Mechanism of Formation of Lined-up V_4C_3 Precipitates in Low Carbon Vanadium Steels*

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Synopsis

The mechanism of formation of lined-up V_4C_3 particles in continuously cooled or isothermally transformed 0.15% C–0.2% V and 0.05% C–0.5% V steels has been studied. There were arrays of long dislocations and dislocations decorated with V_4C_3 precipitates in the proeutectoid ferrite when cooled rapidly from austenite. The size and orientation of lined-up V_4C_3 particles were nearly the same within an array, suggesting that these carbides were formed nearly simultaneously. The formation of lined-up V_4C_3 particles has no relation to the growth rate of the proeutectoid ferrite in these steels. The morphology of lined-up V_4C_3 particles observed by thin foils is the same as that by extraction replicas. Thus, it is suggested that these lined-up V_4C_3 particles are formed by the precipitation not on the advancing γ - α grain boundaries as suggested by Gray and Yeo, but on dislocations introduced by the γ - α transformation.

I. Introduction

It has been well known that lined-up NbC carbides are observed in as-rolled as well as continuously cooled niobium steels. The formation mechanism of such lined-up precipitates has been discussed by many researchers. For instance, Leslie¹⁾ suggested that parallel lines of NbC particles marked the former locations of subboundaries formed during and after hot-rolling, or the successive positions of austenite grain boundaries, or of γ - α boundaries. Morrison,²⁾ on the other hand, considered that the nucleation sites of these carbides were dislocations introduced by the γ - α transformation.

Tanino *et al.*³⁾ found that V_4C_3 carbides also precipitated in fairly parallel rows in the proeutectoid ferrite of 0.15% C–0.2% V steels subjected to continuous cooling from austenite. They considered that the origin of such lined-up V_4C_3 particle was lattice defects introduced by the γ - α transformation. Davenport *et al.*⁴⁾ reported that V_4C_3 carbides formed as bands of very fine particles at the γ - α interface during the transformation, and that this type of precipitation predominated in a 0.2% C–2% V steel, which was solution treated at 1300°C and subsequently transformed isothermally in the range of 500° to 700°C.

Recently, Gray and Yeo⁵⁾ investigated the distribution of NbC particles in a 0.02% C–0.5% Mn–0.1% Nb steel mainly by means of carbon extraction replicas, and proposed a model of the formation mechanism of

lined-up NbC particles; the nucleation and growth of these precipitates occur at the γ - α interface, and the layers of precipitation are formed as the results of the passage of the interface in small, abrupt steps through the matrix during transformation. According to their model, lined-up particles revealed by carbon extraction replicas correspond to sections through the layers of the precipitation, and the spacing between the successive layers of precipitation increases as the cooling rate decreases. They have discussed that general matrix precipitation occurs and precipitate-rows are absent when precipitation is delayed until γ - α transformation is completed. Furthermore, they have insisted that the same model is applicable to lined-up V_4C_3 particles observed in continuously cooled vanadium steels.

When a niobium or vanadium steel is quenched and tempered, these lined-up carbides can not be observed at all. Therefore, it is sure that the formation of the lined-up NbC or V_4C_3 carbides are closely related with the γ - α transformation. However, the mechanism of the γ - α transformation, *i.e.*, the nucleation and growth characteristics of the proeutectoid ferrite and the detailed structure of the γ - α interface have not been elucidated yet. Thus, it seems to be very difficult to correlate directly the formation process of these lined-up carbides with the γ - α transformation.

The present investigation was made to obtain a more systematic evidence concerning lined-up V_4C_3 particles in low carbon vanadium steels through the detailed observation of the growth behavior of the proeutectoid ferrite and the distribution of carbide particles. Most of experimental results were compared with those of niobium steels studied by Gray and Yeo.⁵⁾

II. Experimental

Steels used were prepared by vacuum-melting and cast into 15 kg ingots, which were hot-rolled into slabs of about 7 mm thick. Chemical compositions of steels are shown in Table 1. The 0.2V-steel has a typical ferrite-pearlite structure, and the 0.5V-steel has a pearlite-free ferritic structure when cooled from austenite. Specimens for hardness test, 10 × 10 × 5

Table 1. Chemical compositions of steels (wt%)

Steel	C	V	Si	Mn	P	S	O	N _{sol}	N _{insol}
0.2V	0.16	0.20	0.01	<0.01	0.003	0.003	<0.001	0.0007	0.0012
0.5V	0.046	0.51	0.01	<0.02	0.004	0.004	0.004	0.0003	0.0025

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mm³, and tensile test, 90 × 10 × 0.6 mm³, were austenitized for 1 hr at 1 050° or 1 200°C and were subjected to various types of heat treatments; continuous cooling to room temperature, quenching from various temperature in the course of continuous cooling, and isothermal transformation. "Two-stage aging" was also made using "Formastor-F" dilatometer. Specimens of 4 mm in diameter and 6 mm in length were austenitized for 1/2 hr at 1 200°C, gas quenched to a predetermined intermediate temperature, held for some time at the temperature, then reheated to temperatures just below or above Ac₃ point followed by continuous cooling to room temperature.

The distribution of V₄C₃ particles was examined by means of carbon extraction replicas as well as thin foils. Particular emphasis was laid on the morphology of lined-up V₄C₃ particles.

III. Experimental Results

1. Some Typical Features of Lined-up V₄C₃ Particles

Photographs 1 and 2 show typical electron micrographs of lined-up V₄C₃ particles revealed by carbon extraction replicas in the proeutectoid ferrite of an

isothermally transformed 0.5V-steel. Most of arrays, a group of lined-up particles, ran parallel to each other, while some of them intersected with each other, or branched off or terminated on the way. In some regions, dispersed V₄C₃ particles were also observed among or at the end of these lined-up particles. The morphology of lined-up particles in the 0.2V-steel (ferrite+pearlite) was quite similar to that of the 0.5V-steel (pearlite-free). On the average, 40 to 50% of total precipitates were lined-up except for overaged state. The size of particles became coarser as the cooling rate was decreased or transformation temperature was increased. The spacing between the precipitate line showed similar tendency, but it was widely scattered from 0.01 to 0.1 μ even in a specimen. Thus, in contrast with the results of Gray and Yeo,⁵⁾ no clear correlation between the cooling rate and the spacing could be derived from the present study.

The morphology of lined-up particles observed by thin foils was the same as that of extraction replicas. Typical results of thin foil observations are summarized as follows; there were arrays of long dislocation trails (Photo. 3), straight dislocations decorated with V₄C₃ precipitates (Photo. 4), two groups of parallel rows

Photo. 1. Lined-up V₄C₃ particles in the proeutectoid ferrite of an isothermally transformed 0.5V-steel; isothermally treated for 20 hr at 600°C (extraction replica)

Photo. 3. Long dislocation trails introduced by the γ-α transformation. 0.2V-steel continuously cooled from austenite at 80 deg C/min (thin foil).

Photo. 2. Lined-up V₄C₃ particles intersecting with each other. Same specimen as Photo. 1 (extraction replica).

Photo. 4. Straight dislocations decorated with V₄C₃ particles. 0.5V-steel isothermally treated for 5 hr at 600°C (thin foil).

Photo. 5. Lined-up V_4C_3 particles intersected with each other. 0.5V-steel isothermally treated for 100 hr at 600°C (thin foil).

Photo. 6. Irregularly arranged V_4C_3 particles. 0.5V-steel isothermally treated for 20 hr at 600°C (thin foil).

intersected with each other (Photo. 5), and irregularly arranged lined-up particles (Photo. 6). Furthermore, the size of particles was nearly the same within an array as shown in Photo. 7 (a). Photograph 7 (b) is a dark field micrograph of the area in Photo. 7 (a) taken with a V_4C_3 reflection. The orientation relationship between the carbide and the matrix was found to be the same as that proposed by Baker and Nutting.⁶⁾ It is noted that all of lined-up particles have the same orientation relationship with the ferrite matrix. The configuration of these precipitate lines did not change when a foil was tilted.

2. The Relation between the Growth of the Proeutectoid Ferrite and the Formation of Lined-up V_4C_3 Particles

In order to investigate whether there is a close relation between the nucleation and growth of the proeutectoid ferrite and the formation of lined-up V_4C_3 particles or not, two experiments were performed. One is quenching in the course of continuous cooling and the other is two stage aging.

Photograph 8 shows an optical micrograph taken from a 0.2V-steel which was quenched into iced-brine from 750°C, just below A_{r3} point, in the course of con-

Photo. 7. 0.5V-steel isothermally treated for 5 hr at 600°C (thin foil). Note that the size and orientation of V_4C_3 particles are nearly the same within an array.

- (a) Bright field
- (b) Dark field of the same area as (a)

Photo. 8. Optical micrograph of 0.2V-steel quenched from 750°C, just below A_{r3} point, in the course of continuous cooling from austenite at 20 deg C/min. The arrow indicates the prior austenite grain boundary. ($\times 500$)

tinuous cooling at the cooling rate of 20 deg C/min. The amount of the proeutectoid ferrite was about 30% in volume, and the remaining part was martensite. It is noted that prior austenite grain boundary (indicated by the arrow) and also precipitated particles are visible at the center of this micrograph. In this case, proeutectoid ferrite was nucleated at the austenite grain

boundary and grew at first along it.* When the cooling rate became faster than 60 deg C/min, proeutectoid ferrite grew into the direction perpendicular to the prior austenite grain boundary, and acicular ferrite was formed. Accordingly, arrangement of lined-up particles should be affected by the cooling rate if there is a close correlation between the nucleation and growth of the proeutectoid ferrite and the formation of lined-up particles.

Experimental results, however, did not indicate any correlation between them. Lined-up particles observed by carbon extraction replicas are shown in Photo. 9, which was taken from the same specimen as described in Photo. 8. Relatively regularly arranged lined-up V_4C_3 particles were observed, but the length of each line was not uniform. It was confirmed that precipitated particles seen in Photo. 8 corresponded to lined-up V_4C_3 particles. The optical micrograph shown in Photo. 8, together with the results of carbon extraction replica shown in Photo. 9, makes sure that some of these lined-up particles were arranged at a large angle with the prior austenite grain boundary. The fact that prior austenite grain boundary looked like a denuded zone was also clarified by thin foil observations** (Photo. 10). Furthermore, quite regularly arranged dislocations were often seen in the proeutectoid ferrite grain adjacent to the region of the martensite which was austenite before quenching (Photo. 11). It is noted that fine V_4C_3 particles were observed along these dislocations (Photo. 11 (b)).

Another result which conflicts with the γ - α interface precipitation model is that of two-stage aging treatments. Precipitation characteristic was examined by changing the growth behavior of the proeutectoid

ferrite in the following manner; after small amounts of acicular ferrite was produced at the prior austenite grain boundary by rapid cooling to 690°C, below Ar_3 , remaining part of austenite was transformed into polygonal ferrite by up-quenching the specimen into a higher temperature just below Ac_3 . It might be expected that, if lined-up particles are formed at the advancing

Photo. 9. Extraction replica of the same specimen as Photo. 8. Note that the length of lined-up particles is not uniform (a), and these particles are arranged at an acute angle with the prior austenite grain boundary (indicated by the arrow) (a), (b).

Photo. 10. The configuration of lined-up V_4C_3 particles and the prior austenite grain boundary (the arrow) which looks like a denuded zone. 0.5V-steel isothermally treated for 20 hr at 600°C (thin foil).

* This process is morphologically termed by "grain boundary ferrite allotriomorphs."⁷⁾

** This evidence is consistent with the fact that vanadium carbides do not precipitate in austenite in this steel.⁷⁾

Photo. 11. Dislocation structures in the proeutectoid ferrite of 0.2V-steel quenched from 750°C in the course of continuous cooling. (b) is near area of (a). Note fine V_4C_3 particles are observed along these dislocations.

Photo. 12. Extraction replica of 0.2V-steel.
Heat treatment:
1 200°C × 30 min → 690°C × 1 min → 800°C ×
60 deg C/min 20 deg C/sec
15 min: He Q
Note that there were no lined-up V_4C_3 particles indicative of the precipitation on the advancing γ - α grain boundary.

γ - α grain boundary, the lines of particles would be at first perpendicular to and then along the prior austenite grain boundary. However, there were no lined-up

V_4C_3 particles indicative of the precipitation on the γ - α interface (Photo. 12). It conclusively follows that the growth of the proeutectoid ferrite is not related directly to the formation of lined-up V_4C_3 .

IV. Discussion

The experimental results described above indicate that there are several differences between the present results of low carbon vanadium steels and those of Gray and Yeo⁵⁾ obtained from a niobium steel.

In low carbon vanadium steels, there was no significant difference between the morphology of lined-up V_4C_3 particles observed by carbon extraction replicas and that by transmission electron microscopy. The spacing between each row of precipitates was widely scattered from 0.01 to 0.1 μ even in a specimen, and no clear correlation between the cooling rate and the spacing could be derived from the present studies. Furthermore, a large number of observations made by means of both carbon extraction replicas and transmission electron microscopy showed no evidence of a close relation between the direction of migration of the γ - α interface and the arrangement of lined-up V_4C_3 particles.

If the precipitation of lined-up V_4C_3 particles occurs at the γ - α interface and the layers of precipitation are formed as suggested by Gray and Yeo,⁵⁾ lined-up V_4C_3 particles observed by transmission electron microscopy must be very rare as compared with those by carbon extraction replicas, because most of V_4C_3 precipitates may be observed as dispersed particles and lined-up particles could be observed by thin foils only in the case when each layer arranges nearly parallel to the incident electron beam. In the present case, on the average 40 to 50% of total precipitates were lined-up except for overaged state. Thus, it is difficult to consider that Gray and Yeo's interface precipitation model is applicable to the case of lined-up V_4C_3 particles in low carbon vanadium steels.

The fact that there are lined-up V_4C_3 particles intersecting with each other (Photos. 2, 5) and very irregularly arranged particles (Photo. 6) strongly suggests that these V_4C_3 particles mark former locations of moving dislocations introduced by the γ - α transformation. The role of dislocations is important since V_4C_3 particles preferentially nucleate on dislocations when cooled from austenite in low carbon vanadium steels.⁸⁾ Furthermore, since most of lined-up V_4C_3 particles in the proeutectoid ferrite grain have nearly the same size and the same orientation relationship with the matrix (Photo. 7), it is concluded that these particles nucleate in the ferrite grain nearly simultaneously.

In contrast with the precipitation of niobium carbides in niobium steels, V_4C_3 particles precipitate in the proeutectoid ferrite immediately after the beginning of the γ - α transformation, and they grow and coagulate gradually during further cooling.⁸⁾ When the cooling rate is low enough, not only the number of nucleation sites which are produced by the γ - α transformation will be reduced because of annihilation of dislocations, but also lined-up V_4C_3 particles grow and

coagulate easily during further cooling. Therefore, the size and spacing of each lined-up particles may be controlled by factors such as the annihilation rate of dislocations, diffusion rate of vanadium atoms, and degree of supersaturation of vanadium carbide in ferrite matrix.

V. Summary

The formation mechanism of lined-up V_4C_3 particles in continuously cooled or isothermally transformed low-carbon vanadium steels was investigated by means of carbon extraction replicas as well as thin foils. Main results are as follows:

(1) There were arrays of long dislocations and dislocations decorated with V_4C_3 precipitates in the proeutectoid ferrite.

(2) The size and orientation of lined-up V_4C_3 particles were nearly the same within an array, suggesting that these carbides were formed nearly simultaneously.

(3) There were arrays intersecting with each other, or branched off or terminated on the way.

(4) The size of particles and the spacing between each line became coarser as the cooling rate was decreased, but the spacing was widely scattered from 0.01 to 0.1 μ even in a specimen.

(5) The formation of lined-up V_4C_3 particles had no relation to the growth of the proeutectoid ferrite in these steels.

(6) The morphology of lined-up particles observed by thin foils is the same in nature as that of extraction replicas.

(7) Thus, it is considered from the above-mentioned results that the origin of lined-up V_4C_3 particles is dislocations introduced by the γ - α transformation. It is difficult to interpret the observed lined-up V_4C_3 particles in terms of nucleation and growth of precipitates on the advancing γ - α grain boundaries.

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