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Influence of Yttrium Oxide Doping on the Microstructures of Alumina-Niobium Carbide Composites

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ABSTRACT Ceramic cutting tools have been developed as an alternative material to cemented carbides based ones with the goal of improving cutting speeds and productivity. Among the vast variety of ceramics considered for prospective use as cutting tools materials the preference is given to the composites containing carbides as a second component, i.e., such materials as Al_2O_3-SiC, and Al_2O_3-TiC. In the present work, the influence of Y_2O_3 additives on microstructure of Al_2O_3-NbC composite is studied in order to evaluate the applicability of this material for as ceramic cutting tools manufacturing. The amount of Y_2O_3 additives varied in the ranged, 0 - 3 wt% in the Al_2O_3-NbC 20 wt% composition. Specimens were produced by consequent uniaxial and isostatic pressing followed by pressureless sintering in the flowing argon at 1750 °C for 15 min in a graphite resistance furnace. The achieved densities were up to 99% TD. Microstructure evaluation in terms of grain size distribution were achieved by mean of QUANTIKOV software applied to scanning electron microscope (SEM) micrographs. Optimization of the materials composition in regard of achieving the high densities without compromising the microstructure formation are discussed.

INTRODUCTION

Ceramic-cutting tools can increase the metal removal rate by several times over that obtained with conventional tool materials. Modern ceramic cutting tools are either based on alumina or silicon nitrite, and applications in metal cutting are determined by specific material properties of the tool material in question [1]. The growing interest in application of ceramics for cutting tools manufacturing is justified both from economical and technological perspective. Application of such materials allows tools to be used at higher cutting speeds and higher removal rates, resulting in the increase of removal rates and, consequently, in cost efficient machining [2].

Generally, additives are responsible for secondary phase formation, either inert or not, as well as influencing microstructure formation and densification. The appropriate amounts and types of additives may considerably influence the microstructure and, consequently, the final properties of the product [5]. Another way to improve the properties of ceramics is the introduction of an inert phase. An example of this beneficial effect is the addiction of inert particles of TiC into alumina matrix. These particles increase the hardness and toughness of alumina and allow its use as cutting tool.

It has been known that inert particles of secondary phase can inhibit grain growth and lead to a "pinned" microstructure where the grain growth ceases [12]. Zener at al [12] first quantified this effect in 1948. Predicting the dependence of the pinned (equilibrium) grain size on the volume fraction and radius of particle [12]. "Zener pinning" is a phenomenon in which second-phase particles hinder the coarsening of a matrix phase (grain growth) by pinning the grain boundaries movement. Therefore, the grain size control is a critical issue in regard of the processing and applications of advanced ceramic materials. The inhibition of grain growth by second-phase particles has been extensively studied, for instance, in ceramic systems, where ceramic inclusions were introduced into a ceramic matrix, this class of materials being commonly called ceramic matrix composite – CMC [12,13]. The CMC are materials represent one of the most recent families of structural ceramics [3]. Due to the CMC technique, materials with more preferable properties as compared to monolithic ceramics, such as elevated toughness and prolonged life time [14]. Become available transition metal carbides are used extensively due to their physical properties, such as high melting points, hardness, and electrical conductivity. Transition metal carbides are known to be successfully used as catalysts in chemistry, as well as reinforcing dispersoids in ceramic matrix composite materials in mechanical engineering [15].

Aluminum oxide based materials are among the most frequently utilized high-temperature structural ceramics [3-6]. Al_2O_3 exhibits favorable creep resistance compared to other ceramics. Alumina can be doped with various cations to increase its temperature and stress limits in creep. Currently, one of the most well known additives to alumina aimed for structural applications is yttria, Y_2O_3 [7,8]. Y_2O_3 addictions were shown to improve the high-temperature mechanical properties such as, tensile and compressive creep resistance, and to reduce atomic mobility, which enables better microstructural control [9]. Yttrium has a limited solubility of 10 ppm in bulk α-alumina, above this amount yttrium precipitates out as yttrium aluminate garnet ($Y_3Al_5O_{12}$, YAG) particles. The beneficial effect of yttrium in alumina is closely related to the segregation behavior of the dopant. Several studies have shown that yttrium segregates on free surfaces and grain boundaries, or precipitates out as YAG, if its amount exceeds the solubility limit in the matrix [10]. It is known that YAG is an oxide with cubic structure with high creep resistance, and can be used up to high temperatures (above 1500 °C) in oxidizing atmosphere [11].

The CMC alumina-niobium carbide has been developed as alternative material for commercial cutting tools based on Al_2O_3-SiC and Al_2O_3-TiC. The control of the grain size in ceramic materials is of vital importance, since many of their physical, in particular mechanical, properties show a marked dependency on mean grains size, and on grain size distribution [16].

This work presents the study of yttria effect on microstructure formation in alumina-niobium carbide ceramic composite.

EXPERIMENTAL PROCEDURES

The powders used in this study were: Al_2O_3 (Alcoa, A-16), NbC (Herman C. Starck) e Y_2O_3 (Merck 99,9%). The amount of NbC was fixed at 20 wt%. The composition of the prepared compositions were: undoped Al_2O_3; $Al_2O_3$20wt%-NbC; (Al_2O_3-0.5wt%Y_2O_3)-20wt%NbC; (Al_2O_3-1wt%Y_2O_3)-20wt%NbC e (Al_2O_3-3wt%Y_2O_3)-20wt%NbC, which were designated as: A, AN; A05Y N, A1Y N e A3Y N, respectively.

The powder compositions were prepared by mixing the starting powders in attriction mill for 4 hours, in isopropanol with Al_2O_3 milling media. The undoped alumina material was prepared without any additional powder processing. After milling isopropanol was removed in a rotoevaporater, and the mixtures were further dried in drying box at 110 °C for 24 hours. Pellets of 14 mm diameter were uniaxially pressed at 50 MPa followed by cold isostatic pressing at 200 MPa, and pressureless sintered under flowing argon at 1750 °C for 15 min in a graphite-resistance-furnace. The heating and cooling rates were 20 °C/min. Sintering schedule was developed according to the results of dilatometric experiments [17,18]. The theoretical densities were calculated according to the rule of mixtures, and the apparent density of sintered samples was determinated by Archimedes method. X-ray (Cu $K_{\alpha 1}$ radiation) diffraction analysis was carried out in order to identify phases formed during sintering.

Microstructural characterization was carried out by means of scanning electron microscopy (SEM), on specimens polished with diamond past to 1 μm finish, and thermically etched in vacuum at 1550 °C for 20 min. Grain size distribution was estimated by image analysis of the SEM micrographs using software Quantikov [19].

RESULTS AND DISCUSSION

The powder of all compositions had a mean particle diameter of 0.65 µm as determined by laser diffraction (CILAS).

Densification

The Table 1 shows the results of theoretical green, and sintered densities of the samples.

Table 1- Densities.

Sample	Composition	TD (g/cm^3)	ρ_g (g/cm^3)	% TD	ρ_s (g/cm^3)	% TD
A	Al_2O_3	3.98	2.32	58.1	3.93	98.7
AN	Al_2O_3-20wt%NbC	4.41	2.55	57.9	4.32	99.2
AY05N	(Al_2O_3-0,5wt%Y_2O_3)-20wt%NbC	4.42	2.51	56.9	4.39	99.3
AY1N	(Al_2O_3-1wt%Y_2O_3)-20wt%NbC	4.42	2.52	57.0	4.39	99.5
AY3N	(Al_2O_3-3wt%Y_2O_3)-20wt%NbC	4.44	2.51	56.5	4.42	99.5

Where: TD = theorical density; ρ_g = green density; ρ_s = sintered density.

No significant differences were observed for the green densities values of all prepared samples. After sintering all materials exhibited high densities close to theoretical values.

The crystalline phases formed in the composites, identified by X-ray diffractometry, were: α-Al_2O_3, NbC, and $Al_5Y_3O_{12}$ (YAG). The presence of Y_2O_3 as a separate phase was not determined in any of the sintered Y_2O_3-doped materials. Therefore it may be concluded that Y_2O_3 reacted with Al_2O_3 forming $Al_5Y_3O_{12}$ (YAG), and also was consumed during solid solution formation with α-Al_2O_3.

Microstructural Investigation

SEM analyses were accomplished on the bulk part of sintered samples, which were cut lengthwise for this purpose. Resulting microstructure are presented in Fig.1. Homogeneous distribution of second phase in alumina matrix can be observed. However, due the fact that atomic weights of yttrium and niobium are rather similar, and due to the conditions of the performed analyses (image was formed in secondary electrons), it is not possible to clearly distinguish the YAG and NbC phases, since both appear in micrographs as having the same light contrast.

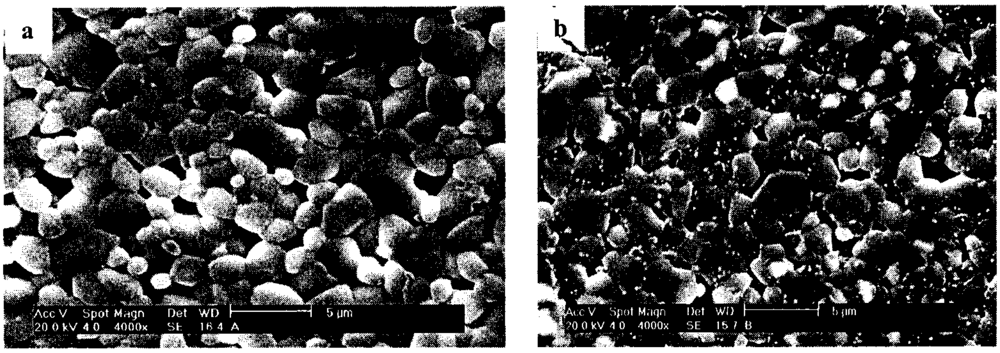


Fig. 1 - SEM images of the samples: (a) A and (b) AN.

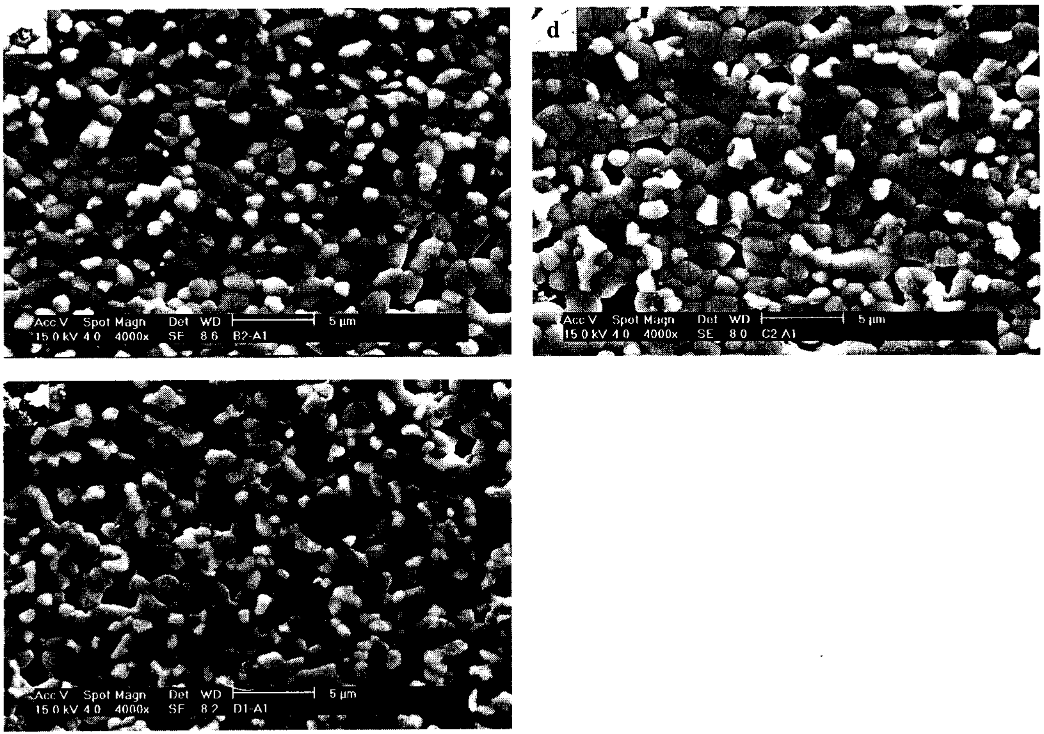
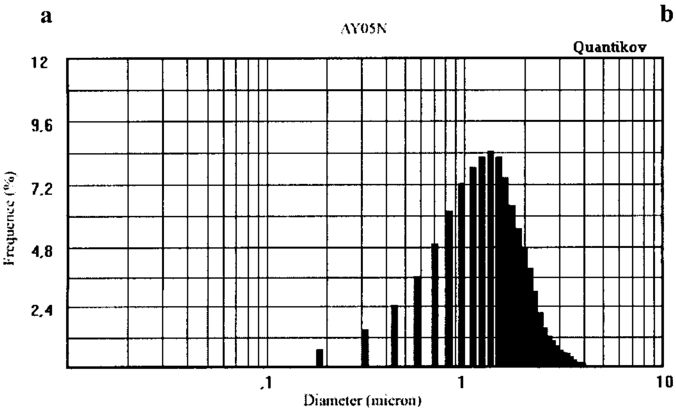
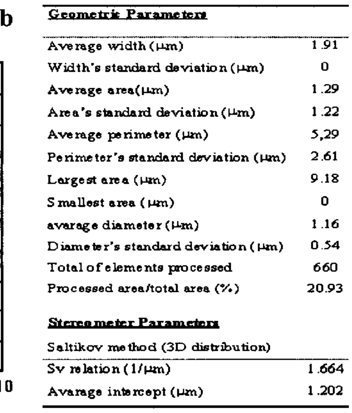


Fig.1 - SEM images of the samples: (c) AY05N, (d) AY1N and (e) AY3N.

Grain Size Distribution

The grain size distribution analyses of sintered samples was estimated using the measurements of mean perimeter of the particles. The typical particle size distribution together with summary table generated by Quantikov software are presented in Fig. 2.





Geometric Parameters	
Average width (µm)	1.91
Width's standard deviation (µm)	0
Average area(µm)	1.29
Area's standard deviation (µm)	1.22
Average perimeter (µm)	5,29
Perimeter's standard deviation (µm)	2.61
Largest area (µm)	9.18
Smallest area (µm)	0
avarage diameter (µm)	1.16
Diameter's standard deviation (µm)	0.54
Total of elements processed	660
Processed area/total area (%)	20.93
Stereometer Parameters	
Saltikov method (3D distribution)	
Sv relation (1/µm)	1.664
Avarage intercept (µm)	1.202

Fig. 2: a) distribution graphic and b) summary table, generated by Quantikov software.

The results of average grain size measurements are presented in Table 2.

Table 2 - Average grain size for the investigated materials.

Samples	Mean diameter (μm)
	20 °C/min – 1750 °C/15 min
A	1.6 ± 1.1
AN	1.4 ± 0.7
A05YN	1.2 ± 0.6
A1YN	1.2 ± 0.7
A3YN	1.2 ± 0.6

The decrease in grain size of alumina from 1.6 to 1.4 μm, was attributed to the efect of NbC addictions which may be considered as an inert second phase. This inert phase acts as a physical barrier during the volumetric shrinkage of alumina matrix. It is known that the presence of inert particles of a second phase can inhibit grain growth due to the so-called "pinning" effect [12]. In fact, there are several studies based on theoretical models and microstructural observations, which deal with sintering and microstructure formation of ceramic matrix composites containing a second, inert phase. The presence of such a phase in terms of shrinkage due to de formation of a three-dimensionally interconnected network of rigid particles, which function as a physical barrier; development of various structural defects, such as cracks, during sintering; non-uniform shrinkage resulting from the variation in the spatial distribution of green density of the matrix caused by the presence of inert inclusions [15]. The latter mechanism was tentatively attributed in the present case.

The addiction of Y_2O_3 to the composite Al_2O_3-20wt%NbC result in a more fine microstructure formation, the mean grain size of alumina decreasing from 1.4 to 1.2 μm. This behavior can be associated with the segregated/precipitated of YAG on the grain boundaries and triple-points junction. YAG is believed to influence the surface of alumina particles causing alteration in diffusion process and, as a consequence, modifying sintering mechanisms in the material[17,20]. One of the effects is the hindering of grain growth of alumina due the fact of its being in contact with the phase with lower surface energy.

Considering the general similarity of the diffusional processes occurring during sintering and high temperature creep tests of alumina it is possible to draw some parallels with the results obtained during the investigations of strengthening mechanisms in alumina ceramics under creep conditions [5]. According to [5], depending on the state of yttria in the ceramics the following phenomena are observed: (a) reduced diffusivity along the grain boundaries due to the interaction of the segregant with the diffusing species (cation, anions, or both), (b) solute and/or precipitate drag on moving grain front, (c) interaction of segregant with the grain-boundary dislocation motion, (d) influence of the segregant with the generation or annihilation of lattice dislocations at the grain boundaries, (e) enhanced resistance to grain sliding due a monolayer or a submonolayer of a second phase, or (f) a combination of these mechanisms. Gulgun et al [5] have suggested that reduced diffusivities along the grain boundaries due to the interaction of the diffusing species with the segregant (mechanism (a) is one of the viable mechanisms responsible for decreased grain size of alumina in Al_2O_3-Y_2O_3 material, which can be also attributed to our materials, Al_2O_3-NbC composite.

CONCLUSIONS

It was shown that both the second phase, NbC and addictions of Y_2O_3, cause the decrease of the mean grain size of alumina matrix, however by means of different mechanisms. While the NbC particles act as physical barriers causing the so-called "pinnong" effect, the Y_2O_3 is believed to cause surface phenomena modifying the diffusion-controlled grain growth mechanisms during sintering. No significant differences both for sintering densities and mean grain size of alumina matrix were observed for the composite ceramics in the investigated range of Y_2O_3 addictive constant, i.e., for 0.5 to 3.0 wt % of Y_2O_3.

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REFERENCES

[1] G. Brandt, Mat. Tech. 14.1 (1999), p. 17.
[2] W. Acchar, P. Greil, A.E. Martinelli, C.A.A. Cairo, A.H.A. Bressiani, J.C. Bressiani, J. Eur. Ceram. Soc. 20 (2000), p. 1765.
[3] R. Naslain, J. Eur. Ceram. Soc. 18 (1998), p.1795.
[4] T. Weon-Pil, T. Watanabe, J. Am. Ceram. Soc. 82 (1999), p. 245.
[5] M. Gulgun, V. Putlayev, M. Ruhle, J. Am. Ceram. Soc. 82 (1999), p. 1849.
[6] T. Ishigaki, K. Sato, Y. Moriyoshi, J. Mater. Sci. Lett. 8, (1989), p. 678.
[7] J. Fang, M. Thompson, M. Harmer, H. Chan, Sintering Technology USA (1996), p. 317.
[8] B. Fenk, H. Opielka, S. Kuhnemann, M. Gulgun, E. Bischoff, Prakt. Metallogr. 36 (1999), p. 433.
[9] A. Towata, H.J. Hwang, M. Yasuoka, M. Sando, J. Am. Ceram. Soc. 81 (1998), p. 2469.
[10] A. M. Thompson, K. K. Soni, H. M. Chan, M. P. Harmer, D. B. Williams, J. M. Chabal, R. Levi-Setti, J. Am. Ceram. Soc. 80, (1997), p. 373.
[11] S. Wang, T. Akatsu, Y. Tanabe, Z. Nakagawa, E. Yasuda, J. Am. Ceram. Soc. 81 (1998), p. 263.
[12] L.C. Stearns, M.P. Hamer, J. Am. Ceram. Soc. 79 (1996), p. 3013.
[13] D. Fan, L-Q. Chen, S-P.P. Chen, J. Am. Ceram. Soc. 81 (1998), p. 526.
[14] K. Niihara, J. Am. Ceram. Soc. Jpn. 99 (1991), p. 974.
[15] O. Dernovsek, J.C. Bressiani, A.H.A. Bressiani, W. Acchar, P. Greil, J. Mater. Sci. 35 (2000), p. 2201.
[16] P.A. Marchlewski, A.R. Olszyna, K.J. Kurzydlowski, B. Ralph, Ceramics International 25 (1999), p. 157.
[17] A.H. Rumbao, R.M. Rocha, A.H.A. Bressiani, J.C. Bressiani, Proceeds of 44^O Ceramic Brazilian Congress (2000), CD.
[18] A.H. Rumbao, A.H.A. Bressiani, J.C. Bressiani, Proceeds of 14° Engineering and Science of Materials Brazilian Congress (2000), CD.
[19] L.C.M. Pinto, V. Vasconcelos, W.L. Vasconcelos, J.C. Bressiani, Acta Microscopica, Supplement B (1996), p. 168.
[20] R.M. Rocha, A.H.A. Bressiani, J.C. Bressiani, Int. J. Refract. Metals Hard Mat. 16 (1998), p. 423.

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