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Investigation of the Chemical Interaction in the TiC-Si_3N_4 System

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Chemical interaction in the TiCSi$_3$N$_4$ system was investigated. Thermodynamic calculations and kinetic analysis were carried out for a number of powder mixtures with various TiC:Si$_3$N$_4$ molar ratios in the temperature range 1300-1750 °C. Stability regions of the TiC-Si$_3$N$_4$ composites were defined. It was shown that the main reaction products are silicon carbide and titanium carbonitride. The overall chemical interaction is described in terms of chemical reaction between titanium carbide and silicon nitride, and the diffusion of carbon and nitrogen through the coherent reaction products layer after completion of the initial direct interaction of the components.

Keywords: *composite materials, silicon nitride, thermodynamic analysis, phase formation, kinetic analysis, chemical interaction, diffusion*

1. Introduction

The majority of titanium carbide and silicon nitride containing materials developed until present time were silicon nitride based ceramic composites with titanium carbide additives serving as particle reinforcing component. Such materials were mainly used for cutting tools and wear-resistant parts production[1,2], as well as ceramic materials with improved thermal and electrical conductivity[3,4]. Processing of such materials can be successfully developed only if the in-depth understanding of thermodynamics and kinetics of the chemical interaction of constituents in the range of temperatures used for materials densification is achieved.

Until now only limited knowledge in this field was acquired. Mach *et al.*[5] investigated Si_3N_4 containing various fractions of *TiC* dispersoid under conditions of hot pressing in nitrogen atmosphere at 1750 °C and suggested that reaction products probably consist of silicon carbide and titanium nitride. Buljan and Zilberstein[6,7] determined that the chemical interaction in the TiC-Si_3N_4 system under conditions of hot pressing and sintering in argon is strongly influenced by impurities, especially iron and free carbon. However, the internal chemical reactions, *i.e.* the chemical interaction between the main components of the system disregarding the effects of glassy phase formed by the conventional oxide sintering additives used for Si_3N_4 densification and of impurities, in the TiC-Si_3N_4 system was not investigated although they may play a determining role in the overall processing procedure of TiC-Si_3N_4 composite materials.

The main problem in silicon nitride processing is its thermo-chemical dissociation at high temperatures. Therefore, densification by means of sintering or hot pressing is normally conducted under nitrogen atmosphere, and often under high nitrogen pressure. However, considering the chemical properties of titanium carbide, namely its ready nitridation in nitrogen atmosphere at high temperatures, it is plausible to assume that its behavior in the mixture with silicon nitride under thermal conditions adequate for densification will be more favorable in the atmosphere of an inert gas, such as argon. In order to elucidate the process of direct chemical interaction between titanium carbide and silicon nitride, in the present work experiments were carried out with mixtures that did not contain any oxide additives, normally used as sintering aids for silicon nitride based ceramics. The emphasis was made on thermodynamic and kinetic analysis of the TiC-Si_3N_4 system behavior. The titanium carbide to silicon nitride molar ratio in the mixtures was chosen as a variable parameter in order to determine its influence on the chemical reaction between the components in the wide temperature range.

2. Experimental

The powders of titanium carbide (laboratory synthesized, Institute for Problems of Materials Science, Kiev,

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Ukraine) of high purity (total impurities content ≤ 0.5 wt.%) and of high specific surface area (12 m^2/g), and silicon nitride (SN E-10, Ube Industries, Tokyo, Japan) of high purity (total impurities content ≤ 0.2 wt.%), high specific surface area (11.5 m^2/g), and high α/β ratio (over 95%) were used for the experiments. The powders were mixed by ball milling in isopropyl alcohol for 24 h with silicon nitride balls as a milling media in a silicon nitride lined vessel. Weights of the milling media and of the vessel measured before and after milling showed the contamination by the ball and vessel material to be negligible. After the mixed slurry was dried in a rotaevaporator, it was passed through a 40 µm sieve in order to crush the soft agglomerates.

Thus prepared mixtures were placed into a boron nitride crucible without any kind of preliminary compaction. Thermal treatment was accomplished in a furnace with a graphite heating element (Astro Industries, Santa Barbara, USA) in a stagnant argon atmosphere under 1 bar pressure. Both heating and cooling rate were 25°/min. Soaking time at the temperatures of heat treatment, which covered the range of 1300-1400 °C, varied from 4 to 240 min.

Thermally treated mixtures were subsequently characterized by X-ray diffraction (XRD) on a powder diffractometer Siemens D5000 (position-sensitive detector, *Ni*-filtered CuK_α radiation, measuring range 10-80° 2Θ) for phase analysis.

3. Results and Discussion

3.1. Thermodynamic analysis of the TiC-Si_3N_4 system stability

Chemical interaction in composite materials is governed by three factors:

- chemical compatibility of constituents;
- internal overall stability, which is mainly determined by the stability of the constituents in the presence of impurities introduced during processing under certain conditions;
- interaction of the constituents with the processing atmosphere.

In our case, chemical interaction may be described by the equilibrium previously proposed by Buljan and Zilberstein in Refs. 6 and 7 for the description of the systems behavior under conditions of hot pressing:

$$xSi_3N_4 + 3TiC\ (s) = 3xSiC\ (s) + 3TiC1_{-x}N_x\ (s) + x/2\ N_2\ (g) \quad (1)$$

A close scrutiny of Eq. 1 leads to a conclusion that *TiC-*Si_3N_4 system may reach equilibrium by several possible courses of chemical interaction:

The first possible equilibrium may be presented as follows:

(1) silicon nitride does not have a real melting point but rather decomposes according to a reaction[8]:

$$Si_3N_4\ (s) = 3Si(s,l) + 2N_2\ (g) \quad (2)$$

$$\Delta G^0_T\ (J\ mol^{-1}) = \Delta G^0_T\ (Si_3N_4)\ (J\ mol^{-1}) = -RT\ln\ (P^{\,2}_{N_2})$$

$$= 723{,}800 - 315\ T\ (K) \qquad T\ (K) \geq 1685$$

$$= 874{,}500 - 405\ T\ (K) \qquad T\ (K) \leq 1685$$

Thermodynamic analysis shows that in the temperature range of 1600-1900 °C thermal dissociation occurs under the pressure of nitrogen of 0.1 MPa[9].

In practice, however, decomposition of silicon nitride is promoted by practically all impurities introduced in the course of processing, carbon in particular[8]. In our case, carbon, which is inherently present in the system, is transported to the place of reaction by means of diffusion, titanium carbide being the source of carbon, will facilitate the thermal decomposition of silicon nitride according to the following reaction[8]:

$$Si_3N_4\ (s) + 3C\ (s) = 3\ SiC\ (s) + N_2\ (g) \quad (3)$$

$$\Delta G^0_T = 3\Delta G^0_T\ (SiC) - \Delta G^0_T\ (Si_3N_4) = -RT\ln\ (P^{\,2}_{N_2})$$

$$\Delta G^0_T\ (J\ mol^{-1}) = -122{,}626 + 37\ T\ (K)$$

The second possible equilibrium may be presented as follows:

(2) titanium carbide has the crystal structure of *NaCl* type, moreover, the atoms of titanium occupy the octahedral voids of the lattice. Since titanium carbide is a nonstoichiometric compound, the vacancies present in the sublattice of carbon may be occupied by nitrogen atoms resulting in the titanium carbonitride solid solution formation according to the following reactions:

$$TiC\ (s)\ x/2\ N_2\ (g) = TiC_{1\text{-}x}N_x\ (s) + xC\ (s) \quad (4)$$

$$\Delta G^0_t = \Delta G^0_T\ (TiC_{\ 1-x}\ N_x) - \Delta G^0_T\ (TiC) = -RT\ln\ (P^{-x/2}_{N_2})$$

$$TiC_{1\text{-}x}N_x\ (s) + (1 - x)/2\ N_2\ (g) = TiN\ (s) + (1 - x)\ C\ (s) \quad (5)$$

$$\Delta G^0_T = \Delta G^0_T\ (TiN) - \Delta G^0_T\ (TiC_{1-x}\ N_x) = -RT\ln\ (P^{-(1-x)/2}_{N_2})$$

In order to simplify the thermodynamic considerations, the titanium carbonitride solid solution will be regarded as an ideal one. In such a case the lattice parameters of the solid solution will obey Vegard's law. Under such conditions the Gibbs free energy change during titanium nitride formation can be described by the following equation:

$$\Delta G^0_T\ (TiC_{\ 1-x}\ N_x) = (1-x)\Delta G^0_T\ (TiC) + x\Delta G^0_T\ (TiN) + RT\ [x\ln x + (1-x)\ \ln(1-x)\ ] \quad (6)$$

where x coefficient of substitution in the solid solution $TiC_{1-x}N_x$, $\Delta G_T^0\,(TiC)\,(J\,mol^{-1}) = -185{,}555 + 14.7\,T\,(K)$, $\Delta G_T^0\,(TiN)\,(J\,mol^{-1}) = -337{,}361 + 96.4\,T\,(K)$

The source of nitrogen in our case are the decomposition products of silicon nitride. In the Eqs. 4 and 5, carbon can be considered as a catalyst of silicon nitride decomposition.

Equations describing the equilibrium of the system under consideration indicate that the chemical interaction in TiC-Si_3N_4 composites is considerably influenced by partial pressure of nitrogen. Thermodynamic analysis enables to evaluate the chemical compatibility of the components and to predict the reaction sequence in the system. Analysis of the equilibrium in the TiC-Si_3N_4 system together with the calculation of the relevant thermodynamic parameters of the system provides the possibility to construct the stability diagram for the constituents and the products of the reaction in coordinates partial pressure of nitrogen - *Ti(C,N)* solid solution composition, *i.e.*, $\log P_{N_2} - x$.

Curves (2) to (5) in Fig. 1 represent the relationship of nitrogen partial pressure and *Ti(C,N)* solid solution composition for equilibrium states in the system at 1500 °C according to Eqs. 2 and 5, respectively. Each curve divides two fields of stability of the constituents under specific nitrogen partial pressure and different solid solution compositions. Curves (4) and (5) define stability fields between titanium carbide and nitrogen, and also define the stability fields of $TiC + C$, $TiC_{1-x}N_x + C$, and TiC. Stability of silicon nitride inside the composite is defined by curves (2) and (3). Therefore, if the value of is higher than the equilibrium value for the Eq. 3 to which corresponds the field above the curve (3), silicon nitride will be in equilibrium with carbon. Consequently, above the curve (3) stability fields of $Si_3N_4 + TiN + C$ and $Si_3N_4 + Ti(C,N) + C$ are located. The field below the curve (3) corresponds to silicon nitride instability, and under such conditions silicon carbide will be formed as a result of the interaction with carbon. Moreover, below the curve (2) lies another field of silicon nitride instability, which corresponds to its thermal decomposition into silicon and nitrogen. The latter decomposition products in turn react with titanium carbide forming titanium carbonitride and silicon carbide. The $SiC + Ti(C,N)$ field corresponds to this reaction. The equilibria in the system are quite similar at higher temperature (Fig. 2), however the curves are shifted to higher nitrogen partial pressure.

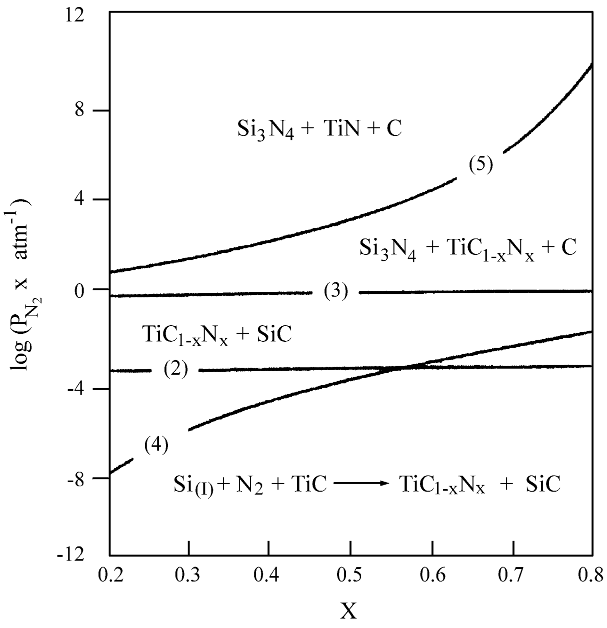

Figure 1. Thermodynamic stability of TiC-Si3N4 at 1500 °C.

As it was shown by thermodynamic analysis, the constituents of the TiC-Si_3N_4 system are chemically incompatible. Therefore, under conditions of sintering or hot pressing normally used for TiC-Si_3N_4 composites densification, pronounced chemical interaction would occur.

3.2. Phase formation during heat treatment

Phase composition evolution during heat treatment of the powder mixtures occurred in complete agreement with the thermodynamic analysis presented above. The main compounds formed as a result of the interaction were silicon carbide and titanium carbonitride. A series of XRD plots taken from the TiC-Si_3N_4 powder mixture with the molar ratio of the components 4:1 heat treated at temperatures in the range of 1300-1750 °C are presented in Fig. 3. Heat treatment was carried out under argon atmosphere.

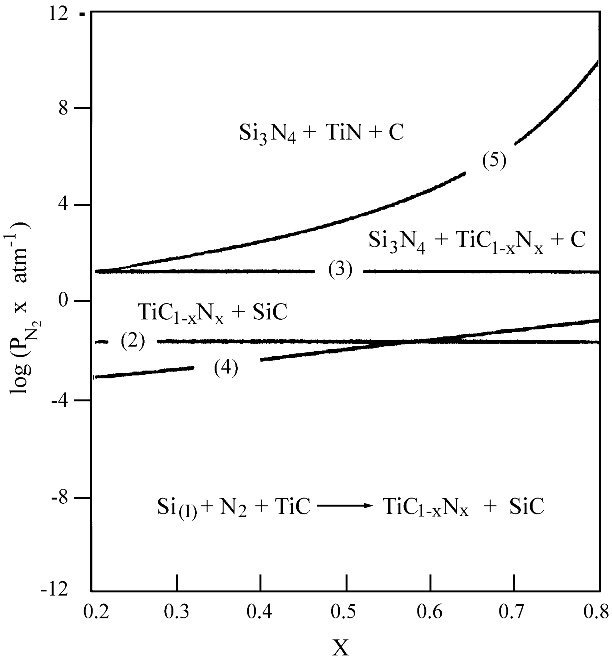

Figure 2. Thermodynamic stability of TiC-Si3N4 at 1750 °C.

Formation of titanium carbonitride and silicon carbide starts at temperatures higher than 1300 °C, which is indicated by the broadening of (111) and (200) planes of titanium carbide diffraction peaks, and by the presence of the (111) plane of β-*SiC* diffraction peak. The amount of above mentioned reaction products increased with the increase of the heat treatment temperature, which can be seen from the increase of the intensities of the silicon carbide and titanium carbonitride diffraction peaks in relation to the ones of silicon nitride and titanium carbide. After heat treatment at temperatures higher than 1700 °C silicon nitride and titanium carbide were not detected. As it was calculated from the XRD data, the titanium carbonitride lattice parameter a_0 values lay in the range of 0.4270-0.4273 nm, which corresponds to the solid solution composition $TiC_{0.5}N_{0.5}$ - $TiC_{0.4}N_{0.6}$ if calculated according to the Vegard's law approach, and were independent from the temperature of the heat treatment. Although according to some literary data[11] silicon nitride was reported to decompose severely at temperatures about 1300 °C in argon atmosphere, no diffraction peaks of silicon were observed in the course of present investigation. αSi_3N_4 to β-Si_3N_4 phase transformation was not observed in the range of heat treatment temperatures applied.

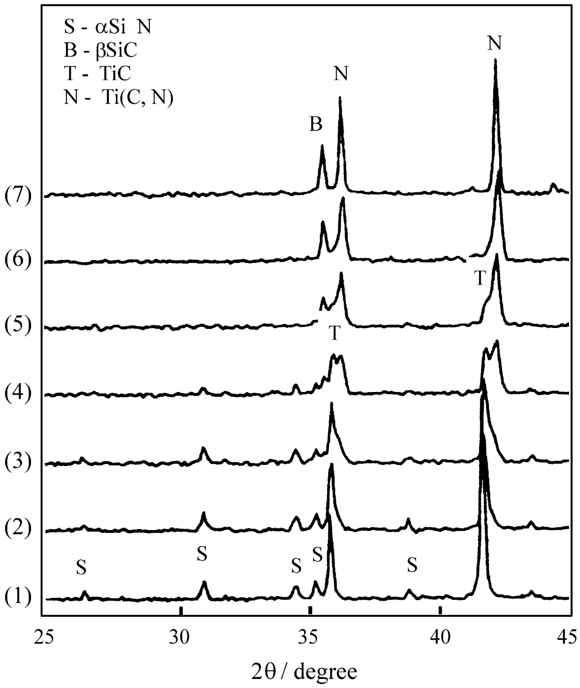

Figure 3. Diffractogramms taken from the TiC:Si3N4 = 4:1 mixture (1) before the heat treatment and after heat treatment at (2) 1300 °C, (3) 1400 °C, (4) 1500 °C, (5)1600 °C, (6) 1700 °C, and (7) 1750 °C, respectively.

3.3. Kinetic analysis

As it was suggested previously, the overall chemical interaction in the TiC-Si_3N_4 system can be described by the Eq. 1. The reaction coefficient of nitrogen for Eq. 1 is dependent on the degree of solubility of nitrogen in titanium carbide, *i.e.*, on the number of carbon vacancies that can be occupied by nitrogen. If the degree of solubility of nitrogen in titanium carbide has some value y, then the Eq. 1 can be transformed into the following one:

$$xSi_3N_4(s) + 3TiC(s) = 3xSiC(s) + 3TiC_{1-x}N_y + z/2N_2(g) \quad (7)$$

where $0 \leq y \leq x$ and $z = 4x-3y$.

Two extreme possibilities may be considered:

- all carbon vacancies are occupied by nitrogen; in this case $y = x = z$, and Eq. 7 transforms into Eq. 1;
- all carbon vacancies are unoccupied (free of nitrogen); in such case $y = 0$, and $z = 4x$.

In the latter case Eq. 7 can be transformed into the following one:

$$xSi_3N_4(s) + 3TiC(s) = 3xSiC(s) + 3TiC_{1-x}(s) + 2xN_2(g) \quad (8)$$

Since nitrogen in all occasions appears as a gaseous product of the interaction between the constituents, any chemical reaction in the TiC-Si_3N_4 system will lead to weight loss. The latter obviously depends on the amount of nitrogen removed from the system.

Therefore, the rate of reactions (1) and (8) can be expressed as:

$$f = [(W_n \quad M_s)/(M_n \quad W_{s0})] \quad 2 \qquad (9)$$

$$f = [(W_n \quad M_s)/(M_n \quad W_{s0})] \quad 1/2 \qquad (10)$$

where W_n - the weight of N_2 formed during the reaction; W_{s0} - initial weight of the silicon nitride constituent in the powder mixture; M_s - molecular weight of silicon nitride; M_n - molecular weight of nitrogen. Substituting W_n by the weight loss value ΔW, and M_s and M_n by the respective values of 140.26 and 28.0 g/mole for silicon nitride and nitrogen molecular weights, Eqs. 9 and 10 may be transformed into:

$$f = 10(\Delta W/W_{s0}) \qquad (11)$$

$$f = 2.5(\Delta W/W_{s0}) \qquad (12)$$

The latter equations for simplification of the further kinetic analysis may be substituted by a generalized one:

$$f = g(y)\Delta W/W_{s0}) \qquad (13)$$

where $g(y)$ is related with the solubility of nitrogen in titanium carbide. In our case this value may be considered as a constant since it was previously established by the

XRD investigations of the lattice parameter a_0 of *Ti(C,N)*. Thus, Eq. 13 unequivocally indicates that the reaction rate in the *TiC-Si$_3$N$_4$* system is directly proportional to the weight loss of silicon nitride during heat treatment. Consequently, the latter fact can be used for kinetic analysis of the chemical interaction in the system under consideration.

Figures 4 and 5 show the reaction curves (relative weight loss *versus* time) for the mixtures with various *TiC:Si$_3$N$_4$* molar ratios under isothermal conditions at 1500 and 1700 °C, respectively. Both sets of curves clearly indicate that the *TiC:Si$_3$N$_4$* molar ratio strongly influences the chemical interaction in the system, and that the weight loss is in direct relation with both the *TiC:Si$_3$N$_4$* ratio and the temperature. Thus, the existence of a strong chemical interaction between *TiC* and *Si$_3$N$_4$* is confirmed.

While the chemical interaction between silicon nitride and titanium carbide proceeds, a coherent layer of reaction products consisting of silicon carbide and titanium carbonitride is formed. The leads to the increase of the reaction products layer thickness and to the decrease of the interaction area due to diminishing of titanium carbide particles diameter. Since the reaction between silicon nitride and titanium carbide under conditions of direct contact occurs rapidly, it is plausible to assume that the rate-limiting process will be the diffusion of carbon through the layer of reaction products. In general, all diffusion models are described by parabolic law[12,13] if the rate-limiting stage is the transport of species through a coherent layer of reaction products. Such parabolic law can be expressed as

$$f = kt^{1/2} \tag{14}$$

where k is a specific constant of reaction rate. In our case Eq. 14 can be transformed into

$$\Delta W/W_{s0} = k't^{1/2} \tag{15}$$

since, as it was shown earlier, relative weight loss is directly proportional to the reaction rate.

Plots of weight loss *versus* square root of time presented in Figs. 6 and 7 exhibit a linear relationship, which supports the supposition that the reaction rate follows a parabolic law and therefore diffusion of species through the layer of reaction products is the rate-limiting stage of reaction. Based on the above described results and conclusions a mechanism of the chemical interaction in the *TiC-Si$_3$N$_4$* system may be proposed. Schematically such a mechanism is shown in Fig. 8. It basically consists of five possible mass-transport routes:

(1) carbon diffuses from titanium carbide through the layer of reaction products to the place of reaction, which is *Si$_3$N$_4$-SiC* interface; (2) silicon diffuses to the *Si$_3$N$_4$-SiC* interface; there carbon will then react with silicon nitride or silicon forming silicon carbide and nitrogen; nitrogen, in turn, can either diffuse through the layer of reaction products to the *Ti(C,N)-TiC* interface and subsequently dissolve in titanium carbide (3), or directly escape along the *Si$_3$N$_4$*-

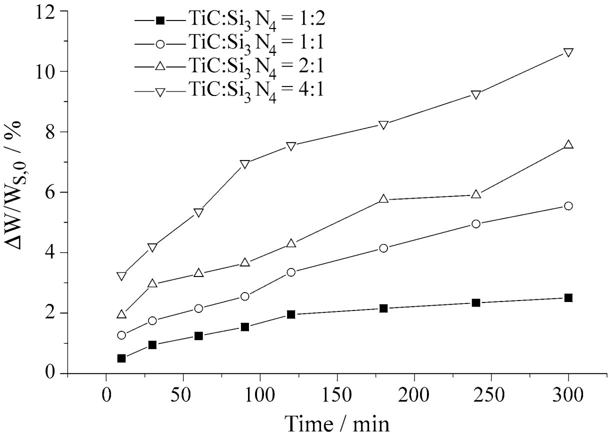

Figure 4. Weight losses of the TiC-Si$_3$N$_4$ mixtures with various ratios of the components during heat treatment at 1500 °C *vs.* heat treatment time.

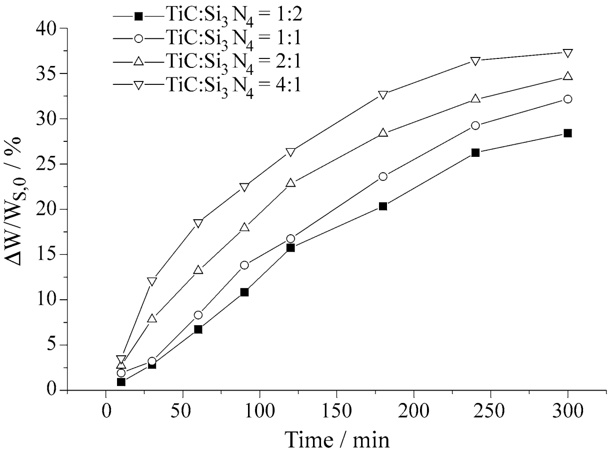

Figure 5. Weight losses of the TiC-Si$_3$N$_4$ mixtures with various ratios of the components during heat treatment at 1700 °C *vs.* heat treatment time.

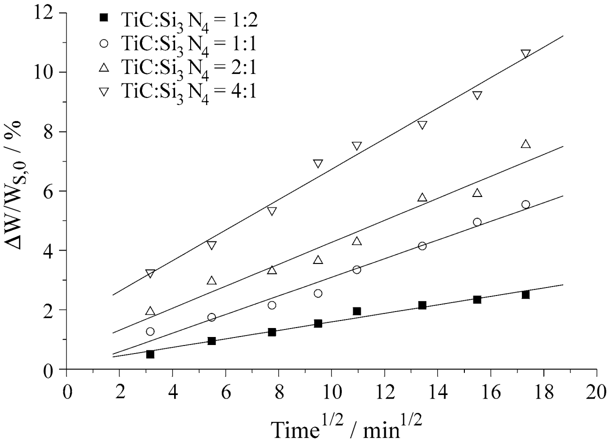

Figure 6. Same relationships as in Fig. 4 presented in parabolic coordinates.

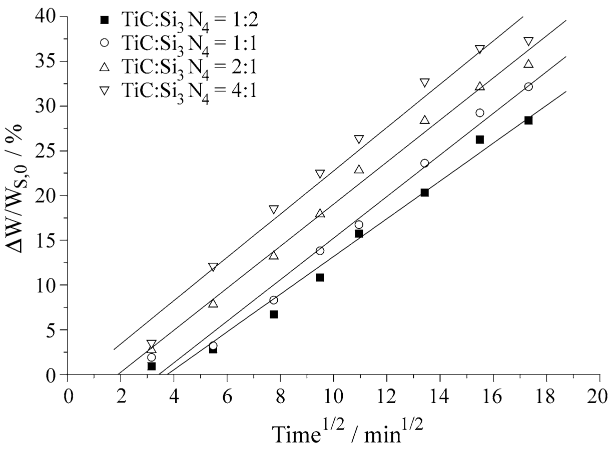

Figure 7. Same relationships as in Fig. 5 presented in parabolic coordinates.

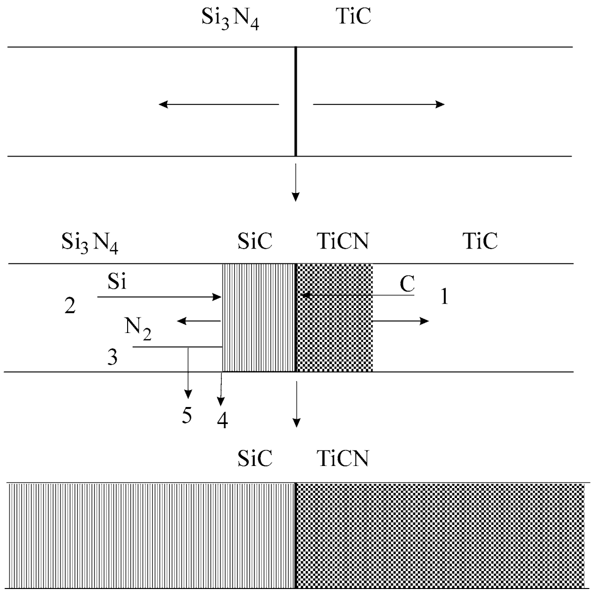

Figure 8. Schematic representation of the chemical interaction in the TiC-Si_3N_4 system (see text for details).

SiC interface into the ambience (4). The decomposition of silicon nitride also results in gaseous nitrogen formation, which can then proceed according to the route (3), or escape into the ambience by route (5), *i.e.*, directly diffusing to the surface of silicon nitride.

It is further plausible to assume that due to intensive gas formation as a result of chemical interaction of the constituents the final structure will be rather porous.

4. Conclusions

Composite material *TiC-Si_3N_4* is unstable under conventional processing conditions.

It was shown that three thermodynamically stable regions exist for the *TiC-Si_3N_4* system, namely *TiN + C + Si_3N_4*, *Ti(C,N) + C + Si_3N_4*, and *SiC + Ti(C,N)*. Stability in these regions is strongly influenced by the nitrogen partial pressure and the temperature. The reaction products mainly consist of β*SiC* and *Ti(C,N)* under present experimental conditions. The equilibrium shifts to the formation of the latter compounds at temperatures higher then 1400 °C. The overall interaction can be described as a chemical reaction between titanium carbide and silicon nitride, which later is controlled by the diffusion of carbon and nitrogen through the coherent layer of the reaction products formed on the initial stages of the process.

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