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Study of the Precipitation Behavior and Strengthening of Carbides during the Partition Process

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***Abstract*—In this paper, the size distribution and quantity of carbides precipitated during the partition process of $60Si_2CrVA$ spring steel treated by Q&P with different partition time were statistically analyzed by SEM. Carbide particles were obtained by electrolytic extraction of $60Si_2CrVA$ treated by Q&P with partition time of 1200s, and the contribution of different kinds of carbides to the yield strength was calculated. The results show: during the partition process of 60Si2CrVA spring steel, the size and volume fraction of carbides increase continuously with the extension of partition time, while the contribution of carbides to yield strength decreases gradually. Carbides rich in V(≤80nm)and carbides rich in Cr(>80nm)are mainly precipitated in the partition process, and carbides rich in V play the key role in precipitation strengthening.**

Keywords-60Si2CrVA spring steel; Q&P process; Partition time; Carbides; Precipitation strengthening

I INTRODUCTION

Spring steel is widely used in aircraft, railway vehicles, such as automobiles and tractors transport and other industrial products. It mainly work in bending periodic, alternating torsion stress conditions, subjected to pull, pressure, shock, torsional fatigue, corrosion and other effects, sometimes bear high short-term sudden load. So the comprehensive mechanical properties of spring steel high requirements.The microstructure of martensite and retained austenite can be obtained by heat treatment of spring steel by Q&P process, and it has the advantages of both high strength and high plasticity in performance[1-4].

Although the Si and Al elements in the spring steel can inhibit the precipitation of cementite in the Q&P process,E.P.Da Siva, D.De knijf, D.V.Edmods and Moor[5-6] all indicate that carbides precipitation in the partition period cannot be completely suppressed even in low carbon steels with relatively high Si and Al content, especially transition carbides[7-8].While precipitation of carbides and the diffusion of carbon in martensite into austenite are a competition mechanism.Carbides precipitation not only lead to the less content of retained austenite at room temperature, but also contribute to poor carbon in martensite,which can reduce comprehensive mechanical properties.As the second phase particle precipitation, the size of carbides will affect the mechanical properties of steel[9-10].The large size carbide particles formed in partition time are easy to cause stress concentration, reduce the plasticity and toughness,and it will result in serious brittle fracture.So,in addition to martensite,precipitation of carbides is also an important factor determining the mechanical properties of spring steel treated by Q&P process[11-12].

There were no systemic study of precipitation of spring steel in the partition of carbides and its effects on the mechanical properties in the domestic and foreign literatures.The purpose of the present work was to explore the influence ofcarbides on mechanical properties by the statistics of carbides precipitation types, quantity and size distribution of spring steel after different Q&P processes,and calculate the contribution to strength.It is determined that In addition to the changes in mechanical properties caused by different tissue structures, the contribution of carbides precipitation strengthening is confirmed ,which can provide guidance for optimizing mechanical properties.

II MATERIALS AND EXPERIMENTS PROCEDURES

The material was cut into φ4 mm × 10 mm small cylinder and then the thermal expansion test was conducted using the DIL805 A / D. The heat treatment process was shown in Table 1. Ac3 point of the 60Si2CrVA spring steel is 790 ℃, specimens were com-pletely austenitized at 860 ℃ for 15 min by dilatometry,and cooled to 200 ℃ (Ms=252 ℃),then partitioning at 360 ℃ of different partition time(30 s,600s,1200s,3600s),finally qenching to room temperature.

The above-mentioned specimens processed by Q & P were mechanically ground and polished,then corroded with 4 voL% nitric acid alcohol solution,and the specimens were analyzed by KYKY-2800B scanning electron microscopy for microstructure and carbides observation.Each sample was selected 100 carbide particles, and carbides size distribution was counted by ImageJ software.In this paper, the method of counting the size of the carbides was the maximum length of the particles and the vertical dimension of the average as the particle diameter[13],and the specimens processed by Q&P with partition time of 1200s were extracted by electrolysis with reference to the extraction standard of carbides.The electrolyte container was made of stainless steel, which was directly used as the cathode; the electrolyte was 8% HCl and 5% citric acid, and the solution pH was about 4, the curret density was 0.05 A/cm2, the extraction time was 10 h, and The temperature was controlled at 5 ℃. When the extraction was completed, the

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carbides powders were washed with alcohol by ultrasonic vibration, and then the carbide powders were dried.The morphology of carbide particles was observed by KYKY-2800B scanning electron microscopy, and chemical element composition was determined by EDS.

At last,150 mm tensile specimens cut by the wire cutting machine was conducted heat treatment, and then finish machining according to the standard tensile specimen drawings.The tensile specimen length was L = 150 mm, d = 5 mm,and the tensile strength, yield strength, elongation and shrinkage were obtained by the MTS electrohydraulic servo universal testing machine,and tension test was conducted according to the national standard GB228-2002,at the beginning of the tensile rate was 1mm/min, and removed the extensormeter, stretching rate was 2mm/min.

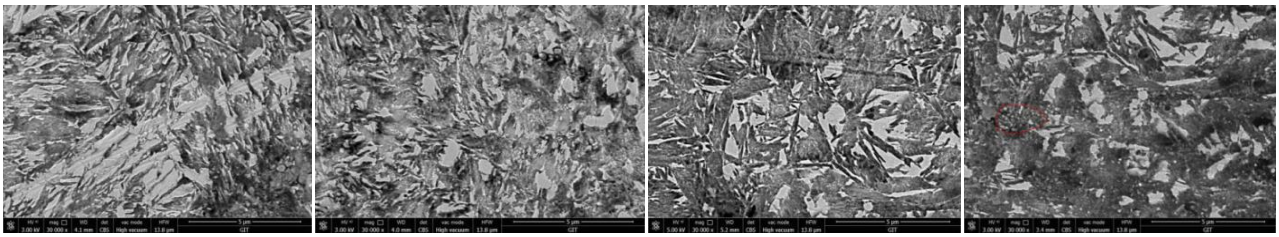
III RESULTS AND DISCUSSIONS

A. *Effects of the partition time on the size distribution of carbides and microstructure*

SEM microstructure of the different partition time as shown Figure 1 .Some larger blocky M/A islands are still visible, and the microstructure of acicular martensite appears, when the partition is set to a temperature of 360 ℃ and partition time of 30s.The microstructure of martensite + bainite + retained austenite appears when the partition time is up to 600 s. With the extension of the partition time, the characteristics of martensite almost disappeared and only some blocky M/A islands existed, but the size of the bright white and dark grey carbides became large.

TABLE I. PARAMETERS OF HEAT TREATMENT

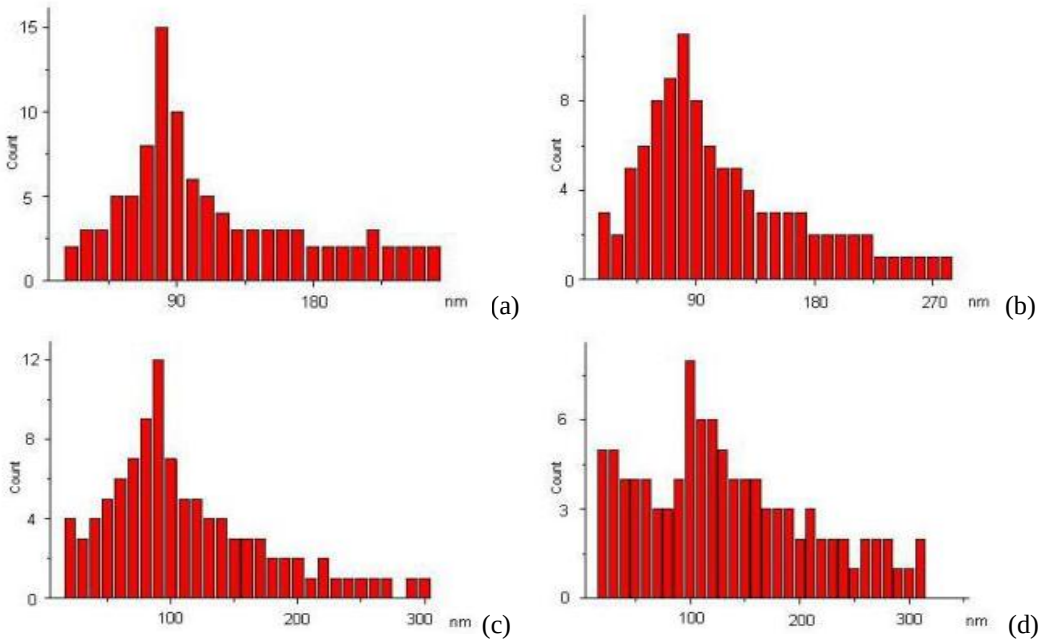
1	860 ℃ ×15min→200 ℃ ×20s→360 ℃ ×30s→cooled to room temperature
2	860 ℃ ×15min→200 ℃ ×20s→360 ℃ ×600s→cooled to room temperature
3	860 ℃ ×15min→200 ℃ ×20s→360 ℃ ×1200s→cooled to room temperature
4	860 ℃ ×15min→200 ℃ ×20s→360 ℃ ×3600s→cooled to room temperature



(a) (b) (c) (d)

(a)200 ℃ -360 ℃ -30s, (a) 200 ℃ -360 ℃ -600s(c)200 ℃ -360 ℃ -1200s, (d) 200 ℃ -360 ℃ -3600s

Figure 1. SEM of different partition time.



(a)200 ℃ -360 ℃ -30s, (a) 200 ℃ -360 ℃ -600s (c)200 ℃ -360 ℃ -1200s, (d) 200 ℃ -360 ℃ -3600s

Figure 2. Size distribution chart of carbides particles.

The size distribution of carbide particles with different partition times is shown in Fig.2.The distribution frequency is the highest, when the size of the particles is about 70 nm. the distribution frequency is the highest the maximum size of 250 nm of the partition time at 30 s. When the partition time is extended to 3600s, the highest frequency particle size of carbides is about 100 nm, and the biggest size is about 300 nm. The more fully atomic diffusion, with the longer time, the more opportunities to grow were provided for carbides, and they could grow up easily. As is shown in distribution charts, although the particles were growing up with the extension of partition time, there was an increasing tendency of small particles of carbides in 10 - 20 nm, the phenomenon of fine carbide clusters could be observed by part of the red circle of Fig1 (d), the reason why led to this phenomenon could be when the temperature reaches a certain temperature and the partition time is long enough, large carbides are decomposed into fine carbides.

B. Effect of carbide size distribution on mechanical properties in different Q&P processes

According to the statistical graph of particle size distribution above, the size of precipitated carbides is larger than 10 nm, Precipitation strengthening effect produced mainly by bypass mechanism. The method of subsection calculation and summation is adopted in this paper to accurately calculate the precipitates contribution to strength. According to McCall-Boyd [14]and Ashby-Orowan [15]correction model. The volume fraction of carbides preci-pitated and the formula of precipitation hardening in the process of partitioning of 60Si2CrVA treated by Q&P process can be written as follows:

$$f_i = \left(\frac{1.4\pi}{6}\right).\left(\frac{N_i D_i^2}{A}\right) \quad (1)$$

$$\sigma_s = \sum_{i=1}^{n} \sigma_i = \sum_{i}^{n} \left[\frac{10\,\mu b}{5.72\,\pi^{3/2} r_i} . f_i^{\frac{1}{2}} \ln\left(\frac{r_i}{b}\right) \right] \quad (2)$$

A is the area of the photograph, Ni for a range of carbon number, Di is the average diameter of carbides in an interval, um; ri is the average radius of a range of carbides, um; fi is the total volume of a range of carbides precipitation; μ is shear coefficient, for steel, the value is 80.26x103 MPa; b is burgers vector, the value is 2.48x10-4 um. The volume fraction of the carbides precipitation and precipitation strengthening can be obtained in this way: starting from 10 nm, the number of precipitates in each interval was calculated by using the span of 10nm as an interval, and the corresponding equivalent mean radius, volume fraction and precipitation enhancement amount were calculated. Finally, all intervals were accumulated. The total volume fraction and the total precipitation strengthening amount are the carbides volume fraction and precipitation strengthening amount of 60Si2CrVA precipitated in the process of Q&P treatment.

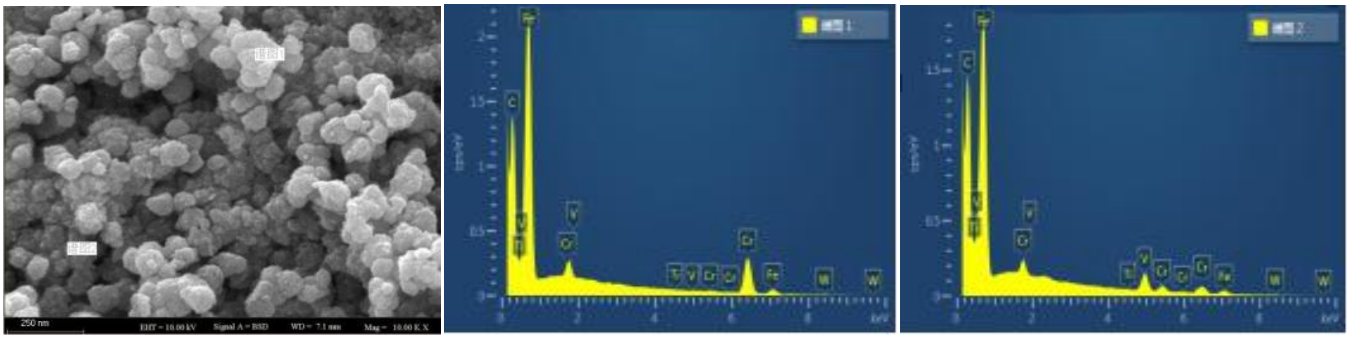
As is shown in table 3, the average size and volume fraction of carbides increase with the extension of partition time, because the diffusion and migration of carbides have enough time, which makes the carbides gather, nucleated and grow gradually. The contribution of carbides to the strength calculated by formula (1) and (2) of each partition time decreases with the prolongation of the partition time. From table 2, it can be observed that the strength of materials increases first and then decreases with the increase of partition time, which proves the change of tissue structure in the partitioning process, and it has greater influence on strength. When the partition time is extended from 30s to 600s, the strength decreases. The reason is the carbon in martensite diffuses to the retained austenite and make it rich in carbon, the increase of retained austenite from table 2 can reflect this phenomenon. When the partition time is extended to 1200s, the strength is increased instead, which is due to the transformation of reduction leaded by decomposition of martensite [16-17].

TABLE II. MECHANICAL PROPERTIES OF DIFFERENT PARTITION TIME

	Ar/%	*σb/Mpa*	*$\sigma_{0.2}$/Mpa*	*HRC*
30s	14.26	1892	1715	49.27
600s	15.15	1753	1627	44.61
1200s	11.86	1823	1684	40.26
3600s	11.51	1789	1643	37.58

TABLE III. CONTRIBUTION OF CARBIDES TO STRENGTH OF DIFFERENT PARTITION TIME

	Average size/nm	Volume fraction /%	Contribution to strength/MPa	The proportion of the total strength /%
30s	72.16	1.83	307.95	17.96
600s	84.25	2.54	286.13	16.52
1200s	99.28	2.86	256.21	15.20
3600s	113.4	3.43	248.87	15.09



(a) (b) (c)

(a)SEM of carbides by electrolytic extraction; (b)EDS1(c)EDS2

Figure 3. Precipitation of carbides during the partitioning process

TABLE IV. CONTRIBUTION OF DIFFERENT KINDS OF CARBIDES TO STRENGTH DURING THE PARTITIONING PROCESS

	Carbides rich in V(≤80nm)	Carbides rich in Cr(>80nm)
contribution value/MPa	183.13	69.96
Contribution ratio /%	72.36	27.64

C. Types of carbides and contribution to yield strength of different types of carbides

The samples treated by Q&P (QT=200 ℃,PT=360 ℃,Pt=1200s), process were extracted by electrolysis to obtain carbide particles. The carbide particles obtained were observed by scanning electron microscope and morphology of carbides were shown in Figure3(a),and Figure(b) was energy spectra of bright white carbide particles in Figure(a),the main alloying elements of the carbides are C and Cr, the mass fraction were 29% and 18% respectively, and it was determined that the carbides were rich in Cr. Figure(c) was energy spectra of gray black carbide particles in Figure(a),the main alloying elements of the carbides are C and V, the mass fraction were 32% and 16% respectively, so It could be concluded that this kind of carbides were rich in V.

The size statistics of two kinds of carbides were calculated respectively, and it is concluded that the size distribution of carbides of V was less than or equal to 80nm,while, the range of size distribution of Cr carbides is greater than 80nm.The content of Cr in 60Si2CrVA is higher, so its carbides tend to aggregate and grow; carbides rich in V and carbides rich in Cr have different nucleation sites, the former is mainly formed in the original austenite crystal[18-20],while the latter is formed at grain boundaries and martensite lath boundaries. The precipitation diffusion rate is higher in the original austenite. Therefore, carbides rich in V distribute dispersedly and have smaller particles [21]. It is calculated according to formula (1) and (2) that the contribution of carbides rich in V to strength is 183.13MPa, and the contribution of Cr to the strength is 69.963MPa.It can be found that the contribution of Cr carbides to the strength is relatively weak, while the carbides of V play a dominant role in precipitation strengthening.

IV CONCLUSIONS

Precipitation behavior and strengthening of carbides is studied by electrolytic extraction technology, SEM and EDS during the application of the Q&P process with different partition time to 60Si2CrVA spring steel and precipitation strength is calculated. The main conclusions are:

(1)The size and volume fraction of carbides increase continuously with the extension of partition time, and the maximum size is about 300nm, while the contribution of carbides to yield strength decreases gradually.

(2)After SEM observation of the carbides obtained by electrolytic extraction, it is found that the bright white precipitate is the carbides rich in Cr, and the dark grey precipitate is the carbides rich in V, both of them are irregular spheres. The former size is larger than 80nm, and the latter is below 80nm.

(3)The calculation of precipitation strengthening of different types of carbides during the partition process of 60Si2CrVA spring steel is described that the contribution of carbides rich in Cr to precipitation strengthening is weak, carbides rich in V play the key role in precipitation strengthening, and their proportion of total precipitation strengthening is 72.36%.

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