Oxidation of boron-titanium thin film coating during cyclic tests on thermal shock

E E Suslov¹, A S Larionov¹, S B Kisliutsin¹,², I I Chernov³, M S Staltsov³, A S Dikov¹ and V V Firsova¹

¹ Institute of Nuclear Physics of the Republic of Kazakhstan, Ibraimov st. 1, 050032 Almaty, The Republic of Kazakhstan
² National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe highway 31, 115409 Moscow, Russia

E-mail: larionov-inp@yandex.kz, i_chernov@mail.ru

Abstract. The results of experiments on cyclic thermal shock tests of promising neutron-absorbing titanium boride coatings are presented. It has been established that the main effect is the high-temperature oxidation of titanium boride with the formation of titanium and boron oxides. The regularities of changes in the oxidation parameters during cyclic thermal shock tests are determined.

1. Introduction

Coatings from titanium boride Ti₂B₅ are intended for use as neutron-absorbing coatings on container structural materials for moving and densified safekeeping of spent nuclear fuel [1–3]. These coatings can significantly increase the efficiency of attenuation of the neutron flux with a decrease in thickness in comparison with existing analogues [4–6]. Coatings in this case should have a sufficient margin of safety, corrosion and thermal resistance.

The most studied and close to Ti₂B₅ modification of titanium boride is titanium diboride TiB₂ [7]. It is known that titanium diboride has high hardness and chemical resistance, as well as a high melting point of 3225 ± 25 °C. Compounds of titanium boride with a high content of boron such as Ti₃B₅ are less detail studied. This is also confirmed by the state diagram of the B–Ti system [8]. Titanium diboride coatings are used in microelectronics and in the manufacture of cutting tools. As a coating material for neutron absorption deposited by the magnetron method, such coatings have not previously been considered. In this regard, the properties of such films were first studied in this work.

It is known that Ti₃B₅, like TiB₂, has high corrosion resistance since an oxide film (borate) is formed on the surface of these compounds [9, 10]. Titanium diboride is prone to high temperature oxidation with the formation of oxide phases of borate B₂O₃ and rutile TiO₂, as well as titanium borate TiBO₃ [11–13].

This paper presents an analysis of the evolution of the structure and phase composition of boride-titanium coatings with a high content of boron.

2. Materials and methods

Austenitic stainless steel 12Cr18Ni9Ti was used as a coating substrate. The samples were cut by spark cutting, the surface was subjected to mechanical grinding and polishing. The size of the samples for
thermal shock tests is 20×5×1 mm³, and the surface roughness is not less than Rₐ = 80 nm. Magnetron sputtering of coatings was carried out according to the proven technique from a composite boron – titanium target, which is made by hot pressing of titanium and boron carbide powders in a weight ratio of 1:1 on a VUP-5M magnetron device [6]. The power supplied to the magnetron was about 42 W and the sputtering time was 1 hour. According to X-ray diffractometry, the coating represents the boron – titanium compound in the form of the ω-phase of titanium hemipentaboride Ti₂B₅ with a small amount of impurity β-phase of titanium dodecaboride TiB₁₂. Integral porosity averaged ~ 1%. It contains impurities of carbon and oxygen (~ 26%). Oxygen is located in defects (pores) mainly, as well as in the form of a thin (not more than 10 nm) oxide film (borate). The phase composition of the oxide film by the applied methods could not be determined due to its small thickness; the intensity of X-ray reflexes is too low for analysis. The coating thickness on the samples for study was ~ 200 nm.

Annealing was carried out in the temperature range of 300–900 °C in the SNOL 7.2 / 1100 muffle furnace in an air medium. The coated sample was placed in a furnace heated to a certain temperature for thermal shock tests. The heating rate of the sample under such conditions was 20–60 s. Cooling occurred with the furnace, the cooling time from 900 to 20 °C was ~ 6 h. The temperature of the sample was controlled using a chromel-alumel thermocouple.

The change in elemental composition after testing was monitored by energy dispersive analysis (EDA) using an EDA attachment on a HITACHI TM3030 scanning electron microscope (SEM). X-ray phase analysis (XRD) was carried out on a D8 ADVANCE ECO diffractometer (Bruker, Germany) using CuKα copper tube radiation. To identify the phases and study the crystal structure, BrukerAXSDIFFRAC.EVAv.4.2 software and the ICDD PDF-2 international database were used. The conditions for obtaining of X-ray diffraction patterns were as follows: Voltage is 40 kV, Current is 25 mA, 2θ = 20–90°, step is 0.03°, standing time at the point is 1 s, a nickel soller was used as an absorber. The depth of X-rays penetration into the material is 8–10 μm under these shooting conditions. The surface morphology of coating was studied by SEM JEOL JSM7500F.

3. Results and discussion

The coating consists of particles with diameters of 100–200 nm and it can be seen that it repeats the relief of the substrate (Figure 1a).

![Figure 1](image-url)
scale on the surface. The dependences of these effects on temperature and the duration of its exposure were determined.

In order to reveal the temperature dependence of the manifestation of effects, annealing was carried out to temperatures of 300, 500, 700 and 900 °C. The maximum temperature was chosen taking into account the fact that the recrystallization of 12Cr18Ni9Ti austenitic steel, which is the substrate material, occurs at a temperature above 900 °C [14]. Since recrystallization is one of the determining factors in the operation of structural materials, a further increase in temperature is not a priority from the point of view of practical use. Scale formation was observed after heating at 900 °C only. An increase in the number of cycles led to the formation of cracks and exfoliation of the oxide layer (flaking). An increase in the oxygen content was observed after heating at 900 °C only. An increase in the number of cycles led to the formation of cracks and exfoliation of the oxide layer (flaking). An increase in the oxygen content was observed until the 3rd test cycle, then the oxygen content decreased, which was caused by the destruction of the oxide layer (Table 1). In the case when no scale was formed, violations of the structure of the titanium boride coating were not observed.

Table 1. Oxygen content in the titanium boride coating after cyclic tests for thermal shock at 900 °C.

| The number of cycles | Before the test | 1  | 2  | 3  |
|----------------------|----------------|----|----|----|
| The oxygen content, at. % | 26.8 | 47.3 | 61.5 | 47.9 |

Cyclical tests for thermal shock at temperatures of 300, 500 and 700 °C did not lead to a change in the phase composition of titanium boride coatings. The phase composition changes after the first test cycle at 900 °C. The position of the reflections in the diffraction patterns indicates the presence of phases corresponding to the TiO$_2$ and B$_2$O$_3$ oxides in the (101) and (022) planes, respectively. As the cycles increase, redistribution of the intensities of diffraction reflections of the main identifiable phases occurs (Figure 2).

![Figure 2](image)

**Figure 2.** Oxide phases reflections intensity change in dependence on (a) temperature and (b) number of cycles: 1 – rutile; 2 – borate.

All diffraction patterns contain reflections corresponding to the austenitic phase, which gives the material of the steel substrate. Titanium oxide is represented in the hexagonal modification of rutile. Iron oxide (hematite) appears during the oxidation of iron in a stainless steel substrate. Boron oxide (borate) has an amorphous structure.

Borate has a melting point of 320–450 °C. The increase in test cycles leads to its burnout. A change in the intensity of the B$_2$O$_3$ phase reflexes shows that the borate formed during the first cycle disappears practically after three cycles. After 5 cycles, the boron oxide reflex appears again, but its
intensity decreases after 10 cycles. The intensity of the titanium oxide reflex varies in the same proportion (see Figure 2b).

After 1 cycle, the scale is not evenly distributed on the surface of the titanium boride coating. After 3 cycles, the scale covers the entire surface, areas appear on which exfoliation occurs. After 5 and 10 cycles, a new oxide layer appears in areas with exfoliated scale; as a result, the surface becomes uneven. In Fig. 3 shows the structure of the oxide layer after 1 test cycle at different magnifications. It can be seen that already after the first cycle a local exfoliation of the formed oxide layer occurs. The oxide layer has a grain structure with grain sizes from 20 to 500 nm.

![Image](image1)

**Figure 3.** Obtained at different magnifications SEM images on a titanium boride coating oxide film after 1 cycle of thermal shock tests at temperature of 900 °C.

After 3 test cycles, the structure of the oxide film has not fundamental differences. Part of the film is exfoliated and areas without an oxide layer are visible in Figure 4. The grain structure of the oxide film does not change. Figure 5b shows a surface area with visible grains of titanium boride after 5 test cycles. It can be seen that the effect of temperature led to a change in the shape of the grains and a decrease in their average size by ~ 1.5 times. These changes have led to compaction of the grain structure of titanium boride.
From the above results we can understand the following. The mechanism of oxide phase formation occurs through the transport of oxygen atoms deep into the material. The accumulation of oxygen at the boundary of the oxide film and titanium boride during heating causes severe embrittlement of the boundary. This mechanism causes flaking and the gradual destruction of the coating. Oxidation in the presence of a large amount of oxygen can occur by reaction

\[ 2\text{Ti}_2\text{B}_5 + 23\text{O} \rightarrow 5\text{B}_2\text{O}_3 + 4\text{TiO}_2. \]

4. Conclusion
Based on the results, we can draw the following conclusions.

Titanium boride coating is prone to high-temperature oxidation in air at temperature of 900 °C as showed investigations of its thermal stability by cyclic thermal shock tests.

Formation of the oxide phase and destruction of titanium boride coating were not detected at temperatures below 700 °C.
Since the storage of spent nuclear fuel involves a temperature of about 350 °C, the characteristics of the developed coating make it possible to use it under these conditions.

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