The Precipitation of Molybdenum Carbides during the Isothermal Decomposition of an Fe-4.10%Mo-0.23%C Austenite*

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Synopsis

The precipitation of carbides during the isothermal decomposition of an Fe-4.10%Mo-0.23%C austenite has been studied by transmission electron microscopy.

In austenite, coarse M_6C particles and Mo_2C fibres were observed to form at temperatures higher than 750°C. The eutectoid reactions occurred with either M_6C at temperatures from 800° to 750°C, or Mo_2C in the range between 750° and 650°C. This M_6C formed in the shape of fine particles aligned parallel to the ferrite/austenite interface, whereas the Mo_2C precipitation exhibited two different morphologies, i.e., the rows of the Mo_2C rods parallel to the ferrite/austenite interface, and the long thin Mo_2C needles with their growth direction nearly perpendicular to the interphase boundary. The crystallographic relationships between these carbides and ferrite were determined and the mechanism of their formation was discussed.

I. Introduction

The creep rupture properties of alloy steels containing molybdenum can remarkably be improved by heat treatment, and it has recently been reported by Yukitoshi and Nishida¹⁾ that the fully annealed steels exhibited much better long time creep properties than those quenched and tempered. Although they explained such behaviours in terms of carbide morphology, the crystallographic aspects of those carbide precipitations have not been fully analysed.

The precipitation of molybdenum carbides during the isothermal decomposition of alloy austenite has been the subject of numerous investigations for these years. Sato *et al.*²⁾ have shown that the carbide phase formed during the isothermal transformation at 700°C varied with increasing the Mo/C atomic ratio from M_3C to $M_{23}C_6$, $M_{23}C_6 + M_aC_b$, $M_aC_b + M_{23}C_6 + Mo_2C$, $Mo_2C + M_aC_b$, $Mo_2C + M_6C$, and finally to M_6C . In the case of comparatively high Mo/C atomic ratio,

both M_6C and Mo_2C precipitate at temperatures from 600° to 850°C,²⁻⁵⁾ and the M_6C particles originate at the austenite grain boundaries,^{4,5)} whereas Mo_2C being formed either as fibres³⁻⁶⁾ or as the very fine needles on parallel sheets.^{4,5)} Berry *et al.*^{4,5)} explained the latter Mo_2C morphology in terms of the austenite/ferrite interphase precipitation in a fashion similar to V_4C_3 particles formed during the isothermal transformation.^{7,8)}

The aim of the present work is to extend the study by Berry *et al.*⁴⁻⁶⁾ and to obtain further information on the carbide precipitation in an Fe-Mo-C alloy.

II. Experimental Procedure

A high purity iron alloy containing 0.23%C and 4.10%Mo was prepared by a 20 kg vacuum induction furnace and was forged into rods of 15 mm square cross section. The 2 mm thick specimens for optical and electron metallographies were sliced from the rods, and austenitized for 10 min at 1200°C in argon atmosphere. They were transformed isothermally in a lead bath held at appropriate temperatures from 400° to 850°C and quenched into iced brine to suppress further isothermal decomposition of the untransformed austenite.

Thin foils were prepared by the technique of Bollmann⁹⁾ using the phosphoric-chromic acid electrolyte and were examined in a HITACHI HU-200 microscope operated at 200 kV.

III. Experimental Results and Discussion

1. T.T.T. Diagram

The T.T.T. diagram was determined by optical

Fig. 1.
The T.T.T. diagram of the Fe-4.10%Mo-0.23%C alloy austenitized at 1200°C for 10 min

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shown in Photo. 3. This indicates that the fibrous Mo_2C carbide formed prior to the precipitation of the fine M_6C particles which are believed to have precipitated at the austenite/ferrite interphase boundaries as described in the following chapter.

3. Eutectoid Reaction

The eutectoid decomposition of the austenite occurred in two different ways, *i.e.*, the one comprised ferrite and M_6C , and the other consisted of ferrite and Mo_2C .

1. Interphase Precipitation of M_6C

Photograph 4 shows an example of the interphase precipitation of M_6C particles which occurred in the

range between 800° and 750°C , and it can be seen that the rows of fine carbide particles lay parallel to the ferrite/austenite (martensite) interface in a similar way as V_4C_3 particles in the isothermally transformed vanadium steels.^{7,8)} It is interesting to note that the carbide free area also exists in the ferrite grain which involves the fine M_6C particles as sheets parallel to the austenite/ferrite interface. This suggests that the growth direction of the ferrite in austenite is quite significant for the carbide precipitation and that the austenite/ferrite interface with a specific orientation

Photo. 4.
The rows of fine M_6C particles parallel to the ferrite/austenite interface formed at 800°C for 1 min

Photo. 3.
The structure consisting of the Mo_2C fibres and the fine M_6C particles formed by the ferrite/austenite interphase reaction at 750°C for 5 min

Photo. 5. The M_6C interphase precipitation occurred at 750°C for 30 min: (a) the bright field image, (b) the dark field image using the $(440)_{\text{M}_6\text{C}}$ reflection, (c) the electron diffraction pattern, and (d) its schematic representation

provides the potent nucleation sites for M_6C particles. Photographs 5 (a) and (b) show also the ferrite grain with the M_6C interphase precipitation formed at 750°C for 25 min, and the selected area electron diffraction pattern and its schematic representation are in Photos. 5 (c) and (d) respectively. The diffraction pattern arising from a similar area is shown in Photos. 6 (a) and (b). These electron diffraction patterns indicate that the M_6C particles formed by the interphase precipitation are related to the ferrite with the orientation relationship given as:

$$\begin{aligned}(2\bar{1}1)_{M_6C} & // ((0\bar{1}1)_\alpha \\ (011)_{M_6C} & // (\bar{1}11)_\alpha \\ (11\bar{1})_{M_6C} & // (211)_\alpha.\end{aligned}$$

The meaning of this relationship is not clear at present because of the insufficient information about the M_6C /austenite relationship.

2. Precipitation of Mo_2C

The eutectoid reaction producing Mo_2C and ferrite occurred in the range between 750° and 650°C, and leads to two distinct morphologies as has been observed by Berry *et al.*,⁴⁻⁶ *i.e.*, the Widmanstätten precipitation of Mo_2C on parallel sheets and the long thin needles of Mo_2C . Photographs 7 (a) and (b) illustrate the parallel rows of Widmanstätten Mo_2C rods, and the analysis of the diffraction pattern (Photos. 7 (c) and (d)) shows that the Mo_2C rods are related to the ferrite by the Pitsch and Schrader orientation relationship,¹² $[001]_\alpha // [1\bar{2}10]_{Mo_2C}$ and $(\bar{1}10)_\alpha // (0001)_{Mo_2C}$, and agrees with the previous observations.⁴⁻⁶ The growth direction of the rods is close to the minimum

misfit direction between Mo_2C and ferrite, *i.e.*, $[001]_\alpha // [1\bar{2}10]_{Mo_2C}$, and is nearly parallel to the austenite/ferrite interface.

Photo. 6. The diffraction pattern arising from an area similar to Photo. 5: (a) the selected area electron diffraction pattern and (b) its schematic representation

Photo. 7. Widmanstätten Mo_2C rods in parallel rows formed at 750°C for 25 min: (a) the bright field image, (b) the dark field image using the $(1120)_{Mo_2C}$ reflection, (c) the diffraction pattern, and (d) its schematic representation

Photograph 8 (a) is, on the other hand, an example of the eutectoid reaction with long thin Mo_2C needles. The Mo_2C /ferrite orientation relationship is, however, definitely not the Jack type¹⁰⁾ but the Pitsch and Schrader type¹²⁾ with the $[001]_\alpha // [\bar{1}2\bar{1}0]_{\text{Mo}_2\text{C}}$

Photo. 8. Parallel Mo_2C needles formed by the eutectoid reaction at 750°C for 5 min: (a) the bright field image, (b) the electron diffraction pattern, and (c) its schematic representation

growth direction. This can be seen in Photos. 8 (b) and (c), where the $(10\bar{1})_\alpha$ is 5° from the $(0\bar{1}11)_{\text{Mo}_2\text{C}}$ and the $(101)_\alpha$ is 5° from the $(\bar{1}101)_{\text{Mo}_2\text{C}}$. These separations are in conformity with what would be expected for the Pitsch and Schrader relationship,¹²⁾ whereas in the case of the Jack relationship¹⁰⁾ they should be 8° and 1° respectively. Thus, the Mo_2C needles formed by the eutectoid reaction can easily be distinguished from the Mo_2C fibres which precipitated in austenite. In this case of the eutectoid reactions, the growth direction of the Mo_2C needles are perpendicular to the previous austenite grain boundary, suggesting that the edgewise growth of the needles which were enclosed by ferrite occurred in austenite.

Photograph 9 (a) shows the previous austenite grain boundary from which the ferrite grains grew into both sides separately. It can be seen that, in one side

Photo. 9. The eutectoid reaction originating at the austenite grain boundary at 650°C for 2 hr: (a) the bright field image, (b) the dark field image using the $(0\bar{1}11)_{\text{Mo}_2\text{C}}$ reflection, (c) the diffraction pattern, and (d) its schematic representation

of this boundary, the fine Mo_2C particles on sheets formed, whereas, in the austenite grain of the other side, the Mo_2C needles originated with their growth direction almost perpendicular to the growing ferrite/austenite interface. The diffraction pattern from the latter area, Photos. 9 (c) and (d), indicates that the Mo_2C was related to the ferrite with the Pitsch and Schrader orientation relationship,¹²⁾ and the dark field image using a Mo_2C reflection confirms that the carbides in the two distinct morphologies are responsible for these reflections.

4. Over-aged Structures

During the isothermal transformation, over-aging took place in the area where the decomposition of the austenite had occurred initially. Thus both newly precipitated carbides after the ferrite formation and the transformation of the carbides during the isothermal holding were able to be observed.

1. The Mo_2C Precipitation in Ferrite

Although the $\langle 11\bar{2}0 \rangle_{\text{Mo}_2\text{C}} // \langle 100 \rangle_\alpha$ growth direction of the Mo_2C which formed during the isothermal transformation aligned specifically either almost parallel or perpendicular to the advancing ferrite/austenite interphase boundaries, the other variants of the growth directions similar to the Mo_2C rods found in tempered martensite^{13,14)} or in quench-aged ferrite¹⁵⁾ were observed as well. Photograph 10 shows such Mo_2C rods with three equivalent growth directions in addition to the parallel rows of Mo_2C with a specific orientation. Photograph 11 illustrates the area where similar Mo_2C rods were precipitated between the rows of M_6C particles formed by the interphase reaction.

The existence of such Mo_2C rods suggests that they formed exclusively in ferrite after the austenite $\rightarrow$ ferrite transformation.

2. The Transformation of Mo_2C into M_6C

In the over-aged specimens, the diffraction patterns corresponding to the M_6C type cubic structure often arose from the carbide similar in appearance to Mo_2C and the orientation relationship between such M_6C and ferrite could not be explained by that described above. Photograph 12 (a) illustrates an example in which the Mo_2C fibres transformed into M_6C , and the selected area electron diffraction pattern, Photos. 12 (c) and (d), and the dark field image using a M_6C reflection indicate that at least some parts of the fibres

were M_6C . Photograph 13 (a) is the area where the Mo_2C rods formed by the interphase reaction decomposed into M_6C , and the dark field image using a M_6C reflection, the associated electron diffraction pattern, and its schematic representation are in Photos. 13 (b), (c), and (d) respectively.

These observations, thus, indicate that the transformation from Mo_2C into M_6C occurred during the isothermal holding.

5. Importance of the Austenite/Ferrite Interface Orientation

In the present work, it was confirmed that the eutectoid reaction occurred with two different carbides, M_6C or Mo_2C . One of the factors which are concerned with the crystal structure of carbides is the temperature range where the reaction occurs, and since M_6C is more stable phase than Mo_2C , M_6C particles will form at higher temperatures.¹⁶⁾ It was, however, observed that both carbides were precipitated at 750°C by the eutectoid reaction, suggesting that there exist some other factors which control the carbide structure. It is interesting to note that the Mo_2C rods or needles formed by the interphase reaction had the growth direction either nearly parallel or perpendicular to the advancing ferrite/austenite interfaces, and that the growth directions inclined to the interfaces with intermediate angles were observed less frequently. Thus, the importance of the advancing ferrite/austenite interface orientation should be recognized, and this can be argued as follows.

When carbides form at the ferrite/austenite interface, the free energy to form the carbides will be much reduced by choosing a suitable orientation relationships among three phases as in the case of the bainitic

Photo. 11. The M_6C interphase precipitation with over-aged Mo_2C rods (transformed for 30 min at 750°C)

Photo. 10. The rows of Mo_2C rods formed by the interphase reaction with the over-aged Mo_2C rods in three equivalent growth directions (transformed for 30 min at 750°C)

Photo. 12. The transformation from Mo_2C fibres to M_6C (transformed for 2 hr at 800°C): (a) the bright field image, (b) the dark field image using the $(224)_{\text{M}_6\text{C}}$ reflection, (c) the diffraction pattern, and (d) its schematic representation

Photo. 13. The transformation from the Mo_2C rods formed by the interphase reaction into M_6C (transformed for 2 hr at 700°C): (a) the bright field image, (b) the dark field image using the $(224)_{\text{M}_6\text{C}}$ reflection, (c) the diffraction pattern, and (d) its schematic representation

reaction where the Isaichev,¹⁷⁾ the Kurdjumov-Sachs,¹¹⁾ and the Pitsch orientation relationship¹⁸⁾ are achieved between ferrite and cementite, between austenite and ferrite, and between austenite and cementite respectively.^{19,20)}

In the case of Mo_2C , similar relationship can be

obtained in a specific way and given as:

$$\begin{aligned} (0001)_{\text{Mo}_2\text{C}} // (110)_\alpha // (111)_\gamma \\ [11\bar{2}0]_{\text{Mo}_2\text{C}} // [001]_\alpha \ 5^\circ \text{ from } [1\bar{1}0]_\gamma \end{aligned}$$

This consists of the Kurdjumov-Sachs relationship¹¹⁾ between ferrite and austenite, the Pitsch and Schrader

relationship¹²⁾ between Mo_2C and ferrite, and the austenite/ Mo_2C orientation relationship close to the familiar one⁴⁾ described as: $(0001)_{\text{Mo}_2\text{C}} // (111)_\gamma$, $(11\bar{2}0)_{\text{Mo}_2\text{C}} // (1\bar{1}0)_\gamma$, and can explain why only the Mo_2C rods or needles with a specific orientation formed by the eutectoid reaction. Since the diffusion of the atoms are much enhanced along the austenite/ferrite interface compared with that in the austenite matrix, it is likely that the Mo_2C rods nucleate with their growth direction parallel to this interface. Whereas if they originate with their growth direction perpendicular to the interphase boundary, the growth directions of both phases are coincident, and the Mo_2C rods can grow cooperatively with the ferrite, resulting in the parallel long thin needles similar in appearance to the pearlite reaction (Photo. 8 (a)).

In order to achieve such requirements, the $[001]_\alpha$ 5° from $[1\bar{1}0]_\gamma$ should be either almost parallel or perpendicular to the advancing ferrite/austenite interphase boundary. Thus the Mo_2C interphase precipitation can occur when these requirements are satisfied at the intermediate temperatures where both M_6C and Mo_2C can form, and the interphase reaction might be accompanied by the precipitation of M_6C particles when the orientation of the interface is deviated from those described above. At lower temperatures, however, the carbides will be confined to Mo_2C and will precipitate with their growth directions determined solely by the orientation relationship described above.

IV. Conclusions

The precipitation of molybdenum carbides in an Fe-4.10%Mo-0.23%C alloy during the isothermal transformation was investigated mainly by means of transmission electron microscopy, and the following results were obtained:

(1) In austenite, two carbide reactions occurred: The one is the precipitation of the coarse M_6C particles at the austenite grain boundaries in the range between 850° and 750°C . The other is the fibrous Mo_2C precipitation in the range between 800° and 750°C .

(2) The eutectoid reaction induces the formation of two different carbides. At temperatures from 750° to 800°C , fine M_6C particles were formed by the austenite/ferrite interfaces as parallel rows. Reducing the transformation temperature in the range between 750° and 650°C , either Widmanstätten Mo_2C rods or long thin Mo_2C needles formed. In the former, the growth direction of Mo_2C was almost parallel to the advancing ferrite/austenite interface, whereas in the latter, it lay nearly perpendicular to the interface.

(3) The M_6C /ferrite orientation relationship in the case of the interphase reaction lay close to:

$$\begin{aligned} (2\bar{1}1)_{\text{M}_6\text{C}} // (0\bar{1}1)_\alpha \\ (011)_{\text{M}_6\text{C}} // (\bar{1}11)_\alpha \\ (11\bar{1})_{\text{M}_6\text{C}} // (211)_\alpha \end{aligned}$$

(4) The Mo_2C formed by the eutectoid reaction was related to the ferrite by that of Pitsch and Schrader¹²⁾ with the $\langle 100 \rangle_\alpha // \langle 11\bar{2}0 \rangle_{\text{Mo}_2\text{C}}$ growth direction, but the Jack type relationship¹⁰⁾ has never been observed except for the precipitation in austenite.

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