Oxidation of cubic complex carbides (Ti xVy Moz)C synthesis by electrospark dispersion method with atmospheric oxygen

Tilebaldy Adilovich, Abduraim Satyvaldievich, and Kalyskan

Abstract. During the joint electrospark dispersion of titanium with VyMoz alloys in hexane, complex carbides (Ti xVy Moz)C with a cubic lattice are formed. Assuming that complex carbides (Ti xVy Moz)C as quasi-binary systems, where complex carbide (Vy Moz)C with a cubic structure is dissolved in cubic titanium monocarbide, the composition of complex carbides (Ti0.75V0.05Mo0.20)C and (Ti0.65V0.31Mo0.04)C, formed by electrospark dispersion of Ti-V0.2Mo0.8 and Ti-V0.2Mo0.8 pairs. Using the method of differential thermal analysis, it was shown that the thermal stability against oxidation of complex carbides (TiVyMoz)C, synthesized by joint electrospark dispersion of titanium and the VyMoz alloy, depends on the ratio of metals. Thermal stability against oxidation increases with an increase in the content of titanium and molybdenum in the composition of complex carbides; their resistance to oxidation increases. It has been established that intensive oxidation of complex carbide (Ti0.75V0.05Mo0.20)C occurs at 595°C, and complex carbide (Ti0.65V0.31Mo0.04)C oxidizes at the maximum rate at 520°C.

1 Introduction

In recent years, the interest of researchers in multicomponent carbides of refractory transition metals has increased, because complex carbides containing two or more metals acquire higher physicochemical and mechanical properties [1].

In work [2], using the method of differential thermal analysis, it was shown that complex carbide (Ti,W)C, synthesized by joint electrospark dispersion of titanium and tungsten, has a higher oxidation temperature with atmospheric oxygen than individual carbides of these metals synthesized under identical conditions.

The authors [3-6] believe that nanopowders of metal carbides are characterized by increased chemical activity, which manifests itself in a decrease in the temperature at which they begin to oxidize compared to coarse-grade ones.

The method of electrospark dispersion is promising for obtaining complex carbides of refractory metals. In this method, the energy of the spark discharge is sufficient to...
transform any refractory metals and their alloys into liquid and vapor states [7]. High
temperatures and pressures accompanying a spark discharge create favorable
thermodynamic conditions for the synthesis of high-
temperature modifications of refractory
metal carbides [8].

The purpose of this study is to study the thermal oxidation by atmosph- e
ric oxygen of a
complex carbide \((\text{Ti}^x\text{V}^y\text{Mo}^z)\text{C}\) (where \(x, y, z\) are the atomic fractions of metals in the
complex carbide and \(x+y+z=1\)), synthesized by the method of electrospark dispersion.

2 Materials and Methods

The synthesis of complex carbide \((\text{Ti}^x\text{V}^y\text{Mo}^z)\text{C}\) was carried out by joint electrospark
dispersion of metallic titanium and the alloy \(\text{V}^{0.9}\text{Mo}^{0.1}\) or the alloy \(\text{V}^{0.2}\text{Mo}^{0.8}\) (where \(0.9\) and \(0.1\); \(0.2\) and \(0.8\) are the mole fractions of vanadium and molybdenum in the
alloy). Hexane was used as a liquid medium, whi- ch also serves as a source of carbon for the
formation of carbide compounds. The energy of a single spark discharge was 0.05 J, which
makes it possible to synthesize highly dispersed carbide compounds.

To study the thermal oxidation of complex carbides \((\text{Ti}^x\text{V}^y\text{Mo}^z)\) with atmospheric
oxygen, the method of differential thermal analysis was used. Derivatograms of carbide
compounds were obtained on a Q-1000/D derivatograph of the F.Paulik, J.Paulik and
L.Erdey system in an air atmosphere in the temperature range \(20-1000^\circ\text{C}\). The sample
heating rate was 10 deg/min. Calcined aluminum oxide \(\text{Al}_2\text{O}_3\) was used as a standard
substance. The mass of the samples was 50 mg with a sensitivity of the balance of 50 mg.

The oxidation process of synthesized carbide compounds was also
studied by calcining
them at temperatures of 400\(^\circ\text{C}\), 600\(^\circ\text{C}\) and 900\(^\circ\text{C}\) in a muffle furnace for 1 hour.

3 Results and Discussions

Previously [9] it was established
that during the joint electrospark
dispersion of titanium
with the alloys \(\text{V}^{0.9}\text{Mo}^{0.1}\) or \(\text{V}^{0.2}\text{Mo}^{0.8}\), two carbide compounds are formed,
 differing in structure and intensity of reflex lines. Carbide compounds with intense lines
have a face-
centered cubic (fcc) crystal lattice of the NaCl type. According to the value of
the fcc lattice parameter, phases with a cubic structure are solid solutions of cubic
monocarbides of titanium (TiC), vanadium (VC) and molybdenum (MoC) of composition
\((\text{Ti}^x\text{V}^y\text{Mo}^z)\text{C}\). The second carbide compound of the products is a complex carbide based
on vanadium and molybdenum semicarbides \((\text{V}^y\text{Mo}^z)\text{C}_2\) with a hexagonal close-
packed (hcp) lattice.

A solid solution of carbides \((\text{Ti}^x\text{V}^y\text{Mo}^z)\text{C}\) can be considered as a quasi-
binary system,
where a complex carbide \((\text{V}^x\text{Mo}^y)\text{C}\) with a cubic structure is dissolved in cubic titanium
monocarbide. It is shown in work [10] that during electrospark dispersion of the alloys
\(\text{V}^{0.9}\text{Mo}^{0.1}\) and \(\text{V}^{0.2}\text{Mo}^{0.8}\), complex carbides \((\text{V}^{0.9}\text{Mo}^{0.1})\text{C}\) and \((\text{V}^{0.2}\text{Mo}^{0.8})\text{C}\) with the
 corresponding lattice parameter value \(a = 4.180 \text{~A}^0\) and \(4.258 \text{~A}^0\). Assuming that the value
of the lattice parameter of the solid solution \((\text{Ti}^x\text{V}^y\text{Mo}^z)\text{C}\) linearly depends on the content
of titanium carbide TiC and complex carbide \((\text{V}^y\text{Mo}^z)\text{C}\) and taking into account the
dispersibility of titanium and alloys \(\text{V}^y\text{Mo}^z\), the compositions of the synthesized complex
carbides (Table 1).

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>Compositions of carbide compounds</th>
<th>Lattice parameters, \text{~A}^0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{Ti}^{0.75}\text{V}^{0.05}\text{Mo}^{0.20}) - (\text{C})</td>
<td>((\text{Ti}^x\text{V}^y\text{Mo}^z)\text{C})</td>
<td>(a = 4.300\text{~A}^0)</td>
</tr>
</tbody>
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Complex carbides \((\text{Ti}_x\text{V}_y\text{Mo}_z)\text{C}\) differ in metal content and therefore the study of their high-temperature oxidation by atmospheric oxygen is of particular interest.

Derivatograms of complex carbides \((\text{Ti}_x\text{V}_y\text{Mo}_z)\text{C}\) and \((\text{V}_y\text{Mo}_z)\text{C}_2\) are presented in Figure 1.

Analysis of derivatograms shows that the number and type of thermal effects on the DTA curve depend on the composition of the initial alloy \(\text{V}_y\text{Mo}_z\). TG curves of derivatograms consist of three sections (Fig. 1).

The first section of the TG curves of derivatograms is in the temperature range of 20-400°C and is characterized by a decrease in the mass of the samples from 5% to 6.75% (Table 2). The decrease in the mass of samples in this area is associated with two processes. In the temperature range of 20-200°C, desorption of heptane adsorbed on particles of carbide compounds occurs. This process is accompanied by broad endothermic effects with a minimum at 170°C. In this case, the mass of the samples decreases by 3%. In the temperature range of 200-400°C, in the first section of TG, oxidation of free \(\text{x-ray carbon}\) occurs in the form of carbon char, formed during the decomposition of heptane molecules:

\[
\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \uparrow
\]

Table 2. The processes occurring during the heating of carbide compounds of the \(\text{Ti}_x\text{V}_y\text{Mo}_z\)-C system up to 1000°C in air.

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>Thermal effects</th>
<th>Processes</th>
<th>(\Delta m) of sample, %</th>
<th>Product of thermolysis</th>
<th>Type</th>
<th>Int. (t)o (\text{C})</th>
</tr>
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<tr>
<td>1</td>
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**Fig. 1.** Derivatograms of complex carbides of the \(\text{Ti}_{0.2}\text{V}_{0.8}\text{C}\) (1) and \(\text{Ti}_{0.9}\text{V}_{0.1}\text{C}\) (2) systems.
In this temperature range, the DTA curves have doublet exothermic effects with maxima at 370°C, 405°C and 375°C, 395°C, respectively. The first peaks of doublets (370°C, 375°C) characterize the process of oxidation of free carbon and this process is accompanied by a decrease in the mass of the samples by 2% and 3.75%, respectively (Table 2). The second peaks at 405°C and 395°C of the exothermic doublets most likely correspond to the oxidation of carbide compounds, as an increase in the sample mass occurs starting from these temperatures.

The second section of the TG curves of derivatograms is in the temperature range of 410°C - 660°C and is associated with an increase in the mass of the samples from 37.0% to 50.5%. In this area, oxidation of carbide compounds occurs and this is indicated by very intense exothermic effects. On the DTA curve of the derivatogram of the product of the Ti-V-Mo-C system, there are doublet intense exothermic effects at 595°C and 620°C, which correspond to the oxidation of two carbide phases (Ti0.75V0.05Mo0.20C) and (V0.2Mo0.8)2C according to the following scheme:

\[
\text{Ti0.75V0.05Mo0.20C} + O_2 \rightarrow \text{TiO}_2 + \text{V}_2\text{O}_5 + \text{MoO}_3 + \text{CO}_2
\]

\[
\text{V0.2Mo0.8} + O_2 \rightarrow \text{V}_2\text{O}_5 + \text{MoO}_3 + \text{CO}_2
\]

The solid solution (Ti0.75V0.05Mo0.20C) is the main phase, therefore a very intense exothermic effect at 595°C corresponds to the oxidation of this carbide compound, and a less intense second exothermic effect at 620°C characterizes the oxidation of the second carbide compound phase (V0.2Mo0.8)2C, the content of which in the product is less compared to complex carbide (Ti0.75V0.05Mo0.20C). The increase in sample mass due to the formation of metal oxides during the oxidation of carbide compounds is 50.5%.
A feature of the derivatogram of carbide compounds of the Ti–V$_{0.9}$Mo$_{0.1}$-C system is the presence of one intense exothermic effect at 520°C. This indicates that complex carbides (Ti$_{0.65}$V$_{0.31}$Mo$_{0.04}$)$_2$C, (V$_{0.9}$Mo$_{0.1}$)$_2$C are oxidized at the same temperature. Their oxidation temperatures are 75°C and 100°C lower than the oxidation temperature of the corresponding complex carbides of the Ti–V$_{0.2}$Mo$_{0.8}$-C system. And the mass of the sample increases by 37.0%.

In the third section of the TG curve of the derivatogram of the product of the Ti–V$_{0.2}$Mo$_{0.8}$-C system, a decrease in the mass of the sample is observed in two stages. The first stage is characterized by an endothermic effect of low intensity at 690°C, and the decrease in the mass of the sample at this stage is correspondingly 4%. At the first stage, most likely, the melting of vanadium oxide V$_2$O$_5$ occurs. According to literature data [11=10] V$_2$O$_5$ melts at 670°C. During melting, the evaporation of this oxide occurs. In the second stage, the sublimation of MoO$_3$ oxide, which has a melting point at 795°C, probably occurs [11-10]. The sublimation process is characterized by an endothermic effect at 805°C, and the decrease in the mass of the sample at this stage is 18.0%.

A feature of the third section of the TG curve of the derivatogram of the product of the Ti–V$_{0.9}$Mo$_{0.1}$-C system is the absence of thermal physical and chemical processes. Therefore, the third section of the TG curve of the derivatogram of this system is rectilinear.

Thus, using the method of differential thermal analysis, it was established that the thermal stability against oxidation of complex carbide (Ti$_x$V$_y$Mo$_z$)$_2$C depends on the ratio of metals. Thermal stability against oxidation increases with increasing content of titanium and molybdenum in the composition of the complex carbide. Therefore, complex carbide (Ti$_{0.75}$V$_{0.05}$Mo$_{0.20}$)$_2$C is characterized by a higher oxidation temperature than complex carbide (Ti$_{0.65}$V$_{0.31}$Mo$_{0.04}$)$_2$C.

The patterns of oxidation of complex carbides of the Ti–V$_y$Mo$_z$-C systems, established by the method of differential thermal analysis, were confirmed during their high-temperature treatment in air (Fig. 2).

When heating complex carbides of the Ti–V$_{0.2}$Mo$_{0.8}$-C and Ti–V$_{0.9}$Mo$_{0.1}$-C systems to 400°C, the mass of the samples decreases by 4-5% due to desorption of hexane and oxidation of free carbon in the form of carbon char.
the corresponding metals. When heating complex carbides from 650°C to 900°C, the mass of samples of complex carbides of the Ti-0.2V-0.8Mo-C system decreases, and this decrease at 900°C is 21.4%, and the mass of a sample of complex carbides of the Ti-0.9V-0.1Mo-C system does not change. The decrease in mass of samples of complex carbides of the Ti-0.2V-0.8Mo-C system, as mentioned earlier, is associated with the sublimation of vanadium and molybdenum oxides. In the composition of complex carbides of the Ti-0.2V-0.8Mo-C system, the molybdenum content is significantly higher than in the composition of complex carbides of the Ti-0.9V-0.1Mo-C system. In the second case, it is possible that a solid solution is formed between the oxides of vanadium and molybdenum and, as a result, sublimation of the oxides of these metals does not occur.

4 Conclusions

Thus, using the method of differential thermal analysis and high-temperature treatment of complex carbides of the Ti-V-0.2Mo-0.8C and Ti-V-0.9Mo-0.1C systems, it was established that the thermal oxidation of complex carbides (Ti-0.3V-0.7Mo)C depends on the ratio of metals. With an increase in the content of molybdenum and titanium, the resistance of complex carbides (Ti-xV-yMo-z)C to high temperature oxidation increases.

References


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