Oxidation of SHS Mo-Si-C Materials in Air

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Abstract—The high-temperature oxidation kinetics of SHS-prepared Mo–Si–C composites, MoSi₂, and Mo₂C were studied in air. The materials were found to exhibit different types of oxidation behavior, depending on temperature and composition. A range of Si/C ratios is revealed in which the oxidation of the composites for as long as 500 h is accompanied by minor weight changes at oxidation temperatures up to 1650 K. This enhanced oxidation resistance is interpreted in terms of the kinetic competition between elementary reactions.

INTRODUCTION

Self-propagating high-temperature synthesis (SHS) can be used successfully to prepare Mo–Si–C composite materials differing in $MoSi_2 : Mo_2C$ ratio. The oxidation resistance of molybdenum carbides and silicides prepared by conventional heat-treatment techniques has been studied in many works. It was of interest to study the oxidation behavior of bulk Mo–Si–C composites prepared by SHS. For comparison, we also prepared the binary compounds $MoSi_2$ and Mo_2C .

RESULTS AND DISCUSSION

Mo₂C and MoSi₂. SHS samples were oxidized in air in the temperature range 860–1350 K for Mo₂C (Fig. 1) and 1450–1650 K for MoSi₂ (Fig. 2). At temperatures of \leq 980 K, Mo₂C oxidation is accompanied by weight gain, in accordance with the reaction

$$Mo_2C + 4O_2 = 2MoO_3 + CO_3$$
.

The Mo_2C surface is covered with a loose oxide layer permeable to gaseous reagents and reaction products. In the range 860-980 K, the apparent activation energy, determined from the initial oxidation rate, is 75 ± 7 kJ/mol. The curves obtained at 860 and 890 K (Fig. 1, curves 1, 2) almost coincide and both show a nearly linear weight gain with time. Further heating, up to 980 K, accelerates oxidation (curves 3, 4). At the same time, with increasing oxidation time, the rate of the process decreases, particularly at higher temperatures. Clearly, as the thickness of the oxide layer increases, it becomes less permeable to gas molecules. As a result, a transition oxidation regime sets in around 1000 K, in which, on the one hand, the oxidation rate is fairly high but, on the other, MoO₃ sublimation begins [3].

The 1000-K kinetic curve (Fig. 1, curve 5) exhibits a complex behavior. During the first ≈ 9 h, the oxide

layer attains a certain thickness and begins to notably impede diffusion. At longer oxidation times, MoO_3 sublimation prevails. As a result, after 9–10 h of oxidation, the sample weight passes through a maximum



Fig. 1. Weight changes during Mo₂C oxidation at (1) 860, (2) 890, (3) 910, (4) 980, (5) 1000, (6) 1090, (7) 1150, (8) 1230, and (9) 1350 K.



Fig. 2. Weight gain during MoSi₂ oxidation at (1, 3) 1450, (2) 1650, and (4) 1500 K; (1, 2) this work, (3, 4) [7].

(curve 5) and then drops sharply. A similar behavior is observed at 1090 K, with the only difference that the maximum in curve 6 is reached in a shorter oxidation time and, accordingly, at a smaller thickness of the oxide layer. In earlier studies of Mo₂C oxidation, no such kinetics were observed. Voitovich and Pugach [4] observed a linear weight gain up to 1100 K and a linear weight loss at 1200 K. According to our data, above the melting point of MoO₃ (1095 K), oxidation is accompanied by no weight gain (curves 7-9). The apparent activation energy in the range 1150–1350 K is 12 \pm 3 kJ/mol, which testifies to a sharp rise in the rate of the process-rapid vaporization of the oxidation products. In this context, the above data are not fully clear. According to x-ray diffraction (XRD) data, the only oxidation product at all temperatures is MoO₃. Voitovich and Pugach [4] obtained single-phase MoO₃ only above 1300 K, while at lower temperatures, the oxide layer consisted of Mo_2O_3 , Mo_4O_{11} , and MoO_3 . It cannot be ruled out that the phase composition of the oxide layer correlates with the oxidation kinetics in the range 1000-1300 K.

MoSi₂ is known to oxidize extremely rapidly below 1300 K, since, at this temperature, the sample surface is not yet covered with a continuous SiO₂ layer [5]. For this reason, we oxidized MoSi₂ in the range 1450–1650 K. Oxidation was found to be accompanied by weight gain (Fig. 2), in accordance with the reaction

$$MoSi_2 + 3.5O_2 = MoO_3 + 2SiO_2$$
.

The apparent activation energy determined from the initial oxidation rate is 110 ± 10 kJ/mol. Oxidation is decelerated by the formation of a dense silica layer; as a result, the diffusion regime sets in rapidly [6]. The rate of diffusion through the solid phase is low. Various, and often conflicting data on the oxidation kinetics of MoSi₂ are available in the literature. Not only different weight gains-and, accordingly, different parabolic oxidation kinetics-for samples oxidized under identical conditions but, occasionally, weight losses have been reported. This is, most likely, associated with the effect of sample purity, since the oxidation of lower molybdenum silicides, Mo₅Si₃ and especially Mo₃Si, is accompanied by weight loss [7]. In our experiments, the phase purity of the samples was checked by XRD, and only single-phase (MoSi₂) samples were studied. Comparison of our results with earlier data [7] (Fig. 2) shows qualitative agreement. In all cases, the 1450-K oxidation curves lie above the higher temperature curves, in agreement with the report [8] that a dense SiO_2 film is formed only above 1500 K.

Thus, the oxidation behavior of SHS $MoSi_2$ in air is identical to that of the materials prepared by conventional heat-treatment techniques, while our results for Mo_2C differ markedly from earlier data. Note, however, that the available data are insufficient to correlate these distinctions with the synthesis method or other factors.

Mo-Si-C composite materials. The oxidation behavior of this system in air was studied [1, 2] on samples with different Si/C atomic ratios. The results for oxidation temperatures between 1230 and 1650 K are presented in Fig. 3. As in the case of Mo₂C, all of the curves show weight loss throughout the temperature range examined. The introduction of silicon (Si/C =0.45) slightly decelerates the oxidation process. Comparison of the oxidation curves in Figs. 1 and 3a indicates, for a particular weight loss and T = 1350 K, an increase in oxidation time from 70 to 130 min. The apparent activation energy determined from the initial, linear portion of the curves is 94 ± 7 kJ/mol, which is fairly close to that for MoSi₂. Increasing the Si/C ratio to 2.25 leads to a substantially higher oxidation resistance (Fig. 3b), and the apparent activation energy increases to 210 ± 15 kJ/mol. It follows from the data in Fig. 3b that a further increase in silicon content (Si/C = 3.74) notably reduces the net weight loss $(\leq 2.2\%)$, and the curves level off after 100–150 h of oxidation. Since the initial oxidation kinetics are nonlinear, there is no point in assessing the apparent activa-







Fig. 4. Weight changes during oxidation of Mo–Si–C composites with Si/C = (1-3) 7.14 and (4, 5) 16.04 at (1) 1350, (2, 4) 1450, and (3, 5) 1650 K.

tion energy. Figure 3c illustrates the oxidation kinetics of the Si/C = 4.17 samples. The initial stages of oxidation are seen to be accompanied by an even smaller weight loss (0.2-0.4%). In this case, the apparent activation energy of the initial stages also cannot be accurately evaluated. After the rapid weight loss in the initial stages, the curves in Fig. 3c become almost linear. As the temperature is raised from 1230 to 1450 K, both the weight loss and the slope of the curves increase.

An interesting feature was revealed in studies of the Si/C = 7.14 samples between 1350 and 1650 K. Similar to the curves in Fig. 3, curves 1 and 2 in Fig. 4 show weight loss. Oxidation at 1450 K is accompanied by a slight weight change (curve 2), and that at 1650 K (curve 3) by a sizeable weight gain, as in the oxidation of MoSi₂. In other words, there are Mo–Si–C materials whose oxidation is accompanied by weight loss at lower temperatures and weight gain at higher temperatures. In both cases, the oxidation rate decreases with time and the curves are nearly parabolic. Note that the data points for oxidation at 1350 K scatter widely. With increasing oxidation temperature, the scatter decreases,



Fig. 5. Weight change as a function of Si/C for long-term ($\tau = \tau_{max}$) annealing of Mo–Si–C materials at (1) 1230, (2) 1350, (3) 1450, and (4) 1650 K; numbers at the data points indicate τ_{max} , h.

and the 1650-K curve is quite smooth. These changes seem to be associated with the formation of a dense silica film.

The data in Figs. 3c and 4 demonstrate that, at certain oxidation temperatures and Si/C ratios, the sample weight may remain virtually constant over a fairly long time. This, however, does not necessarily testify to a high oxidation resistance. Rather, the state of the material should be thought of as quasi-stationary, resulting from an interplay between elementary steps underlying the oxidation of the composite material.

A further increase in silicon content (Si/C = 16.04) produces no radical changes in the oxidation behavior of the material. As in the case of the Si/C = 7.14 sample (Fig. 4, curve 2), oxidation of the Si/C = 16.04 sample at 1450 K (Fig. 4, curve 4) is accompanied by a minor weight loss during the first 20–30 h. At longer oxidation times, the processes leading to weight gain prevail because of the high silicon content in this sample. No stationary state was achieved in the range of oxidation times studied, because this temperature is not high enough. The oxidation at 1650 K (Fig. 4, curve 5)



Fig. 6. Calculated constant-weight curve for the 1450-K oxidation of a Mo-Si-C material with Si/C = 16.04.

favors the formation of a dense SiO_2 film. Curve 5 is similar to curve 3 but lies higher, in accordance with the higher silicon content of the sample. On the whole, curves 3 and 5 resemble those given in [8] for the oxidation of MoSi₂ at 1500 K and above.

These results suggest that a stable weight of the composites in question during oxidation (quasi-stationary oxidation behavior) can be achieved not only by adjusting the oxidation temperature at a particular composition of the material but also by optimizing its composition, in particular, the silicon content. The curves in Fig. 5 summarize the data above. It can be seen that, in the range Si/C = 4.17-16.04, the Mo–Si–C composites can be exposed to high temperatures for a long time, up to 500 h according to our results, without significant weight changes.

Consider now the processes responsible for the quasi-stationary state during high-temperature oxidation, using the Si/C = 16.04 material as an example. At the beginning of oxidation, the Mo : Si : C atomic ratio on the surface is 1.1 : 1.8 : 0.1. During the high-temperature oxidation, molybdenum oxidizes to the volatile oxide MoO₃, carbon to CO₂, and silicon to the nonvolatile oxide SiO₂. Assuming that carbon burns out fully on the sample surface and calculating the

amount of vaporized molybdenum oxide for a given fraction of oxidized silicon, one can plot a constantweight curve for high-temperature oxidation of a particular Mo–Si–C composite, the process in which molybdenum loss is compensated for by the weight gain due to the formation of silicon oxide. Such a curve for the Si/C = 16.04 material is displayed in Fig. 6. This curve is the locus of points corresponding, under a given temperature, to the constant-weight oxidation behavior.

CONCLUSION

Bulk Mo₂C prepared by SHS exhibits different types of oxidation behavior in the range 980–1150 K. Oxidation between 1000 and 1090 K is accompanied first by weight gain and then by weight loss. The oxidation time corresponding to the maximum sample weight depends on the oxidation temperature. Since these results differ markedly from those reported in the literature, they are likely to reflect the specifics of the SHS process.

During long-term (up to 500 h) oxidation in air between 1230 and 1650 K, SHS Mo–Si–C materials with Si/C = 0.45–16.04 exhibit an oxidation behavior that is opposite to that of Mo₂C: with increasing oxidation temperature and Si/C ratio, a transition from weight loss to weight gain occurs. Under certain conditions, the sample weight decreases with time in the initial stage of oxidation and then rises. This behavior is due to the formation of a dense film of the nonvolatile oxide SiO₂.

In the composition range Si/C = 0.45-16.04, the sample weight varies very little during oxidation. The observed quasi-stationary state is due to kinetic competition between vaporization of the forming MoO₃ and the weight gain related to the formation of a SiO₂ film on the sample surface.

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