

## Sintering Behavior of the $\text{Al}_2\text{O}_3$ -NbC Composites with $\text{Y}_2\text{O}_3$ Addition

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**Abstract.** Sintering behavior of  $\text{Al}_2\text{O}_3$ -NbC powders mixtures with  $\text{Y}_2\text{O}_3$  addition was investigated under condition of constant heating rate in dilatometric experiments. Three different compositions containing 10, 20 and 40 wt% of niobium carbide were prepared. The amount of yttria, which was used as a sintering aid, was kept constant at 3 wt%. Identical sintering schedule was applied to all compositions. The constant heating rate of 20 °C/min up to 1750 °C was applied followed by an isothermal dwell time of 15 minutes. Experimental results imply that NbC modifies the  $\text{Al}_2\text{O}_3$  sintering behavior by shifting the sintering stages to higher temperatures, thus hindering densification of the matrix. Mixtures with yttria additions exhibited systematic delay of the initial shrinkage stage. An anomalous peak on the densification rate curves on a certain densification stage is also observed. These characteristics indicate that yttria modifies the diffusion process of the alumina matrix.

### Introduction

Alumina based ceramic composites, with a reinforcing phase of transition metal carbide or nitride, are suitable for applications where high hardness and wear resistance are necessary. The additions of hard carbides to  $\text{Al}_2\text{O}_3$  improve not only fracture toughness, but also thermal shock resistance by increasing the thermal conductivity of the material. On the other hand, the difficulties for sintering of covalent compounds, such as transition metal carbides, are avoided by incorporating of the latter into alumina matrix [1].

The carbide most commonly used as a reinforcing component in alumina matrix ceramic is titanium carbide in the amount of 20-40% in weigh. These composites are commercially used for cutting tool inserts fabrication by hot pressing and subsequent diamond machinery. However, conventional pressureless sintering presents a more economically viable fabrication route compared to hot pressing or hot isostatic pressing [2]. There are two main obstacles preventing the use of pressureless sintering for such composite materials fabrication:

- interaction of alumina with free carbon present in the carbide additions or with the carbide itself is expected to result in volatile phases formation [3], which may hinder the overall densification by shifting the sintering mechanism from bulk diffusion to evaporation-condensation;
- the presence of a inert, rigid second phase inclusions can cause substantial reduction of densification rates of the composite matrix [4].

Therefore, considerable efforts have been made to understand the factors controlling the pressureless sintering of oxide-matrix-carbide ceramic composites in order to develop an improved processing route for such materials.

Niobium carbide, NbC, due to its remarkable properties, such as high melting point, good electric conductivity and high hardness, was considered as an even better candidate for alumina matrix composites reinforcement. Such composites are expected to find application as wear resistant materials and cutting tools. Alumina-niobium carbide composite material has been successfully produced by pressureless sintering in a near-dense (relative density higher than 96% of theoretical) state [5].

The goal of the present paper was to thoroughly investigate densification behavior of  $\text{Al}_2\text{O}_3$ -NbC composites with and without  $\text{Y}_2\text{O}_3$  additions. The influence of NbC content and  $\text{Y}_2\text{O}_3$  additions on densification kinetics and their role in sintering mechanism modification were studied.

### Experimental Procedure

Powders of  $\text{Al}_2\text{O}_3$  (A-16 SG, Alcoa, mean particle size  $\approx 0.4 \mu\text{m}$ ), NbC (H. C. Stark, mean particle size  $\approx 2.3 \mu\text{m}$ ), and  $\text{Y}_2\text{O}_3$  (Merck) were used as raw materials. Two groups of composition were prepared:  $\text{Y}_2\text{O}_3$ -free, and with a fixed amount of  $\text{Y}_2\text{O}_3$  added to alumina that was chosen as 3wt%. Inside each group the NbC content was a variable parameter, the amounts added being 10, 20 and 40 wt% in relation to  $\text{Al}_2\text{O}_3$ . Two NbC-free compositions (pure  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ -3% $\text{Y}_2\text{O}_3$ ) were prepared as a reference. Overall, the compositions prepared for the present study can be described as  $\text{Al}_2\text{O}_3$ -xNbC and  $(\text{Al}_2\text{O}_3$ 3% $\text{Y}_2\text{O}_3$ )-xNbC, where x=0, 10, 20, 40 wt%.

The powders were mixed in a ball milling for 10 h in isopropanol with alumina milling media. The mixture was dried at 110 °C for 4h in a drying chamber and subsequently crushed in an agate mortar and passed through a 32- mesh sieve in order to disintegrate soft agglomerates.

Green bodies of cylindrical shape (6 mm diameter and 10 mm height) were subsequently uniaxially and cold isostatically pressed under 100 and 200 MPa, respectively. The resulting green densities increased with the increase of NbC content from 57 to 61% for 0 and 40 wt% of NbC additions. Such behavior can be explained by the fact that NbC powders being coarser provide better packing of the powder particle in the compact.

The investigation of sintering behavior was accomplished in a Netsch-402 dilatometer with a graphite resistance furnace that allowed continuous in situ measurements of linear shrinkage during the whole sintering cycle. The same sintering schedule was applied to all compositions. Samples were heated at the rate of 20 °C/ min up to 1750 °C, followed dwell time of 15 min. Sintering experiments were conducted in flowing argon. Sintered samples were then characterized by density measurements and scanning electron microscopy (SEM). The samples for SEM were prepared by standard ceramographic procedure.

### Results and Discussion

The results of dilatometric investigation of the fine-grain  $\text{Al}_2\text{O}_3$ -NbC composites sintering behavior is presented in a form of linear shrinkage versus temperature curves in Fig.1. The curves in Fig. 1(a) correspond to the samples without  $\text{Y}_2\text{O}_3$  addition and the ones in Fig. 1(b) to the samples with 3 wt%  $\text{Y}_2\text{O}_3$  addition. The curve of pure  $\text{Al}_2\text{O}_3$  is added for comparison. The results clearly show that with increasing amount of NbC added the shrinkage curves shift to higher temperatures. It can be further noted that no significant densification occurred at temperatures exceeding 1700°C, as well as during isothermal part of the experiment.

The plots of the shrinkage rate versus temperature for pure  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  doped  $\text{Y}_2\text{O}_3$ , NbC, and NbC 3 wt%  $\text{Y}_2\text{O}_3$ , are presented in Fig 2. It can be observed that the main peak which corresponds to the maximum shrinkage rate lies in the same temperature regardless yttria addition. However the curves of the containing yttria samples exhibit a systematic delay of about

100 °C in the initial shrinkage. It is noted also that the temperature of maximum shrinkage is slightly shifted to higher temperature according to the increasing in NbC concentration. Table 1 summarizes the temperatures of initial shrinkage (onset Temperature) and the maximal shrinking rate for all samples. The influents of the NbC particles and the Y<sub>2</sub>O<sub>3</sub> doping on the shrinkage rate will be discussed in detail further.

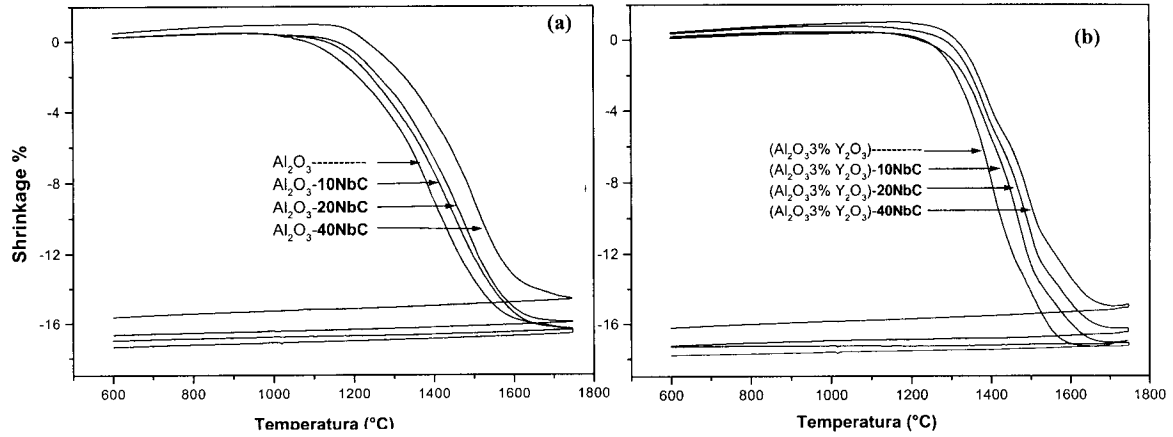


Fig.1: Densification curves (linear shrinkage as a function of temperature) for Al<sub>2</sub>O<sub>3</sub> -xNbC samples, where x= 0,10, 20 and 40 %wt. (a) samples with 0% Y<sub>2</sub>O<sub>3</sub>; (b) samples with 3 %wt Y<sub>2</sub>O<sub>3</sub> added to Al<sub>2</sub>O<sub>3</sub>

It is observed some secondary peaks in Fig. 2. In the increasing of shrinkage rate stage the peak is clearly defined for samples with Y<sub>2</sub>O<sub>3</sub>, whereas samples without the additive present some shoulders. Samples with Y<sub>2</sub>O<sub>3</sub> also exhibit systematic anomalous peak in the stage of shrinking rate decreasing, which lies on 1500 °C and 1580 °C for alumina component only and for the composite, respectively.

From a theoretical standpoint, the total amount of shrinkage that can occur during sintering,  $\rho(T)$ , is related only to the green density,  $\rho_0$ , through the expression:

$$\rho(T) = \rho_0 \left( \frac{L_0}{L(T)} \right)^3 \quad (1)$$

where  $L_0$  is the linear dimension of the green body and  $L(T)$  is the sample length measured during sintering.

However, if the shrinkage rate is plotted versus the relative density of the samples the information about overall sintering behavior as well as about each sintering stage described by the model of solid-state sintering [6] may be obtained. Such plots for the investigated materials are presented in Fig. 3. The densities of all samples after sintering exceed 95% of the theoretical density, which shows that neither of the dopants hinders overall densification. The first peak lies in the range of relative densities of 64 to 67%, which corresponds to the first sintering stage of the model of solid-state sintering. Some differences concerning the intermediate sintering stages can be observed. Thus, the addition of NbC causes a shift of the main maximum of the shrinkage rate toward higher relative densities, in the range of 73 to 82%. The last peak presented in Fig 3(b), for samples with Y<sub>2</sub>O<sub>3</sub>, occurs at practically the same range of relative density and close to 90% of the theoretical density.

Table 1: Onset temperature of the initial shrinkage (T-Onset) and the temperature of the maximum shrinkage rate (T<sub>m</sub>).

Sample	T-Onset (°C)		T <sub>m</sub> (°C)	
	0% Y <sub>2</sub> O <sub>3</sub>	3%Y <sub>2</sub> O <sub>3</sub>	0% Y <sub>2</sub> O <sub>3</sub>	3%Y <sub>2</sub> O <sub>3</sub>
Al <sub>2</sub> O <sub>3</sub>	985	1117	1397	1403
Al <sub>2</sub> O <sub>3</sub> -10NbC	1000	1112	1465	1470
Al <sub>2</sub> O <sub>3</sub> -20NbC	1019	1124	1495	1499
Al <sub>2</sub> O <sub>3</sub> -40NbC	1081	1177	1505	1503

#### *Effect of NbC reinforcement and its concentration on densification behavior*

At least three effects, resulting from the increasing amount of NbC additions, can be observed on Fig. 2 and Table 1, as compared with the shrinkage behavior of pure Al<sub>2</sub>O<sub>3</sub>: (i)- the gradual shift of the maximum shrinkage rate to higher temperatures (up to about 100 °C higher with 40% NbC); (ii)-the alteration of the slope of the shrinkage rate curve; (iii)- formation of two shoulders on the shrinkage curve on the initial stage of sintering, more visible for 40 wt% NbC samples.

The observed effects can be explained in terms of the presence in a system undergoing solid-state densification, which occurs due to diffusion process, of an inert component, in this case the NbC. The shift of the maximum of shrinkage rate to higher temperatures is caused by the energetic considerations since the inert particles of NbC hinders bulk diffusion, and therefore higher temperatures are necessary to provide sufficient driving force for densification. After this energetic barrier is overcome, the diffusion occurs faster, which causes the change of the slope of the shrinkage rate curve as well as the slight increase of the absolute values of the latter.

#### *Effect of Y<sub>2</sub>O<sub>3</sub> additive on densification behavior*

The sintering kinetics of Al<sub>2</sub>O<sub>3</sub>-NbC composite is markedly affected by the presence of 3%wt of Y<sub>2</sub>O<sub>3</sub>. The following effects can be attributed to the Y<sub>2</sub>O<sub>3</sub> additions: (i) the shift of the temperature of the onset of shrinkage to higher temperatures by about 100 °C; (ii) the change of the slope of the shrinkage rate versus temperature curve; (iii) an increase of absolute maximal shrinking rate values by about 50% in relation of yttria free samples; (iv) emphasizing of the peak in the first sintering stage in combination with NbC presence followed by a pronounced decrease of shrinkage; (v) the formation of a shoulder on the shrinkage rate curve on the final stage of sintering.

The influence of yttria and other rare-earth oxide additives on alumina sintering behavior and microstructure development were previously investigated [7,8]. Two effects resulting from such additions were unambiguously established: the hindering of sintering kinetics and of the grain-growth of alumina. Although the exact operating mechanisms of rare-earth oxides influence are still under discussion, it was postulated that the large yttrium cations at the grain boundaries block the diffusion of ions along grain boundaries, leading to the reduced grain boundary diffusion [8]. This seems to be a plausible explanation for the delay of the shrinkage onset in this present work.

The combination of yttria effect with the NbC presence in the alumina sintering mechanisms results in a formation of a defined peak before the main peak (Fig. 2). This peak means that in a certain sintering stage the shrinkage rate decrease significantly with the increasing volume fraction of the inclusion phase, starting from quite low NbC content. For all concentrations this peak lies about 1390 °C which is practically the same temperature of alumina maximal shrinking rate peak, though they occur in different sintering stages (Fig. 3).

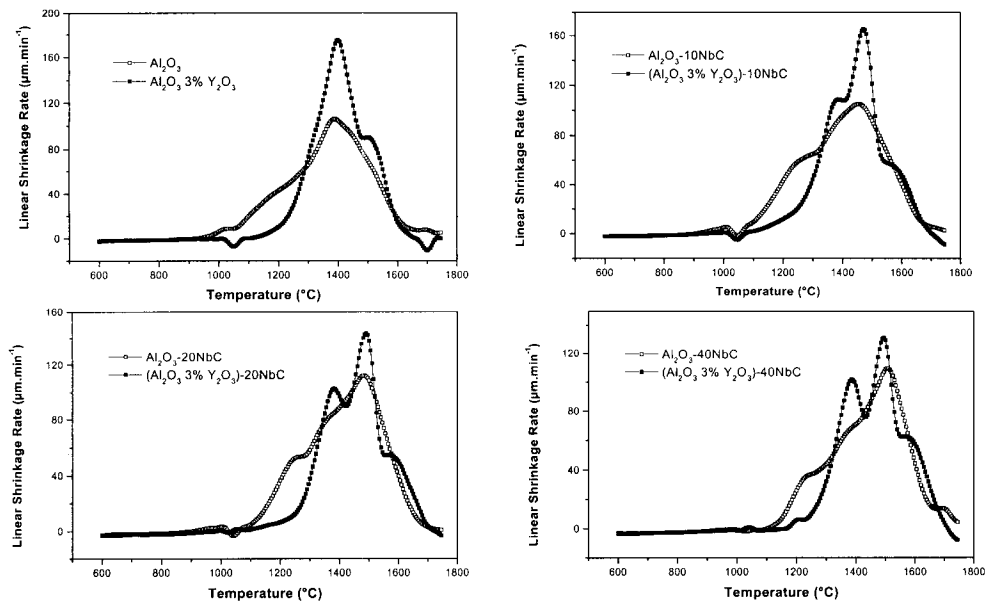


Fig. 2: Linear Shrinkage rate vs. temperature, comparing curves of the samples with and without Y<sub>2</sub>O<sub>3</sub>. (a) Al<sub>2</sub>O<sub>3</sub>; (b) Al<sub>2</sub>O<sub>3</sub> 10NbC; (c) Al<sub>2</sub>O<sub>3</sub> 20NbC; (d) Al<sub>2</sub>O<sub>3</sub> 40NbC.

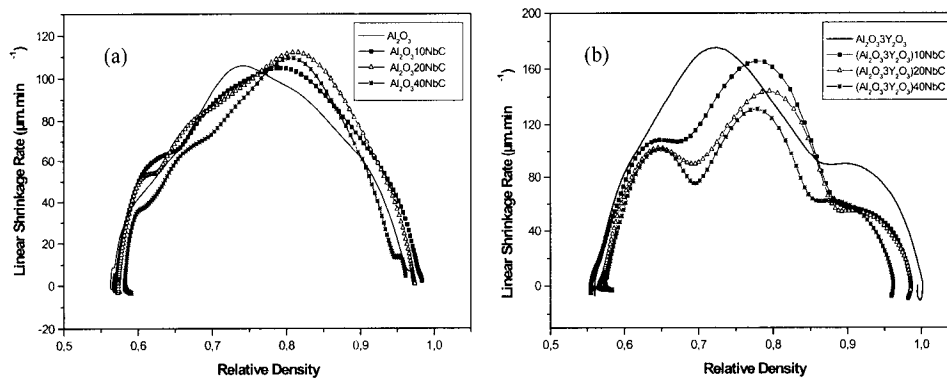


Fig. 3: Linear Shrinkage rate as a function of relative density for Al<sub>2</sub>O<sub>3</sub>-xNbC samples, where x= 0, 10, 20 and 40 %wt. (a) samples with 0% Y<sub>2</sub>O<sub>3</sub>; (b) samples with 3 %wt Y<sub>2</sub>O<sub>3</sub> added to Al<sub>2</sub>O<sub>3</sub>

The anomalous peak that corresponds to a slight increase in shrinkage rate curves occurs in the final sintering stage of all compositions (Fig. 3). Formation of these peaks can be attributed to the saturation level of yttrium at the alumina grain boundaries, resulting in the intergranular precipitation of yttrium-rich secondary phase. In fact previous studies have detected fine precipitates of yttrium aluminum garnet (YAG: 3Y<sub>2</sub>O<sub>3</sub>.5Al<sub>2</sub>O<sub>3</sub>) scattered throughout the microstructure [5,9,10]. The presence of this phase along grain boundaries and at three point junctions can be acting as a pin providing physical constraint for the Al<sub>2</sub>O<sub>3</sub> grain growth, allowing an increase in the densification rate. At any rate the effect of Y<sub>2</sub>O<sub>3</sub> on the overall shrinkage behavior together with the well-defined peak formation on the shrinkage rate curves needs further research.

The results of microstructural investigations of sintered ( $\text{Al}_2\text{O}_3$  3% $\text{Y}_2\text{O}_3$ )-NbC composites are presented in Fig 4. As it can be seen the final grain size of alumina is strongly influenced by the second phase (white grains) additions indicating that pinning mechanism is involved in the sintering process.

Fig.4: Scanning electron micrographs of ( $\text{Al}_2\text{O}_3$  3% $\text{Y}_2\text{O}_3$ )-NbC composite polished and thermally



etched at 1450 °C in vacuum. (a) 10%NbC; (b) 20% NbC; (c) 40%NbC.

### Conclusions

Sintering behavior of ceramic particulate composites, consisting of fine-grained  $\text{Al}_2\text{O}_3$  matrix with 3%wt of  $\text{Y}_2\text{O}_3$  addition and coarse, inert NbC inclusions was investigated using constant heating rate technique. The dilatometer records provided interesting results about the sintering behavior of these materials. The presence of inert rigid particles of NbC shifts the shrinkage to higher temperatures and hinders matrix densification on the first sintering stage. The combination of  $\text{Y}_2\text{O}_3$  and NbC effects on the densification mechanisms leads to a pronounced decrease of shrinkage rate on the initial stage of sintering.  $\text{Y}_2\text{O}_3$  addition retards the initial shrinkage possibly due to the inhibition of grain boundary diffusion mechanism. It can also be tentatively stated that  $\text{Y}_2\text{O}_3$  presence enhances the composite densification in the final sintering stage due to the pinning effect of yttrium rich phase precipitated along alumina grain boundary.

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### References

- [1] J.G. BALDONI and S.T. BULJAN, Am. Ceram. Soc. Bull., 67-2 (1988), p. 381-387.
- [2] R. A. CUTLER., A. C. HURFORD, A. V. VIRKAR, Int. J. Refract. Met. Hard Mater., June (1989), p. 114-120.
- [3] Y.K. WOOK, J.L. GUNN., J. Am. Ceram. Soc., 72-8 (1989), p. 1333-1337.
- [4] C. L. FAN and M. N. RAHAMAN, J. Am. Ceram. Soc., 75-8 (1992) p. 2056-2065.
- [5] R.M.R. PASOTTI, J. C. BRESSIANI, A.H.A. BRESSIANI, Int. J. Refract. Met. Hard Mater., 16 (1998), p.423-427.
- [6] N. J. SHAW, Powder Metall. Int. , 21 (1989), p. 16-21.
- [7] E. SATO and C. CARRY, J. Am. Ceram. Soc., 78-8 (1998), p. 2156-2160.
- [8] J. FANG, A.M. THOMPSON, M.P. HARMER, H. M. CHAN, J. Am. Ceram. Soc., 80-8 (1997), p. 2005-2012.
- [9] R.C. McCUNE, W. T. DONLON, J. Am. Ceram. Soc., 69-8 (1985), p. C196-C199.
- [10] A. TOWATA, H. J. HWANG, M. YASUOKA, M. SANDO, J. Am. Ceram. Soc., 81-9 (1998) p. 2469-2472.

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