SCALING RESISTANCE IN BINARY TITANIUM AND CHROMIUM CARBIDES MADE BY SHS

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Double titanium-chromium carbide DTCC has considerable wear resistance, high heat resistance, and good scaling resistance; it is widely used as a component in materials working at high temperatures [1]. One method of making DTCC is self-propagating high-temperature synthesis SHS, which is increasingly used to make various compounds [2, 3].

We have examined the oxidation of DTCC powders in air at 600°C for grain size 80/40 μm, which were made in a laboratory SHS reactor; we used PTM titanium, PKh1-S chromium, and carbon as PM-15TS carbon black. All the DTCC powders were first analyzed chemically. The contents of titanium, total carbon, and oxygen were determined by the methods described in [4], while chromium was determined by the titrimetric persulfate method [5], iron by atomic absorption [6], and free carbon (as carbon dioxide) by coulometric titration with an AN-7529 analyzer by combusting the carbon black collected on asbestos remaining after dissolving the DTCC in acids. The x-ray phase analyses were performed by the [7] method.

The mass increase and the total carbon content were determined with 2 g of DTCC powder oxidized in air in a muffle furnace at 600°C; sometimes, the powder after oxidation was used again in x-ray phase analysis. Table 1 shows that the amount of free carbon increases with the chromium carbide content in the DTCC. There were considerable heat losses in the laboratory reactor, so the reaction in the combustion zone did not go to completion. The finished product therefore contains not only unreacted carbon but also the lower chromium carbide Cr7C3 than metallic chromium (from x-ray phase analysis).

The lattice parameter in the DTCC was determined before and after vacuum annealing for 4 h at 1200°C (Fig. 1); solid solutions of chromium carbide (over 15 mol.%) in titanium carbide are probably out of equilibrium, so chromium carbide segregates on annealing under those conditions. Annealing for 3 h at 1800°C under vacuum did not alter the compositions of solid solutions containing less than 15 mol.% chromium carbide, nor was there any effect on the lattice parameter or on the peak intensities [2]. DTCC containing 15 mol.% chromium carbide or less represents an equilibrium solid solution.

X-ray phase analysis of the initial powders showed that DTCC containing up to 25 mol.% chromium carbide is a single-phase solid solution, but a separate chromium carbide phase is formed at higher levels, i.e., the product consists of two phases, which agrees well with the solubility of chromium carbide in titanium carbide [8].

Figure 2 shows the mass increase in DTCC on oxidation in air at 600°C; for comparison, we show the increases for titanium and chromium carbide powders. The DTCC curves for 40 and 45 mol.% and the initial part of the curve for 35 mol.% chromium carbide lie below 100 %, which means that the mass is reduced, evidently because gaseous carbon oxides are formed, i.e., there is a reduction in the content of C-free, which is not balanced by the formation of metal oxides. DTCC containing 40 mol.% of chromium carbide contains only 0.15 mass % free carbon after oxidation for 50 min.

Discontinuous DTCC oxidation produces almost the same results as continuous, so it was possible to increase the treatment time. Figure 3 shows the variation in total carbon in the DTCC during oxidation. The degree of oxidation for the metals in the DTCC is given by Figs. 2 and 3 as

$$\alpha = \frac{(M/M_0 - 1) \cdot 100\% + (C_{\text{tot}}^0 - C_{\text{tot}}^t) \cdot 100\%}{O_{\text{max}}}$$

in which $M_0$ and $M$ are the masses of the powder before and after oxidation in g, $C_{\text{tot}}^0$ is the initial content of total carbon in mass %, and $C_{\text{tot}}^t$ is the content of total carbon in the powder after t min of oxidation reckoned on the initial mass of powder in mass %, and $O_{\text{max}}$ is the content of oxygen in the completely oxidized powder in mass %.

Fig. 1. Effects of DTCC composition on the lattice constant for the single-phase solid solution of chromium carbide in titanium carbide: 1) before annealing; 2) after annealing for 4 h at 1200°C and [8] data (solid straight line).

Fig. 2. Mass change M/M₀ for DTCC powders during oxidation in air at 600°C. Here and in Figs. 3, 4, and 6 the numbers 1-9 correspond to the numbers of the powders in Table 1, while 10 is chromium carbide and 11 is titanium carbide.

Fig. 3. Reduction in total carbon content in DTCC powders on oxidation in air at 600°C.

Fig. 4. Variation in degree of oxidation for DTCC powders in air at 600°C.

Figure 4 shows kinetic curves for the powder oxidation; specimens containing 35, 40, and 45 mol.% chromium carbide oxidize at almost the same rate.

Figure 5 shows how the composition affected the mass change in the powders on oxidation for 3 and 9 h; a small amount of chromium carbide added to titanium carbide increases the oxidation. There is least resistance to oxidation with 15 mol.% chromium carbide, and maximum resistance for 35-45 mol.%, but even in the latter case, the scaling resistance was less than with the higher chromium carbide. This type of curve has been observed [9] for the mass change after oxidation in relation to the amount of chromium carbide in solid solution in titanium carbide. That behavior occurs because the random introduction of chromium atoms into the titanium carbide lattice on synthesis reduces the binding of the titanium to the carbon and thus