

OSTWALD GROWTH OF CARBIDE IN ISOTHERMAL SPHEROIDIZING PROCESS OF HOT-DEFORMED HIGH-CARBON CHROME CAST STEEL

WANG HAIYAN

In isothermal spheroidizing process, spheroidizing growth of the carbide formed from hot-deformed high-carbon chrome cast steel under high temperature is investigated. It shows that spheroidizing growth of carbide proceeds in such a way that the bigger carbide particles swallow the smaller ones and the short rhabdoid carbide dissolves and spheroidizes by itself. When isothermal time exceeds 3 hours, its spheroidization is not obvious. The feature of the process is the increment of the size of carbide particles and the decrement of their amount. The growth process accords well with Ostwald Ripening Law.

1. Introduction

High-carbon chrome cast steel shows good strength, hardness, and wear-resistance, and it has been widely used in high-speed abrasion and extrusion applications. Since the carbide in cast steel is distributed in the form of continuous network structure, its brittleness limits its wider application. Former experiment results show that if high-carbon chrome cast steel is hot-deformed, the network structure of carbide is broken, a large amount of granular carbide is precipitated from matrix, and its general mechanics properties are improved. However, the isothermal spheroidization of high-carbon chrome cast steel hot-deformed under high temperature is not studied in detail yet. Since the cast steel spheroidization quality determines its property [1], we investigate the appearance, the size, and the content change of carbide in isothermal spheroidization process of hot-deformed high-carbon chrome cast steel. Our experiment shows that spheroidizing growing of carbide is essentially the coarsening process of carbide dispersion-separated and accords with the Ostwald Law [2]. It perfects the traditional opinion that spheroidal carbide gradually precipitates and grows, with carbide particles left after austenitizing being its nucleating center. And it is instructive for investigating the carbide spheroidizing growing after this material is hot-deformed, for perfecting its spheroidization mechanism, and for determining spheroidizing technology.

2. Experimental Procedure

Experimental material is high-carbide chrome cast steel with carbon 2.15 wt %, silicon 0.58 wt %, manganese 0.82 wt %, chromium 6.15 wt %, phosphorus 0.035 wt %, and sulfur 0.031 wt %. It's smelted in medium frequency

electric induction furnace (250 Kg), and is cast in permanent mold into circular sample ($\phi 50 \times 60$ mm).

The sample is heated to 1000°C in electric resistance furnace KJX-8-13, and is held at this temperature for 40 min. The sample undergoes one-way compression deformation between flat anvils by air hammer 400 Kg, and its deformation amount is 40%. The deformed sample is immediately put into electric resistance furnace at 850 °C and is cooled to room temperature. After this, the cooled sample is taken out from the furnace and is cut into samples with the size of 10 \times 10 \times 20mm. Then the samples with the same size are put into another electric resistance furnace at 720°C and are kept at this temperature respectively for 30min, 60min, 120min, 180min, 240min, and 360min.

The appearance of the carbide in samples at different time during isothermal treatment is observed with metalloscope NEOPHOJ21 and

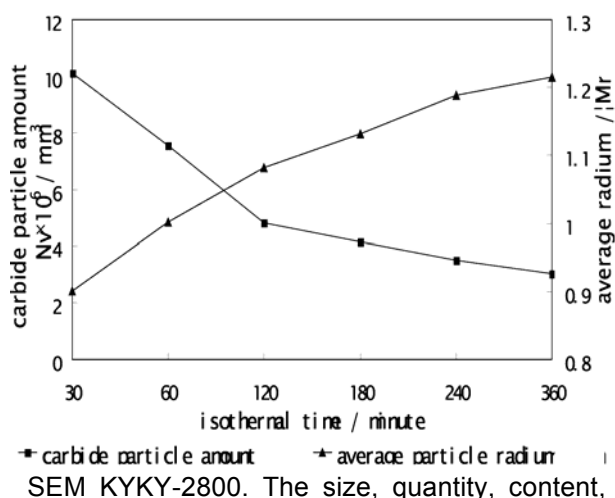


Fig. 1. Relationship between carbide particle amount or average particle radius with isothermal time

and growing rate of carbide are determined by means of the methods mentioned in literature [3, 4].

3. Results and Discussion

3.1 The Formation and Growth of Granular Carbide

The following phenomena are observed with metalloscope and SEM. At the beginning of isothermal treatment, most carbide in matrix is fine granular and few is short rhabdoed. Then the short rhabdoid carbide begins to dissolve and changes into granular ones. With isothermal treatment going on, short rhabdoid carbide vanishes gradually, and granular carbide grows up spheroidally, the appearance of carbide becomes more integrated, and its amount becomes less and less (see Fig.1).

Defects, such as dislocation, appear in austenite after high-carbon chrome cast steel is hot-deformed, which induces precipitation of the fine granular carbide at the place of the defects. During the following cooling process, the carbon atoms dissolved in austenite precipitate in the form of carbide M_3C for the lowered temperature. This precipitation attaches to surface of the existed granular carbide firstly [5]. When temperature is lower than eutectoid temperature, carbon atoms also precipitate as the above form. On one hand, the amount of existed granular carbide is limited; On the other hand, precipitation of the carbon atoms far from existed granular carbide area is limited by diffusion distance, so formation of this area accords with lamellar pearlite formation mechanism. SEM shows that the short rhabdoid and the fine granular carbide also appear in matrix (see Fig.2).

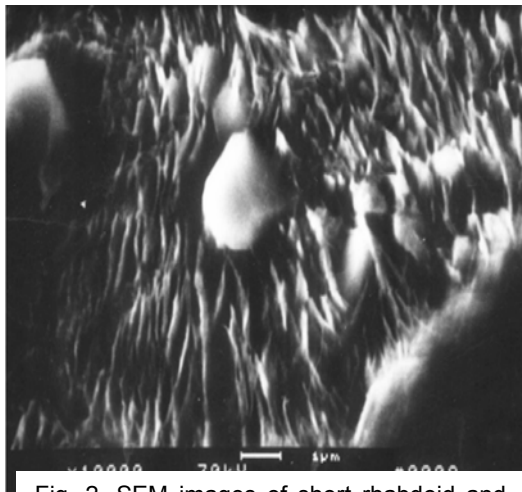


Fig. 2. SEM images of short rhabdoid and fine granular carbide

In the following isothermal, growth behavior

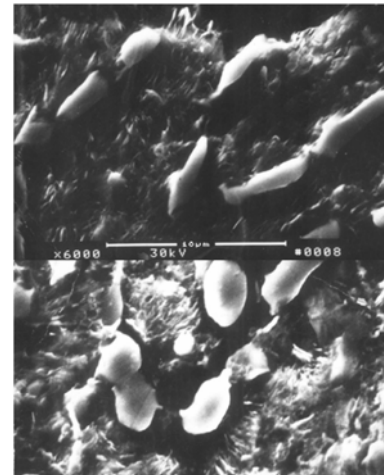


Fig. 3. Spheroidization of rhabdoid carbide: (a) Isothermal treatment for 60 min (b) Isothermal treatment for 240 min

of the short rhabdoid and the fine granular carbide is as follows:

(1) Spheroidization of short rhabdoid carbide

Because there are lattice defects inside short rhabdoid carbide, such as dislocation and grain sub-boundary, these parts would be where rhabdoid carbide dissolves. Existence of grain sub-boundary brings interfacial tension inside carbide, so groove is generated. Bilateral of the groove is camber. As we know, the radius of curvature of the camber is smaller than plane. According to colloidal state equilibrium theory, the smaller the radius of curvature of the chamber is, the higher the solubility of the solid solution carbide contacted with the chamber. Therefore, the carbide at the chamber solves so as to increase the radius of curvature. This thus destroys the equilibrium of interfacial tension here. In order to keep tension equilibrium, groove is deepen further. This process continues cyclically till carbide dissolves in two. Carbide at dissolved parts dissolves at sharp edge and precipitates on its plate, so that its radius of curvature approaches to each other and its spheroidization is realized finally. The Fig.3 and Fig.4 show rhabdoid carbide's dissolution and spheroidization process.

(2) Spheroidizing growth of granular carbide Gibbs free energy equation can be written as:

$$\Delta G = -\Delta V \Delta G_v + \Delta S \cdot \sigma. \quad (1)$$

Where ΔG_v is the free energy of carbide particle per unit volume; σ is the boundary energy of carbide particle per unit area; ΔV is the

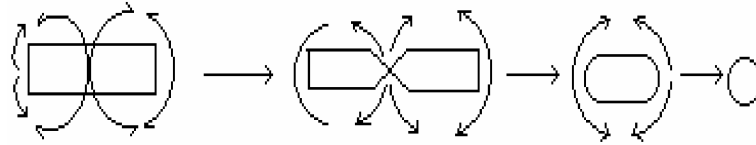


Fig. 4. Schematic drawing of dissolve and spheroidizing of rhadoid carbide

volume of carbide particle; and ΔS is the area of carbide particle.

Assuming that the radius of two spherical carbide particles is r_1 and r_2 respectively and the two particles form a closed system. Free energy of the system can be deduced from the above equation:

$$\Delta G_1 = -\frac{4}{3}\pi(r_1^3 + r_2^3)\Delta G_v + 4\pi(r_1^3 + r_2^3)\sigma. \quad (2)$$

Assuming that a part of carbide in small sphere is moved into big sphere and the shape of the carbide is not changed after the movement, then change of their volume and area is shown as follows:

$$dV_1 = 4\pi r_1^2 dr_1; \quad (3)$$

$$dV_2 = 4\pi r_2^2 dr_2; \quad (4)$$

$$dA_1 = 8\pi r_1 dr_1; \quad (5)$$

$$dA_2 = 8\pi r_2 dr_2. \quad (6)$$

Free energy of the system can now be expressed as:

$$\Delta G_2 = -\frac{4}{3}\pi(r_1^3 + r_2^3)\Delta G_v + \frac{4}{3}\pi(r_1^3 + r_2^3)\sigma + (4\pi r_1^2 dr_1 + 4\pi r_2^2 dr_2)\Delta G_v + (8\pi r_1 dr_1 + 8\pi r_2 dr_2)\sigma. \quad (7)$$

$$\text{Because } dV_1 = dV_2. \quad (8)$$

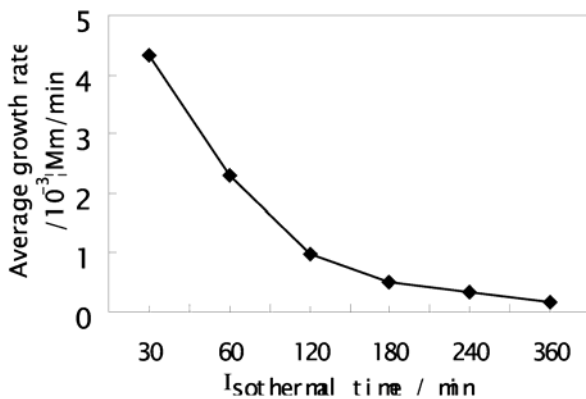


Fig. 5. Relation between average growth rate of spherical carbide and isothermal time

Then the change of system free energy before and after the movement is:

$$\Delta G = \Delta G_2 - \Delta G_1 = (dA_2 - dA_1)\sigma. \quad (9)$$

By substituting Eq.(3)-(6) and Eq.(8) into Eq.(9), and we obtain:

$$\Delta G = 8\pi r_2 \sigma (1 - \frac{r_2}{r_1}) dr_2. \quad (10)$$

Because $r_2 > r_1$, then $\Delta G < 0$, i.e. $\Delta G_2 < \Delta G_1$.

We can obtain from the above analysis that the process of the bigger carbide particles swallowing the smaller ones goes on spontaneously and the process is completed by diffusion of carbon atoms. This is theoretical explanation of the result shown in Fig.1.

3.2 Growth speed of granular carbide

We can see from Fig.1 that average diameter of carbide increases much fast at the beginning. The relationship between radius and time ($\bar{d} - t$), according to the above experimental data, coincides well with the curve of the following equation:

$$y = \frac{kx}{a + bx} + c. \quad (11)$$

By substituting experimental data into the above equation, we can obtain: $k=0.0035$, $a=0.325$, $b=0.0063$, $c=0.715$. In Eq.(11), y is average diameter of granular carbide (\bar{d}), and x is isothermal time (t), i.e.

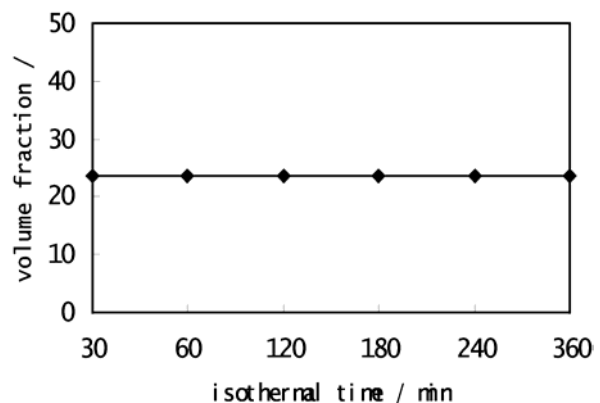


Fig. 6. Relation between volume fraction of carbide and isothermal

Table 1

Error of empirical equation				
Time / minute	Average diagram /mm		Error	
	Experimental data	Computed data	Absolute error/mm	Relative error / %
30	0.978	0.972	-0.006	-0.61
60	1.065	1.077	0.012	1.13
120	1.182	1.174	-0.008	-0.68
180	1.214	1.221	0.007	0.58
240	1.252	1.249	-0.003	-0.24
360	1.360	1.355	-0.005	-0.38

It seems that they coincide very well.

$$\bar{d} = \frac{0.0035t}{0.325 + 0.0063t} + 0.715. \quad (12)$$

Table 1 shows comparison between the experimental data and the computed data according to Eq.(12).

According to Eq.(13), the first derivative of with respect to t obtains average growth linear rate of carbide particle:

$$\bar{v} = \frac{1.138 \times 10^{-3}}{(0.325 + 0.0063t)^2}. \quad (13)$$

Eq.(13) is shown in Fig.5.

Growth rate of carbide is very high at the beginning of isothermal process, and then, it lowers down. This can be explained as follows:

At the beginning of isothermal process, size difference of carbide ($r_2 - r_1$) is the greatest. According to Eq.(10), the greater the size difference of carbide ($r_2 - r_1$) is, then, the greater its free energy (ΔG) is, the higher its diffusion pressure is, and the faster its growth rate is. With isothermal process going on, on one hand, amount of carbide decreases so that diffusion distance of carbon atoms becomes longer; on the other hand, size difference of the existed carbide ($r_2 - r_1$) decreases, then, its free energy (ΔG) approaches the limit zero, and its spontaneous diffusion pressure reduces. As the result, growth rate of carbide lowers.

3.3 Volume fraction of carbide

We can see from Fig. 6 that volume fraction of carbide keeps constant (about 23.5%) in the isothermal process.

It shows that precipitation of granular carbide from matrix in high-carbon chrome cast

steel occurs at very beginning of isothermal process and no new carbide precipitates from matrix any longer in the following process. Spheroidizing growth of carbide proceeds under the condition that solute concentration in matrix is in equilibrium. Therefore, growth nucleus of carbide is not fixed in the carbide spheroidizing growth process. Only the bigger carbide particles may become growth nucleus of spherical carbide, while the smaller carbide particles are swallowed granually by bigger ones. Consequently, with isothermal process going on, average size of carbide particles increases, their amount decreases gradually, and their volume fraction keep constant. This accords well with Ostwald Ripening Law. It perfects the traditional opinion that spheroidal carbide gradually precipitates and grows, with carbide particles left after austenitizing being its nucleating center.

4. Conclusion

(1) Isothermal spheroidizing growth of hot-deformed high-carbon chrome cast steel proceeds in such a way that the carbon atoms diffuse, bigger carbide particles swallow smaller ones, and short rhabdoid carbide dissolves and spheroidizes by itself. It appears as increment of the size of carbide particles and volume fraction of carbide keeping constant. The growth process accords well with Ostwald Ripen Law.

(2) When isothermal time exceeds 3 hours, its spheroidization is not obvious. This result perfects the traditional opinion that spheroidal carbide gradually precipitates and grows, with carbide particles left after austenitizing being its nucleating center. And it is instructive for investigating the carbide spheroidizing growing after this material is hot-deformed, for perfecting its spheroidization mechanism, and for determining spheroidizing technology.

REFERENCES

1. Akehisa Inoue. Microstructures of Deformation and Fracture of Cementite in Pearlitic Carbon Steels strained at Various Temperatures. Met. Trans, 1997, 8A:1689.
2. Li Xinli. Stability of Microstructure in Metal System. Beijing: Science press, 1984.
3. Ren Huailiang. Metallography Experimental Technique. Beijing Metallurgical Industry Press, 1986.
4. Sun Huilin. Quantitative Metallography. Beijing: Mechanical Industry press, 1982.
5. Hewitt W. The Spheroidise Annealing of High-carbon Steels and Its effect on Subsequent Heat Treatment. Heat Treat Met, 1982, 9(3):56.

*Materials Science and Engineering College,
Yanshan University, Qinhuangdao, 066004,
China*

Article is delivered in editing 9.07.2002