

High-temperature oxidation of AlN–SiC–TiB₂ ceramics in air

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Abstract

The oxidation behaviour of AlN–SiC–TiB₂ composite materials with 2, 5 and 10 mass% TiB₂ and 3 mass% Fe additive obtained using powder metallurgy methods was studied in air up to 1500 °C by thermogravimetry (TG) and differential thermal analysis (DTA) techniques. The phase composition and structure of the oxide films formed were investigated using metallography, X-ray diffraction (XRD) and electron probe microanalysis (EPMA) methods. The two-stage character of non-isothermal oxidation kinetics (heating rate of 15 grade/min) of composites was established. During the first oxidation stage (up to 1350 °C), the formation of α -Al₂O₃, TiO₂ (rutile), B₂O₃ and β -cristobalite as well as different aluminium borates was found. They formed as a result of interaction between Al₂O₃ and melted B₂O₃. During the second stage (above 1350–1400 °C), the mullite 3Al₂O₃·2SiO₂ proved to be a main oxidation product in the scale; besides, some amounts of β -Al₂TiO₅ were formed as well. The iron additive dissolved in the mullite and aluminium titanate phases that led to the stabilization of a scale formed. It was established that for the three different TiB₂ contents, oxidation isotherms follow the parabolic or parabolic rate law. The slope change on the Arrhenius plot given by the dependence of the parabolic rate constants on the reciprocal temperature, suggests a change of the oxidation mechanism in the temperature range of 1300–1350 °C. For example, for the (AlN–SiC)–5% TiB₂ composite specimen, the calculated values of apparent activation energy are equal to 285 kJ/mol (1100–1300 °C) and 500 kJ/mol (1350–1550 °C), respectively. The AlN–SiC–TiB₂ ceramics developed here can be recommended as high-performance materials for a use in oxidizing medium up to 1450 °C.

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1. Introduction

AlN-based ceramics can be considered as the only non-oxide ceramics to compete with Si₃N₄ and SiC for high-temperature applications.^{1–5} Oxidation of AlN–TiB₂ and AlN–SiC binary ceramic systems has been studied earlier.^{6,7} Oxidation behaviour of a HIPed AlN–TiB₂ composite has been investigated in flowing oxygen in the temperature range 700–1300 °C.⁶ It was established that the material under study possesses a very good oxidation resistance below 1050 °C. Therefore, the enhanced oxidation and formation of thick oxide scales at higher temperatures can limit its high-temperature application. Nevertheless, the formation of

the aluminium borates (Al₄B₂O₉ and Al₁₈B₄O₃₃) by entrapment of boron oxide by alumina is interesting because it reduces the volatilization of boron oxide, which seals pores and cracks.

Concerning AlN–SiC ceramics, it was shown⁷ that the scale formed in air at the temperatures up to 1550 °C consists of three oxide layers. In the inner layer, both Al₁₀N₈O₂ oxynitride and β -cristobalite phases were found; in the intermediate one, the β -SiAlON was determined for the samples with a lower content of SiC and α -Al₂O₃ for the greater AlN content. The outer layer contains mullite (3Al₂O₃·2SiO₂) as the main phase, which ensures high protective properties of the scale. The AlN–SiC ceramics can be related to materials having an extremely high oxidation resistance up to 1400 °C.^{7,8} It has been hypothesized that the corresponding ternary system AlN–SiC–TiB₂ will have a high corrosion resistance too, in

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addition to the significant improvement of mechanical characteristics by comparison with the AlN–SiC system.

2. Materials and experimental

The AlN–SiC–TiB₂ composite materials were manufactured by hot pressing of ternary powder mixture (AlN and SiC: average particle size <2 μm, and TiB₂ <5 μm). The powders were preliminarily ground inside a ball mill with the iron balls during 10 h. The duration of hot pressing process was 30–40 min in the temperature range of 1750–1820 °C under pressure of 30–40 MPa. The final porosity of samples was less than 3%. They had a heterogeneous structure with an average grain size of 1–3 μm. TiB₂ preserves its lattice parameters while AlN and SiC are known to form a solid solution.

In this work, the oxidation of AlN–(28–20) mass% SiC–(2–10) mass% TiB₂ ceramics was studied up to 1500 °C in air. Three batches (samples—with 2, 5 and 10 mass% TiB₂) were studied. Kinetics of high-temperature oxidation was investigated using TG and DTA method (a Setaram device-1600), the oxidation products and the scale peculiarities were established with the aid of XRD (a DRON-2.0 apparatus), SEM and EPMA (a Camebax MS 46) methods.

3. Results and discussion

The oxidation of the first powder grade (70% AlN–28% SiC–2% TiB₂) starts at 770 °C. Three DTA peaks are observed during non-isothermal oxidation—at 880, 990 and 1280 °C (Fig. 1). In the case of the composite of same composition, there are only two DTA peaks (1220 and 1420 °C), and at 1450 °C the mass gain per surface unit reaches 0.5 mg/cm².

In the range of 1300–1350 °C, an evolution of the oxidation mechanism takes place. Undoubtedly, this behaviour may be related to a change of the scale composition (see Table 1). At lower temperatures (1200–1350 °C), the scale consists essentially of rutile (TiO₂), Fe₂O₃ and Fe₂TiO₅. At the same time, near the substrate, some amounts of Al₁₀N₈O₂ and β-cristobalite were detected. Between 1400 and 1500 °C, the inner scale layer contains TiO₂, α-Al₂O₃, and β-SiO₂ (cristobalite), growing together with a fine-dispersed β-

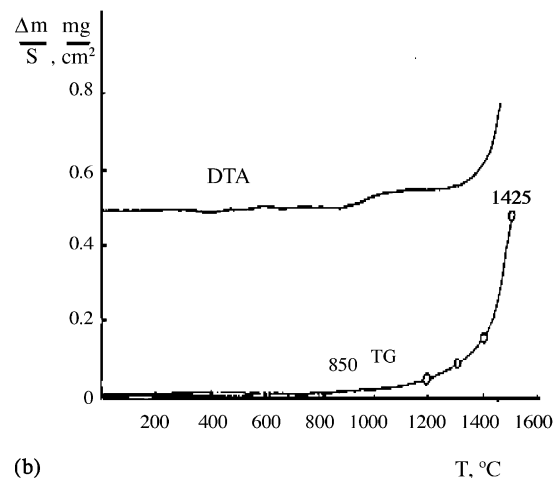
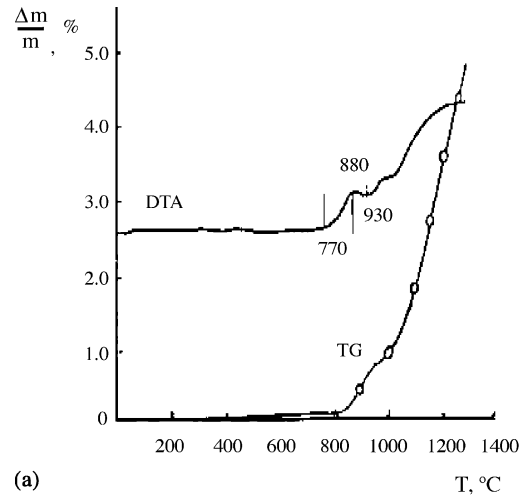


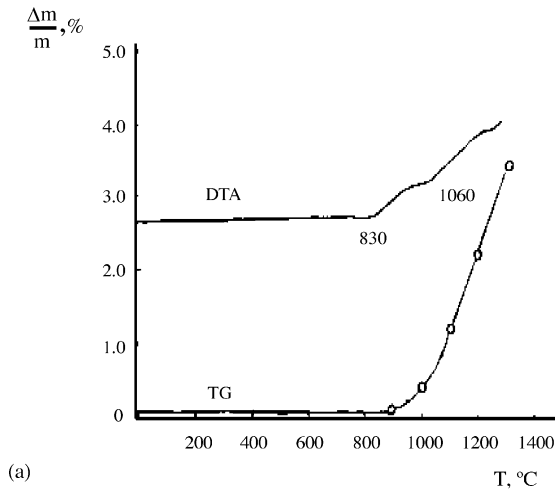
Fig. 1. DTA and TG curves for high-temperature oxidation of 70% AlN–28% SiC–2% TiB₂ samples: (a) powders; (b) hot-pressed ceramics.

Al₂TiO₅ titanate phase which was formed by solid-phase reaction of Al₂O₃ and TiO₂. The outer scale layer is only 3Al₂O₃·2SiO₂ mullite; it has a strong adhesion to the inner film.

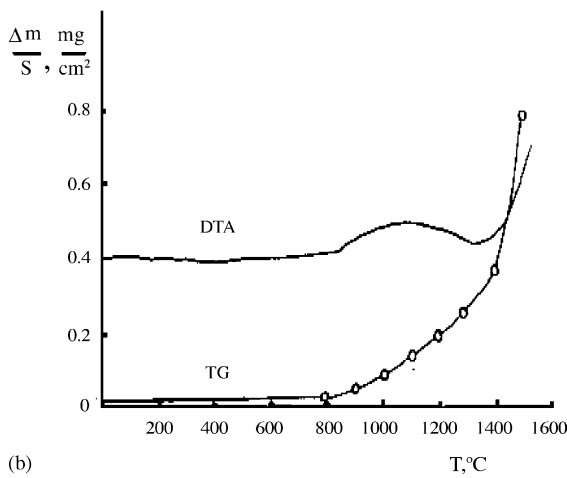
The oxidation of 70% AlN–25% SiC–5% TiB₂ powders starts at 830 °C, and up to 1350 °C only two peaks are noticed on DTA curve (1000–1050 and 1200 °C) while the oxidation

Table 1
Phase composition of oxide film on different AlN–SiC–TiB₂ ceramics (XRD data)

Type of ceramics (mass%)	Temperature range (°C)	Composition of oxide film (main phases)
70% AlN–28% SiC–2% TiB ₂	1200–1250	TiO ₂ (rutile), Al ₁₀ N ₈ O ₂ , β-SiO ₂ cristobalite, Fe ₂ O ₃ (traces)
	1350	α-Al ₂ O ₃ , β-SiO ₂ cristobalite, Fe ₂ TiO ₅ (traces), β-Al ₂ TiO ₅ (small amount)
	1450	β-Al ₂ TiO ₅ alloyed with Fe ₂ TiO ₅ , α-Al ₂ O ₃ , 3Al ₂ O ₃ ·2SiO ₂ (mullite)
70% AlN–25% SiC–5% TiB ₂	1200–1250	TiO ₂ (rutile), Al ₁₀ N ₈ O ₂ , β-SiO ₂ cristobalite
	1350	α-Al ₂ O ₃ , β-Al ₂ TiO ₅ , β-SiO ₂ cristobalite, Fe ₂ TiO ₅ (traces)
	1450	α-Al ₂ O ₃ , β-Al ₂ TiO ₅ alloyed with Fe ₂ TiO ₅ , 3Al ₂ O ₃ ·2SiO ₂
70% AlN–20% SiC–10% TiB ₂	1200–1250	TiO ₂ (rutile), Al ₁₀ N ₈ O ₂ , β-SiO ₂ cristobalite, Fe ₂ O ₃ (traces)
	1350	α-Al ₂ O ₃ , β-Al ₂ TiO ₅ , β-SiO ₂ cristobalite, Fe ₂ TiO ₅ (traces), 3Al ₂ O ₃ ·4B ₂ O ₃ (small amounts)
	1450	α-Al ₂ O ₃ , β-SiO ₂ cristobalite, β-Al ₂ TiO ₅ alloyed with Fe ₂ TiO ₅ , 3Al ₂ O ₃ ·2SiO ₂



(a)



(b)

Fig. 2. DTA and TG curves for oxidation of 70% AlN–25% SiC–5% TiB₂ samples: (a) powders; (b) hot-pressed ceramics.

of the dense composite material is characterized by only peak at 1100 °C (Fig. 2). The composite ceramics has a similar oxidation resistance in air (Fig. 4). For this grade, the oxide film formed in air at 1450 °C consists of two main phases: elongated β -Al₂TiO₅ grains tight together with the mullite grains. Herein the mullite has in its lattice up to 1% TiO₂ and 2–3% Fe₂O₃ as dissolved additives; it conforms to the appropriate phase diagrams. The oxide film on these ceramics is very dense, without porosity and prevents oxygen access to the core.

The isothermal oxidation of ceramics with 2% TiB₂ follows a parabolic rate law only in the temperature range of 1200–1250 °C whereas at higher temperatures the paralin-ear dependence of mass gain on time duration takes place (Fig. 3). For the ceramics with 5% TiB₂ the paralin-ear law of oxidation (Fig. 4) is observed in all temperature range (1200–1450 °C). Both these kinds of samples show a high oxidation resistance.

The 70% AlN–20% SiC–10% TiB₂ powder begins to oxidize at a significantly lower temperature, 600 °C (Fig. 6). A greater amount of TiB₂ in the ceramics leads to a lower

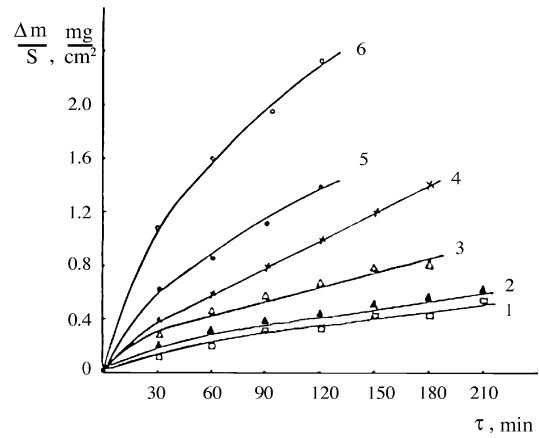


Fig. 3. Oxidation isotherms for 70% AlN–28% SiC–2% TiB₂ ceramics: (1) 1200 °C; (2) 1250 °C; (3) 1300 °C; (4) 1350 °C; (5) 1400 °C; (6) 1450 °C.

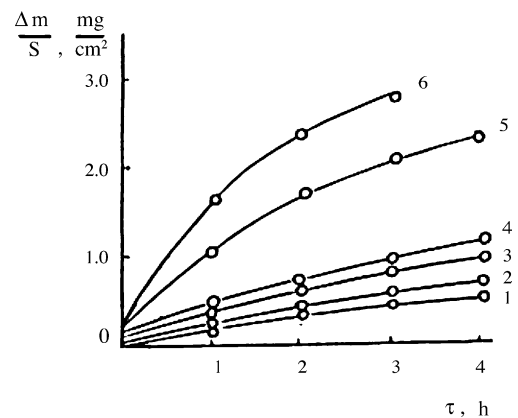


Fig. 4. Oxidation isotherms for 70% AlN–25% SiC–5% TiB₂ ceramics: (1) 1200 °C; (2) 1250 °C; (3) 1300 °C; (4) 1350 °C; (5) 1400 °C; (6) 1450 °C.

of oxidation resistance (Fig. 5). The mass gain in this case was somewhat higher at the same temperatures although here comparatively small $\Delta m/S$ values are, obviously, compensated by essential contribution of B₂O₃ evaporation. It must

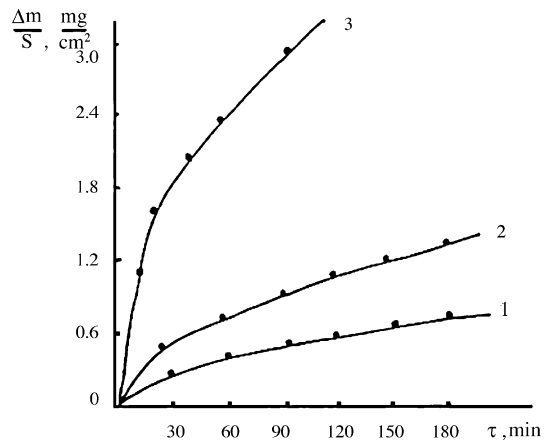


Fig. 5. Oxidation isotherms for 70% AlN–20% SiC–10% TiB₂ ceramics: (1) 1200 °C; (2) 1250 °C; (3) 1300 °C.

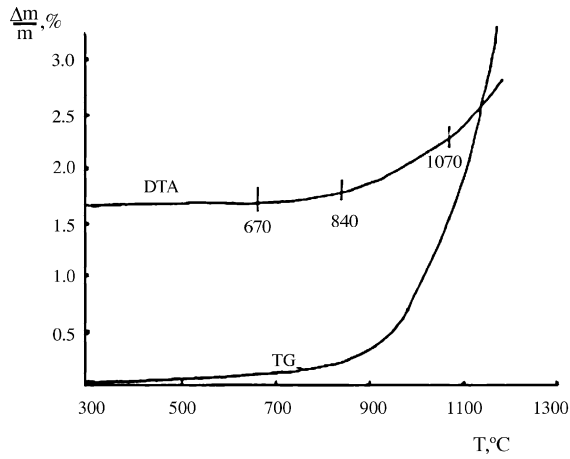


Fig. 6. DTA and TG curves for high-temperature oxidation of 70% AlN–20% SiC–10% TiB₂ powders.

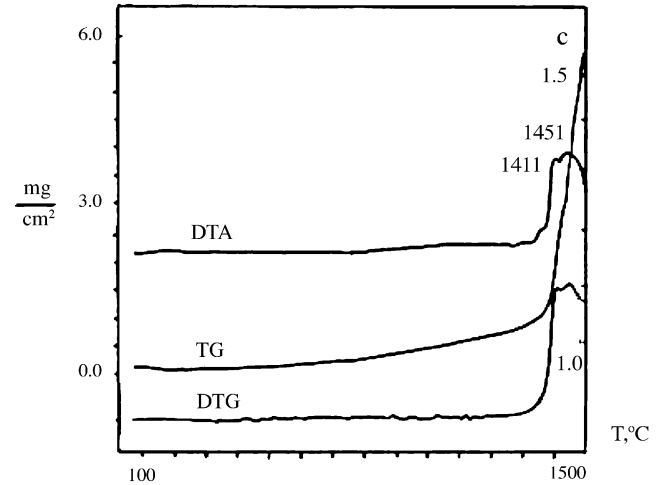
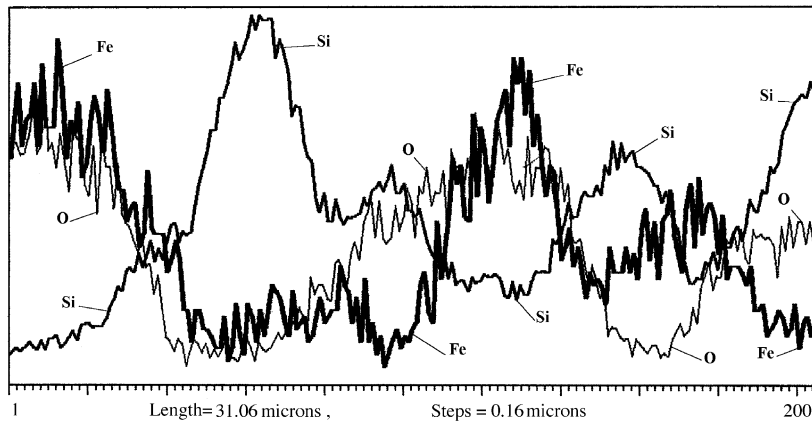


Fig. 7. DTA, TG and DTG curves for oxidation of 70% AlN–20% SiC–10% TiB₂ compact samples.

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10-JUL-98, File: S1 PAN1 . LIN, Beam= 59.73nA, KeV =15.
 Sp .=1, Element : O , Scala= 150
 Sp .=2, Element : Al , Scala= 700
 Sp .=3, Element : TI , Scala= 550

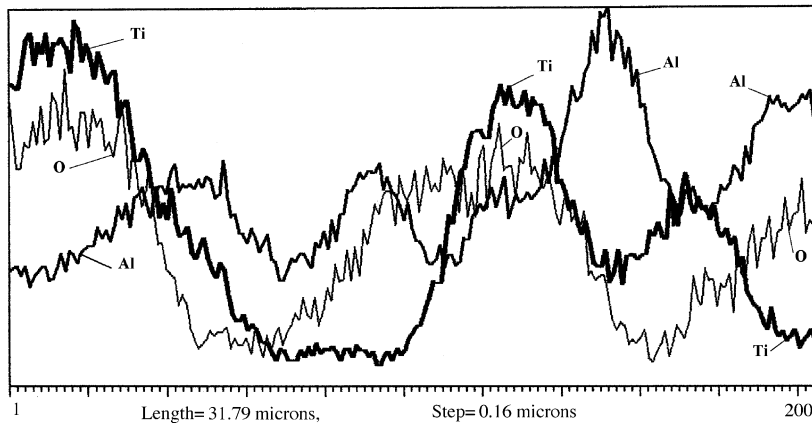


Fig. 8. EPMA spectra of elements distribution on the surface of scale formed on 70% AlN–25% SiC–5% TiB₂ ceramics at 1450 °C.

be noted that under non-isothermal oxidation of monolithic samples (Fig. 7) at 1500 °C, $\Delta m/S = 5.5 \text{ mg/cm}^2$ that is almost by seven times higher than that for ceramics containing 5% TiB_2 (Fig. 2).

For the ceramics with 10% TiB_2 , the composition of scale formed at 1350 and 1450 °C is essentially differed

from the previous cases. In particular, at 1450 °C the outer scale layer consists of mullite with elongated inclusions of $\beta\text{-Al}_2\text{TiO}_5$, and the inner scale layer consists of AlN , $\alpha\text{-Al}_2\text{O}_3$, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (traces), Fe_2TiO_5 and $\beta\text{-SiO}_2$ cristobalite (Table 1). The aluminium borate $2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ was partially decomposed with formation of boron oxide. As a

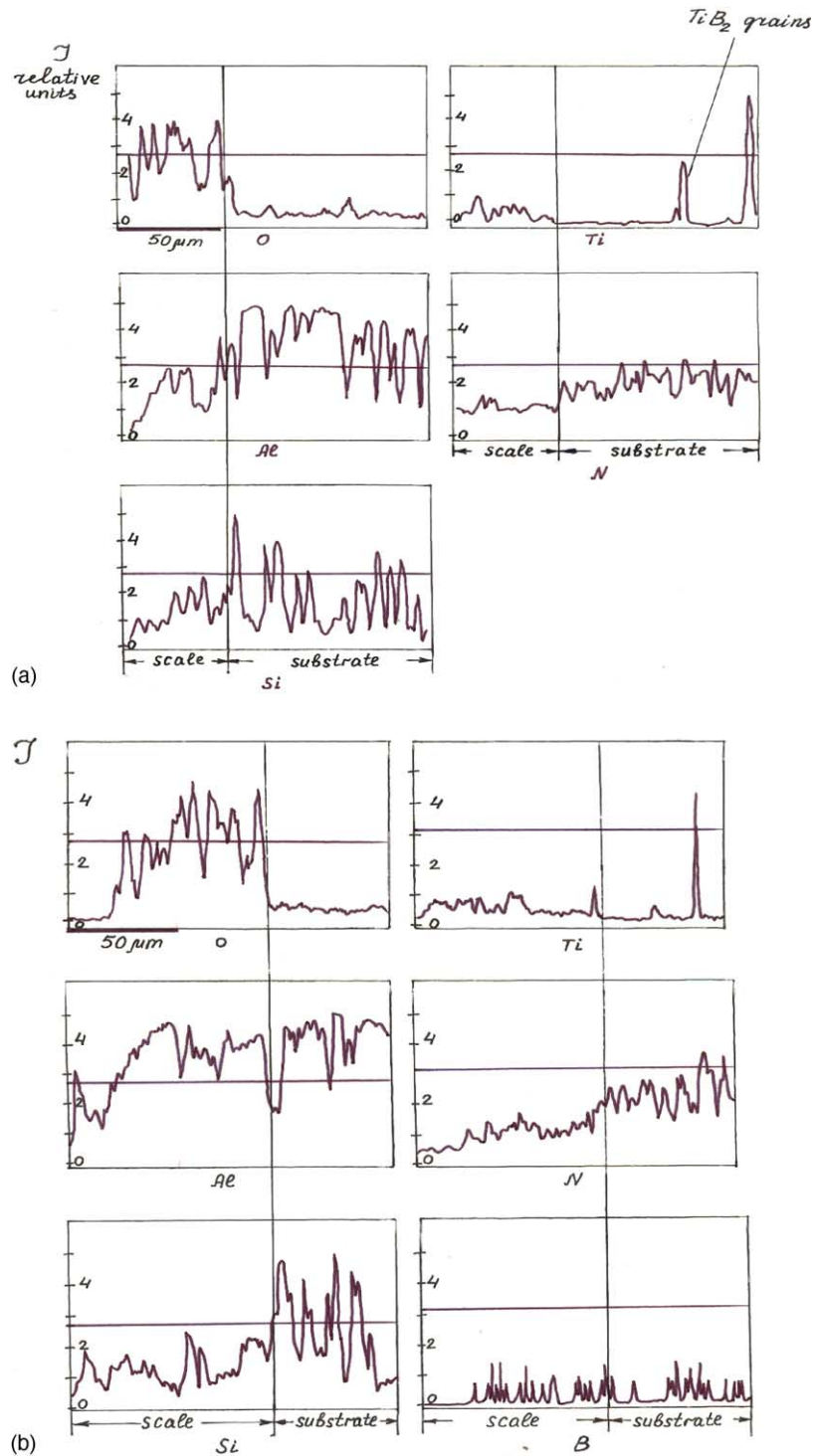


Fig. 9. Distribution of elements through a cross section of scale formed on 70% AlN–28% SiC–2% TiB_2 ceramics at: (a) 1250 °C; (b) 1450 °C (duration of oxidation: 2 h).

result of B_2O_3 evaporation, the formation of pores and loosening of a scale took place.

In Fig. 8 one can see the distribution of different elements on the surface of 70% AlN–25 SiC–5% TiB_2 ceramics sample which was oxidized in the air at 1450 °C during 2 h. Herein the images of Al, Ti and oxygen spectra are presented on the upper picture while the Si, Fe and also O ones—on the lower picture. These data confirm the XRD data concerning the presence on this surface of Al_2TiO_5 , $3Al_2O_3 \cdot 2SiO_2$ as well as the small amounts of Fe_2TiO_5 and SiO_2 phases. In Fig. 9 as an example the distribution of different elements (Al, Si, Ti, B, O, and N) through the cross section of scale formed under oxidation at 1250 and 1450 °C of 70% AlN–28% SiC–2% TiB_2 ceramic sample is given (Fig. 9a and b, EPMA images, respectively). Here one can see in the scale a sharp enough increase of oxygen and decrease of nitrogen content compared with the substrate but two scale layers (see Fig. 9a and b) are characterized by different elements profiles.

The values of parabolic rate constants for oxidation of all the kinds of AlN–SiC– TiB_2 ceramics were calculated on the base of experimental mass gain data. For ceramics with 5% TiB_2 content, proceeding from the dependence of parabolic rate constants on the reciprocal temperature, according to the Arrhenius plot (Fig. 10), the values of the apparent activation energy (E) were calculated for different temperature ranges. In this case, for the 1100–1300 °C range, this value is equal to 285 kJ/mol (E_1), whereas for 1350–1550 °C one $E_2 = 500$ kJ/mol. Taking into account the data obtained, we can conclude that there is a change of oxidation mechanism between 1300 and 1350 °C.

If for the first stage (<1350 °C), the oxidation is limited by individual components interaction with oxygen and corresponding diffusion processes in the film formed, for the second one ($T > 1350$ °C), the solid-phase reactions of mul-

lite and Al_2TiO_5 formation begin to play the main role. These lead to an essential change of elements diffusion rate in the scale. Besides, due to a high adhesion of the oxide scale to the substrate and the sintering of the scale that takes place at the higher temperature, the oxidation rate significantly slows down.

For the 70% AlN–28% SiC–2% TiB_2 ceramics and the same temperature ranges, $E_1 = 180$ kJ/mol and $E_2 = 335$ kJ/mol whereas for the oxidation of 70% AlN–20% SiC–10% TiB_2 ceramics in the temperature range of 1200–1300 °C, $E_1 = 660$ kJ/mol. However, in this case, the parabolic rate law is observed only up to 1300 °C (see Fig. 5).

4. Conclusion

1. An influence of both composition and phase characteristics on kinetics evolution and mechanism of oxide scale formation as well as on the composition of reaction products was noticed. At short time exposure in air and comparatively low temperatures (1200–1300 °C), TiO_2 (rutile), $\alpha-Al_2O_3$ and β -cristobalite were detected whereas at longer oxidation time and higher temperatures (1350–1550 °C), mullite ($3Al_2O_3 \cdot 2SiO_2$) and $\beta-Al_2TiO_5$ are the main oxides. The high adhesion of mullite phase (growing together with the aluminium titanate) ensures the high protective properties of the scale.
2. The AlN–SiC– TiB_2 ceramics containing 2–5% TiB_2 has the best oxidation resistance. At higher content of titanium diboride (10% and more), the initial formation of B_2O_3 and its further evaporation can lead to the partial loss of protection of a scale due to pore formation.
3. Finally, the AlN–SiC– TiB_2 ceramics developed here may be recommended as corrosion-resistant composite materials for their application in air up to 1400 °C.

Acknowledgement

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References

1. Gogotsi, Y. G., Desmaison, J., Andrievski, R. A. et al., AlN-based ceramics—an alternative to Si_3N_4 and SiC in high-temperature application? *Key Eng. Mater.*, 1997, **132–136**, 1600–1603.
2. Tampieri, A. and Bellosi, A., Oxidation resistance of Al–Ti–N and Al–Ti–C composites. *J. Am. Ceram. Soc.*, 1992, **75**(6), 1688–1690.
3. Costa Oliveira, F. A., Baxter, D. J. and Ungeheuer, J., The oxidation kinetics of an yttria-doped hot pressed silicon nitride. *Key Eng. Mater.*, 1997, **132–137**, 1580–1583.
4. Jacobson, M. S., Corrosion of silicon-based ceramics in combustion environments. *J. Am. Ceram. Soc.*, 1993, **76**(1), 3–28.
5. Janney, M. A., Mechanical properties and oxidation behaviour of a hot pressed SiC–15 vol.% TiB_2 composite. *Am. Ceram. Soc. Bull.*, 1987, **66**, 322–324.

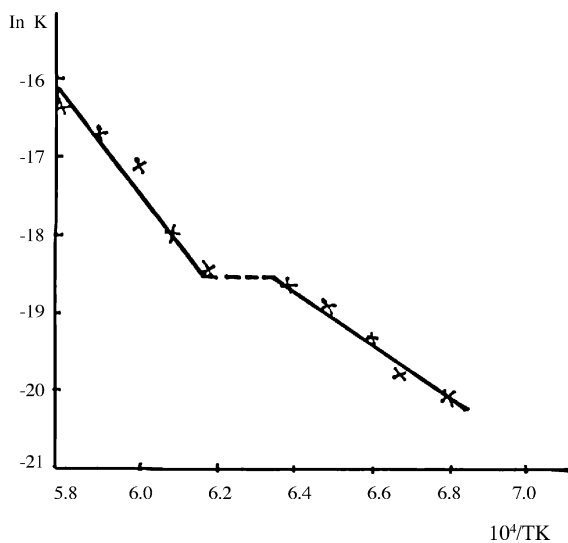


Fig. 10. Dependence of the parabolic rate constants on reciprocal temperature for oxidation of 70% AlN–25% SiC–5% TiB_2 ceramics.

6. Schneider, S. V., Desmaison-Brut, M., Gogotsi, Y. G. and Desmaison, J., Oxidation behaviour of a hot isostatically pressed TiB_2 -AlN composite. *Key Eng. Mater.*, 1996, **113**, 49–58.
7. Lavrenko, V. A., Desmaison-Brut, M., Panasyuk, A. D. and Desmaison, J., Features of corrosion resistance of AlN-SiC ceramics in air up to 1600°C. *J. Eur. Ceram. Soc.*, 1998, **18**, 2339–2344.
8. Xu, Y., Zangvil, A. and Ruh, R., Formation of SiAlON as intermediate oxidation product of SiC-AlN ceramics. *J. Am. Ceram. Soc.*, 1995, **78**, 2753–2762.