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Oxidation behavior of TiC-TiB₂ multiphase ceramics

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Abstract: The isothermal oxidation behavior and mechanism of the TiC-TiB₂ multiphase ceramics fabricated by self-propagating high temperature synthesis were studied. The result shows that the oxidation kinetics agrees to the parabolic rule within the temperature rang of RT to 1000°C. First at 600°C TiB₂ was oxidized to be TiO₂. Then both TiB₂ and TiC were oxidized to be TiO₂ when temperature increased to 1000°C. A compact TiO₂ film, the oxidation product, formed on the sample surface, which prevented further oxidation and resulted in a very high oxidation resistance of the sample.

Key words: TiC-TiB₂ multiphase ceramics; oxidation resistance; oxidation mechanism

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1 Introduction

TiC-TiB₂ multiphase ceramics are potential candidates for heat-resisting parts, cutting tools, moulds and armor materials because of their hardness, high melting-point, low density. But the high cost of the raw materials powder B or TiB₂ and the conventional sintered-technology are not only time and energy wasting but also hard to be densified. So these materials were hard to extensive use because of their high cost. At present, TiC or TiB₂ composites can be fabricated by SHS technology, which is energy saving, simple equipment and processing, simple product, low cost. The writer of this paper had ever successfully fabricated TiC-TiB₂ multiphase ceramics by the way of adopting self-propagating high temperature synthesis and pseudo hot isostatic pressing (SHS/PHIP) technology and low cost B₄C powder instead of B powder.

2 Experimental

2.1 Preperation of TiC-TiB₂ multiphase ceramics

The fabrication of TiC-TiB₂ multiphase ceramics uses these materials; Ti powder (average particle size is less than 44μm, purity is 99%), amorphous carbon (average particle size is 1 μm, purity is 99.5%) and B₄C powder(average particle size is less than 10 μm, purity is 93%). Put these materials in the vacuum drying oven under 90°C for 24 h, the power mixture ratios is separately 2 : 1, 1 : 1, 1 : 2, according to the system of Ti-C-B chemical reaction, and put the mixture in the mixer-machine to ball mill for 24 h, the blends were pressed into pellets with about 55% relative density, with the Φ55 mm×70 mm dimension cy-

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lindrical pellets, and put the pellets into the reactor. After the combustion synthetic reaction, quickly exerted the axial pressure of 180 MPa, and kept the pressure for a certain time, then fetched the pellets, buried them into sands to cool down and prevent from oxidation. All the numbers of the samples, composition, technological conditions and properties were shown in Table 1. In addition, to adjust the sample 3[#] match and their technological parameter, we can get the test samples with various porosity.

2.2 Oxidation experiment

The oxidation resistance test-pieces, with dimension of 2.5 mm×5 mm×12 mm, were cut by the linear cutting and the surface were polished, cleaned and dried. The high temperature oxidation experiments were carried out in cabinet-type electric furnace. When the furnace reached the orient-temperature, put the samples and proceeded static oxidation experiments in the air environment. After keeping the temperature in different temperatures, fetched the samples from the furnace and cooled them in the air. Used the 10⁻⁴ balance to measure the different changes of the mass. The material oxidation characters were evaluated by unit time, unit surface, and mass changes. The phase and structure of the material composition are analyzed by XRD and SEM to study the oxidation mechanism.

Table 1 Composition of sample and experimental conditions

Sample number	Composition (mole ratio)	Technological condition			Flexural strength /MPa	Fracture toughness /MPam ^{1/2}	Relative density /%
	n(TiC); n(TiB ₂)	Delay time /s	Holding time /s	Pressure /MPa			
1	2 : 1	10	5	180	410	4.0	93.8
2	1 : 1	8	5	180	0	5.2	91.5
3	1 : 2	10	5	180	450	5.8	96.8

3 Results and discussions

3.1 The oxidation behavior of TiC-TiB₂ multiphase ceramics

Fig. 1 is the curve describing the material of different composition after oxidation at 600°C. It can be seen that all the samples showed oxidation liveweight growth with TiB₂ content increasing and the variable tendency of the three curves are the same, and the curves are almost parabolic shape. The oxidation liveweight growth of sample 1[#] is apparently low, which is related to the high content of TiC. The hot-pressed TiB₂ ceramics pellets are oxidized from about 500°C, and the oxidation temperature of the TiB₂ is lower than TiC. So the TiB₂ was prior to be oxidized in the TiC-TiB₂ multiphase ceramics. In sample 1[#], the low content of TiB₂ and the high content of TiC lead to the lower oxidation liveweight growth, which can be seen from the curve tendency. TiC is not oxidized at this temperature (it was taken from the curve of XRD). In addition, because of the self-healing oxidation resistance, as the oxidation persisting, the oxidation resistance rate decreased obviously, and gradually accessed into passive oxidation stage. Fig. 2(a) is the mass changes of the sample 3[#] oxidized in different temperature. It

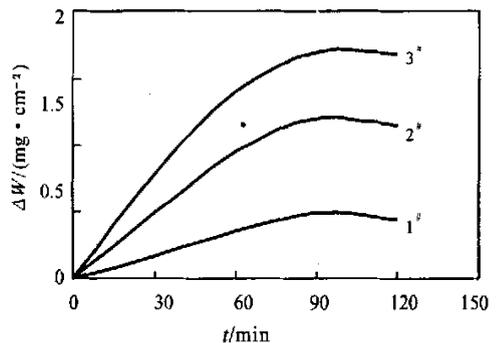


Fig. 1 Weight changes of the composites with different compositions after oxidation at 600°C

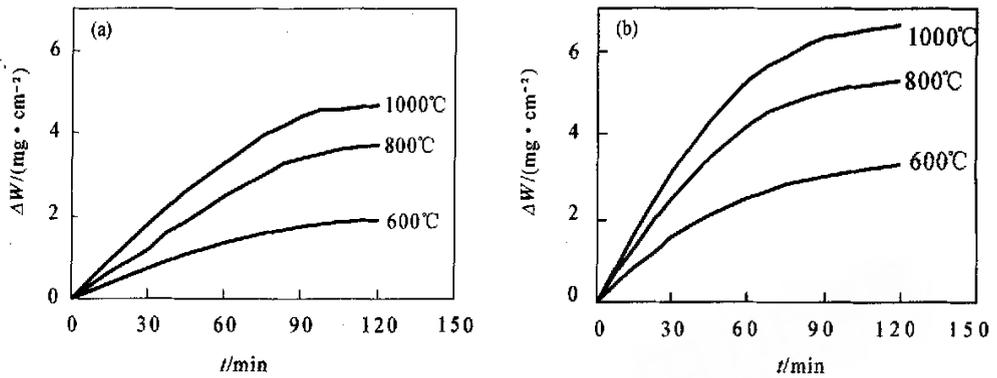


Fig. 2 Results of 3[#] specimen oxidized at different temperature
(a) — Porosity 6%; (b) — Porosity 18%

seems that sample 3[#] all showed oxidation liveweight growth. But in different temperature, the oxidation liveweight growths are various. In the low temperature, only part of the TiB₂ is oxidized, and the oxidation liveweight growth is lower. Within 800–1000 °C, because the TiB₂ is completely oxidized, and TiC also starts oxidation, so sample 3[#] shows greater tendency of oxidation liveweight growth. At the same time with the extension of the time, it also comes to the passive oxidation stage. Fig. 2(b) shows the oxidation liveweight of the sample 3[#] whose porosity is 18%. Compared to Fig. 2(a), under the same condition, oxidation liveweight growth of sample 3[#] increases extremely. It indicates that the material density has great influence on their oxidation resistance, the pores in undensified material lead to the permeation of oxygen and accelerated the speed of oxidation. The remainder porosity lows the activation energy in oxidation course, so that lows the material oxidation resistance and makes the porosity wider. In addition, from the oxidation sample appearance, we could made the same conclusion; the non-oxidation sample appeared grey dark, with the temperature increasing, the oxidation sample appeared grey dark → light yellow → yellow → dark yellow.

3.2 Oxidation mechanism of TiC-TiB₂ multiphase ceramics

Because the oxidation resistance of the material was closely related to the composition and dense of the material, and generated characteristic of the oxidize, analyzing the changes of the materials phase has important meaning to study oxidation mechanism. During the oxidation course, the TiC and TiB₂ phase mainly occurred such chemical reactions in the TiC-TiB₂ multiphase ceramics.



It can be seen that only TiO₂, B₂O₃ and carbon oxidation gases existed in the reaction product, but in the air, the degree of the every reaction and the order of the reaction is various. According to the thermodynamic data, we had counted the generated enthalpy and free energy of (1)–(5) chemical reaction (as shown in Fig. 3 and Fig. 4). From the figures, during the temperature range which was counted, the generated enthalpy and the free energy both were negative value. It indicated that all the reactions could realize in the thermodynamic. However, whatever generated enthalpy and free energy compared with other reac-

tions, the negative value of the reaction (1) is minimum. It indicated that the reaction (1) was the easiest to occur. It is easily accepted that around a certain temperature in the air reaction (1) was previous to occur. This agreed to the reference [7]. Fig. 5 showed that sample 3[#] XRD result in various temperatures after 30 min. At 400 °C, the oxidation result was uniform to the normal temperature (1). There was no obviously changes, only the two phases of TiC and TiB₂. At 600 °C, TiO₂ occurred. With the temperature increasing, the phases of TiC and TiB₂ gradually decreased. At 1000 °C, completely converted to phase TiO₂, in this time the oxidation completely finished. Compared with the samples diffraction peak intensity varied after oxidation, it can be seen that, with temperature increasing, peak intensity of TiB₂ decreased fastest and amplitude variation increased largest. However, TiC is relatively slow. It showed that TiB₂ was previous to be oxidized. When at the 800 °C, part of TiC began to oxidize, these results conformed to Fig. 4.

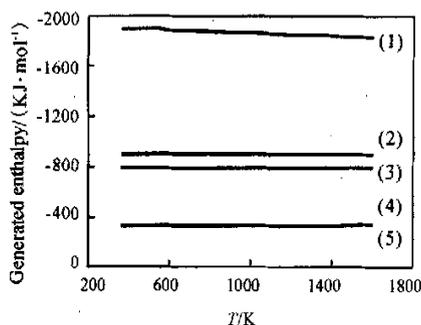


Fig. 3 The curves of enthalpy temperature for different oxidation reactions

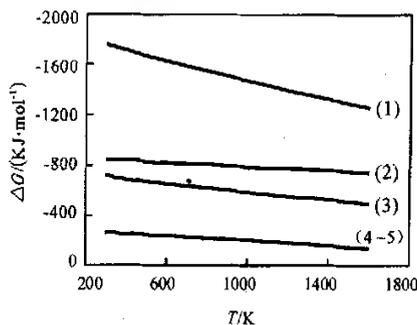


Fig. 4 The variety curve of free energy temperature for different oxidation reaction

By analyzing the thermodynamic data and XRD result, the high temperature oxidation procedure of TiC-TiB₂ multiphase ceramics are: TiB₂ firstly react with oxygen and the products are TiO₂ and B₂O₃. These products are able to form protective layer to prevent the inner material to form further oxidation. Secondly TiC reacts with oxygen and the products are TiO₂, CO, CO₂. But B₂O₃ has low melting-point (550 °C). With the temperature increasing, the B₂O₃ volatilize or react with TiO₂ to form the new phase, TiBO₃. So that B₂O₃ lose the protection effect. Above all, it is found that the oxidation resistance would be relatively weakened with the content of TiB₂ increasing. In addition, in the XRD results of all the oxidized samples, there is no B₂O₃ crystal phase but only TiO₂ crystal phase. The reason is that low melting-point of B₂O₃ leads to the volatilization in the high temperature, or it exists in amorphous state. Fig. 6 shows the pictures of sample 3[#] surface. At 400 °C, after being oxidized 300 min, it could be seen that there were no oxidation in the material surface. In the picture, the cauliflower-like flaws were created in the grilling course. At 600 °C, oxidation layer started in the sample surface, but not dense and homogenous, and some place did not occur to oxidize. The reason was that only TiB₂ was oxidized at 600 °C (as shown in Fig. 5). Because of the high content of TiB₂, there were many indications that TiB₂ had been oxidized into TiO₂. With the temperature coming to 800 °C, TiB₂ had been completely oxidized and TiC started to be oxidized. In this time, more oxidation layer surface or boundary, and volatilized at the high temperature, made the surface some bubbles. At 1000 °C, the sample surface was completely oxidized and homogeneous (as showed in Fig. 6).

After comparing, we found that the layer oxidant TiO₂ showed the tendency of gradually increasing with the temperature increasing. At 1000 °C, the size of the TiO₂ crystal grains obviously grew bigger, and many crystal

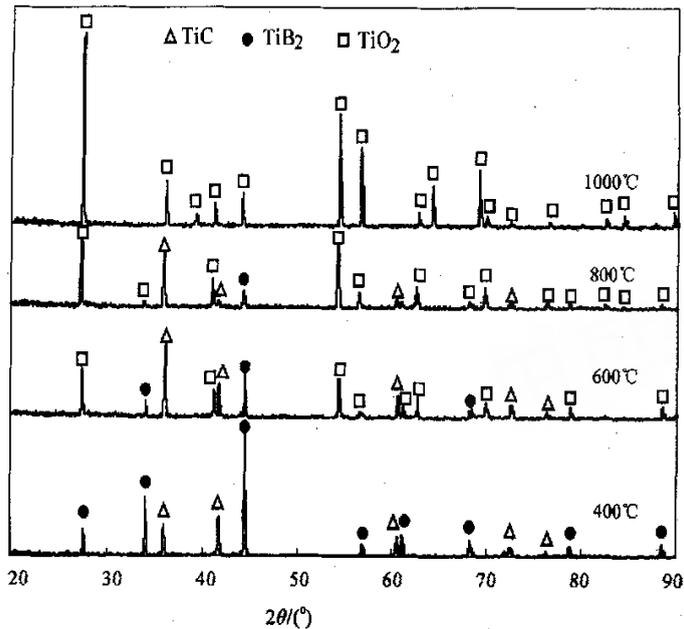


Fig. 5 XRD patterns of the sample 3# oxidized at different temperatures

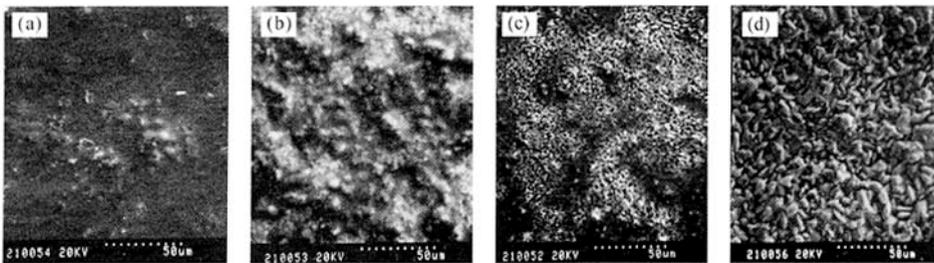


Fig. 6 SEM micrographs of the sample 3# oxidized at different temperatures
(a)–400°C; (b)–600°C; (c)–800°C; (d)–1000°C

grains wrapped the material surface, which made the material show perfect oxidation resistance.

4 Conclusion

(1) The oxidation kinetics of TiC-TiB₂ multiphase ceramics materials agrees to the parabolic rule within temperature range of 600°C to 1000°C. With the content of TiB₂ increasing, the materials oxidation kinetics shows the increasing tendency. The rate of oxidation obviously decreases with the extension of the oxidation time, so it gradually comes into the oxidation resistance stage.

(2) The oxidation of the TiC-TiB₂ multiphase ceramics materials was found to start at 600°C, and TiB₂ oxidation was first to occur, with TiB₂ being oxidized into TiO₂. There were no B₂O₃ crystal phase which was low-melting point, because of the TiO₂ melting point is 1840°C and boiling point is 2227°C, so it made the material have excellent oxidation resistance.

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