UDK 666.3/.7:546.28
Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 37(1-2)25(2003)

THE CARBOTHERMAL PREPARATION OF SILICON NITRIDE WHISKERS

KARBOTERMIČNA PRIPRAVA VISKERJEV IZ SILICIJEVEGA NITRIDA

[1]Gabriel Sučik, [1]Tarzicius Kuffa, [2]Damir Hršak

[1]Faculty of Metallurgy, Technical University of Košice, Letna 9, Košice, Slovakia
[2]Faculty of Metallurgy, University of Zagreb, Aleja narodnih heroja 3, 44103, Sisak, Croatia

Prejem rokopisa - received: 2002-11-18; sprejem za objavo - accepted for publication: 2003-01-06

The type of silicon nitride (Si_3N_4) whiskers prepared in this study can be used for reinforcement in plastics, metals or ceramic composites, since silicon nitride has a high strength at high temperatures, high thermal shock resistance, and the whiskers have a tensile strength, close to the theoretical value. Condensed silica fume (CSF) and graphite was used as the precursors. The precursors must be in the amorphous phase and be particles that are as small as possible. Iron oxides from the precursors have an important role in the carbothermal preparation of silicon nitride whiskers, too. The optimum reaction conditions for preparing the silicon nitride whiskers were found to be: a reaction temperature in the interval 1380-1400 °C, a C/SiO_2 molar ratio of 4 and a gas-phase composition (in vol. %) of 72 % N_2 and 28 % NH_3. The best efficiency rate was 40 mass. % of Si_3N_4 whiskers.

Key words: silicon nitride, whiskers, carbothermal preparation, reaction temperature, molar ratio C/SiO_2, gas phase composition

Viskerji iz silicijevega nitrida (Si_3N_4), ki smo jih pripravili, se lahko uporabijo za utrditev kompozitov z matico iz kovine, plastike in keramike. Silicijev nitrid ima visoko trdnost pri visoki temperaturi, veliko odpornost proti toplotnim šokom in natezno trdnost, ki je blizu teoretične. Kondenzirani hlapi silicija (CSF) in grafit sta bila uporabljena kot prekursorja. Grafit mora biti amorfen in v čim manjših zrnih. Železov oksid iz prekursorja ima pomembno vlogo pri pripravi viskerjev iz silicijevega nitrida. Optimalni pogoji, določeni za pripravo viskerjev, so: reakcijska temperatura (1380-1400) °C, molsko razmerje C/SiO_2 4 in volumski delež plinske faze 72 % N_2 in 28 % NH_4. Najboljši izkoristek je bil 40 % viskerjev Si_3N_4.

Ključne besede: viskerji silicijevega nitrida, karbotermična priprava, reakcijska temperatura, molsko razmerje C/SiO_2, sestava plinske faze

1 INTRODUCTION

Silicon nitride is one of the most extensively studied structural ceramic materials, and the most important construction material for replacing steel in high-temperature and/or corrosive environments, for example in a gas turbine engine. It possesses high strength, fracture toughness, wear resistance, and thermal shock resistance, and is stable in oxidizing and other corrosive atmospheres, all of which are necessary for engineering applications at high temperatures[1-4]. Silicon nitride whiskers can be used for reinforcement in plastics, metals or ceramic composites[5].

Carbothermal reduction and nitriding of silica is a more rapid process if inexpensive but pure reactants are used, and it is now established as one of the most promising alternatives to the silicon nitriding method in the production of silicon nitride of high purity[6-11]. The conditions for the preparation of silicon nitride from silica by carbothermal reduction and nitriding as well as the occurrence of other phases in the Si-C-O-N system can be predicted for different conditions of temperature and pressure[12]. Impurities that are present in the reactants, for example small concentrations of iron oxides, are also known to play an important role in determining the phase formed and their effects cannot be explained entirely with equilibrium thermodynamics[13]. The silicon nitride can be in the form of powder, fibres or a needle-like shape. The shape of the silicon nitride particles is the result of a nucleation mechanism.

Condensed silica fume is a very fine non-crystalline silica produced by electric-arc furnaces as a by-product of the production of metallic silicon or ferrosilicon alloys. It is a powder with particles sized between 0.1 and 0.2 μm. From the economic point of view it is very important to find a good way of exploiting this waste material.

2 EXPERIMENTAL

All the experiments for preparing silicon nitride whiskers were realized in a laboratory semi-batch tube reactor with a controlled reaction temperature.

The starting materials were Slovakian condensed silica fume and graphite. The chemical composition (in mass. %) of condensed silica fume was: amorphous SiO_2 95.6 %, Fe_2O_3 0.2 %, Al_2O_3 0.1 %, MgO 0.9 %, CaO 0.1 % and Na_2O + K_2O 0.9 %. The ignition loss was 1.4 mass. %. A granulometric analysis showed that 90 % of particles were under 2 μm. The graphite used had a carbon mass portion over 97.9 %, and a particle size of 1-5 μm.

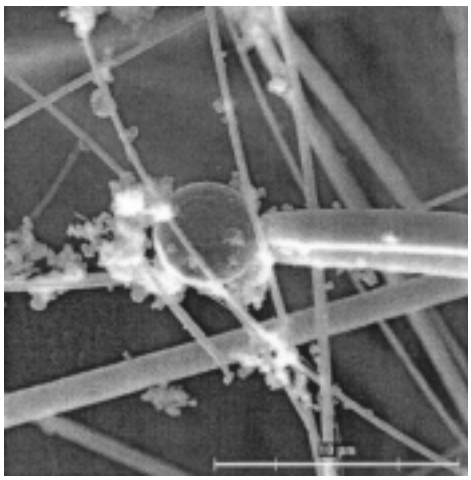

Figure 1: SEM photograph of two forms of α-Si_3N_4 whiskers
Slika 1: SEM-posnetek dveh oblik viskerjev α-Si_3N_4

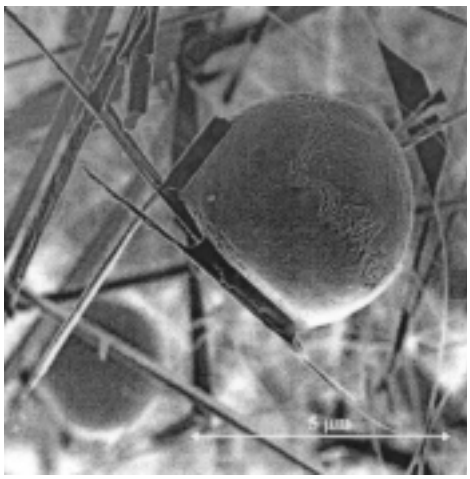

Figure 2: SEM photograph of broken Fe-Si droplets separated by whiskers
Slika 2: SEM-posnetek prelomljenih kapljic Fe-Si, ločenih z viskerji

The total gas flow rate was 2.1 dm^3/h, and the reaction time was 15 hours. The reaction temperature, the C/SiO_2 molar ratio, and the gas-phase composition were varied.

3 RESULTS AND DISCUSSION

After the set of experiment was completed, the optimum reaction conditions for preparing the silicon nitride whiskers using condensed silica fume and graphite as precursors were found to be: reaction temperature, 1380-1400 °C; C/SiO_2 molar ratio, 4; and gas phase composition (in vol. %), 72 % N_2 and 28 % NH_3. The best efficiency rate, using these parameters, was 40 mass. % of Si_3N_4 whiskers.

At temperatures lower than 1380 °C the reaction kinetics for the formation of silicon nitride whiskers is insufficient, and at temperatures higher than 1400 °C we get unwanted silicon carbide as one of the reaction products. The highest efficiency rate was achieved when the molar ratio C/SiO_2 was 4; a stoichiometric molar ratio of 2 is insufficient. Not surprisingly, a lot of excess carbon is needed because a full conversion at the stoichiometric coefficient can only be realized in the case of a full contact between the carbon and the silica particles, which is unlikely to occur under actual reaction conditions.

The gas-phase composition has a great influence on the formation of silicon nitride whiskers. For the preparation of α-Si_3N_4 whiskers it is necessary to use a mixed nitrogen atmosphere because a pure N_2 atmosphere results in the preferential formation of β-Si_3N_4 whiskers. The best results are achieved with a gas-phase composition of 72 volume % of N_2 and 28 volume % of NH_3. In the carbothermal preparation of silicon nitride whiskers, as with the carbothermal

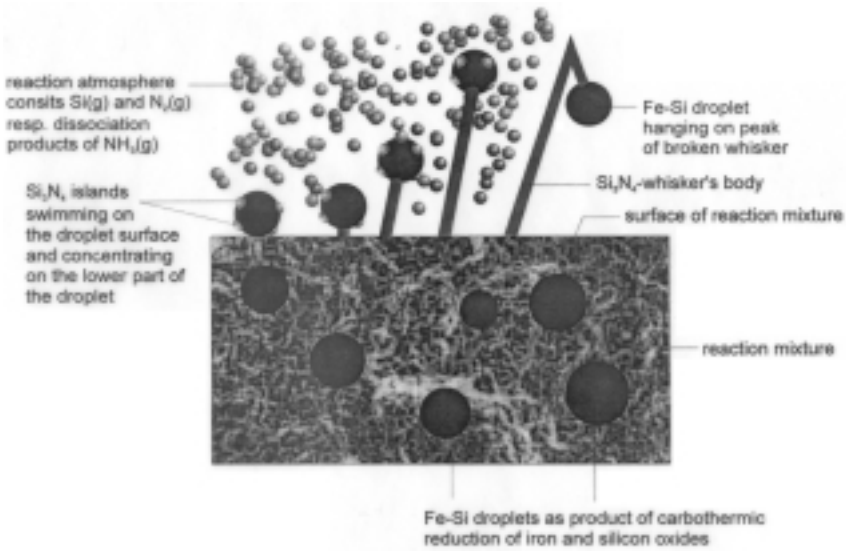

Figure 3: Presumed mechanism for the growth of silicon nitride whiskers
Slika 3: Predpostavljeni mehanizem rasti viskerjev silicijevega nitrida

preparation of silicon nitride powder, the α-Si_3N_4 form is preferable.

In this paper two forms of silicon nitride whiskers were produced. Needle-shaped crystals of silicon nitride were produced on the surface of the reaction mixture and grew in the [001] crystallographic direction. These crystals have Fe_xSi_y droplets on their upper ends and were formed via a VLS (vapor-liquid-solid) mechanism. The existence of a fibrous product formed on the internal surface of the tubular reactor proved the transport through the gaseous phase and the formation of silicon nitride whiskers via the heterogeneous nucleation of $Si_3N_{4(s)}$ through the condensation of Si(s) from a supersaturated Si(g) vapor on a solid substrate and the consequent reaction of Si(s) with nitrogen from the gaseous phase. **Figure 1** shows both forms of silicon nitride whiskers.

The critical size of the whiskers depends on the direction of their growth. The connection between the droplet and the whisker is interrupted and the whisker growth is finished when the critical size is exceeded. An SEM photograph of separated, broken Fe-Si droplets is shown in **Figure 2**.

Figure 3 presents the presumed mechanism for the growth of silicon nitride whiskers.

4 CONCLUSION

The optimum reaction conditions for preparing silicon nitride whiskers using condensed silica fume and graphite as the precursors in carbothermal reduction and subsequent nitridation of amorphous silica were found to be: a reaction temperature between 1380-1400 °C, a C/SiO_2 molar ratio of 4, and a gas-phase composition (in vol. %) of 72 % N_2 and 28 % NH_3. The best efficiency rate, using these parameters, was 40 mass. % of Si_3N_4 whiskers.

Two forms of silicon nitride whiskers were produced: needle-shaped crystals on the surface of the reaction mixture and fibre-shaped crystals on the internal surface of the tubular reactor.

The results presented in this paper will be useful in the further development of the process of silicon nitride whiskers preparation using Slovakian raw materials.

5 LITERATURE

[1] T. Yamada, Ceram. Trans. 42 **(1994)** 15-27
[2] N. N. Ault, R. L. Yeckley, Am. Ceram. Soc. Bull. 72 **(1993)** 117-118
[3] J. M. Schoenung, Ceram. Bull. 70 **(1991)** 112-116
[4] G. Schwier, G. Nietfeld, G. Franz, Mater. Sci. Forum 47 **(1989)** 1-20
[5] T. Hashishin, Y. Kaneko, H. Iwanaga, Y. Yamamoto, J. Mater. Sci. 34 **(1999)** 2193-2197
[6] F. K. van Dijen, A. Kerber, U. Vogt, W. Pfeiffer, M. Schulze, Key Eng. Mater. 89 **(1994)** 19-27
[7] T. Ličko, V. Figusch, J. Puchyova, J. Eur. Ceram. Soc. 9 **(1992)** 219-230
[8] Y. W. Cho, J. A. Charles, Mater. Sci. Technol. 7 **(1991)** 289-298
[9] D. L. Segal, Br. Ceram. Trans. J. 85 **(1986)** 184-187
[10] S. Zhang, W. R. Cannon, J. Am. Ceram. Soc.67 **(1984)** 691-695
[11] K. Komeya and H. Inoue, J. Mater. Sci. 10 **(1975)** 1243-1246
[12] S. J. P. Durham, K. Shanker, R.A. L. Drew, Can. Metall. Q. 30 **(1991)** 39-43
[13] S. A. Siddiqi, A. Henry, J. Mater. Sci. 20 **(1985)** 3230-3238