The spheroidizing tendency and spheroidization mechanism of 75Cr1 steel

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Abstract. Spheroidization annealing process was carried out on 75Cr1 steel after cold rolling. Using TEM, SEM and image analysis software Image-Pro Plus 6.0, the effects of cold rolling and spheroidization processes on microstructure and mechanical properties were analyzed. The result shows that the cold rolling leads to fragmentation of the cementite and formation of the defects, which induces faster lamellae break-up and accelerates the annealing process. With the increase of isothermal temperature and holding time, the dimension of the spheroidized carbides increase as driven by Ostwald ripening mechanism, whereas the hardness of the steel decreases. The prior cold rolling before annealing process causes the yield strength improve slightly, however shows little effect on the cold formability. The optimum heat treatment process is, holding the samples at 705°C for 6 hours with cold deformation ratio (ϵ) of 0.6.

1 Introduction

75Cr1 steel, which belongs to Germany 1.2003 grade, is a cold-work alloy tool steel by German standard and mainly used in the manufacture of small tools. The high value in hardenability and toughness, and good property in shearing and wearing resistance of 75Cr1 steel makes it preferential in tool steel using[1-2], however, the high hardness and strength of 75Cr1 steel deteriorate the plasticity, thus a spheroidization annealing is required prior to industrial production to improve plasticity [3-4].

Many researches were found investigated on the quenching and tempering heat treatment processes of 75Cr1 steel, however few result is reported about the spheroidization annealing process. As been reported, the deformation usually accelerate the rate of spheroidization annealing and increase the spheroidization degree[5-6]. Nowadays most of the manufactures provide cold-rolled steel plates to company so as to reducing the cost of subsequent production and achieving rapid completion of spheroidization. In this paper, the effect of prior cold rolling on annealing process in 75Cr1 steel was investigated, which was expected to provide a theoretical base for annealing process design in 75Cr1 steel.

2 Experimental procedures

The chemical composition of the 75Cr1 steel was given in Table 1. A_{c1} and A_{c3} were detected to be 730°C and 753°C. The microstructure was detected using TEM JEM-2100 and SEM JEM-6700. At first, the cold rolled sample with the intermediate deformation ($\epsilon=0.4$) was used as the research object in determining the spheroidization

annealing temperature and holding time. Then, the spheroidization annealing of different cold rolling deformation samples ($\epsilon=0, 0.2, 0.4, 0.6$) were studied. The annealing process were simulated in a CARBOLITE tube furnace, the accuracy of the heat controller was $\pm 5^\circ\text{C}$. The heat treatment process was shown in Fig. 1.

Table 1. Chemical composition of the 75Cr1 steel (mass %)

C	Si	Mn	P	S	Cr	Cu	V	Ti
0.75	0.29	0.77	0.01	0.002	0.46	0.02	0.003	0.004

Figure 1. Spheroidizing annealing process of the investigated steels

Metallographic specimens were firstly prepared according to the standard procedure of the spheroidized sample and then etched with nital (2% HNO_3 in ethanol) for a few seconds. The vickers hardness of all specimens were measured with a loading force of 0.5 kgF (4.905 N) with a dwell time of 10 s. The tensile test was conducted at room temperature according to ISO 6892:1998 standard, during which, the test speed was 30 mm/min.

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The degree of spheroidization was quantified by image analysis over randomly selected SEM micrographs (at 7000 times magnification). Particles with an area smaller than $0.001\mu\text{m}^2$ were not considered in the analysis. Cementite particles with an aspect ratio lower than 2 were considered to be spheroidized in this study. Aspect ratio is defined as the relation between the length

and the width of the cementite, and it is provided by the image analysis software Image-Pro Plus6.0 [7-8].

3 Results and discussions

3.1 Raw materials

Figure 2. The microstructure of 75Cr1 steel with different cold rolling deformations (a) $\varepsilon=0$, (b) $\varepsilon=0.2$, (c) $\varepsilon=0.4$, (d) $\varepsilon=0.6$

Figure 3. Microstructure of the samples annealed at different temperatures (a) 630°C, (b) 660°C, (c) 690°C, (d) 705°C, (e) 720°C

With the cold rolling deformation increased, the hardness increased because of the deformation strengthening, as shown in Table 2. The SEM microstructure with different cold rolling deformations were shown in Fig. 2. Because the pearlites in the original structure had different orientations, the cold rolling made the microstructure transformed through a process of “uniform→uneven→uniform”. In the case that pearlite

interlaminar has a large intersection angle with the strain direction, the microstructure will be refined during cold deformation. On the contrary, if the pearlite interlaminar parallels to the strain direction, the cementite would be bent and fractured, as shown in Fig. 2c. It can be seen from Fig. 2d nearly all the pearlite structure were parallel to the strain direction, and the microstructure was refined as the deformation reached up to 60% [9].

Table 2. The hardness of 75Cr1 steel under different cold rolling deformations

Deformation%	0	0.2	0.4	0.6
Hardness HV	298.0	398.6	419.0	427.8

3.2 Effect of isothermal temperature on microstructure of the annealed steel

Isothermal temperature is one of the most important factors affects the spheroidization annealing process. Supposing the carbides volume fraction is same, the larger the carbides size is, the lower the steel hardness becomes[10]. In the present work, 75Cr1 steel samples ($\varepsilon=0.4$) were heated individually to 630oC, 660oC, 690oC, 705oC and 720oC, then preserved by a time of 6h. After heat preservation, the samples were cooled to 300oC at a rate of 1oC/min and then air-cooled to room temperature. The final microstructure was shown in Fig. 3.

Image-pro Plus6.0 was used to calculate diameter, aspect ratio and spheroidization rate of the SEM micrographs (at 7000 times magnification) at different isothermal temperature, and the results were shown in Figs. 4 and 5. The cementite particles showed an increasing tendency with the higher isothermal temperature, which was considered because the lamellae spheroidization kinetic was temperature dependent[11-13]. When the sample was annealed at 630°C, most of cementite particles were smaller than 0.2 μm , however the globular shape of these particles with an aspect ratio more than 2. With the temperature continued to increase, the cementite particles with diameter less than 0.3 μm decreases rapidly in number. After this sharp decrease, the production of globular particles slowed down and the globular particles became coarsen. When the sample was annealed at 705°C, the spheroidization rate grew up to 93.8%, however, the spheroidization rate decreased to 89% at 720°C. It was indicated that the temperature improvement accelerated the diffusion of carbon and thus induced the spheroidization become faster, that was, made the small particles grew into larger particles by Ostwald mechanism. However, the temperature which was close to A_{c1} , will lead to the coarse of the particle and even induce some particle grew to lamellae, causing the spheroidization rate decreased. The hardness curve with respect to isothermal temperature after spheroidization annealing was shown in Fig. 6. With isothermal temperature increased, the hard phase number decreased and the hardness reduced. When the sample was annealed at 720°C, the minimum hardness was 191.2 HV, however

the spheroidizing effect was terrible and the cementite coarsen heavily. Therefore, the reasonable spheroidization annealing temperature is 705°C.

Figure 4. The arrange law of carbide sizes in samples with different annealing temperature

Figure 5. Evolution of the spheroidization degree in samples with respect to annealing temperature

Figure 6. Hardness variety in the samples annealed at different temperature

Figure 7. Microstructure of the sample annealed at 705°C with different holding time(a)3h, (b)6h,(c)9h, (d)12

3.3 Effect of spheroidizing time on the microstructure of annealed steel

During heat treatment, cementite lamellae was split to globular units and coarsen as driven by the Ostwald ripening process, as shown in Fig. 7. It can be seen from Figs. 8 and 9 that the size of carbides in these samples increased with the extension of holding time. At the time of 3h, most of the particles were at the range of 0.1-0.2 μ m. The spheroidization degree was higher with time prolonged, but the spheroidization degree decreased a little when holding time was 12h due to the coarsen of cementite.

Figure 8. The arrange law of carbide sizes in samples with different holding temperature

Figure9.Evolution of the spheroidization degree with different holding time at 705°C

With the holding time prolonging, some small carbides were dissolved, while the remained carbides trended to become the nucleation core of newly generated carbides. When holding time was short, the amount of small carbides ($<0.3\mu$ m) was large because the lamella carbides were dissolved into particles, and the hardness was higher than the other samples, as shown in Fig. 10. Although the hardness decreased when extending the holding time, it must be considered as well that abnormal grains may generated, which are harmful to cold formability[14]. Thus, the duration of the annealing should be adjusted with the aim of satisfying not only a minimum hardness but also a appropriate microstructure. When the holding time was 6h, the spheroidization rate was higher, the hardness reached the value (<250 HV) required for cold working, and the carbide size was uniform. Therefore, to get a proper microstructure, the holding time of 6h can be chose for this heat treatment.

Figure10. Hardness variety in the samples annealed with different holding time at 705°C

3.4 Effect of cold rolling on the microstructure of annealed steel

Figure 11. The microstructure of 75Cr1 steel with different cold rolling deformations that (a) $\epsilon=0$, (b) $\epsilon=0.2$, (c) $\epsilon=0.4$, (d) $\epsilon=0.6$ after annealing by 6 hours at 705°C

It is reported that besides defect migration and cementite break-up, cementite sub-boundary splitting also accelerates spheroidization[15-16]. The microstructure evolution after deformation at different ratio for 6h at 705°C was shown in Fig. 11. For the non-deformed sample, it was observed that several pearlite colonies still lied in the microstructures, despite the cementite lamellae being partially fragmented into short units, the spheroidization rate was the lowest in the four microstructures with different deformation ratio. It can be seen from Figs. 11 and 12, when the deformation continued to increase, the spheroidization became more complete. After spheroidizing, the cementite began to grow, and the diameter in samples with deformation ratio (ϵ) of 0.6 was significantly larger than that of 0.4, as shown in Figs. 11c and 11d. It can be concluded that the cold deformation can significantly shorten the spheroidization annealing time and accelerate the spheroidization process

Figure12. Evolution of the spheroidization degree with different cold rolling deformations

3.5 The role of cold deformation in spheroidization annealing

During spheroidization annealing, the changes on the cementite are mainly through the mechanism of the

defects migration in cementite lamella and the Rayleigh instability theory. The cementite in the spheroidization annealing process of the test steel after cold rolling mainly fragment through two mechanisms, one is that the cementite is broken by cold rolling process, and the other is that the cementite is broken due to the cementite dissolution during annealing[17-19]. As shown in Figs. 13b and 13f, the pearlite before deformation was laminae, and the diffraction patterns was regular. When ϵ was 0.6, the diffraction pattern of the cementite became circular, it was indicated that the cementite had rotated to different directions during the deformation process, and the interface between the ferrite and the cementite became blurred. The increase in cold rolling deformation caused a large number of defects inside the structure, generated deformation energy, and provided more channels for the diffusion of carbide, as shown in Fig. 13e.

It can be seen from Figs. 14, 15 and 16 that before deformation, the interlamellar pearlite space was 4.1nm and the thickness of cementite was about 0.6 nm. When ϵ was 0.2, part of pearlite had been broken into granules which became the nucleation core of newly generated carbides, but most of them still stayed as a laminated structure. When ϵ was 0.6, the cementite layer spacing was about 0.6 nm, and the thickness was reduced to 0.25 nm. According to the spheroidization kinetics, the relationship between the instantaneous growth rate of the carbide aggregation and the interlamellar pearlite spacing is shown in the equation (1) [20-21]:

$$\frac{\partial r}{\partial t} = \frac{4D\Omega C_0 \sigma}{RTrl_0} \cdot \frac{(1/r_1 - 1/r_2)}{(1/r_1 - 1/\lambda)} \quad (1)$$

Where D represents diffusion coefficient, C_0 represents the concentration of alloying elements in the matrix when the position is at the radius with zero curvature, Ω is molar volume, σ is the interfacial energy, T is absolute temperature, R is diffusion

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radius, r_1 and r_2 is the radius of diffusion, l_0 is the length of cementite, λ is the interlamellar pearlite spacing. When the cementite is finer and the interlamellar spacing is smaller, the diffusion distance of the alloy elements becomes short, and this is beneficial for the aggregation of the cementite. Therefore, the microstructure after cold rolling deformation is more favorable for the spheroidization of the cementite.

Figure 15. Evolution of pearlite interlamellar spacing with respect to cold rolling deformation

Figure16. Evolution of the cementite width with respect to cold rolling deformation

3.6 Mechanical properties discussions

The mechanical properties of the experimental steel which were affected by grain size, cementite distribution and ferrite matrix were shown in Table 3. It can be seen that the tensile strength and yield strength increased at first, and then decreased to their minimum values of 223.3 HV and 680 MPa with the increase of deformation, and this tendency was same as that of hardness. However, the tensile elongation decreased first and then increased. The yield strength of samples with prior deformation was higher than non-deformed samples, it may be resulted from the presence of deformation energy. During these treatment, the deformation samples will recrystallize. When the cold rolling deformation increases, the grains become finer after recrystallization [22-23], some reseraches have reported that the grain size has weak effect on cold formability[24]. When ϵ was 0.2, the fine cementite particles formed by annealing were dispersed on the ferrite matrix which can contribute to the steel strength improvement through second phase strengthening, thus the tensile strength increased whereas the tensile decreased. Besides, the resistance to overcome when dislocation bypasses spherical carbides during stretching is the formula (2):

$$\tau = Gb/L \quad (2)$$

Where G is the shear modulus of the material, b is the Burgundian vector, and L is the average space of the second phase. When L increases, τ decreases, and the value of tensile strength as well as yield strength reduces.

The tensile elongation of non-deformed sample was 11.78%. It can be seen from Fig. 17a that the distribution of dimple was uneven, even some area presented river pattern, thus non-deformed samples had unsatisfied performance in deformation ability. It was indicated that the deformation ability of the steel was also influenced by the degree of spheroidization, and the cold formability cannot be considered only from the parameters such as hardness or cementite particle size [25]. When ϵ was 0.2, the dimple was the smallest and shallowest of the four SEM micrographs, and the cold formability was the worst of the four samples. The size of the dimple was equivalent to the carbide particles[26]. As the cold rolling deformation futher increased, the fracture dimple became larger, and the plasticity was better. When ϵ was 0.6, the hardness after annealing was 223.3 HV, the maximum tensile elongation was 13.01%, and the tensile strength was 680 MPa.

Table 3. Mechanical properties of steel sample after spheroidizing annealing with different cold rolling deformations

Applied strain	Tensile strength (MPa)	Yield strength (MPa)	Tensile Elongation (%)	HV
0	759	440	11.78	234.7
0.2	787	660	10.75	235.6
0.4	733	651	11.42	232.8
0.6	680	620	13.01	223.3

4 Conclusion

- (1) The best spheroidization annealing process for 75Cr1 steel is as follows: Firstly, cold roll the steel with the deformation ratio (ϵ) of 0.6; then isothermal the steel at 705 °C for 6 hours. After this annealing process, the tensile strength of the steel is more than 680 MPa, the hardness is 223.3 HV, and the maximum elongation is 13.01%.
- (2) During the spheroidization annealing process of the 75Cr1 steel, the carbide size increases in Ostwald mechanism, and the steel hardness is reduced from 311.4 HV to 191.2 HV. With the increase of isothermal temperature, the degree of spheroidization rate first increases rapidly to 93.8%, and then decreases to 76.3%.
- (3) After cold rolling, not only a great many of small particle carbides in the 75Cr1 steel can directly contribute to spheroidization as the core of spheroidization annealing, but also a large number of dislocations and subgrain boundaries will accelerate the kinetics of spheroidization.

Figure13. The TEM microstructure and diffraction spot of 75Cr1 steel with different cold rolling deformations at high magnification;(a)(b) $\epsilon=0$, (c) $\epsilon=0.2$, (d) $\epsilon=0.4$, (e)(f) $\epsilon=0.6$

Figure14. The TEM microstructure of 75Cr1 steel with different cold rolling deformations at low magnification (a) $\epsilon=0$, (b) $\epsilon=0.2$, (c) $\epsilon=0.4$, (d) $\epsilon=0.6$

Figure 17. The SEM micrographs of tensile fracture of 75Cr1 steel with different cold rolling deformations that (a) $\epsilon=0$, (b) $\epsilon=0.2$, (c) $\epsilon=0.4$, (d) $\epsilon=0.6$ after annealing by 6 hours at 705°C

- (4) After spheroidization annealing to 75Cr1 steel, the hardness decreases with the increase of carbide size, because the resistance will decrease when the dislocations bypassing the carbide.
- (5) The yield strength of the cold rolled samples increases slightly compared with the un-deformed ones after annealing, because of the recrystallizing in them. The main factors that affect the cold formability are: spheroidization rate, cementite size and the distribution of cementite particles.

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