G. SUČIK, T. KUFFA, D. HRŠAK

ISSN 0543-5846
METABK 43 (2) 93-95 (2004)
UDC - UDK 553.625:66.09=111

THE USE OF DIATOMACEOUS EARTH IN PREPARATION OF SiAlON POWDER

Received - Primljeno: 2003-09-01
Accepted - Prihvaćeno: 2003-12-15
Preliminary Note - Prethodno priopćenje

In this paper the SiAlON powder was prepared by carbothermal reduction and nitridation of diatomaceous earth. The origin of raw material was deposit Lučenec, in the central region of Slovak Republic. The aim was investigate potential use of this natural source as a main precursor for production of low-cost SiAlONs by carbothermal reduction and nitridation.

Key words: *SiAlON powder, carbothermal preparation, diatomaceous earth*

Uporaba dijatomejske zemlje u pripravi SiAlON praha. U ovom je radu SiAlON prah pripravljen karbotermijskom redukcijom i nitridacijom dijatomejske zemlje. Porijeklo sirovine je nalazište Lučenec u središnjem dijelu Slovačke. Cilj rada bio je istražiti mogućnosti te prirodne sirovine kao ishodišta za dobivanje jeftinih SiAlON-a postupkom karbotermijske redukcije i nitridacije.

Ključne riječi: *SiAlON prah, karbotermijska priprava, dijatomejska zemlja*

INTRODUCTION

With technological progress, natural materials become insufficient to meet increasing demands of product capabilities and functions. There are many combinations of metallic and non-metallic atoms that can combine to form ceramic components and also several structural arrangements are usually possible for each combination of atoms. This led scientists to invent many new ceramic materials to meet increasing requirements and demands in various application areas.

Generally speaking SiAlONs is a common name for a huge family of the ceramic alloys based on silicon nitride. Initially, they were discovered before approximately 30 years [1 - 3] and have been continually developed since until today. There are two SiAlON phases that are of interest as engineering ceramics, α-SiAlON and β-SiAlON, which are solid solutions based on α-Si_3N_4 and β-Si_3N_4, structural modifications.

Sufficient understanding of basic regularities of interrelation between starting powder properties, processing parameters and properties of consolidated materials was achieved. The vast amount of data accumulated was critically evaluated and summarized in several reviews [4 - 6]. Although the initial goal of creating a single-phase silicon nitride based ceramics without any intergranular amorphous phases due to the transient liquid phase sintering was not achieved, SiAlON ceramics became one of the commercially produced high-technique ceramic material.

Diatomaceous earth is sediment of many kinds of diatoms, unicellular algae that live in fresh water or sea water. Diatomaceous earth from a sea layer is composed of amorphous silicon dioxide and a small amount of clay and volcanic ash. Diatomaceous earth collected from a lake layer has silicon dioxide content higher than that from the sea layer.

Possible usage of diatomaceous earth from Lučenec deposit as a precursor in β-SiAlON production by carbothermal reduction and nitridation is very interesting from economical point of view and will be a great contribution in better valorisation of Lučenec deposits.

EXPERIMENTAL

All experiments were done in alumina-mullite tubular reactor with two silicon carbide heating bodies. After intensive homogenisation precursors were put in corundum boat and pushed in reaction space of reactor. Before heating reaction space was flushed with N_2 and NH_3 gas mixture. For that purpose nitrogen was purified by deoxidisation. Atmospheric pressure was used. Reaction temperature was 1400 °C and reaction time 12 hours [7].

G. Sučik, T. Kuffa, Faculty of Metallurgy, Technical University of Košice, Košice, Slovakia, D. Hršak, Faculty of Metallurgy, University of Zagreb, Sisak, Croatia

Different combination of diatomaceous earth and graphite carbon with some aluminium compounds: aluminium oxide α-Al_2O_3, aluminium hydroxide $Al(OH)_3$ as well as aluminium oxyhydroxide gel (AlOOH) were used as precursors.

Table 1. **Chemical composition of diatomaceous earth**
Tablica 1. **Kemijski sastav dijatomejske zemlje**

Component	SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	K_2O
Portion / mass %	65,40	15,35	0,08	5,03	0,56	0,61	1,08

The chemical composition of used diatomaceous earth is shown in Table 1. Dry loss at 110 °C was 2,59 mass % and ignition loss at 850 °C was 9,98 mass %. The chemical composition of graphite carbon is shown in Table 2. Ignition loss at 850 °C was 99.35 mass %.

Table 2. **Chemical composition of graphite carbon**
Tablica 2. **Kemijski sastav grafitnog ugljika**

Component	C	CaO	MgO	SiO_2	Al_2O_3	H_2O
Portion / mass %	96,08	0,06	0,04	0,09	0,05	0,22

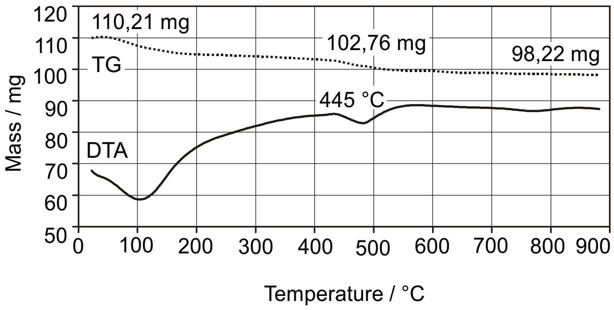

Figure 1. **Thermogravimetric analysis of diatomiceous earth from Lučenec**
Slika 1. **Termogravimetrijska analiza dijatomejske zemlje iz Lučenca**

Thermogravimetric and x-ray analysis of used diatomaceous earth are presented in Figures 1. and 2.

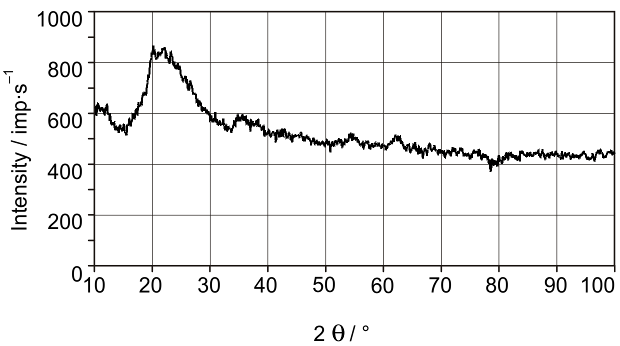

Figure 2. **X-ray analysis of diatomiceous earth from Lučenec**
Slika 2. **Rentgenska analiza dijatomejske zemlje iz Lučenca**

RESULTS AND DISCUSSION

The best precursors mixture were diatomaceous earth with alumina gel (ADE) and graphite carbon. Diatomaceous earth was in-situ doped by pseudobohemite-like gel to achieve the best possible contact between atomic layers of silicium and aluminium [8]. In that case, during carbothermal reduction of precursors some aluminium atoms, because of thermal degradation of aluminium oxyhydroxide, becomes a part of growthing silicon nitride structure. That fact is essential for SiAlON preparation.

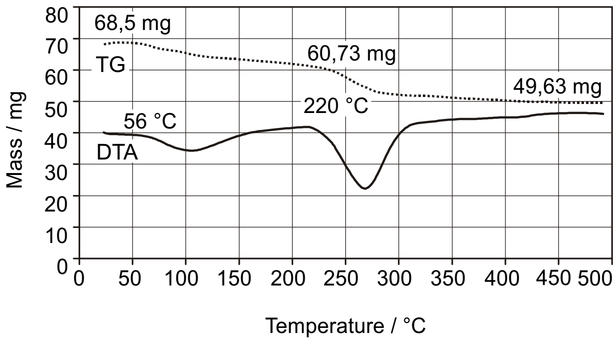

Figure 3. **Thermogravimetric analysis of aluminium acetate**
Slika 3. **Termogravimetrijska analiza aluminijevog acetata**

Alumina gel was prepared by reaction between aluminium nitrate $Al(NO_3)_3$ and ammonia hydroxide in water solution acidified by acetic acid to set pH value. Precipitation started of pH of 4 and ended at pH 7. Figure 3. shows thermogravimetric analysis of used precipitated dried gel. A quick precipitation leads to a very poorly crystalline material with main endothermic effect started at 220 °C with peak at 275 °C. Small endothermic effect starts at 50 °C shows the release of powder residual moisture. The loss of mass was above 18 %. Thus, it follows that precipitated gel was AlOOH.

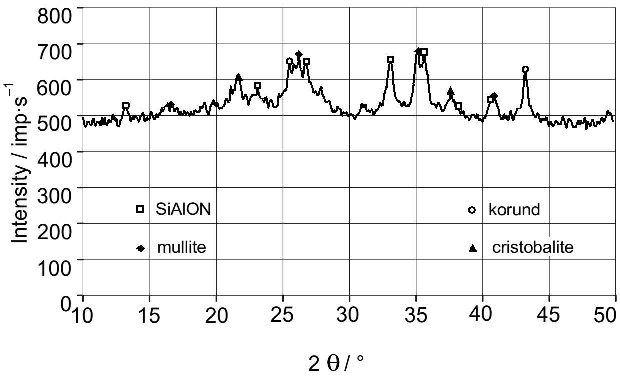

Figure 4. **X-ray analysis of SiAlON preparation final products**
Slika 4. **Rentgenska analiza konačnih produkata priprave SiAlON-a**

However, the yield of SiAlON phase in final product is relatively poor.

CONCLUSION

It can be concluded that it is possible to use diatomaceous earth from Lučenec deposit as precursor in SiAlON production by carbothermal reduction and subsequent nitridation. It is confirmed that it is not necessary to have a compound with SiAlON-like structure in precursor mixture.

Acetation of diatomaceous earth by acetic acid and consequently in-situ precipitation of aluminium oxyhydroxide was necessary to achieve a good contact between atomic layers of silicium and aluminium.

Chemical composition of prepared SiAlON was $Si_3Al_{2.67}O_4N_4$ which is close to β-SiAlON type. High content of alkaline metals in diatomaceous earth can be a significant disadvantage.

At atmospheric pressure here applied the total conversion of starting oxides was not achieved.

REFERENCES

[1] Y. Oyama, K. Kamigaito, Jpn. J. Appl. Phys. 10 (1971), 1637 - 1642.

[2] K. H. Jack, W. I. Wilson, Nature Phys. Sci. 238 (1972), 28 - 29.

[3] K. H. Jack, Trans. J. Brit. Ceram. Soc. 72 (1973), 376 - 378.

[4] T. Ekström, M. Nygren, J. Am. Ceram. Soc. 75 (1992), 259 - 276.

[5] S. Hampshire, R. A. L. Drew, K. H. Jack, Phys. and Chem. of Glasses 26 (1985), 82 - 86.

[6] J. E. Shelby, J. T. Kohli, J. Am. Ceram. Soc. 73 (1990), 39 - 42.

[7] G. Sučik, PhD. Thesis, Faculty of Metallurgy Technical University of Košice, 1998.

[8] R. C. Mackenzie, G. Berggren: Differential Thermal Analysis, Volume 1, Chapter 9, Oxides and Hydroxides of Higher-Valency Elements, Academic Press, London and New York, (1970), 279 - 286.