Impact of nitrogen atmosphere on sintering of alumina ceramics

JUDIT CSÁNYI TAMÁSNÉ ▪ University of Miskolc ▪ femjuci@gold.uni-miskolc.hu

LÁSZLÓ A. GÖMZE ▪ Department of Ceramics and Silicate Engineering ▪ femgomze@gold.uni-miskolc.hu

A nitrogén atmoszféra hatása az alumínium-oxidkerámiák zsugorítására

Hagyományos szennyezettségű Al_2O_3 porok semleges nitrogén gázközegben történő zsugorítása során az $\alpha\text{-Al}_2\text{O}_3$ mellett egy új fázis is megjelenik, amely javítja a kerámia mechanikai jellemzőit.

A tanulmány ismerteti a zsugorított minta mikroszerkezetét, amelyet SEM, EDAX s RTG-diffrakciós módszerrel vizsgáltak. A vizsgálatok alapján megállapítható, hogy a hőkezelés egy új fázis, az ALONC kialakulásához vezet.

1. Introduction

Several industries, like electronics have been using products made of very high purity ($>99,9\%$) Al_2O_3 powder because of their excellent mechanical and electrical properties. These products are mainly produced by dry pressing, sintering. In order to achieve the special mechanical features the use of the right technology is as important as the selection of the raw material.

Many studies are investigating the sintering behaviour of alumina, its microstructure [1, 2, 3]. Our work until now has focused on obtaining deeper knowledge about these properties and on the description of mechanical characteristics of alumina, heat treated in nitrogen atmosphere [4].

Heat treatment in nitrogen gas is a well-known technology for steels, resulting the increase of surface hardness of steels, their wear resistance, resistance to repeated use and corrosion. In this procedure alloy elements – carbon, nitrogen, silicon, and aluminum – are entered into the surface layer of the steel by diffusion – modifying, improving its mechanical and chemical properties [5, 6, 7].

The purpose of the present study is to present the results of heat treatment in nitrogen inert gas of alumina ceramics, and to discover the changes in the microstructure of the surface layer.

According to the literature several authors are dealing with the use of nitrogen atmosphere by adding other additives (AlN) [8, 9, 10, 11]. During the sintering the nitrogen – entered in the form of gas or solid substance (AlN) – and its reaction with the rigid, solid material produces a new substance, a very tough material, keeping its mechanical properties. The result of heat treatment in nitrogen inert gas is the production of AlN and ALON, besides Al_2O_3 . ALON has several excellent properties, its thermal conductivity, specific resistance is high, the dielectric constant is moderately low. AlN cannot be found in the nature. It can be produced by nitridation of metal aluminum powder, or by the carbothermic reaction of alumina powder [12]. ALON is a kind of polycrystalline material, the structure of which is just the inverse of spinel. It is a glass-like, poreless material of great hardness, but with low heat conductivity. Among the methods to be used for the production of alumina nitride phase the most popular are simultaneous reduction and nitridation of Al_2O_3 , oxynitridation of metal aluminum during firing, its gas phase reaction with AlCl_3 , direct reaction between Al_2O_3 and AlN [9].

Tamásné Csányi Judit

Anyagmérnöki diplomát szerzett 2001 nyarán a Miskolci Egyetem Anyag- és Kohómérnöki Karán.

Tanulmányait doktoranduszként a jelenlegi Kerámia- és Szilikátmérnöki Tanszéken folytatta 2001–2004 között. 2003-ban tanulmányi ösztöndíjat nyert, így az Epcos Deutchlandsberg AG elektronikai vállalatnál kerámia-filmek fémzését tanulmányozta. 2004 óta, Szombathelyen az Epcos Elektronikai Alkatrész Kft. fejlesztőmérnökeként dolgozik. 2007-ben sikeresen megvédte műhelyvitáját.

Dr. Gömze A. László

1973-ban szerzett gépészmérnöki oklevelet a Moszkvai Építőmérnöki Egyetemen. Szilikátvegyész oklevelét 1979-ben kapta a Mengerlejev Kémia-technológiák Egyetemen. 1985-ben a műszaki tudományok kandidátusa - kitüntetés-

sel. Szakmai pályafutását az Épületkerámia-ipari Vállalatnál kezdte, ahol részt vett a Kerámia Téglagyár, a Padlólap II. és az új Örbottyán II. Téglagyár tervezésében. 1977-ben már a KEVITERV Egyedi Gépek és Létesítmények tervező osztályát irányította. Még ebben az évben tanársegéd lett Szaladnya Professor mellett a Miskolci Egyetemen. Ugyanitt 1999-től a Kerámia- és Szilikátmérnöki Tanszék vezetője. Több szabadalom és találmány szerzője. Hazai és külföldi publikációinak száma meghaladja a 200-at.

According to the literature the reaction of Al_2O_3 and AlN produces ALON phase above 1650°C , which can be made by plasma spraying, adding AlN, sintered in nitrogen gas.

In the *plasma spraying technology* first the $\text{Al}_2\text{O}_3/\text{AlN}$ composite powder is sintered in Ar/N_2 plasma ($\approx 10000\text{K}$), which is direct nitridation of alumina. With this method cubic lattice AlN can be produced, containing N- and O-ions. The AlN and $\gamma\text{-Al}_2\text{O}_3$ content of the thus produced material is growing compared to the AlN and Al_2O_3 content of the original (starting) material. Thus further heat treatment is required in nitrogen gas at $800\text{--}1200^\circ\text{C}$ for 2 hours with temperature holding. As a result of later heat treatment the AlN will be of hexagonal lattice, the AlN quantity will increase, but the $\gamma\text{-Al}_2\text{O}_3$ content will decrease. [13]

The quantity of AlN added to Al_2O_3 and the sintering temperature influence significantly the material microstructure.

Fig. 1. Phase diagram of AlN- Al_2O_3

1. ábra AlN- Al_2O_3 fázisdiagram

(Taken from: Allen M. Alper: Phase Diagrams in Advanced Ceramics 29. [14])

During sintering in nitrogen gas homogenous microstructure is achieved with lower (<10 mol%) AlN content, AlON appears on the contact surface of alumina. At higher AlN content the produced ALON is around the grain boundary of alumina.

McCauley and Corbin sintered *in situ* the AlN and Al₂O₃ powders, grinded together. Several combinations of production parameters were discovered. As shown by Figure 1 the liquid phase can be found in a very narrow stripe of the solid phase at high temperature. The results of sintering at 1975 °C are grain porosities, but the higher temperature (2025 °C) produces much less porosity and ALON.

The method was improved later, the starting powder is 0,5µm and smaller grain size distribution ALON powder, formed by preliminary reactions [15]. Reaction of the starting powder:

Tabary, Servant and Alary observed, that carbon is present in two forms. On the one hand in the form of graphite, not entering into reaction during melting, on the other in a form embedded into separations, becoming an Al-O-N-C quaternary system.

Figure 2 shows the phase structure of „ALONC” in Mol quantity along the line connecting points P₁ (25% Al₂O₃ – 75% AlN) and P₂ (60% Al₂O₃-20% AlN – 20% Al₄C₃). The intersection point of Al₂O₃-Al₄C₃ section can be 26,5mol% Al₄C₃, not following the literature value. Thus Al₄O₄C can be found at 20 mol% Al₄C₃ and Al₂OC, and also at 50 mol% Al₄C₃. Three dominant AlN based compositions can be distinguished. The general form is AlN-Al₂O₃ in pseudo-binary system it is Al_nO₃N_(n-2). In the Al₂O₃-Al₄C₃ pseudo-binary phase this formula becomes Al_(x+4)O_(1.5x)C₃, where x = 8; 6; 5; 4,4 and 4; and the M/X = n/n+1 ratio is equal to 4/5, 5/6, 6/7, 7/8, and 8/9, where M = (n_{Al}) and X = (n_O+n_C). [16]

Fig. 2. Content of ALONC phase in Al₂O₃-AlN-Al₄C₃ pseudo-ternary system

2. ábra Az „ALONC” fázis összetétele az Al₂O₃-AlN-Al₄C₃ pszeudo-ternér rendszerben

(Taken from: Tabary, Servant, Alary: Journal of the European Ceramic Society p. 1918)

2. Test conditions

During the experiment the sintering abilities of alumina powders of different purity were investigated with the use of nitrogen gas. Table 1 shows the compound of the powders

applied by us, according to the datasheet of the manufacturer partly 3% polyvinyl-ester, polyvinyl-ethanol, polyvinyl-glycol, partly 6% magnesium-silicate and 5% alkali-earth metal carbonate are needed to the preparation of pressing powders. Of the Kreutz SPG 95 and Alcoa CT 3000 SDP alumina powder, shown in Table 1. annular specimen were made with bilateral pressing by the mechanical press of Mikeron Kft, where the diameter of the pressing tool dowel was 34,6 mm, the diameter of the housing was 47,7 mm.

Compound	Kreutz SPG 95	Alcoa CT 3000 SDP
Al ₂ O ₃	≈ 95%	99,7%
SiO ₂	2,2%	0,02%
MgO	1,40%	0,1%
CaO	1,10%	0,03%
Na ₂ O	< 0,2%	0,08%
Fe ₂ O ₃	< 0,3%	0,02%

Table 1. Content of applied pressing powder

1. táblázat A felhasznált prészor összetétele

Part of the raw specimen was pre-sintered in normal way, at 1250 °C, the remaining part in nitrogen gas at 1420 °C in composition-type resistor furnace. The pre-sintered semi-finished product was sintered at 1640 °C in Nabel HT128 type furnace of Mikeron Kft.

The additive content of pressing powders was tested by DSC-equipment. Microstructure of the burnt specimen was tested by SEM, EDAX and X-ray diffraction meter.

3. Results

The DSC diagram of Al₂O₃ powders was taken into account to the establishment of test conditions (Figure 3). The investigation confirmed that in the presence of oxygen the organic materials begin to evaporate at 240–250 °C out of the 95 and 99,7% content

Fig. 3. DSC analysis of 95% Al₂O₃

3. ábra 95% tartalmú Al₂O₃ kerámia DSC vizsgálata

pressing powder. The evaporation process lasts nearly until the attainment of 800 °C. Thus in our test during the pre-sintering process the N₂ gas had been continuously flown from 500 °C. It is known that with the reduction of oxygen the dissociation of organic materials cannot be completed, thus some percentage carbon is left in the biscuit baked, sintered ceramics [17].

Fracture surface of samples pre-sintered in nitrogen gas and burnt in normal atmosphere (Figure 4) was tested, analyzed.

It can be seen on Figure 4, that in the external layer of the specimen a new, characteristically different – form the traditionally sintered Al₂O₃ ceramic – structure had developed.

Fig. 4. Fracture surface of N₂ heat treated, sintered Al₂O₃ by SEM (95% Al₂O₃; pressure: 177,1MPa; max time of pressure: 15s)

4. ábra Nitrogén atmoszférában hőkezelt próbatestek töretfelületének SEM felvétele (95%-os Al₂O₃, sajtólónyomás: 177,1 MPa, a sajtólónyomás max. határideje: 15 s)

Fig. 5. Fracture surface of N₂ heat treated, sintered Al₂O₃ by EDX

5. ábra Nitrogén atmoszférában hőkezelt próbatestek töretfelületének EDX felvétele

Fig. 6a. Fracture surface of N₂ heat treated, sintered 95% Al₂O₃

6a. ábra Nitrogén védőgázban előégetett 95% Al₂O₃ töretfelületének felvétele a felszín közelében

Fig. 6b. Inert part at fracture surface of N₂ heat treated, sintered 95% Al₂O₃

6b. ábra N₂ védőgázban előégetett 95% Al₂O₃ kerámia belső részének töretfelülete

Figure 5 shows the spectrum of the average composition of the fracture surface. The picture shows that besides aluminum and oxygen, carbon has also appeared.

Figure 6 shows outer layer of the fracture surface of 95% Al₂O₃ ceramic with M = 10000X enlargement. Square granules typical of alumina, as well as the great number of tiny granules left out of consideration until now were observed! The tiny granules are only of 0,1-1 μm size. Here the traces of a new phase in the middle of the specimen could be seen.

Fig. 7. Roentgen diffraction of ceramic sample

7. ábra A vizsgált minta röntgendiffrakciós felvétele

The structure of ceramics heat treated in nitrogen gas was determined on the basis of X-ray diffraction test. The results are shown on Figure 7. It can be seen that next to the tips of Al_2O_3 carbon in crystal form, and also $\text{Al}_4\text{N}_3\text{CO}$ (ALONC) had appeared. Most of the ALON tips fit to the diffractogram, its presence is still not completely proved. The results of our experiments are significant, since we have proved, that already at relatively low temperature ALONC is produced in alumina ceramics of traditional „contamination” pre-sintered in nitrogen gas.

Observations of Tabary, Servant and Alary support our findings, that carbon is present in two forms. Once in the form of graphite, which does not enter into reaction during melting, and in the form of *Al-O-N-C* quaternary system.

4. Conclusion

1. Our tests clearly confirm that during sintering of Al_2O_3 nitrogen gas exercises similarly positive impact on the material structure and mechanical behaviour of the ceramics, as is the case with nitriding, or carbo-nitriding of steel alloys. It was proved by SEM photos that close to the surface of the sintered body 0,1 μm granules develop and distribute in large volume in the material structure, owing to the presence of which the water and gas compactness and mechanical stability of the material system is significantly increasing.

2. On the basis of the tests it can be stated, that with the use of the right production technology (pressing, sintering atmosphere, sintering temperature) excellent quality products can be produced of the 92 – 99,7% Al_2O_3 -content basic materials of traditional „contamination”, which had only be produced until now of the 4th and 5th generation high purity Al_2O_3 .

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