Effects of Chromium, Molybdenum and Vanadium on Spheroidization of Carbides in 0.8% Carbon Steel*

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Synopsis

Effects of chromium, molybdenum and vanadium on spheroidization of carbides in 0.8% carbon steel by slow cooling annealing have been investigated.

An addition of chromium remarkably accelerates spheroidization of carbides, while additions of molybdenum and vanadium do a little. X-ray analysis of carbides indicates that M_3C and M_7C_3 are only carbides observed throughout the annealing process in 2% and 5% chromium steels, respectively. In molybdenum and vanadium steels, however, carbides formed by the eutectoid reaction are proved to differ from those surviving in austenite on annealing, i.e., $M_{23}C_6$ and M_3C are eutectoid carbides in molybdenum and vanadium steels respectively, while Mo_2C and VC survive in austenite in the steels respectively. Although the addition of any of these elements results in increasing amounts of undissolved carbides in austenite, the fact that chromium has a marked effect on spheroidization of carbides strongly suggests that an undissolved particle of carbides in austenite of chromium steels act as a center for the precipitation of eutectoid carbides since undissolved carbides coincide with eutectoid carbides. Thus it is concluded that coincidence of carbide precipitating during eutectoid reaction with that surviving in austenite will be of a primary importance in spheroidization of eutectoid carbides by slow cooling annealing.

I. Introduction

Spheroidizing of carbides is of primary importance to give ductility and toughness to high carbon steels such as tool steels and bearing steels. Although various annealing processes for this purpose are proposed, the process that the austenitized material is subject to the eutectoid transformation under sufficiently low super-cooling is widely used. The annealing cycle may be divided into two processes, that is austenitizing and cooling. Honda and Saito¹⁾ suggested that an inhomogeneous distribution of carbon atoms in austenite is necessary when the steel is austenitized, and locally concentrated carbon atoms in austenite may be assumed to favor the nucleation of carbide in subsequent eutectoid reaction, resulting in spheroidal carbide structure. Whiteley²⁾ proposed that undissolved carbide in austenite, which may be indispensable to spheroidize carbide may act as a center of precipitation of carbide in eutectoid transformation and consequently lead to a development of spheroidal structure. Nakano and Kawatani³⁾ performed a detailed investigation on the relation between the numbers of carbide particles retained in austenite when steels were austenitized and those existing after cooling, and found that the numbers of them coincided before and after cooling, which led them to the con-

clusion that retained carbide particles in austenite acted as centers of precipitation of carbide during subsequent eutectoid reaction.

The rate of cooling subsequent to austenitizing is also known to be an important factor to develop a spheroidized carbide structure. Miyoshi⁴⁾ studied the influence of reaction temperature on spheroidization of carbides using chromium steel by isothermal reactions at various temperatures below A_1 temperature and found that there was a critical temperature below which lamellar structures formed. Nakano and Kawatani³⁾ investigated the effect of the number of retained carbide on the rate of cooling necessary to obtain the fully developed spheroidized structure, and found that there existed a critical rate of cooling at and below which a fully spheroidal carbide structure was given and it was dependent upon the number of carbide particles retained in austenite, an increase of which resulted in the increase of the critical cooling rate.

The purpose of the present study is to investigate the effect of alloying elements on the spheroidization of carbide and the relation of the type of carbide retained in austenite to that formed during eutectoid reaction.

II. Experimental

0.8% carbon steels with and without an alloying element were employed. The chemical composition is given in Table 1. The steels were cast into 90 kg ingots after induction air melted, and forged into bars of 15 mm in diameter. The forged bars were homo-

Table 1. Chemical composition of steels (wt%)

Steel	C	Si	Mn	P	S	Cr	Mo	V
0.8%C	0.80	0.23	0.45	0.011	0.011	0.06	—	—
0.5%Cr	0.79	0.18	0.41	0.014	0.011	0.50	—	—
1%Cr	0.78	0.13	0.41	0.010	0.010	1.03	—	—
2%Cr	0.70	0.18	0.42	0.016	0.011	2.05	—	—
3%Cr	0.78	0.17	0.40	0.017	0.011	2.86	—	—
5%Cr	0.80	0.24	0.48	0.016	0.012	5.12	—	—
0.5%Mo	0.80	0.15	0.40	0.014	0.009	—	0.49	—
1%Mo	0.79	0.14	0.38	0.016	0.010	—	0.96	—
2%Mo	0.79	0.27	0.39	0.014	0.013	—	2.07	—
0.5%V	0.80	0.18	0.43	0.014	0.008	—	—	0.52
1%V	0.78	0.17	0.42	0.013	0.008	—	—	1.06

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genized in vacuum at 1 200°C for 50 hr before going any farther in the study. Microstructural measurement of carbide particles was carried out using a microscopic particle analyzer and carbide particles with ratios of the major axis to the minor less than 2 were defined to be spheroidal.⁵⁾

In order to make the structure pearlitic before spheroidizing carbides, molybdenum and vanadium steels and carbon and chromium steels were subjected to isothermal reactions at 600° and 700°C, respectively, for 15 hr after austenitizing at 1 000°C for 1 hr. Cooling at a rate of 20°C/hr followed for spheroidizing carbide austenitizing at 760° and 800°C for molybdenum and vanadium steels and at temperatures varying from 760° to 960°C for chromium steels. X-ray diffraction analysis was conducted on carbides extracted with the solution shown in Table 2.

III. Results

Photograph 1 illustrates microstructures of 0.8% carbon steel cooled at 20°C/hr after austenitizing at 760° and 800°C for 2 hr. It can be seen in Photo. 1 that austenitizing at 760°C makes, to a large extent, spheroidal carbide structures develop, while austenitizing at 800°C favors the development of lamellar structures. Degrees of spheroidization were examined

Table 2. Extraction solutions for carbides

Carbide	Method	Solution
Fe ₃ C (FeV) ₃ C	Electrolytically extracted	30% citric acid, 15% sodium citrate, 1.2% potassium bromide
(FeMo) ₃ C (FeCr) ₃ C	Electrolytically extracted	5% HCl in ethanol
Mo ₂ C Cr ₇ C ₃	Chemically extracted	55% phosphoric acid
VC	Electrolytically extracted	7% HCl, 3% FeCl ₃ , ethylene glycol

Photo. 1. Microstructures obtained by cooling 0.8% carbon steel at 20°C/hr after heating at (a) 760°C and (b) 800°C for 2 hr ($\times 1\,000$)

in chromium steels and results are shown in Fig. 1 as functions of chromium contents and austenitizing temperature where austenitizing time was 2 hr. It is seen in Fig. 1 that although 0.5% addition of chromium is not sufficient to give a fully spheroidal structure under the condition used here, increases of chromium addition expand to a great extent the range of austenitizing temperature to permit fully spheroidized carbide structures and thus are favorable to it. Photograph 2 illustrates carbide structures of molybdenum steels spheroidization-annealed by austenitizing at 760° and 800°C for 2 hr and subsequently cooling them at a rate of 20°C/hr. A large amount of spheroidal carbide is observed when austenitized at 760°C, comparing with that in 0.8% carbon steel in Photo. 1. A raise of austenitizing temperature to 800°C reduces the amount of spheroidized carbides and increases that of lamellar in the molybdenum steels. A small amount of molybdenum addition as little as 0.5% makes little difference from no addition in the amount of spheroidal carbide. Increasing amount of it, however, appears to increase the amount of spheroidal carbide to a lesser extent than that in chromium addition. A fully spheroidized carbide structure failed to develop in any molybdenum steels examined here under the condition used in present study. Since the amount of spheroidal carbides will be affected by the number of carbide particles retained in austenite, retained carbide particles in austenitized molybdenum steels were micrographically examined which are illustrated in Photo. 3. As seen in Photo. 3 the number of carbides in austenite increases with increase of molybdenum content and decreases with an increase of austenitizing temperature.

The carbide structure in vanadium steels was also investigated after austenitizing at 760° and 800°C for 2 hr and cooling at 20°C/hr, which is revealed in Photo. 4. It can be seen that addition of 0.5% vanadium does not affect markedly the amount of spheroidal carbides when austenitized at 760°C. An addition of 1% vanadium makes carbides massive. A raise of austenitizing temperature from 760° to 800°C results in the increasing amount of lamellar carbides in 1% vanadium steel. Addition of 1% vanadium increases the amount of spheroidized carbides when the steel is austenitized at 800°C, as seen

Fig. 1. Degree of spheroidization as a function of austenitizing temperature in steels containing various amounts of chromium cooled at 20°C/hr after austenitizing

(a) and (d): 0.5% molybdenum steel (b) and (e): 1% molybdenum steel (c) and (f): 2% molybdenum steel

Photo. 2. Microstructures obtained by cooling molybdenum steels at 20°C/hr after heating at (a), (b), (c) 760°C and (d), (e), (f) 800°C for 2 hr ($\times 1000$)

incomparison of Photo. 4 with Photo. 1. Although the increasing amount of vanadium addition increases the amount of spheroidized carbide, it could not develop fully spheroidized carbide structure under the condition used in the present study. Photograph 5 illustrates retained carbide in 1% vanadium steel when it is austenitized at 760°C for 2 hr. Thus it is noticed that chromium addition to 0.8% carbon steel is more favorable to spheroidizing carbide than molybdenum and vanadium additions.

An X-ray diffraction analysis of extracted carbides was performed. Results are summarized in Table 3 where carbides in as preheat treated, in austenitized, and in spheroidized states are shown. Although the amount of carbide extracted from the austenitized 0.5% molybdenum steel was too small to detect by means of X-ray diffraction technique, an electron microscopic observation of the steel revealed fine particles of carbide retained in austenite and they were presumed to be Mo_2C .⁶⁾ VC observed in the austenitized 0.5% vanadium steel, as shown in Table 3, may have presumably survived due to insufficient time for austenitizing. It should be noted that in the chromium steels type of carbides existing in the austenitized condition coincides with that observed after spheroidization whereas both in molybdenum and vanadium steels types of carbides observed in the austenitized state are different from those after spheroidization.

It was found, as illustrated typically in Photo. 6, that electron microscopic observations of carbides extracted from both molybdenum and vanadium steels after spheroidization-annealing revealed mixed morphologies of plate-like and globular carbides and an electron diffractometry proved plate-like carbide and globular one to be M_{23}C_6 and Mo_2C , respectively, in the molybdenum steels and M_3C and VC, respectively, in the vanadium steels. This observation strongly suggests that newly formed M_{23}C_6 and M_3C in eutectoid transformations in the molybdenum and vanadium steels, respectively, develop into plate-like whereas Mo_2C and VC retaining in austenite in molybdenum and vanadium steels, respectively may grow during the transformations, resulting in globulars. Coincidence of the type of carbides in the austenitized state with that after eutectoid reaction seems to play an important role in the development of spheroidal carbide structures.

IV. Discussion

In general, the formation of lamellar structure may be of the most favorable process in a sense that on the eutectoid transformation a large amount of carbide relative to the number of preferred nucleation site in austenite from which lamellar pearlite forms can precipitate without any increase of migration distance of the atoms associated with the transformation. How-

(a) and (d): 0.5% molybdenum steel (b) and (e): 1% molybdenum steel (c) and (f): 2% molybdenum steel
 Photo. 3. Microstructures obtained by quenching molybdenum steels after heating at (a), (b), (c) 760°C and (d), (e), (f) 800°C for 2 hr ($\times 1\,000$)

(a) and (c): 0.5% vanadium steel
 (b) and (d): 1% vanadium steel

Photo. 4. Microstructures obtained by cooling vanadium steels at 20°C/hr after heating at (a), (b) 760°C and (c), (d) 800°C for 2 hr ($\times 1\,000$)

Photo. 5. Microstructure obtained by quenching 1% vanadium steel after heating at 760°C for 2 hr

ever, the existence of a sufficient number of retained carbide particles in austenite will allow the development of spheroidal structure to become competitive, when undercooling is not large, as results of the dispensation of the nucleation process of carbide which is energy consuming and a favor with diffusion distance of the atoms.

Thus it is likely that the effect of retained carbide particles as precipitation sites in austenite in chromium steels is the most important factor to make a spheroidized carbide structure to develop under the condition of low undercooling. It should be recognized that carbide retained in austenite in chromium steels is the same in type with what is to be formed in the subsequent eutectoid transformation, which permits to dispense with the nucleation of carbide. In the molybdenum and vanadium steels, however, retained carbides in austenite are different in type from those formed in the subsequent eutectoid reaction which prevents retained carbides from acting as sites of precipitation of eutectoid carbide, although there are a large number of carbide particles survived in austenite. As indicated in Table 3, Mo_2C and VC are carbides retained in austenite in the molybdenum and vanadium steels, respectively which are known to be able to form on isothermal transformation of the steels.^{7,8)} Since solubility limits of substitutional elements in M_2C are as little as 0.3 for Cr, 0.3 for V, and 0 to 0.2 for Fe⁹⁾ in atomic ratio and that in MC is 0.15 for $\text{Fe}+\text{Cr}+\text{Mo}$ ⁹⁾ in atomic ratio, only a small amount of iron atoms can contribute to the formation of the carbides. Therefore, the amounts of molybdenum and vanadium in the steels used in the present study are too small to catch a large amount of carbon as Mo_2C and VC which is squeezed out of austenite in eutectoid transformation of the steels and the excessive amount of carbon squeezed out of austenite will be forced to form a different type of carbide, which grows into plate-like as shown in Photo. 6. Thus, the carbide to be retained in austenite should be the same in type as that formed in subsequent eutectoid reaction, in order to establish a well spheroidized carbide structure by spheroidizing annealing. Whether retained carbides in austenite can contribute to a sub-

Photo. 6. Carbide extracted from (a) 2% molybdenum steel and (b) 1% vanadium steel, spheroidization-annealed with cooling from 800°C at 20°C/hr

sequent eutectoid reaction or not may be governed by how much of carbon it can catch in the subsequent eutectoid reaction of the steel with a particular chemical composition. In low alloy steels the contribution of iron atoms becomes very large to catch a big amount of carbon as carbide, which is squeezed out of austenite in the eutectoid reaction, because the amount of substitutional carbide-forming alloying elements such as molybdenum, vanadium and chromium is not sufficient to produce their own carbide without including any other substitutional alloying element. M_{23}C_6 can include a large amount of iron as typically indicated by $\text{Fe}_{21}\text{Mo}_3\text{C}_6$ ¹⁰⁾ in molybdenum steels. On the other hand, M_7C_3 can dissolve 60% of iron to chromium in atomic ratio.⁹⁾ Even in 5% chromium steel, chromium content is stoichiometrically insufficient to form Cr_7C_3 but M_7C_3 can be formed with aid of iron dissolving in it, which allows particles of M_7C_3 retained in austenite to become centers of precipitation of the carbide which takes place during the eutectoid transformation. One of the reasons why the addition of the increasing amount of chromium favors development of spheroidized carbide structure is that it shifts the eutectoid composition of steels to a lower carbon side and consequently the temperature range where carbide can equilibrate with austenite is extended.

It is found that as another important factor to obtain a fully spheroidized structure, it is necessary to cool the steel from austenitic region at a rate below the critical cooling rate which is determined by the number of carbide particles retained in austenite.³⁾ In the present study, however, the failure of the development of a fully spheroidized structure in the molybdenum and vanadium steels will be ascribed to the dissociation of the carbide to precipitate during subsequent eutectoid transformation at austenitization, but not to the inadequacy of cooling rate. Therefore it is necessitated that the molybdenum and

Table 3. X-ray analysis of carbides in various steels examined

Steel	Preheat treatment	As preheat treated	In austenite	Spheroidized
2%Cr	1 000°C×1 hr → 700°C×15 hr	M ₃ C	M ₃ C*	M ₃ C*
	1 000°C×1 hr → 600°C×15 hr	M ₃ C	M ₃ C*	M ₃ C*
5%Cr	1 000°C×1 hr → 700°C×15 hr	M ₇ C ₃	M ₇ C ₃ *	M ₇ C ₃ *
0.5%Mo	1 000°C×1 hr → 600°C×15 hr	M ₃ C+M ₂₃ C ₆	trace*	M ₂₃ C ₆ +†Mo ₂ C*
1%Mo	1 000°C×1 hr → 600°C×15 hr	M ₂₃ C ₆	—	M ₂₃ C ₆ +†Mo ₂ C*
2%Mo	1 000°C×1 hr → 600°C×15 hr	M ₂₃ C ₆ +Mo ₂ C	Mo ₂ C**	M ₂₃ C ₆ +†Mo ₂ C*
0.5%V	1 000°C×1 hr → 600°C×15 hr	M ₃ C+VC	M ₃ C+VC**	M ₃ C+VC*
1%V	1 000°C×1 hr → 600°C×15 hr	M ₃ C+VC	VC**	M ₃ C+VC*

* 800°C×2 hr,

** 760°C×2 hr,

† identified by electron diffraction analysis

vanadium steels must be austenitized in such a manner that the appropriate number of particles of M₂₃C₆ and M₃C are retained in molybdenum and vanadium steels, respectively undissolved in austenite, and subsequently cooled down through eutectoid temperatures at an adequate rate.

V. Summary

The effects of chromium, molybdenum and vanadium on spheroidizing of carbides were investigated in 0.8% carbon steels and results obtained are summarized as follows:

(1) An increasing addition of chromium to 0.8% carbon steel makes it easy to give a fully spheroidized carbide structure. Additions of molybdenum or vanadium also increase the amount of spheroidized carbide, but fully spheroidized structures are failed to be obtained within their additions in the present study.

(2) X-ray analyses of extracted carbides disclose that carbides retained in austenite and after spheroidization are M₃C in 2% chromium steel and M₇C₃ in 5% chromium steel and retained carbides in austenite are Mo₂C in molybdenum steels and VC in vanadium steels, whereas M₂₃C₆ and Mo₂C are carbides in molybdenum steels and M₃C and VC in vanadium steels after spheroidizing annealing.

(3) Electron diffraction analyses reveal that plate-like carbides after spheroidizing annealing are M₂₃C₆ and M₃C in molybdenum and vanadium steels re-

spectively and globular Mo₂C and VC in molybdenum and vanadium steels respectively.

(4) The coincidence of the type of carbide surviving in austenite with that precipitating during eutectoid reaction subsequent to the austenitizing will be of primary importance in spheroidizing eutectoid carbides.

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