion

Table 1 summarises the physical and mechanical properties of Al_2O_3–NbC composites. Densification was a function of the temperature and the sintering process. Pressureless sintering at 1650°C without additives did not result in significant densification. Increasing the sintering temperature to 1800°C improved the density of the material from ~90% TD to ~96% TD. Hot-pressing resulted in density values in the range of ~98 and 99.5% TD. Similar densities have been reported for cold-isostatically pressed Al_2O_3–TiC composites pressureless sintered at 1870°C.[6] It has also been shown that the relative density of Al_2O_3–TiC composites varies within a wide range (75%TD to >99) according to the sintering method and temperature.[14]

The hardness values obtained were consistent with the composite processing method. Pressureless sintering resulted in relatively low hardnesses, ranging from ~9.6 to a maximum of 13.9 GPa obtained for Al_2O_3–30 wt% NbC sintered at 1800°C/15 min. Hardness did not increase at high NbC contents, probably because of the low density of the material. This is further confirmed by examining the density and hardness of hot-pressed specimens. As compared to pressureless sintering, hot-pressing resulted in denser materials also characterised by hardness in excess of 19 GPa, such as that obtained for

Table 1
Properties of Al_2O_3–NbC composites

Composition (wt%)	Density (% TD)	Al_2O_3–D50 (μm)	H_v (GPa)	K_{1C} (MPa m$^{1/2}$)
Uniaxial pressing — sintered at 1650°C/30 min				
Al_2O_3	93.0	3.0	9.5±0.8	3.0±0.5
Al_2O_3 + 5% NbC	91.8	1.9	12.9±0.7	3.6±0.6
Al_2O_3 + 10% NbC	91.6	1.6	9.6±0.9	3.2±0.5
Al_2O_3 + 20% NbC	89.6	1.8	9.8±0.8	3.1±0.6
Uniaxial pressing — sintered at 1800°C/15 min				
Al_2O_3 + 5% NbC	96.1	–	9.8±0.6	2.5±0.8
Al_2O_3 + 10% NbC	96.5	–	12.6±0.5	3.1±0.7
Al_2O_3 + 20% NbC	96.2	–	9.9±0.4	3.7±0.4
Al_2O_3 + 30% NbC	95.3	–	13.9±0.6	3.0±0.8
Hot-pressed at 1650°C/30 min				
Al_2O_3 + 5% NbC	99.5	2.3	16.5±1.1	2.9±0.6
Al_2O_3 + 10% NbC	99.5	1.4	15.7±1.2	2.8±0.6
Al_2O_3 + 20% NbC	98.2	1.4	19.7±1.2	4.5±0.5
Al_2O_3 + 30% NbC	97.7	1.3	19.0±1.3	4.2±0.4

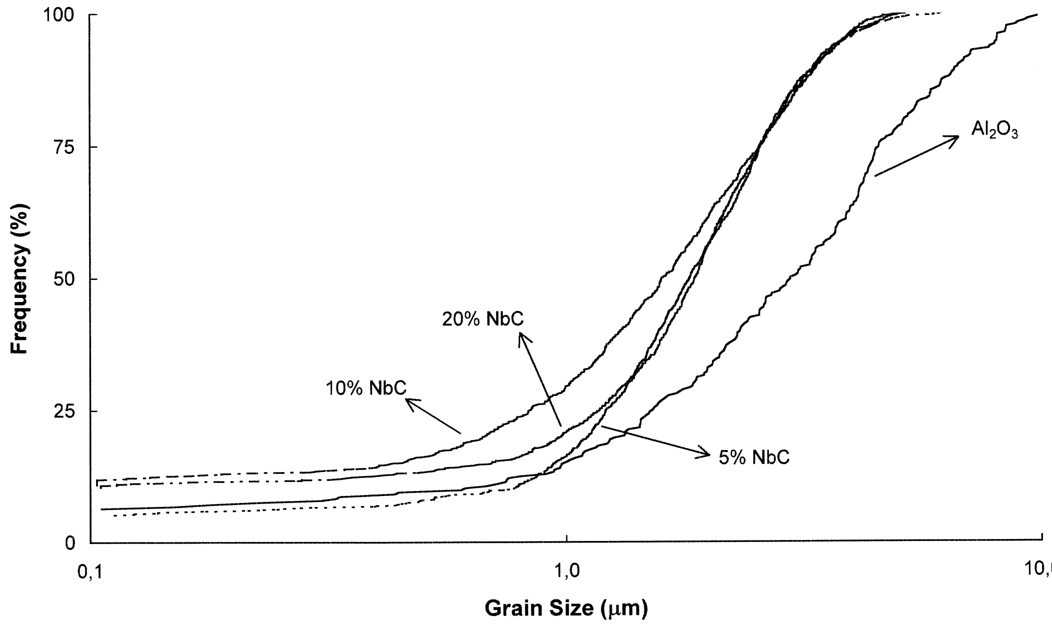

Fig. 1. Size distribution of alumina grains for plain alumina and Al_2O_3–NbC composites sintered at 1650°C/30 min.

Al_2O_3 reinforced by 20–30 wt% NbC hot-pressed at 1650°C/30 min. These values are compatible to other cutting tools materials, such as cemented carbides (12–20 GPa)[1] Al_2O_3 (19 GPa),[5] Al_2O_3–TiC (19–23 GPa),[5,15] and Si_3N_4 (19 GPa).[16] Fracture toughness of pressureless sintered Al_2O_3–NbC composites remained roughly unchanged within the margin of error. Average values ranged from 2.5 to 3.7 MPa $m^{1/2}$, regardless of the sintering temperature and NbC contents. A slight increase to ~4.5 MPa $m^{1/2}$ was obtained hot-pressing specimens with NbC contents in excess of 20 wt%. These values are compatible to those obtained from hot-pressed and hipped Al_2O_3–TiCiC (3.4–4.5 MPa $m^{1/2}$),[15,17] and grant NbC particular interest in its application as reinforcement for Al_2O_3 cutting tools.

The addition of NbC to Al_2O_3 restrained grain growth, resulting in pinned microstructures. This can be implied from an analysis of the D50 values included in Table 1. Although the increasing concentration of NbC did not result in a steady reduction in the average grain size of the Al_2O_3 grains for composites sintered at 1650°C, the difference in grain size distribution of plain and reinforced alumina is evident from Figs. 1 and 2. Grain growth inhibition has been observed in a variety

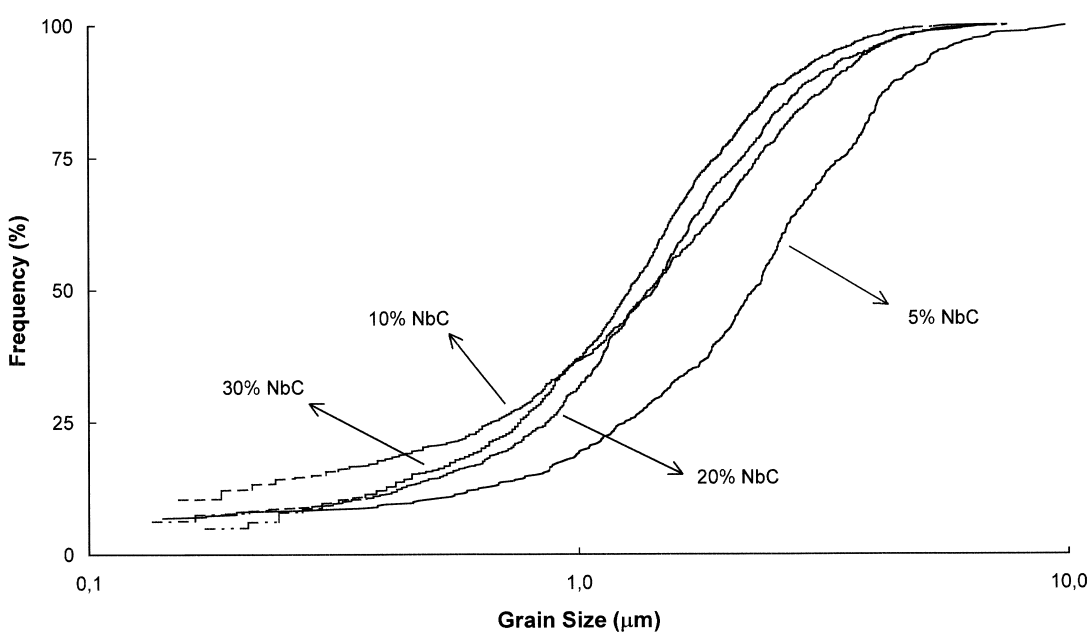

Fig. 2. Size distribution of alumina grains for Al_2O_3–NbC composites hot-pressed at 1650°C/30 min.

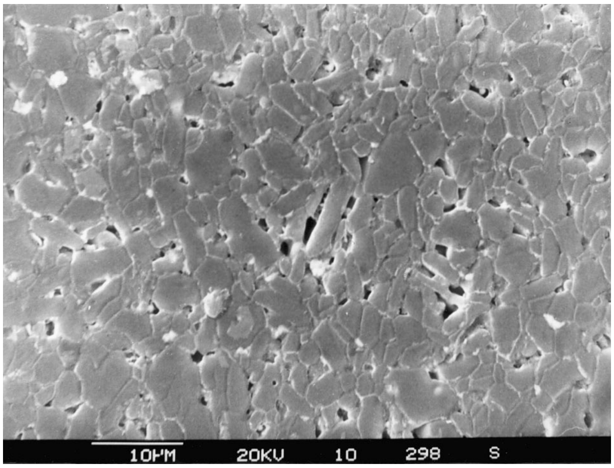

Fig. 3. Microstructure of pure Al_2O_3 sintered at 1650°C/30 min.

of particulate composites, both metallic and ceramic, such as carbide-reinforced Fe–Ni–Cr alloys,[18] Al_2O_3–ZrO_2[19] and Al_2O_3–SiC.[11] Several models have been proposed to quantitatively describe the pinning effect in composite materials.[20–22] However, they all apply to highly dense composites (<99.5%TD). In porous composites, not only dispersed particles but also remained pores restrain grain growth, which prevents a further analysis based on such models for the results obtained herein.

Figs. 3 and 4 show the microstructure of plain Al_2O_3 and Al_2O_3–5 wt% NbC composite, respectively. Both were sintered at 1650°C/30 min. The reduction in Al_2O_3 grain size caused by the addition of NbC particles is rather evident from the pinned microstructure of the composite. X-ray diffraction patterns from both sintered and hot-pressed specimens revealed that Al_2O_3 and NbC were the only crystalline phases present, as it should be expected from such composites processed without additives.

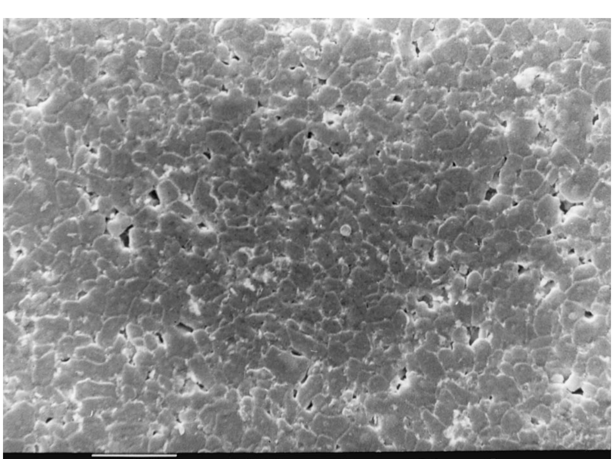

Fig. 4. Microstructure of Al_2O_3–5 wt% NbC composite sintered at 1650°C/30 min.

4. Conclusions

The results obtained from the characterisation of pressureless sintered and hot-pressed Al_2O_3–NbC composites revealed that:

1. Pressureless sintering resulted in densities ranging from 90% TD to 96% TD. Hot-pressing resulted in denser specimens (~98 and 99.5% TD).
2. The hardness of the composites appeared to be a function of both NbC content and density. Hot-pressed materials resulted in the highest hardness values, exceeding 19 GPa, which is appropriate for cutting tool materials.
3. Hot-pressing increased the maximum fracture toughness from 3.7 to 4.5 MPa $m^{1/2}$. These values are compatible to similar hot-pressed and hipped Al_2O_3–TiC.
4. The addition of NbC restrained the grain growth of Al_2O_3.

Acknowledgements

The authors acknowledge the financial support for this research granted by CAPES-Brazil and DAAD-Germany under the PROBRAL international cooperation program.

References

1. Brandt, G., Ceramic cutting tools, state of the art and development trends. *Mat. Tech.*, 1999, **14**(1), 17–24.
2. Minyoung, L. and Borom, M. P., Rapid rate sintering of Al_2O_3–TiCiC composites for cutting-tool applications. *Adv. Ceram. Mater.*, 1988, **3**(1), 38–44.
3. Xingzhong, Z., Jiajun, L., Hezhou, M. and Zhenbi, L., Wear behavior of Si_3N_4 ceramic cutting tool material against stainless in dry and water-lubricated conditions. *Ceram. Int.*, 1999, **25**, 309–315.
4. Chae, K. W., Kim, D. Y. and Niihara, K., Sintering of Al_2O_3–TiC composite in the presence of liquid phase. *J. Am. Ceram. Soc.*, 1995, **78**(1), 257–259.
5. Ishigaki, T., Sato, K. and Moriyoshi, Y., Pressureless sintering of TiC–Al_2O_3 composites. *J. Mater. Sci. Lett.*, 1989, **8**, 678–680.
6. Kim, Y. W. and Lee, J. G., Pressureless sintering of alumina-titanium carbide composites. *J. Am. Ceram. Soc.*, 1989, **72**(8), 1333–1337.
7. Chae, K. W., Kim, D. Y., Kim, B. C. and Kim, K. B., Effect of Y_2O_3 additions on the densification of an Al_2O_3–TiC composite. *J. Am. Ceram. Soc.*, 1993, **76**(7), 1857–1860.
8. Tai, W. P. and Watanab, T., Fabrication and mechanical properties of Al_2O_3–WC-Co composites by vacuum hot pressing. *J. Am. Ceram. Soc.*, 1998, **81**(6), 1673–1676.
9. Pasotti, M. R. R., Bressiani, A. H. A. and Bressiani, J. C., Sintering of alumina–niobium carbide composite. *Int. J. Refractory Metals & Hard Materials*, 1998, **16**, 423–427.
10. Dernovsek, O., Bressiani, J. C., Bressiani, A. H. A., Acchar, W. and Greil, P., Reaction bonded niobium carbide–alumina composite ceramics from polymer-filler mixtures. *J. Mater. Sci.*, in press.

11. Stearns, L. C. and Harmer, M. P., Particle-inhibited grain growth in Al_2O_3–SiC. *J. Am. Ceram. Soc.*, 1996, **79**(12), 3013–3028.
12. Lyakishev, N. P., Tulin, N. and Pliner, Y. L., Niobium in steels and alloys. *Revista da Companhia Brasileira de Metalurgia e Mineracao*., 1984, 1–14.
13. Evans, A. G. and Charles, E. A., Fracture toughness determinations by indentation. *J. Am. Ceram. Soc.*, 1976, **59**(7–8), 371–372.
14. Ishigaki, T., Sato, K. and Moriyoshi, Y., Pressureless sintering of TiC–Al_2O_3 composites. *J. Mater. Sci. Lett.*, 1989, **8**, 678–680.
15. Cutler, R. A., Hurford, A. C. and Virkar, A. V., Pressureless-sintered Al_2O_3–TiC composites. *Mater. Sci. Eng.*, 1988, **105A**, 183–192.
16. Xingzhong, Z., Jiajun, L., Baoliang, Z., Hezhou, M. and Zhenbi, L., Wear behaviour of Si_3N_4 ceramic cutting tool material against stainless steel in dry and water-lubricated conditions. *Ceram. Int.*, 1999, **25**, 309–315.
17. Burden, S. J., Hong, J., Rue, J. W. and Stromsborg, C. L., Comparison of hot-isostatically-pressed alumina–titatium–carbide cutting tools. *Ceram. Bull.*, 1988, **67**(6), 1003–1005.
18. Koul, A. K. and Pickering, F. B., Grain coarsening in Fe–Ni–Cr alloys and the influence of second-phase particles. *Acta Metall*, 1982, **30**, 1303–1308.
19. Okada, K., Yoshizawa, Y. and Sakuma, T., Grain size distribution in Al_2O_3–ZrO_2 generated by high-temperature annealing. *J. Am. Ceram. Soc.*, 1991, **74**(11), 2820–2823.
20. Zener, C. and Smith, C. S., Grains, phases and interfaces: an interpretation of microstructure. *Trans. Am. Inst. Min. Metall. Eng.*, 1948, **175**, 15–51.
21. Srolovitz, D. J., Anderson, M. P., Grest, G. S. and Sahni, P. S., Computer simulation of grain growth — III, Influence of a particle dispersion. *Acta Metall.*, 1984, **32**(9), 1429–1438.
22. Hillert, M., Inhibition of grain growth by second-phase particles. *Acta Metall.*, 1988, **36**(12), 3177–3181.