

Aluminosilicates Assisted Pressureless Sintering of Sialon Ceramics

Azhar Hussain, Matteo Pavese, Luca Settineri, P. Fino, S. Biamino, C.F. Badini, M. R Abdul Karim, and E. Padovano

Abstract—The effect of aluminosilicates on the pressureless densification of a ceramic with composition in the sialon region was studied. Aluminosilicates (kaolinite and muscovite) were used as sintering aids. Kaolinite addition caused a linear increase in densification up to 10 weight percent. Kaolinite increased density and hardness at high temperature as compared to the muscovite-modified samples which showed discordant results in density and hardness values.

Keywords: Densification, Kaolinite, Muscovite and Sialon

I. INTRODUCTION

SIALON ceramics are an important class of nitride-based materials. They are used as structural as well as functional ceramics. Sialon ceramics development in structural engineering applications allowed to obtain good mechanical properties coupled with ease of fabrication as compared to the pure silicon nitride ceramics [1]. Addition of sintering additives in addition to the native surface oxide (i.e. SiO_2 on the surface of Si_3N_4 and Al_2O_3 on the surface of alumina) helps to improve the sinterability of Si_3N_4 [2]. Addition of Al_2O_3 and Y_2O_3 as sintering additives helps in promoting a liquid phase by forming a ternary eutectic [3]. Addition of Al-O units in the Si_3N_4 structure results in a solid solution of Si_3N_4 with structure similar to the Si_3N_4 one but good toughness, combined with a simpler fabrication. This phase can be sintered using conventional liquid phase sintering [4], and is represented as β -Sialon on the Jancke Prism [5]. β -Sialon is a tough phase but it lacks the minimum hardness necessary to rank this material as a structural ceramic. On the other hand there is another substitutional solid solution of Si_3N_4 called α -Sialon, limited in the composition range given by formula, $\text{M}_x\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$. It is a hard and strong phase but difficult to be synthesized. Development of α -Sialon starting from Si_3N_4 involves the substitution of the Si-N units typical of the Si_3N_4 with m Al-N units, and n Al-O units [6]. For α -Sialon, though, replacement of Si-N units in Si_3N_4 with Al-N and Al-O units requires special treatments and equipment, and has been investigated using SPS and HIP [7]. β -Sialon is

instead synthesized, in the literature, in many different ways, like carbothermal nitriding [8].

If pressure is not applied it is possible to improve the densification by using liquid phase sintering. In this case, by using a controlled amount of liquid at the Si_3N_4 dissociation temperature, it is possible to facilitate dissolution and precipitation of Si_3N_4 , and α -Sialon is formed [9]. In this paper, densification of sialon without pressure, in the presence of aluminosilicates (kaolinite and muscovite) was tried to facilitate the liquid phase sintering of a composition very close to the α -Sialon region, with the intent to obtain a combination of α and β -Sialon. Moreover, aluminosilicates may also react with Y_2O_3 to form an eutectic which can facilitate densification. The eutectic may transform, at high temperature, into other polycrystalline phases which do not have a negative effect on the properties. Finally, it is also possible to adjust the composition to reduce or even eliminate the glass phase or the unwanted crystalline phases that can form on the grain boundaries between the grains of the main phases [9]

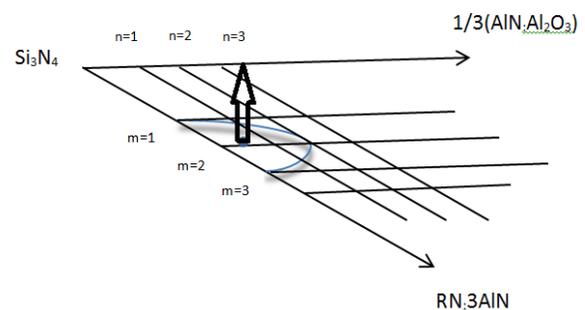


Fig. 1 Compositions of starting material on α -Sialon zone, a point in the Jancke prism.

II. EXPERIMENTAL

Starting composition was chosen with $m=2$ and $n=1.5$ in the α -Sialon region, as shown in Fig. 1. Powder of Si_3N_4 (a product of H.C. Starck, grade M11-A), AlN (a product of HC Starck, grade C-A), Y_2O_3 (a product of HC Starck, grade C-A), Al_2O_3 (provided by the ABCR, 1~5micron size) were mixed with 5, 10, 15 and 20% kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and muscovite ($\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$), provided by Alfa Aesar. Samples containing 5, 10, 15 and 20 percent silicate (kaolinite or muscovite) were designated as K5, K10, K15, K20 and

Azhar Hussain is with the Department of Production Systems and Industrial Design, Politecnico di Torino, Torino, Corso Duca Degli Abruzzi 24-10129, Italia (phone: +393273377226; e-mail: azharhussain1150@hotmail.com).

Matteo Pavese is with Department of Applied Sciences and Technology, Politecnico di Torino, Torino, Corso Duca Degli Abruzzi 24-10129, Italia (e-mail: matteo.pavese@polito.it).

Luca Settineri is with Politecnico di Torino, Torino, Corso Duca Degli Abruzzi 24-10129, Italia (e-mail: luca.settineri@polito.it).

M5, M10, M15, M20 for kaolinite and muscovite additions, respectively. Addition of aluminosilicates moved the composition away from the single phase region as indicated in Fig. 1, but it remains in alpha-beta region. Raw materials were mixed in the mixture of ethanol and butanol for 36 hours in plastic containers with alumina balls inside. After mixing the slurry was dried on a hot plate for 24 hours at the temperature of 50-60 °C. Powder was mixed again in an agate mortar and pestle and pressed in the form of 25 mm pellets, applying a pressure of 4 tons for 3-4 seconds. Pressed pellets were sintered in a furnace under 600-800 mbar of N₂; samples were heated at 5 °C/min to 1650 °C and 1700 °C, and cooled inside

The effect of increasing the densification temperature seems to be a reduction of the overall density of the samples, in particular for 5% case, but also for other samples. At higher temperature, kaolinite addition is better than muscovite. This is also confirmed by the hardness values, that are often well correlated with the density. Figures 4 and 5 show the effect of the kaolinite addition (Fig. 4) and of the muscovite addition (Fig. 5) on the density values for both temperatures (1650 °C, marked as L, and 1700 °C, marked as H). Again it can be seen a rather flat trend for kaolinite and an increasing one for muscovite, except for the points at 5% of silicate at 1700 °C, where a much lower density was obtained. This effect might be due to the dissociation of Si₃N₄ into its constituents, since not enough liquid phase is present to prevent dissociation.

TABLE I
VARIATION IN PROPERTIES AS EFFECTED BY THE COMPOSITION AND TEMPERATURE

Silicate Additive	Silicate quantity	Name	Sintering at 1650 °C			Sintering at 1700 °C		
			BD	RD	Hardness	BD	RD	Hardness
	%		g/cm ³	%	GPa	g/cm ³	%	GPa
No additive	0	S	2.31	68%	11.2	1.76	52%	17.7
Kaolinite	5	K5	3.2	96%	15.2	2.53	76%	20.3
	10	K10	3.09	94%	20.5	3.16	96%	23.4
	15	K15	3.16	97%	19.5	3.21	98%	21
	20	K20	3.05	95%	15.7	3.12	97%	14.3
Muscovite	5	M5	2.84	86%	19.3	2.63	79%	20.6
	10	M10	2.96	91%	21.2	3.01	91%	16.5
	15	M15	3.06	94%	22.6	2.99	92%	19.4
	20	M20	3.11	97%	20	2.79	87%	19.2

the furnace to room temperature. Bulk density and hardness testing was carried out to evaluate the densification. Bulk density of sintered samples was measured by Archimedes' principle using ethanol as a medium, and values are given in Table I along with Vickers hardness and relative density.

III. RESULTS AND DISCUSSION

At 1650 °C, as shown in Fig. 2, the muscovite-modified samples showed a roughly linear increase in density as the silicate addition passed from 5 to 20%. Instead for kaolinite, the density was maximum at the 5%, and slowly decreased afterwards. It must however be noted that density values changed abruptly for the 5% additions of both kaolinite and muscovite. Shrinkage behaved in a somewhat different way, with a monotonic increase for kaolinite addition and more flat for muscovite case.

The samples sintered at 1700 °C containing kaolinite showed a similar behavior, as shown in Fig. 3, even if K5 sample was less dense than expected. In the case of muscovite

samples the maximum density was close to 90% for all samples, again with the exception of M5 sample.

A high quantity of partially detached scale was observed on the surface of specimens and significant porosity is observed.

Porosity size and quantity differed widely for the different samples, as shown in Fig. 6 and Fig. 7. Kaolinite modified samples were sintered much better than muscovite ones both at 1650 °C and 1700°C. Visibly porosity in the kaolinite modified samples decreased with aluminosilicate addition and was present in small amounts, confirming the density results shown in Table I.

Muscovite containing samples showed instead very large porosity as shown in Figs. 6 and 7. This is partially in contrast with the density values shown in Table I, and could be due to the detachment of inclusions from the samples during polishing. Further analysis of these discrepancies must be performed to fully understand the occurring phenomena. Hardness values measured on samples sintered at 1650 °C and 1700 °C are shown in Fig. 8 and Fig. 9 respectively. For kaolinite modified samples, the trend shows a maximum

between 10 and 15% for both temperatures. For muscovite the behaviour is different at the two temperatures.

At 1650 °C sintering temperature, the trend is somewhat similar to that of the kaolinite, with a maximum around 15%, at 1700 °C the values show no clear trend. Again, for muscovite containing samples, the high porosity level shown in Fig. 6 and 7 is not coherent with the values of hardness, that suggest instead a good densification behaviour at least for 1650 °C.

The variation of hardness of observed in both kaolinite and muscovite containing samples does not follow exactly the same trend than the density. This could be explained by the formation, in particular for high aluminosilicate content, of softer glassy phases, that reduce the hardness even if the density is further increasing.

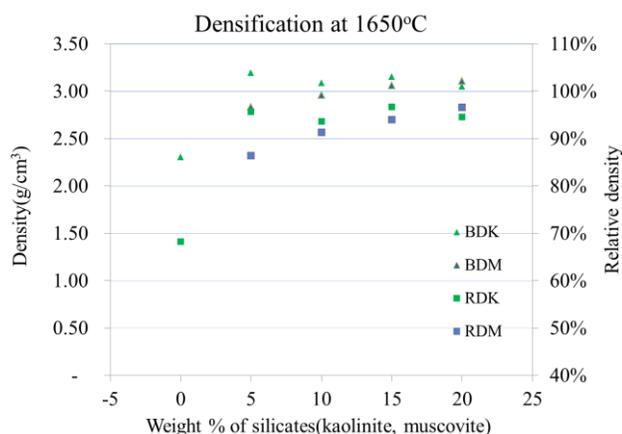


Fig. 2 Bulk density and relative density for kaolinite (respectively, BDK and RDK) and muscovite (respectively, BDM and RDM) modified samples, sintered at 1650°C.

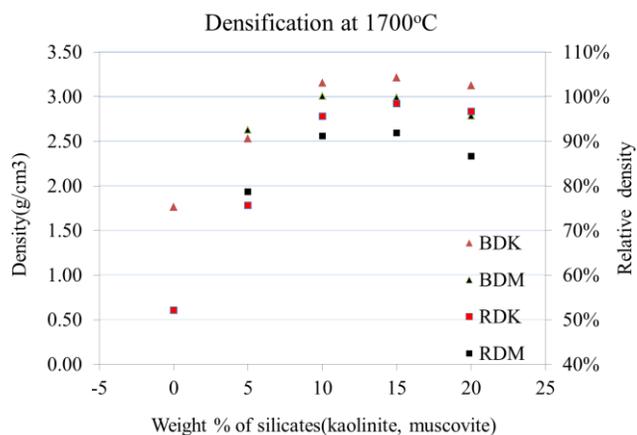


Fig. 3 Bulk density and relative density for kaolinite (respectively, BDK and RDK) and muscovite (respectively, BDM and RDM) modified samples, sintered at 1700°C.

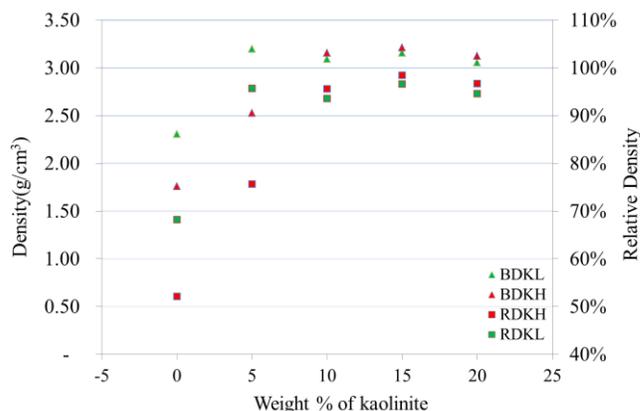


Fig. 4 Density variations with kaolinite additions at 1650°C, (BDKL= Bulk density with kaolinite at low temperature, i.e., 1650°C) and 1700°C (BDKH= Bulk density with kaolinite at high temperature, i.e., 1700°C). And RDL and RDH stands for relative density for low and high temperature sintered samples, respectively..

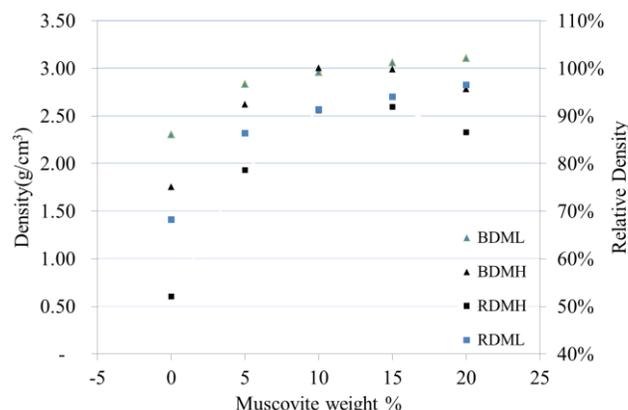


Fig. 5 Density variations with muscovite additions at 1650°C, (BDML= Bulk density with muscovite at low temperature, i.e., 1650°C) and 1700°C (BDMH= Bulk density with muscovite at high temperature, i.e., 1700°C). And RDL and RDH stands for relative density for low and high temperature sintered samples, respectively.

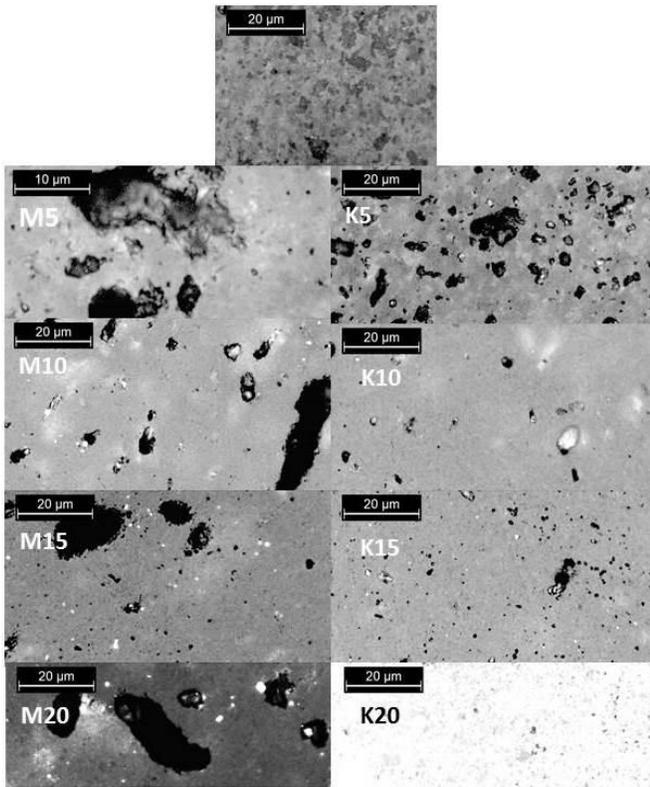


Fig. 6 Micrographs of samples sintered at 1650°C. Samples containing muscovite are represented with M and K stands for kaolinite whereas 5,10,15 and 20 is increase in percentage of silicates, muscovite and kaolinite, repectively

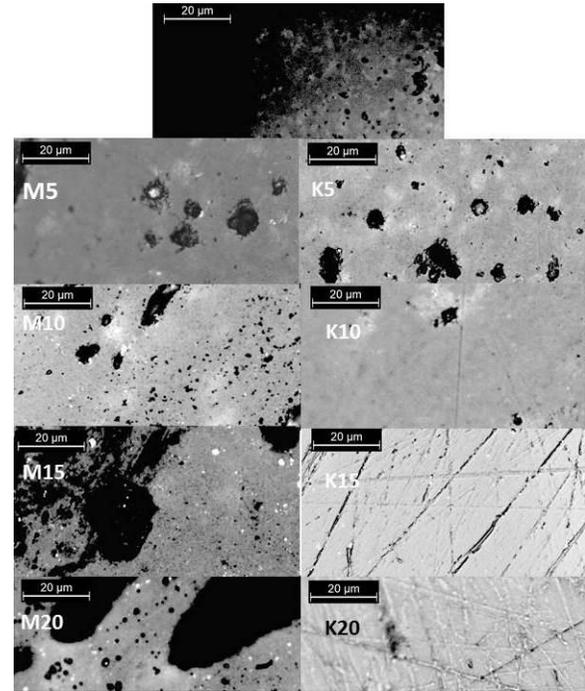


Fig. 7 Micrographs of samples sintered at 1700°C. Samples containing muscovite are represented with M and K stands for kaolinite whereas 5,10,15 and 20 is increase in percentage of silicates, muscovite and kaolinite, repectively

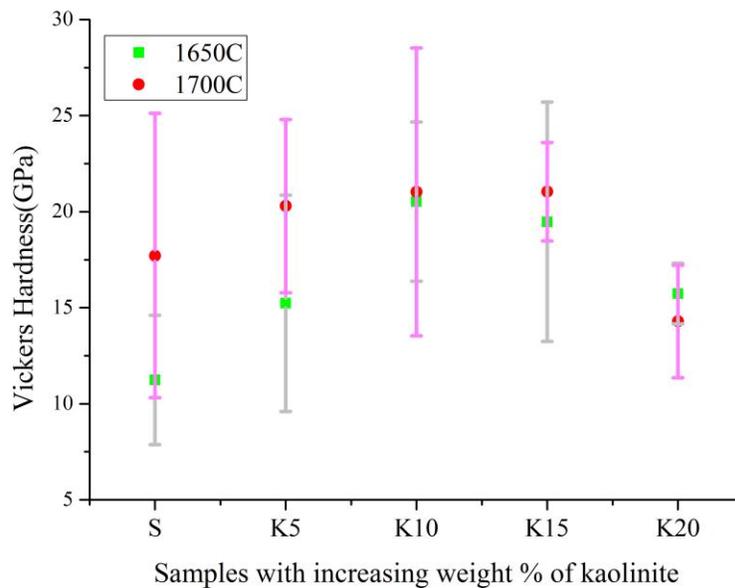


Fig. 8 Hardness values as a function of temperature and kaolinite additons at 1650°C and 1700°C.

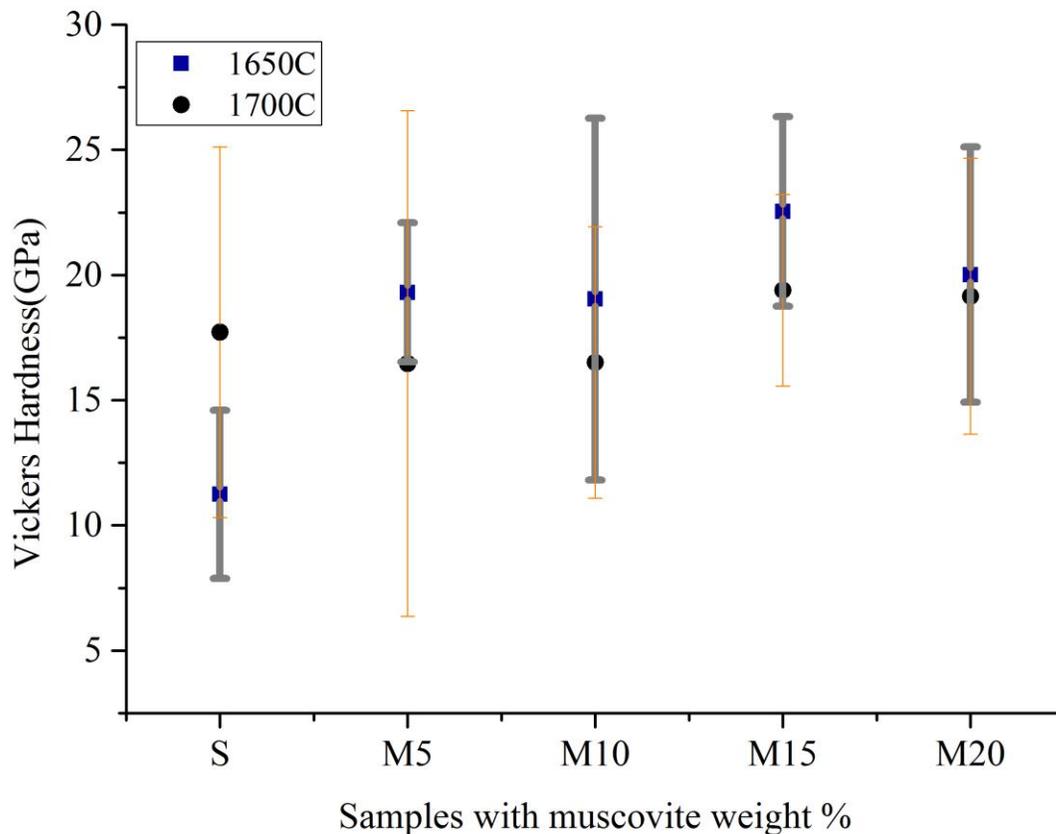


Fig. 9 Hardness values as a function of temperature and muscovite additions at 1650°C and 1700°C

IV. CONCLUSIONS

In this work the densification behavior of sialon with composition $m=2$ and $n=1.5$ were studied. Two aluminosilicates, kaolinite and muscovite, were added from 5 to 20% to the sialon, and two temperatures, 1650°C and 1700°C, were studied. The main results obtained can be summarized as follows.

1. Kaolinite was effective in achieving a good densification both at 1650 and 1700 °C, but at the highest temperature too small a quantity of kaolinite was not sufficient to avoid Si₃N₄ decomposition, with formation of porosity.

2. Muscovite was good in achieving densification only at 1650 °C. At 1700 °C porosity developed, probably due to the Si₃N₄ decomposition .

3. Samples containing kaolinite showed the maximum hardness values at lower weight fraction than the maximum density. This suggests the formation of softer phases at larger aluminosilicate additions.

REFERENCES

- [1] H., New developments in α -SiAlON ceramics. *Journal of the European Ceramic Society*, 1999. 19(13-14): p. 2349-2357.
- [2] Lewis, M.H. and R.J. Lumby, Nitrogen Ceramics: Liquid Phase Sintering. *Powder Metallurgy*, 1983. 26(2): p. 73-81.
<http://dx.doi.org/10.1179/pom.1983.26.2.73>
- [3] Kolitsch, U., et al., Phase equilibria and crystal chemistry in the Y₂O₃-Al₂O₃-SiO₂ system. *Journal of Materials Research*, 1999. 14(02): p. 447-455.
<http://dx.doi.org/10.1557/JMR.1999.0064>
- [4] Zhang, C., R. Janssen, and N. Claussen, Pressureless sintering of β -sialon with improved green strength by using metallic Al powder. *Materials Letters*, 2003. 57(22-23): p. 3352-3356
[http://dx.doi.org/10.1016/S0167-577X\(03\)00073-9](http://dx.doi.org/10.1016/S0167-577X(03)00073-9)
- [5] Janecke, E. 2. *Phys. Chem.* 1908,51, 132.
- [6] Jack, K.H., Sialons and related nitrogen ceramics. *Journal of Materials Science*, 1976. 11(6): p. 1135-1158.
<http://dx.doi.org/10.1007/BF02396649>
- [7] Bartek, A., et al., Yttrium. alpha. -sialon ceramics by hot isostatic pressing and post-hot isostatic pressing. *Journal of the American Ceramic Society*; 1992. 75(2): p. 432-439.
<http://dx.doi.org/10.1111/j.1151-2916.1992.tb08198.x>
- [8] Kokmeijer, E., et al., The influence of process parameters and starting composition on the carbothermal production of sialon. *Journal of Materials Science*, 1990. 25(2): p. 1261-1267.
- [9] Shen, Z., et al., Formation of tough interlocking microstructures in silicon nitride ceramics by dynamic ripening. *Nature*, 2002. 417(6886): p. 266-269.
<http://dx.doi.org/10.1038/417266a>
- [10] Lange, H., G. Wötting, and G. Winter, Silicon Nitride—From Powder Synthesis to Ceramic Materials. *Angewandte Chemie International Edition in English*, 1991. 30(12): p. 1579-1597.
<http://dx.doi.org/10.1002/anie.199115791>