

Original Papers

INFLUENCE OF Cr, Fe, Ni AND Ti ADDITIVES ON THE NITRIDATION KINETICS OF SILICON POWDER COMPACTS

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The influence of small amounts (0.2–1.0 wt%) of Cr, Ni, Fe, and Ti on the nitridation of pure Si was studied. An accelerating effect of metals on nitriding kinetics became evident above the eutectic temperature of the systems metal – silicon. The time of nitridation of silicon in the presence of a metallic aid was shortened. The initial significant increase of the conversion rate of Si to Si₃N₄ was in the samples with the lowest metal content (0.2 wt%), although the total conversion was greater for the samples with higher metal addition. A slight influence of the type of metal on the phase composition was observed.

INTRODUCTION

Reaction-bonded silicon nitride (RBSN) remains a promising high-temperature engineering material with many established applications, e. g. components of gas turbine engines as rotors and stators, combustion chambers, metallurgical equipment, etc. The advantage of RBSN in comparison with other Si₃N₄ based materials is that the product has the shape and dimensions of the compacted silicon powder from which it was formed. The products retain their good mechanical properties (high-temperature creep resistance, strength) up to high temperatures (1400°C) due to the absence of glassy phase on grain boundaries at the end of nitridation. In the liquid phase sintered Si₃N₄ the grain boundary glassy phase is responsible for the degradation of mechanical properties. The next not negligible advantage of this process is the relative low price of silicon powder. On the other hand the factor significantly influencing the price of the final product is a long time of nitridation, from 20 to 100 hours, depending on the dimensions of the nitrated body. Suitable choice of the reaction conditions can result in shortened nitridation. Influence of temperature, pressure, impurities in the gas (He, Ar, H₂), gas flow rate, and Si₃N₄ seeding have been well described [1–6]. Metallic impurities in the silicon powder, particularly iron, also affect the reaction rate. Boyer et al. [7] have shown that Fe enhances the nitridation reaction. Fe promotes devitrification of silica layer present on the surface of silicon particles, which is subsequently disrupted and the reaction of underlying Si with nitrogen can proceed. Another view explaining the role of Fe was proposed by Jack

[8], who suggested that Fe forms a liquid phase by reaction with Si to form an eutectic or with SiO₂ to form a silicate melt at high temperatures. All of above-mentioned variables, individually and in combination, have a remarkable effect on the microstructure and the time of nitridation of the product. However, despite the large effort dedicated to understanding the nitridation mechanisms, some questions have remained.

The purpose of this work is better understanding of the role of impurities on the reaction kinetics. The promoting role of Fe [7–9] and other additives as Mn, Co, Pd, Pt, Ni have been also reported [10], however, more knowledge about the effect of metallic elements on nitridation is needed. From this reason the influence of intentionally introduced metallic additives such as Fe, Cr, Ni, and Ti on the reaction kinetics is studied in this work.

EXPERIMENTAL

The starting silicon powder (Ventron m 2N5) was prepared by wet milling in acetone in a planetary steel ball mill. Impurities (Fe, Ni) introduced during the milling were removed by washing of the batch in HCl. Spectrographic analysis showed the following levels of impurities (wt%): 0.03 Fe, 0.01 Ni, 0.01 Mg, and 0.01 Ca. The Si powder grain size after milling varied from 0.1 to 10 μm with a BET surface area of 8 m²g⁻¹. The contents of added metals (Me=Fe, Ni, Cr) were 0.2, 0.5, and 1.0 wt%, respectively. They had been added in a form of nitrates and after the homogenization were coagulated with urea. Hydrolysis of urea according to reaction



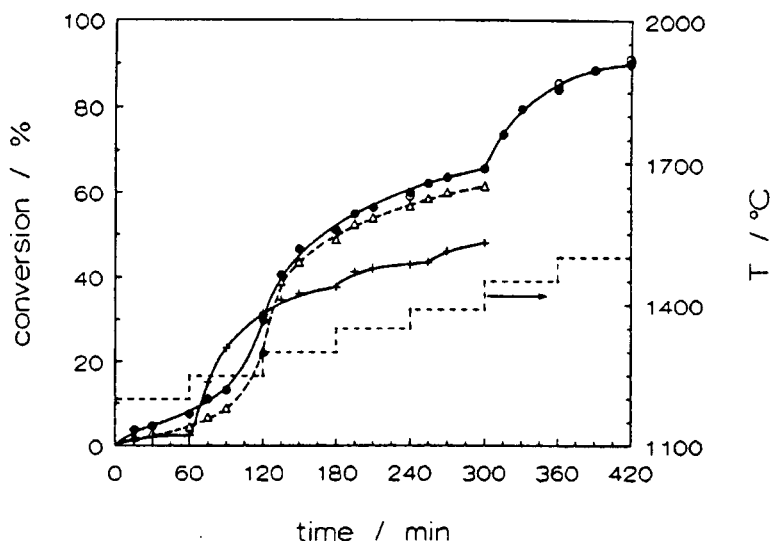
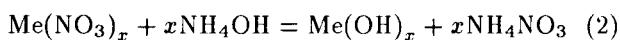


Fig. 1. Time dependence of conversion of Si to Si_3N_4 with Fe addition (+ 0.2 wt%Fe, Δ 0.5 wt%Fe, \bullet, \circ 1.0 wt%Fe).

and subsequent formation of metal hydroxides by reaction



have been carried out in temperature range of 90–100°C. Hydroxides in the filter cake were decomposed at 450°C for 1h. Cylindrical compacts (6 mm diameter, 4 mm height) were pressed from the powders under a uniaxial pressure of 100 MPa. The green densities of pellets were approximately 55% of the theoretical one. These pellets were nitrided in a graphite resistance furnace and therefore, powder bed of composition 10% Si + 90% Si_3N_4 was used as a protection against the formation of SiC in the product. The nitridation was performed in a static gaseous mixture of 90 vol% N_2 and 10 vol% H_2 at a pressure of 0.15 MPa. Hydrogen was supplied by hydrogen generator HG 1410 Tesla. The strong reduction conditions (C, CO, H_2) insured a direct reduction of metal oxides to metals. Microanalysis of the products of nitridation showed that this method provides a good distribution of metals. A main disadvantage of used method was that the oxygen content increased from 1.6% to 2.3%. Three heat treatments were used:

I: 1200°C, 1250°C, 1300°C, 1350°C, and 1390°C for 1h each;

II: the same as I followed by 1450°C and 1500°C for 1h each;

III: 1350°C for 2h, 1450°C for 3h, and 1520°C for 1h. The samples were pre-treated for 20 min in vacuum at 700°C prior to admission of the nitriding gas. The heating-cooling rate of 100°C min^{-1} was used for all experiments. Microstructural analysis was performed by optical (Carl Zeiss Jena) and scanning electron

microscopy (Jeol JSM 35). The measurement of the extent of reaction was based on the assumption that measured weight gain corresponds to the theoretical conversion of Si to Si_3N_4 . The nitridation was interrupted for the weight gain determination, the sample was removed from the cooled furnace and weighed on Sartorius balance (precision 0.0001 g). Phase composition was determined by X-ray diffraction analysis using the quantitative method described by Käll [11]. The $\beta/(\alpha+\beta)$ ratio was calculated from the intensity of diffraction lines (102), (210) for α - and (101), (210) lines for β - Si_3N_4 .

RESULTS AND DISCUSSION

The weight gain of the sample without metallic additives was only 2 wt% after the nitridation at 1250°C for 60 min. Because of this low degree of conversion materials without metallic additives were not considered in the next study. The weight gain of samples with metallic additives was measured after 15, 30, and 60 minutes of nitridation at all temperatures. From these data an 'effective' conversion was calculated. 'Effective' conversion means that for its calculation the evaporation of Si and formation of SiC during nitridation was omitted (its formation is accompanied by lower weight gain in comparison with Si_3N_4). The results are given in Figs. 1–3. The influence of interruption of nitridation on the degree of conversion of Si to Si_3N_4 was investigated for the samples with 1 wt% metal content. The heat treatment II was also interrupted after each 2 hours in the second case, but the conversions were nearly the same ($\pm 3\%$; opened circles in Figs. 1–3), so the effect of interruption of nitridation is negligible.

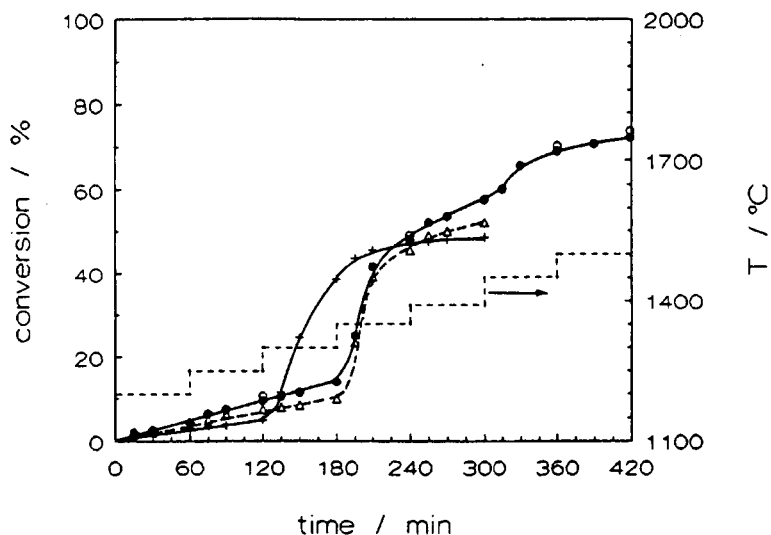


Fig. 2. Time dependence of conversion of Si to Si_3N_4 with Cr addition (+ 0.2 wt% Cr, Δ 0.5 wt% Cr, ●, ○ 1.0 wt% Cr).

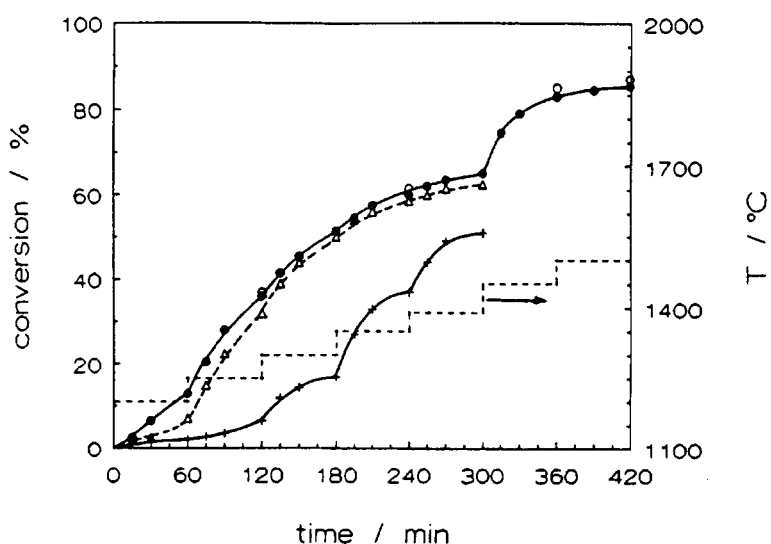


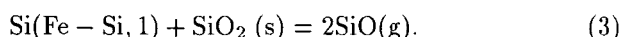
Fig. 3. Time dependence of conversion of Si to Si_3N_4 with Ni addition (+ 0.2 wt% Ni, Δ 0.5 wt% Ni, ●, ○ 1.0 wt% Ni).

The Si samples with Fe and Cr additions (Figs. 1 and 2) have nearly linear increase of conversion up to their eutectic temperature, which is 1208°C for Fe - Si [12] and $1305 \pm 10^\circ\text{C}$ for Cr - Si [13]. As is pointed out in [14], in the beginning stage of nitridation a gaseous nitrogen is chemisorbed onto the silicon surface and silicon is transported to the reaction site by surface diffusion and by evaporation - condensation with resultant formation of nitride nuclei. The kinetics rate for this stage is linear. The subsequent lateral and vertical growth of nuclei is a function of arrival of N_2 to the growth sites. Often the reaction rate decreases.

The initial part of conversion curves for the samples containing Fe and Cr is possible to describe by these mechanisms. The conversion decreases with decreasing metal content. It can be proposed that with decrease of the conversion degree of Si to Si_3N_4 also the thickness of nitride layer decreases. Metals also affect the reaction because of their effect on the nitrogen atmosphere. Hot iron catalyzes the formation of active (possibly atomic) nitrogen, which is more reactive than molecular nitrogen [2]. Chromium, as a transition element, exposes a similar effect. The presence of hydrogen in the nitriding atmosphere also cannot

be neglected, because of its promoting role, especially in the initial stage of reaction. The added hydrogen affects the thermal diffusion of the gas and supports the removal of the protective silica layer covering the silicon grains [3]. The hydrogen content was the same for all experiments. Thus, its accelerating effect on the reaction extent was the same and this allow to compare an influence of different metals on nitridation of silicon. Finally, the conclusion can be drawn, that unequal conversion depends on the amount and the kind of metal impurity.

The first significant increase of conversion unexpectedly appears in the samples with the lowest metal content (0.2%) after 15 minutes of nitridation at 1250°C for Fe and at 1300°C for Cr (Figs. 1 and 2). In the last mentioned samples the formed nitride layer is probably discontinuous up to the eutectic temperature of Me – Si system. Over this temperature the gradually formed liquid phase is directly accessible for N₂. As is described by Lange [15], Fe at eutectic temperature form a silicon-rich liquid in equilibrium with the ambient Si. Active oxidation of this liquid results in production of gaseous SiO probably by the reaction



SiO(g) reacts with N₂ to form α -Si₃N₄. As further SiO is volatilised, equilibrium is maintained by dissolving the surrounding silicon. On the other hand, also formation of the β -Si₃N₄ phase within a liquid FeSi₂ was observed as a consequence of diffusion of N₂ into this melt and its reaction with Si [7]. The earliest increase of conversion for the samples with the lowest metal addition can be explained in this manner. After separation of reactants (Si and N₂) by formed Si₃N₄ layer the reaction is possible only by diffusion of N₂ through this layer. The reaction rate is lowered.

Significant increase of conversion begins later for the samples with higher metal content. For the samples with Fe addition after 60 minutes of nitridation at 1250°C (Fig. 1) and for the Cr-containing samples after 15 minutes of nitridation at 1350°C (Fig. 2). It is supposed that increase of conversion is caused by destroying of the reaction barrier which is probably in the form of an unpenetrable Si₃N₄ layer, which is formed in the first part of nitridation. The disruption of this nitride layer is caused either by increasing of partial pressure of Si (p_{si}) or by different thermal expansion coefficient of Si and Si₃N₄. More effective nitridation in the presence of liquid phase takes place. The reaction rate is also diffusion controlled in this case, but the diffusion coefficient of nitrogen in liquid silicon is much higher than in solid Si₃N₄ [16, 17]. This is indicated by rapid increase of conversion. The total conversion is higher for the samples with higher metal content (up to 1 wt% Me) because of higher amount of liquid phase formed.

Elucidation of reaction mechanism for the nickel-containing samples seems to be more complicated. The phase diagram of Si – Ni system [18] shows the formation of solid solution up to 2 wt% Ni at 993°C. The lowest eutectic temperature of this binary system is 964°C. In the equilibrium state in the samples with low additions of Ni (0.2–1.0 wt%) no liquid phase is present at temperatures of 1200°C and 1250°C because of formation of solid solution at these temperatures and compositions. According to the observed kinetics, which is comparable with previous ones, formation of Si₃N₄ by diffusion of N₂ through solid phase (nitride or silicide) is less probable. However, it can be assumed, that the solubility of Ni in Si is locally exceeded or non-equilibrium state prevails, so then the formation and transient existence of liquid phase is possible. The sample with 0.2 wt% Ni differs from the other samples in its specific form of conversion curve (Fig. 3). The formation rate of nitride at each temperature is higher in the initial stage and later is continuously lowering. This step-like increase of conversion is observed also in the other samples, but it is not so conspicuous. One of the possible reasons for such shape of conversion curve is as follows: during the first two nitriding cycles (1200°C and 1250°C) a relatively unpenetrable nitride layer formed, because the temperature of the first dwell was 236°C over the eutectic temperature of Si – Ni. Nickel can influence the nitriding atmosphere in the similar way as in previous case and/or the formed Ni_xSi_z affords easier diffusional way for N₂ or Si to the reaction site. Both effects positively influence the density and thickness of Si₃N₄ layer, respectively. The small amount of liquid phase and the partial pressure p_{si} at lower temperatures (< 1300°C) are not able to disrupt a formed nitride layer. At 1300°C and higher temperatures, when the step-like increase of conversion arises, the reaction seems to be diffusion controlled. However, Fig. 4 shows that the kinetics of Si₃N₄ formation does not obey strictly parabolic rate law at the given temperatures. Except diffusion, also other process should contribute to the formation of Si₃N₄. It can be supposed, that microcracks are forming in a nitride layer [19] at higher temperature, when the p_{si} is enough high, and due to the different thermal expansion of Si and Si₃N₄. Silicon with higher thermal expansion coefficient than Si₃N₄ initiates internal stress on the interface during relatively high heating rate (100°C min⁻¹) which can disrupt the compact nitride layer and creates free area for the motion of reactants (N₂, Si) together and/or for the formation of liquid phase between Ni and Si. At the end of the nitriding cycle the most pores or cracks are filled with Si₃N₄ and diffusion becomes the controlling step. Therefore, the reaction slows down. By increasing of temperature the mentioned mechanisms are repeated with a result-

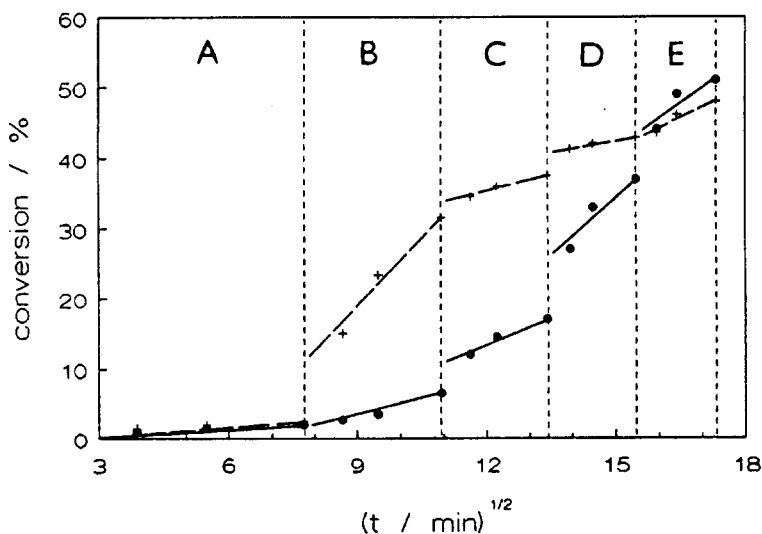


Fig. 4. Dependence of conversion of Si to Si_3N_4 on $t^{1/2}$ (A - 1200°C , B - 1250°C , C - 1300°C , D - 1350°C , E - 1390°C , + 0.2 wt%Fe, ● 0.2 wt.%Ni).

tant step-like increasing of conversion. Final stage of the nitridation for all samples is diffusion controlled. Relatively short total nitriding time caused, that on the polished surface of the sample nitrided by heat treatment I, unreacted silicon was identified in the centre of large grains and agglomerates (Fig. 5). The fracture surface of the product (1 wt% Ni) is shown in Fig. 6.

The influence of liquid phase on the nitridation was proved by addition of titanium to silicon. Titanium was added in a form of TiH_2 which is decomposing at 400°C . After nitridation of Si +1 wt% Ti at 1300°C for 1 hour 3% conversion was obtained, and after the same nitriding time at 1350°C (20°C over the eutectic temperature of binary system Si - Ti [18]) the conversion was 40%. The influence of liquid phase is evident. X-ray analysis of the product shows 48% $\beta\text{-Si}_3\text{N}_4$ content.

Obtained phase composition of the products are given in Table I. After the same heat treatment the $\beta/(\alpha+\beta)$ ratio increased with increasing metal content. The reason is in the higher liquid phase formation which promotes $\beta\text{-Si}_3\text{N}_4$ growth. The part of the total amount of β -phase is a result of the reaction between solid silicon and nitrogen at higher temperatures. Higher β -phase yield was obtained after heat treating III (course of conversion see in Fig. 7) in comparison with II one, because the temperature was raised to 1350°C directly. At this higher temperature the formation of $\beta\text{-Si}_3\text{N}_4$ is preferred. The α -phase content in the products is higher after heat treatment I and II, respectively. It is due to the used nitriding conditions (lower nitriding temperature, H_2

content in the nitriding gas) supporting the formation of $\alpha\text{-Si}_3\text{N}_4$. This confirms, that the type of nuclei has a decisive role on the phase composition of the product. In the presence of liquid phase, when the highest increase of 'effective' conversion is obtained, α - and β -crystals grow competitively, although $\beta\text{-Si}_3\text{N}_4$ often occurs in combination with liquid, and $\alpha\text{-Si}_3\text{N}_4$ often originates from vapour phase reaction by the nitridation of $\text{Si}(\text{g})$ which vaporizes from liquid. Depending on the metal type the highest $\alpha\text{-Si}_3\text{N}_4$ content is obtained for the samples with Ni addition and higher, nearly the same $\beta\text{-Si}_3\text{N}_4$ content for the samples with Fe and Cr additions.

CONCLUSIONS

The experiments confirmed a positive influence of metal additions (Fe, Ni, Cr, Ti) on the reaction kinetics of RBSN which becomes evident over the eutectic temperature of added metal and silicon.

The final conversion of Si to Si_3N_4 is nearly the same for 0.5 and 1.0 wt% metal addition, therefore, lower amount of metal (0.5 wt%) is sufficient for remarkable influence of reaction kinetics.

The phase composition is slightly influenced by metal additon. The nucleation and crystallization of $\alpha\text{-Si}_3\text{N}_4$ is positively influenced by the presence of Ni and $\beta\text{-Si}_3\text{N}_4$ content increases by addition of Fe, Cr, and Ti.

The nitriding schedule has a higher effect on phase composition than the type of metal addition. RBSN with $\alpha\text{-Si}_3\text{N}_4$ content can be prepared by slow nitridation of silicon compact with Ni addition in a temperature range $1100\text{--}1300^\circ\text{C}$, while high β -phase con-

Table I
Phase Composition of the Products

Metal content [wt.%]	$\alpha - \text{Si}_3\text{N}_4$ [wt.%]	$\beta - \text{Si}_3\text{N}_4$ [wt.%]	Si [wt.%]	Heat treatment
1.0 Cr	61.2	13.3	25.5	I
1.0 Fe	64.5	14.8	20.7	
1.0 Ni	66.9	12.0	21.1	
0.5 Cr	61.1	10.1	28.8	
0.5 Fe	65.7	11.2	23.1	
0.5 Ni	69.3	8.2	22.5	
0.2 Cr	60.0	9.1	30.9	
0.2 Fe	58.1	10.7	31.2	
0.2 Ni	63.4	7.1	29.5	
1.0 Cr	67.6	15.6	16.8	II
1.0 Fe	76.9	17.1	6.0	
1.0 Ni	76.1	15.2	8.7	
0.2 Cr	67.8	19.9	12.3	III
0.5 Cr	71.0	21.2	7.8	
1.0 Cr	70.3	21.9	7.8	

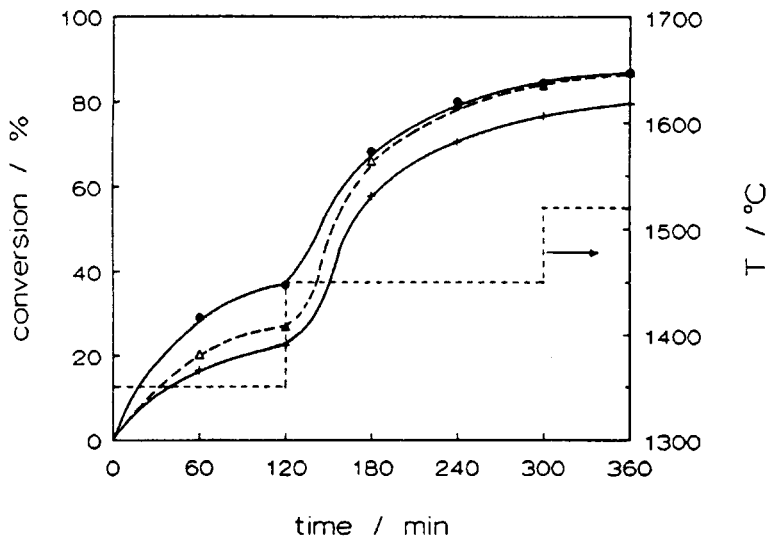


Fig. 7: Time dependence of conversion of Si to Si_3N_4 with Cr addition (+ 0.2 wt%Cr, Δ 0.5 wt%Cr, \bullet, \circ 1.0 wt%Cr).

tent can be obtained after nitridation in temperature range 1350–1500°C with Fe, Cr or Ti addition.

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VPLYV Cr, Ni, Fe A Ti NA KINETIKU NITRIDÁCIE KREMÍKA

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Sledoval sa vplyv rôznych prechodných kovov na kinetiku nitridácie kremíka. Kovy (Cr, Ni, Fe a Ti) sa pridávali

vo forme dusičnanov, z ktorých sa vyzrážali pomocou mčoviny, čím sa dosiahla dobrá disperzia kovových prísad. Vplyv kovov na kinetiku nitridácie sa prejavil nad eutektickou teplotou systému kremík – kov, nakoľko difúzia dusíka cez tvoriacu sa kvapalnú fázu je o niekoľko poriadkov vyššia ako cez tuhý Si alebo Si_3N_4 . Celková konverzia Si na Si_3N_4 bola vyššia u vzoriek s vyšším obsahom kovovej prísady, i keď v prípade Fe a Cr mali vzorky s nižším obsahom prísady zpočiatku rýchlejší vzostup konverzie (obr. 1, 2). Konverzia vzorky s 0.2 hm.% Ni mala špecifický, stupňovitý priebeh (obr. 3). Reakciou medzi Si s prísadou Ni a N_2 postupne vznikala súvislá vrstva Si_3N_4 , reaktanty sa od seba oddelili a reakcia sa zpomalila. Riadiacim mechanizmom reakcie v tejto etape nitridácie bola difúzia. Zvýšením teploty sa v dôsledku rôzneho koeficientu teplotnej rozťažnosti Si a Si_3N_4 a rastúceho parciálneho tlaku Si celistvosť zreagovanej vrstvy narušila, čím sa opäť umožnil priamy priebeh reakcie medzi Si a N_2 . Ako naznačuje závislosť na obr. 4, tieto mechanizmy mali vplyv na celkový stupeň konverzie najmä v počiatočnom štádiu nitridácie pri danej teplote.

Vhodnou voľbou kovovej prísady možno do určitej miery modifikovať aj fázové zloženie produktu.

Obr. 1. Priebeh konverzie Si na Si_3N_4 s prísadou Fe v závislosti od doby nitridácie. (+ 0.2 hm.%Fe, Δ 0.5 hm.%Fe, \bullet , \circ 1.0 hm.% Fe)

Obr. 2. Priebeh konverzie Si na Si_3N_4 s prísadou Cr v závislosti od doby nitridácie. (+ 0.2hm.%Cr, Δ 0.5 hm.%Cr, \bullet , \circ 1.0 hm.%Cr)

Obr. 3. Priebeh konverzie Si na Si_3N_4 s prísadou Ni v závislosti od doby nitridácie. (+ 0.2 hm.%Ni, Δ 0.5 hm.% Ni, \bullet , \circ 1.0 hm.%Ni)

Obr. 4. Závislosť konverzie Si na Si_3N_4 od odmerniny z času. (A – 1200°C, B – 1250°C, C – 1300°C, D – 1350°C, E – 1390°C, \bullet 0.2 hm.%Ni, + 0.2 hm.%Fe)

Obr. 5. Mikrofotografia vyleštenej plochy vzorky RBSN obsahujúcej nezreagovaný Si v strede aglomerátu.

Obr. 6. Mikrofotografia (SEM) lomovej plochy RBSN s prísadou 1 hm.% Ni.

Obr. 7. Priebeh konverzie Si na Si_3N_4 s prísadou Cr v závislosti od doby nitridácie. (+ 0.2 hm.%Cr, Δ 0.5 hm.% Cr, \bullet , \circ 1.0 hm.%Cr)