Stability of Lamellar Structure in a Mo-TiC Eutectic Composite under a Low Vacuum at High Temperatures*

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The thermal stability of lamellar structure in a Mo-TiC eutectic composite has been investigated at 1523–2223 K for 5.76×10⁴–3.6×10⁵ s under a low vacuum of 13 mPa.

It was found that the TiC phase in the eutectic lamellar disappeared near the surface of specimens above a critical temperature of about 1750 K, but below that temperature the TiC phase remained and TiO film was formed on the surface. The Mo matrix phase was not oxidized and was stable at all test temperatures, since its affinity for oxygen is lower than that of carbon and titanium.

It is presumed that at higher temperatures the disappearance process of TiC phase is controlled by the diffusion of carbon atoms through the matrix to the surface, and the carbon and titanium atoms on the surface are removed by CO gas formation and TiO evaporation, respectively, but at lower temperatures the evaporation of TiO is so slow that the TiO film is formed on the surface.

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I. Introduction

Along with the development of various kinds of heat engines, the metal matrix composites with excellent high-temperature properties are required to develop in order to improve the heat efficiency by increasing their operating temperatures. The mechanical properties at high temperatures are most important for this purpose. However, many other problems also must be settled for the practical application. For example, there are problems about the reaction between the component phases at high temperatures(1), the thermal fatigue(2) which may occur due to the difference in their thermal expansions, and the compatibility with the environment. They are especially important because the mechanical properties may be deteriorated by them.

Various eutectic-composites have been investigated(3) because the eutectic-composite is believed to be stable at high temperatures and not serious in the problem of the reaction mentioned above, together with the easiness of manufacturing.

The present authors(4) have investigated the mechanical properties of the lamellar eutectic composite of high melting-point materials, i.e. Mo and TiC, and reported that the composite has an excellent high-temperature strength as well as a good toughness at room temperature and it is a hopeful candidate for high-temperature applications.

Since the difference in thermal expansion coefficient between Mo and TiC phases is as small as $2.0 \times 10^{-6} \text{ K}^{-1}$, which is fairly smaller than those in the usual metal-matrix composites (for example $1.4 \times 10^{-5} \text{ K}^{-1}$ in Cu-W composite(6)), the thermal fatigue due to the temperature variation may be out of the problem.

On the other hand, the problem of compatibility with environment may be serious in this material. The problem should be studied under a definite condition for a practical application.

As an example of environmental problem, Igata et al.(7) recently, investigated the effect of neutron irradiation on the Mo-TiC eutectic-composite, and reported that the radiation embrittlement is extremely small in comparison...
with other metallic materials, and this composite is a hopeful candidate for the first wall material of a nuclear fusion reactor.

It is well known that the matrix Mo has a good strength at high-temperatures but has a poor oxidation resistance because of its high affinity for oxygen. Since the vapor pressure of MoO₃ is so high⁷ that the mass loss due to the oxidation and evaporation is serious at high temperatures even under a low oxygen pressure, some techniques such as coating are necessary for the high-temperature applications. However, no investigation has been carried out on the oxidation behavior of Mo base composites containing second phases such as TiC, not only in the atmosphere but also in a vacuum. The experimental data on the compatibility with environment should be accumulated for practical applications.

The present work is to investigate the stability of the composite structure under a low vacuum at high temperatures, in order to clarify the usefulness of the composite as the material of high-temperature vacuum-furnace such as a first wall material of a fusion reactor.

II. Experimental Procedure

After mixing Mo powder (4.0 μm in diameter, 99.9 mass% purity) and TiC powder (1.9 μm in diameter, 99.54 mass% purity) to the eutectic composition of Mo-23.5 mol% TiC, the mixture was pressed under a hydrostatic pressure of about 250 MPa for 60 s to a green compact about 12 mm in diameter and 170 mm in length.

After degassing and sintering under a vacuum of 13.3 Pa at about 1500 K for 3.6 ks, the compact was melted and directionally solidified under a helium atmosphere (6 N purity) of 0.15 Pa at a rate of 1.66 × 10⁻⁵ m/s (60 mm/h) by using a floating zone technique with a radio frequency induction heating to make a rod sample of 8 mm in diameter and 150 mm in length. The sample obtained was bisected parallel or perpendicular to the solidification direction.

The sections were observed by SEM and found to be of lamellar structure consisted of black and white layers as shown in Fig. 1 which is a typical example of the section perpendicular to the solidification direction. The observation on the parallel section showed that the lamellar structure was almost the same along the whole length. The structure observed on the parallel and perpendicular sections were not very different. From X-ray diffraction and EPMA, the black layers were identified as TiC phase and the white layers as Mo phase.

The lamellar structure covered almost all parts of the specimens, but locally a rod-like structure of TiC phase was also observed. The mean width of the lamellars was measured to be 0.7 μm for Mo phase and 0.25 μm for TiC phase. The eutectic colonies were observed to be elongated to the solidification direction. The diameter of the colonies was about 150 μm on the transverse section. The rod-specimens were cut perpendicular to the solidification direction every 5 mm and further bisected.
parallel to the direction. The resultant specimens were semi cylindrical discs of 4 mm in radius and 5 mm in thickness.

After isothermal heating under a vacuum of 13.0 mPa (=1×10⁻⁴ Torr) at 1523−2223 K for 5.76×10⁴−3.6×10⁵ s (16−100 h) the specimens were bisected again parallel to the solidification direction. In order to reveal the structure change during the heating, the original and new sections were examined by using the Shimadzu Auto X-ray Diffractometer (Cu target), Hitachi XPMA and Hitachi SEM.

By using Tokuda hot-cathode ionization gauge, the vacuum during the heating was determined to be 13 mPa and the fluctuation of the pressure was too small to detect. During the heating the temperature of the specimen was measured by using a two color pyrometer. The fluctuation of the temperature was controlled within ±10 K in the reference to a setting temperature.

III. Experimental Results

Figure 2 shows the scanning electron micrographs of the new section after heating at 2223 K for 3.6×10⁵ s (100 h), whose original structure before heating was almost the same as that shown in Fig. 1. Figure 2(a) shows the structure in a large colony near the surface of the specimen. By comparing the structures in Fig. 2(a) and Fig. 1 it is found that a layer of lamellar free zone (hereafter called LFZ) is produced parallel to the surface by the heating.

Figure 2(b) shows the structure around a colony boundary which intersects the surface. The formation of LFZ is more remarkable in the region around the colony boundary than in the inner region of the colony. As shown by arrows, some voids are formed on the colony boundary. Voids were also sometimes observed in the inner region of the place where TiC phases seemed to have been present before the heating. However, the size of these voids was much smaller than those on the colony boundary.

On the other hand, in the inner region of the specimen the eutectic lamellar structure was quite similar in a colony as well as around a colony boundary to that before the heating.

The observations show that the structure change exclusively occurs near the surface exposed to the environment.

From the above results, it is presumed that the LFZ is formed by a process of decomposition of the TiC lamellae and diffusion of the decomposed Ti and C atoms through the matrix to the surface where they disappear. The mechanism of the void formation is not clear at present. But, the voids seem to be a kind of Kirkendall voids, which may be formed due to the insufficient volume compensation by Mo atoms for the decomposition and diffusing away of the TiC phase.

To determine the temperature dependence of the width of LFZ, E, the specimens were held at temperatures in a range of 1523−2223 K for 3.6×10⁵ s (100 h) and the result is shown in Fig. 3. Here the width, E, was measured at the region of relatively uniform width without
any colony boundary. The LFZ was hardly observed at lower temperatures from 1523 K to 1673 K, but clearly observed at higher temperatures above 1873 K. As seen in Fig. 3, $E$ increases as the temperature rises, and attains to 16.5 μm at 2223 K.

Figure 4 shows the scanning electron micrographs of the surface of the specimens after holding at 1673 K and 2223 K for $3.6 \times 10^5$ s. A typical example of the surface structure with LFZ is shown in Fig. 4(a), which was obtained after heating at 2223 K for $1.8 \times 10^5$ s (50 h). It is found that the surface is relatively smooth and there are many voids in the colonies as well as at the colony boundaries. These voids may be of the same kind of the voids found in the interior region of the specimen.

X-ray diffraction on the surface did not show any other peaks than those of Mo. This, together with the microscopic observation, shows that the TiC phase near the surface has completely disappeared after the heating.

Figure 4(b) is the structure after holding at 1673 K for $3.6 \times 10^5$ s (100 h). This is a typical example of the surface structure in the case of undetectable LFZ. It is seen that the surface is uneven and covered with films with some cracks. The size of the cells observed on the uneven surface is almost the same as the colony size. Accordingly, it is assumed that the grooves are formed by the preferential thermal-etching at the colony boundaries. From the results obtained by X-ray diffraction, these films were identified as TiO. In short, the LFZ was not detected in the specimen with the oxide film.

Figure 5 shows the relationship between the holding time, $t$, and the width of LFZ, $E$, at the higher temperatures where LFZ was formed. Although the datum points are not many, a linear relationship seems to hold between $E^2$ and $t$ from the results at 2073 K. Then, it is assumed that the growth of LFZ is controlled by the diffusion of some Ti-C complex or dissociated Ti and C atoms toward the surface. The activation energy for the process will be discussed in section IV.

Figure 6 shows a typical example of concentration profiles of the elements of C, Ti and
Mo in the LFZ, which were measured by EPMA. The intensity profiles of Mo-L\(_\alpha\), Ti-K\(_\alpha\) and C-K\(_\alpha\) on the scanning line of Fig. 6(a) are shown in Fig. 6(b). Except that the intensity of Mo-L\(_\alpha\) suddenly drops in TiC phase, the intensity of Mo-L\(_\alpha\) is almost constant up to the surface. From the intensity profile of Ti-K\(_\alpha\), it is clear that the concentration of titanium increases with the distance from the surface. Although the gradient of carbon concentration is not clear because of the low resolved concentration\(^9\), the concentration is considered also to increase with the distance from the surface. Thus, it is presumed that the TiC phase once resolves into the Mo matrix and dissociate to Ti and C atoms, and then they diffuse through the Mo matrix to the surface of the specimen.

IV. Discussion

1. Disappearing rate of TiC lamellae

From the result of Fig. 5, \(E\) and \(t\) have the following relationship,

\[
E^2 = kt. \quad (1)
\]

Here, \(k\) is the rate constant for the disappearance of TiC lamellae. If the disappearance is controlled by a thermal activation process, \(k\) is expressed by,

\[
k = k_0 \exp \left( -\frac{Q}{RT} \right). \quad (2)
\]

Here, \(k_0\) is a constant independent of temperature, \(R\) the gas constant and \(Q\) the activation energy for the disappearing process.

The disappearance of the TiC phase probably consists of the following three processes: firstly resolution of the TiC phase into the Mo matrix, secondly diffusion of the resolved Ti and C atoms through the matrix to the surface, and thirdly surface reaction for removing these atoms from the surface. Of these processes, the diffusion to the surface may be the most probable rate-controlling process, because the relation of \(E^2 \propto t\) holds.

Figure 7 shows the relationship between the temperature, \(T\), and the gradient of the straight lines in Fig. 5, \(k\). As expected from eq. (2), a good linear relationship holds between \(T^{-1}\) and \(\ln k\). From the slope of this line, the activation energy, \(Q\), for the disappearing process is calculated to be 117 kJ/mol.

It has been reported that the activation energy for C diffusion in Mo is 115 kJ/mol\(^{10}\) and for Ti diffusion 209 kJ/mol\(^{11}\). Since the activation energy obtained by the present experiment is very close to that for C diffusion.
but much smaller than that for Ti diffusion, the disappearing process is considered to be controlled by the diffusion of C atoms to the surface. Ti atoms having lost the associated C atoms dissolve into the matrix phase of Mo, and then the TiC phase disappears.

2. Mechanisms of the formation of oxide film and the disappearance of lamellar structure

As shown in Fig. 4, the TiO film was not detected on the surface of the specimen held at the higher temperatures, but was formed on the surface when held at the lower temperatures, where the LFZ was hardly observed. The critical temperature for this transition was about 1750 K. It will be shown in the following that the critical temperature is understandable on the basis of a free energy concept.

In the early stage of heating at the higher temperatures, both of the TiC(δ) and Mo(β) phases coexist at the surface region of the specimen in the thermal equilibrium state. Therefore, the activity of Mo atoms dissolved in the δ phase should equal the activity of Mo in the β phase. The same is true of C and Ti atoms in the δ and β phases.

Assuming that the thermodynamic properties of the δ and β phases are not much different from those of pure TiC and pure Mo phases, respectively, the following oxidation reactions of TiC and Mo phases may occur at the surface in the early stage.

From reference (12),

\[ \text{Ti(s)} + \frac{1}{2} \text{O}_2(\text{g}) = \text{TiO(s)}; \]
\[ \Delta G_{3a}^0 = -122300 + 21.3T. \tag{3a} \]
\[ \text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) = \text{CO(g)}; \]
\[ \Delta G_{3b}^0 = -26700 - 20.95T. \tag{3b} \]
\[ \text{TiC(s)} = \text{Ti(s)} + \text{C(s)}; \]
\[ \Delta G_{3c}^0 = 44600 - 3.16T. \tag{3c} \]

Then,

\[ \text{TiC(s)} + \text{O}_2(\text{g}) = \text{TiO(s)} + \text{CO(g)}; \]
\[ \Delta G_3^0 = -104400 - 2.81T. \tag{3} \]

and

\[ \text{Mo(s)} + \text{O}_2(\text{g}) = \text{MoO}_2(\text{s}); \]
\[ \Delta G_4^0 = -140500 - 4.61T \log T + 56.8T. \tag{4} \]

Here, s denotes solid state and g gas state under the standard state, \( \Delta G^0 \) the standard free energy change for the reaction at the pressure of 1 atm (unit in cal) and \( T \) the absolute temperature.

Assuming the partial pressures of \( \text{O}_2 \) and \( \text{CO} \) gas’s, which are denoted by \( P_{O_2} \) and \( P_{CO} \), respectively, are nearly equal to the vacuum pressure of 13 mPa (= 1.3 \times 10^{-7} \text{ atm} ), the free energy change for the reactions under these partial pressures is described as follows,

\[ \Delta G_3 = \Delta G_{3a}^0 + RT \ln \left( \frac{P_{CO}}{P_{O_2}} \right) \approx \Delta G_{3a}^0, \tag{3'} \]
\[ \Delta G_4 = \Delta G_{4a}^0 + RT \ln \left( \frac{1}{P_{O_2}} \right) \]
\[ \approx \Delta G_{4a}^0 + 31.7T. \tag{4'} \]

Since \( \Delta G_3 \ll \Delta G_4 \) in the whole temperature range in the present experiment, the reaction of eq. (3) will prevail. As mentioned above, the activity of Ti and C atoms in the β phase may be considered to be almost the same as that in the TiC phase. Accordingly TiO phase should be formed on the surface of the both δ and β phases.

According to Grovers, Hoch and Johnston (13), the equilibrium vapor pressure of TiO, \( P_{\text{TiO}} \), is given as a function of temperature,
$\text{TiO(s)} = \text{TiO(g)}$

$$\log P_{\text{TiO}}^0 = -\frac{29421}{T} - 0.583 \times 10^{-3} \times T + 10.43,$$ \hspace{1cm} (5)

where the unit of $P_{\text{TiO}}^0$ is atm. The value of $P_{\text{TiO}}^0$ in eq. (5) strongly depends on temperature and above 1810 K it increases and overrides 13 mPa. Because the solid TiO phase is in equilibrium with TiO(g) of that vapor pressure, the free energy change for the reaction under the vapor pressure of $P_{\text{TiO}}$ is given by

$$\Delta G_5 = RT \ln \left( \frac{P_{\text{TiO}}}{P_{\text{TiO}}^0} \right).$$ \hspace{1cm} (6)

In present experiment, the vacuum pressure was maintained in a nearly constant of 13 mPa. Therefore, it is reasonable to assume that at the lower temperatures, where $P_{\text{TiO}}^0$ is smaller than the environmental pressure of 13 mPa, $P_{\text{TiO}}$ is equal to $P_{\text{TiO}}^0$, and at higher temperatures, where $P_{\text{TiO}}^0$ is larger than 13 mPa, $P_{\text{TiO}} = 13$ mPa. On this assumption and from the criterion of $\Delta G_5 < 0$, the critical temperature for the evaporation of TiO, $T_c$, is calculated to be 1810 K. This is naturally a rough approximation, because the actual partial pressure of TiO is not equal to the environmental pressure. However, the estimated critical temperature is approximately equal to the experimental one, 1750 K, as shown in Fig. 3.

From the above discussion, it is considered that the disappearance of TiO film above 1750 K arises from the direct evaporation of the TiO film under vacuum pressure.

Obviously from eq. (6), the critical temperature determined by the criterion of $\Delta G_5 < 0$ strongly depends on the vacuum pressure or $P_{\text{TiO}}$, and decreases with the decrease in the vacuum pressure.

From the evidence that the growth rate of the LFZ is controlled by the diffusion of C atoms at the higher temperatures where the TiO film is not formed, the C atoms are considered to be removed from the surface by the reaction,

\[ 2\text{[C]} + \text{O}_2 \rightarrow 2\text{CO}; \]
\[ \Delta G^\circ_7 = -53400 - 41.90T. \] \hspace{1cm} (7)

With the reduction of C concentration in the matrix, the TiC phase dissolves into the matrix and disappears. The solid solubility of Ti in Mo rapidly increases with the decrease of C content. At the present test temperatures, Mo and Ti make a homogeneous solid solution.

The fact that the concentration of Ti in the LFZ decreases toward the surface as shown in Fig. 6, shows that the Ti atoms are also removed from the surface by means of evaporation as TiO gas.

At the lower temperatures where the TiO film is formed on the surface, the diffusion of C atoms toward the surface, which is necessary for the reaction of eq. (7) is considered to be retarded by this oxide film.

It is well known that the vapor pressure of MoO$_3$ is very high. Then, the formation of MoO$_3$ by the oxidation of Mo phase (Mo$\rightarrow$MoO$_2$$\rightarrow$MoO$_3$) might also participate in the surface reaction mentioned above. However, the formation of MoO$_3$ is hardly considered under the present experimental conditions, because above 1917 K the value of $\Delta G = \Delta G^\circ + RT \ln P_{\text{O}_2}$ for eq. (4) becomes positive, and at all test temperatures the reactions of (3a)$\rightarrow$(3c) and (3) prevail. As a result, the Mo phase is stable as far as the resolved C and Ti atoms are present in it.

### V. Conclusions

In order to investigate the thermal stability of lamellar structure, a Mo-TiC eutectic lamellar composite was heated at 1523$\sim$2223 K for $5.76 \times 10^4 \sim 3.6 \times 10^5$ s (16$\sim$100 h) under a vacuum of 13 mPa and the structure change was examined. The results obtained are as follows.

1. Above the critical temperature of about 1750 K, TiC phase near the surface of the specimen disappears and a lamella free zone (LFZ) is formed. Further a lot of voids are formed in the LFZ.
2. On the other hand, below the critical temperature the formation of LFZ is hardly observed, and TiO film is formed on the surface.
3. The width of LFZ increases proportionally with 1/2th power of the holding time.
The activation energy for the disappearance of TiC phase is about 117 kJ/mol, which is very close to the value for the diffusion of C atoms in Mo matrix.

This shows that the disappearing process is controlled by the diffusion of C atoms through the Mo matrix to the surface.

(3) The critical temperature for the disappearance of TiC phase and the formation of TiO film is determined by a balance of the equilibrium vapor pressure of TiO and the vacuum pressure around the specimen.

Above the critical temperature, the equilibrium vapor pressure is higher than the vacuum pressure and TiC phase disappears near the surface, which is considered to occur by the process that the C and Ti atoms dissolved in the matrix are removed at the surface by CO gas formation and TiO evaporation, respectively.

On the other hand, at the lower temperatures the equilibrium vapor pressure of TiO is lower than the vacuum pressure, and then the evaporation of TiO is so slow that the TiO film is formed on the surface.

Therefore, the fact that the width of the LFZ is hardly observed at the lower temperatures shows that the diffusion of C atoms toward the surface is retarded by the oxide film.

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