Effect of Organic Additives on Silicon Combustion in Nitrogen

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Abstract

The work shows some peculiarities of silicon combustion in nitrogen in the presence of additives of organic compounds. Organic compounds with different composition were used. Combustion of samples was carried out in a constant-pressure bomb. The combustion products are composite powders and containing α-, β- Si_3N_4, SiC, Si_2N_2O. The addition of organic additives suppressed coagulation of Si particles, improved the extent of conversion, and promoted combustion of coarse Si powders which can't be ignited by any other methods. Introduction of organic dopants to Si powders was found to intensify their combustion without significant influence on the combustion temperature. Active transition of silicon to the gas phase occurs in the low-temperature zone of the combustion wave at the temperature lower than the melting point of silicon. At the temperatures lower than the melting point of Si the quenched combustion products contain two types of crystals of SiC and Si_3N_4. SiC is formed within a low-temperature zone of the combustion wave. SiC is formed by fine crystals and large spherical particulates which are formed by a bunch of very thin web-like crystals. SiC and Si_3N_4 formation provides a protective coating on silicon particles. It prevents coagulation at the temperature increase. The experiments have proved that it is enough to introduce 1-7 M of the organic additive to 1000 M of silicon for the combustion initiation. Meanwhile, adding different inorganic salts, including ammonium chloride, did not promote combustion. After initiation of combustion to continue Si powder must contain additives or organic compounds or addition of carbon black; carbon black is necessary for keeping the combustion on.

Introduction

Synthesis of silicon nitride Si_3N_4 by combustion of silicon powder in nitrogen is known to require dilution of starting Si powder with a refractory compound [1-4]. Otherwise, the yield of Si_3N_4 is normally low. Due to a high combustion temperature Tc attained in the rapidly propagating combustion wave, Si undergoes melting and thus forms an obstacle for penetration of nitrogen gas into the reaction zone. In order to suppress the coagulation of melted Si particles, a starting Si powder is diluted, up to 30-70 wt.%, with the end product (Si_3N_4). Analysis of the literature and preliminary experiments allowed us to suppose that there exist an alternative approach to the SHS of Si_3N_4: instead of strong dilution with final product, we are going to suggest low dilution with organic compounds.

The experiments result in the conclusion that introduction of small additives of organic compounds allows one not only to prevent silicon coagulation and increase nitriding degree but also to carry out combustion of coarse-grained silicon which can't be ignited by any other methods [5, 6]. Combustion of silicon powders containing organic dopants in nitrogen gas under pressure was found to yield a mixture of α-Si_3N_4 - up to 60%, β-Si_3N_4 - up to 100%, SiC - up to 80% and Si_2N_2O - up to 70%. Relative amount of these compounds in combustion product was found to depend on the pressure of nitrogen gas, type and concentration of dopants, combustion geometry, and cooling rate.

The work shows some peculiarities of silicon combustion in nitrogen in the presence of additives of organic compounds.

Experimental

Combustion of silicon powders containing organic additives in nitrogen was performed under nitrogen pressures $P(N_2)$ ranging between 20 and 150 atm. In experiments we used nitrogen gas of either commercially pure grade (containing up to 2 vol.% oxygen). Two different Si powders were

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used in experiments: powder 1 with a particle size $d < 50\,\mu m$, powder 2 with $d < 130\,\mu m$. Figure 1 shows the size distribution of particles in powders Si-1 and Si-2. Organic and inorganic additives (D) with different composition were used: Tetraphenyl silane $C_{24}H_{20}Si$, Tetraphenyl silanol $C_{18}H_{15}SiOH$, Naphthalene $C_{10}H_8$, Dipyridyl $(C_6H_4N)_2$, Naphthol $C_{10}H_8O$, Dichlorobenzene $C_6H_4Cl_2$, Acrylamide $C_2H_3CONH_2$, Oxalic acid $(COOH)_2 \times 2H_2O$, Ammonium oxalate $(NH_4)_2(COO)_2 \times 2H_2O$, Urea $CO(NH_2)_2$, Ammonium hydrocarbonate NH_4HCO_3, Ammonium carbonate $(NH_4)_2CO_3$, Carbon black C, Salmiac NH_4Cl, Ammonium hydrosulfate NH_4HSO_4, Ammonium sulfate $(NH_4)_2SO_4$, Calcium carbonate $CaCO_3$.
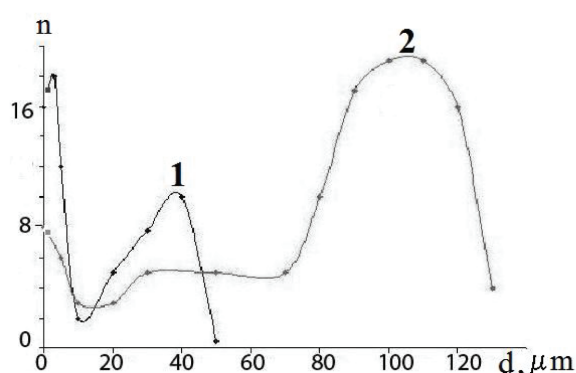

Fig. 1. Size distribution of particles in Si powder Si-1 (curve 1) and powder Si-2 (curve 2).

Powders (Si+D) were mixed in a porcelain mortar and then charged into a quartz tube of 35 mm in diameter. Combustion of thus prepared bulk density samples was carried out in a constant-pressure bomb preliminary purged with nitrogen gas. Vertically placed samples were ignited from the top with a tungsten coil via a thin layer of Ti powder (about 1 g in weight). The combustion temperature Tc was determined (with an accuracy of $\pm$ 50 K) by thermoelectric method [7] using W–Re thermocouples (VR-5/20) 100 or 200 μm in diameter placed at the sample center. Combustion products were characterized by XRD (DRON-3M, Cu-Kα radiation) using the Powder Diffraction File (PDF-2) database and by EDS (LEO-1450 electron microscope equipped with an INCA ENERGY 350 analyzer).

Results and Discussion

Preliminary experiments have shown that powder Si-1 can burn in nitrogen gas of $P(N_2) > 70$ atm, but incompletely and with product sintering. The values of combustion temperature Tc measured in the presence of different additives D ([D] = 5 wt.%) are presented in Fig. 2. As it could be expected, Tc

values are nearly independent of the type of dopant and fall within the range of 2270 $\pm$ 50 K.

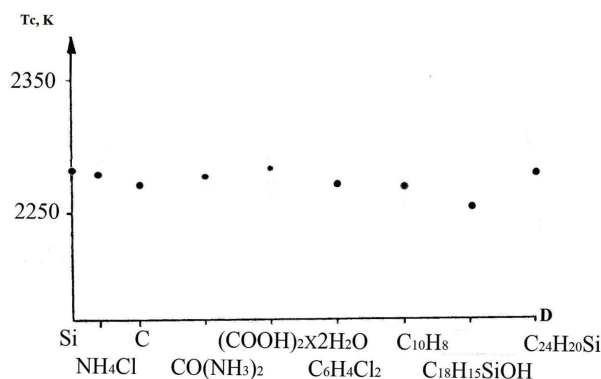Fig. 2. Measured values of Tc for combustion of Si-1 powder at $P(N_2) = 70$ atm and [D] = 5 wt.%.

In these experiments, combustion of Si + 4 wt.% $C_{24}H_{20}Si$ mixture was arrested upon rapid depressurization of the reactor. The fracture surface of quenched samples exhibited several colored concentric zones: an outer black zone about 1 mm wide was followed by a narrow blue zone, a wide green zone, and a grey central zone. The data of XRD (Fig. 3) suggest that the blue zone should correspond to SiC (Fig. 3a). Then the phases of α-Si_3N_4 and β-Si_3N_4 appear (in nearly equal amounts), the SiC phase remaining predominant (fraction of the green zone adjacent to the blue one) (Fig. 3b). On going to the sample center, the amounts of α-Si_3N_4 and β-Si_3N_4 initially grow at nearly the same pace, after which the reflexes from β-Si_3N_4 and SiC get stronger, along with a decrease in the intensity of the signal from unreacted silicon. Within the grey zone (Fig. 3d), β-Si_3N_4 is predominant, while the reflexes from α-Si_3N_4, SiC, and Si get weaker.
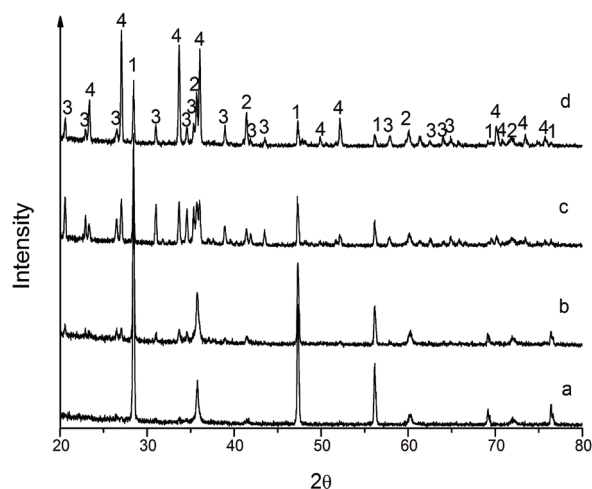

Fig. 3 (a-d). X-ray diffraction pattern of: the blue zone (a), beginning of the green zone (b), the green zone (c), the grey central zone (d).

It was established, that the outer black layer of starting Si, is covered with a thin layer of carbon black (Fig. 4a). The blue zone is formed by fine crystals and large spherical particulates (Fig. 4b,c). As it is seen in Fig. 4d, the spheres are formed by a bunch of very thin web-like crystals. In Fig. 3f, there is a beginning of the green zone, where silicon nitride appears. Here we can see an individual particle of silicon. Some erosion traces are obvious. They are explained by evaporation. The melting traces are not seen. Active transition of silicon to the gas phase occurs in the low-temperature zone of the combustion wave at the temperature lower than the melting point of silicon. At the temperatures lower than the melting point of Si, the quenched combustion products contain two types of crystals of silicon carbide and silicon nitride. Silicon carbide is formed within a low-temperature zone of the combustion wave. SiC and Si_3N_4 formation provides a protective coating on silicon particles. It prevents coagulation at the temperature increase.
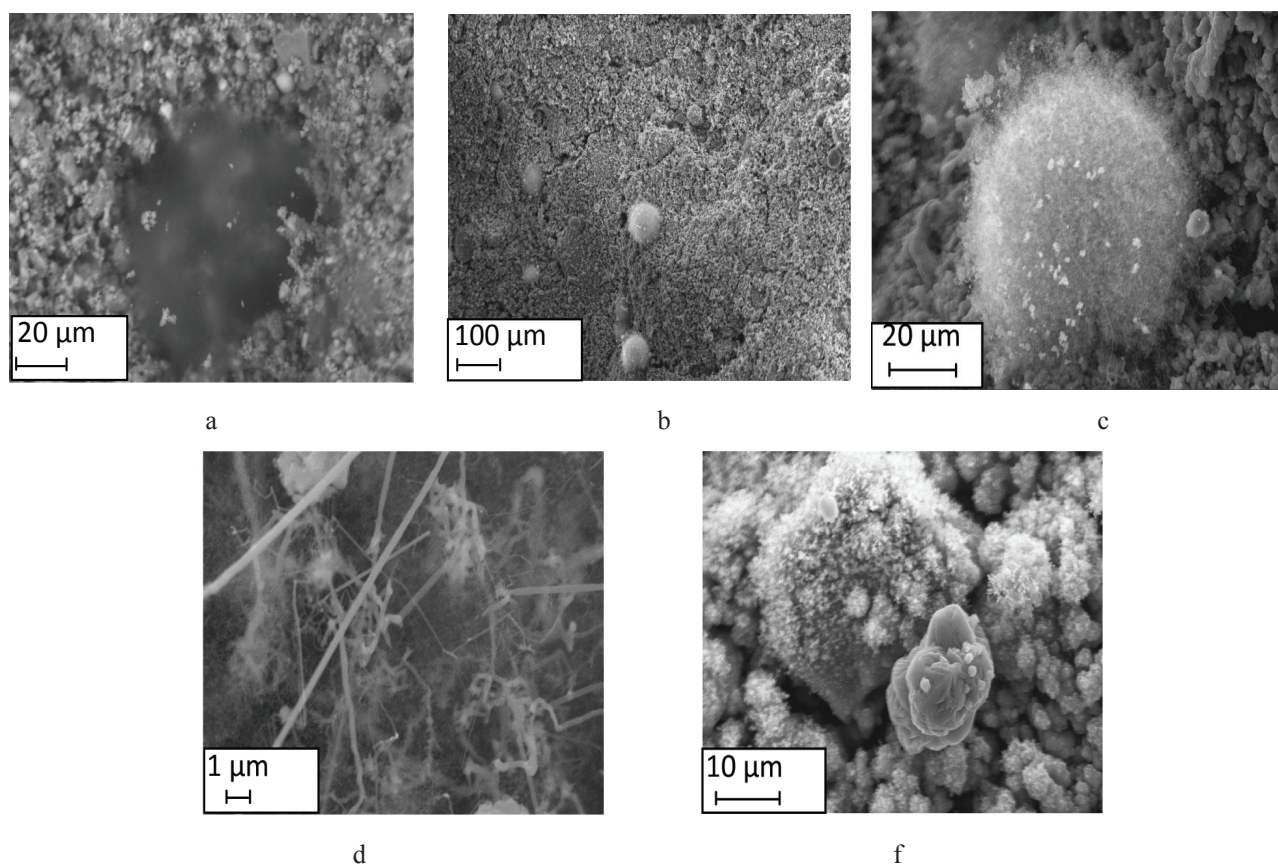

Fig. 4. (a-f). Microstructure of fracture surfaces of the quenched samples: a – beginning of the blue zone (Si + C black spot + SiC fine crystals); b – a blue zone (Si + SiC); c – fine crystals (background) and large spherical particulate; d – web-like crystals, f – beginning of the green zone (Si + SiC+Si_3N_4).

The experiments with arresting the combustion front of Si-1 containing oxygen-containing additives $(NH_4)_2(COO)_2 \times 2H_2O$, $(COOH)_2 \times 2H_2O$ and NH_4HCO_3 were carried out in a quartz glass. These additives are characterized by low decomposition temperatures, so we used the samples pressed in the glass. When the first two additives were used, black carbon was observed in the quenched combustion products in the layer next to the starting mixture, and in the following layer SiC was discovered that is analogous to the experiments with $C_{24}H_{20}Si$, though silicon carbide was absent in the final product. The absence of silicon carbide in the final products in the case of oxygen-containing additives was mentioned in paper [8]. When NH_4HCO_3 was used, black carbon and silicon carbide were not observed.

Powder Si-2 could not be ignited even at $P(N_2) = 150$ atm, as well as upon preheating to 573 K or upon an increase in the amount of igniting Ti powder. But in the presence of organic dopants (up to 5 wt.%), powder 2 could be ignited already at $P(N_2) = 70$ atm. For Si-2 powder, the minimal

amount of additives necessary for ignition combustion at $P(N_2)$ 90 atm was found to be 1.3 wt.% in the case of $C_{24}H_{20}Si$ and 3 wt.% in the case of $(COOH)_2 \times 2H_2O$. Therefore, that it is enough to introduce 1-7 M of the organic additive to 1000 M of silicon for the combustion initiation. Meanwhile, the addition of 5 wt.% H_2O, $CaCO_3$, C, NaCl, NH_4Cl, NH_4HSO_4, NH_4HCO_3 did not promote combustion.

For comparison 5 mass % of NH_4HCO_3 and 3-5 mass % $(NH_4)_2(COO)_2 \times 2H_2O$ were introduced into Si-2 powder. From the viewpoint of the quality and quantity their elemental composition is the same. At the same amount of gaseous products the combustion could be initiated in the case of 3% of oxalate. In the case of 5 mass % of NH_4HCO_3 it was not observed. Different effect of the additives on combustion can be connected with their different behavior at high temperatures. E.g., at heating NH_4HCO_3 decomposes with formation of molecular compounds, while at heating of $(NH_4)_2(COO)_2 \times 2H_2O$ hydrocarbon radicals can be formed leading to black carbon formation which was observed in the above mentioned experiments.

The following experiments were carried out at $P(N_2)$ 70 and 90 atm. The amount of the introduced additives ($C_{24}H_{20}Si$, C_6H_4Cl, $C_{10}H_8$, $(COOH)_2 \times 2H_2O$) was 5 mass %. In this case the combustion temperature did not depend on the additive composition and was equal to that of silicon (Fig. 2).

1. The sample consisted of two layers. The upper layer of 3-5 mm in height consisted of the organic additive. The lower layer consisted of Si-2 powder. The additive decomposed, the upper layer didn't start burning. The product of the decomposed additive was loose X-ray amorphous powder of the black color.
2. The sample of 60 mm in height consisted of Si-2 powder and black carbon. The concentration of the black carbon ranged from 0.1 to 5 mass %. It appeared to be impossible to ignite the sample.
3. The sample consisted of two layers. The upper layer of 10 mm in height consisted of Si-1 powder containing 5 mass % of the additive. Before the experiment we had established that if the layer was 10 mm high, the combustion reaction in the mixture of silicon with the additive was complete. The lower layer of 50 mm in height consisted of Si-2 and black carbon. The concentration of black carbon in the lower layer was equal to that of carbon in the upper layer. The combustion of the lower layer spread along the entire height.
4. The upper layer of 10 mm in height consisted of Si-1 with 5 mass % of the additive. The lower layer of 50 mm in height consisted of Si-2 powder without the additive. The combustion was realized completely only in the upper layer. In the lower layer the combusted penetrated to some depth, and the combustion wave got to a cone.
5. The sample consisted of two layers. The upper layer of 10 mm in height consisted of Si-1 powder without additives. The lower layer of 50 mm consisted of Si-2 powder without additives. After the combustion of the upper layer the lower layer failed to burn.

As it was established Si-2 powder at the terms under study without additives could not be ignited, it wasn't ignited even in the case of black carbon introduction (Exp. 2) or after the complete combustion of the layer consisting of Si-1 powder (Exp. 5). However, experiment 3 proved that the mixture of Si-2 powder and black carbon can be ignited by the burning layer of silicon and the additive. Also it is possible to ignite Si-2 powder without additives in the same way (Exp. 4). The depth of the combustion front penetration into the lower layer depended on the dispersion of the starting silicon. If silicon of 20 to 40 μm (which couldn't be ignited at 70 atm) is used instead of Si-2 powder, the combustion will penetrate deeper. So, we can conclude that the additives initiate combustion but for keeping it on black carbon is required. In the presence of black carbon combustion penetrates to the entire depth (Exp. 3). We can suppose that at combustion of the upper layer consisting of silicon and the additive (Exp. 3, 4) active intermediate gaseous products are formed and get into the lower layer with the gas flow where they initiate combustion which can be kept on only in the presence of black carbon. It is well known that different compounds can create ion-radical forms on black carbon surface by sorption; these forms provide fast reactions like chain ones, and perhaps, due to black carbon active products are formed in the lower layer. So, black carbon provides continuation of the combustion process. In Experiment 4 the active products which got from the upper layer to the lower one were consumed and the ignition didn't start. That is why the combustion which was started in the lower layer damped away.

Conclusions

The addition of organic additives suppressed coagulation of Si particles, improved the extent of conversion, and promoted combustion of coarse Si powders. The experiments have proved that it is enough to introduce 1-7 M of the organic additive to 1000 M of silicon for the combustion initiation. Carbon black is necessary for keeping the combustion on. Active transition of silicon to the gas phase oc-

curs in the low-temperature zone of the combustion wave. Two types of crystals of SiC and Si_3N_4 are formed in the combustion wave at the temperature lower than the melting point of silicon; they create a protective coating preventing coagulation of silicon particles at the temperature increase.

Acknowledgment

References

1. Mukasyan, A.S., Martynenko, V.M., Merzhanov, A.G., Borovinskaya, I.P., and Blinov, M.Yu., Fiz. Goreniya Vzryva 22:43 (1986).
2. Zakorzhevskii, V.V. and Borovinskaya, I.P., Int. J. SHS 9 : 171 (2000).
3. Grachev, V.V., Shatalov, B.N., and Borovinskaya, I.P., Proc. All-Russia Conf. on Combustion and Explosion in Physical Chemistry and Process Engineering of Inorganic Materials, Moscow, 2002, p. 89.
4. Hirao, K., Miamoto, V. and Koizumi, M., J. Am.Ceramic Soc. 69:60 (1986).
5. Barinova, T.V., Borovinskaya, I.P., Int. J. of SHS 18:25 (2009).
6. Barinova, T.V., Borovinskaya, I.P., Int. J. of SHS 18:30 (2009).
7. Maslov, V.M., Borovinskaya, I.P., and Merzhanov, A.G., Fiz. Goreniya Vzryva 14:79 (1978).
8. Cano, I.G., Perez Baelo S., Rodriguez, M.A., de Aza, S., J. of the European Ceram. Soc. 21:291 (2001).

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