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Cu Partitioning Behavior and Its Effect on Microstructure and Mechanical Properties of 0.12C-1.33Mn-0.55Cu Q&P Steel

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> Abstract: Cu, as an austenitic stable element, is added to steel in order to suppress the adverse effects of high content of C and Mn on welding. Based on C partitioning, Cu and Mn partitioning can further improve the stability of retained austenite in the intercritical annealing process. A sample of low carbon steel containing Cu was treated by the intercritical annealing, then quenching process (I&Q). Subsequently, another sample was treated by the intercritical annealing, subsequent austenitizing, then quenching and partitioning process (I&Q&P). The effects of element partitioning behavior in intercritical region on the microstructure and mechanical properties of the steel were studied. The results showed that after the I&Q process ferrite and martensite could be obtained, with C, Cu and Mn enriched in the martensite. When intercritically heated at 800 °C, Cu and Mn were partitioned from ferrite to austenite, which was enhanced gradually as the heating time was increased. This partitioning effect was the most obvious when the sample was heated at 800 °C for 40 min. At the early stage of $\alpha \rightarrow \gamma$ transformation, the formation of γ was controlled by the partitioning of carbon, while at the later stage, it was mainly affected by the partitioning of Cu and Mn. After the I&Q&P process, the partitioning effect of Cu and Mn element could be retained. C was assembled in retained austenite during the quenching and partitioning process. The strength and elongation of I&Q&P steel was increased by 5 305 MPa% compared with that subjected to Q&P process. The volume fraction of retained autensite was increased from 8.5% to 11.2%. Hence, the content of retained austenite could be improved significantly by Mn and Cu partitioning, which increased the elongation of steel.

> **Key words:** low carbon high strength steel; intercritical annealing; element partitioning behavior; retained austenite; mechanical properties

1 Introduction

As the automobile industry has been developed, a series of environmental and safety problems have arisen. Nowadays, automobile steel requires both high strength and high toughness. High strength steel with Martensite+Austensite as the main microstructure is necessary. Speer *et al*^[1,2] have proposed a novel heat treatment called the Q&P (quenching and partitioning) process in 2003. The Q&P process produces a lath martensite and retained austensite multi-phase microstructure. The steel is quenched to a temperature between martensite start (Ms) and finish (Mf) temperatures and held for a moment, accompanied by the partition of C from supersaturated martensite to austensite. Consequently, the stability of austensite can be improved due to the enriching of C in austensite. After it is quenched to room temperature, more retained austensite can be obtained. The strength and toughness of the steel can also be improved^[3-5]. Therefore, the C content of Q&P process steel is generally high in order to improve the volume fraction and stability of retained austensite.

However, with the C content becoming high, the hardenability of steel and the heat affected zone are increased during welding, respectively, which will lead to welding cracks, and degeneration of welding performance^[6,7]. To solve this contradiction,

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recent researches^[8-10] have introduced Mn partitioning behavior from ferrite to austenite during intercritical heat preservation using intercritical annealing, subsequent austenitizing, and finally the quenching and partitioning process (I&Q&P). The mass fraction of Mn in some micron order areas is higher than that in the steel matrix after austenitizing. Mn-rich austenite is dispersed in the steel matrix. The stability of Mn-rich austenite is better than that of Mn-lacking austenite. Part of the Mn-rich austenite produced can be retained in the subsequent process. Therefore, when experimental steel gains more austenite at first quenching, more C can be partitioned to the austenite in the partitioning process. When the secondary quenching to room temperature occurs, more retained austenite is preserved^[11-17].

Mn partitioning can be used effectively to regulate the retained austenite content and improve the product's strength and elongation. However, if the Mn content is too high, difficulties arise in smelting, casting, and welding. To ensure the positive effects of Mn partitioning, an appropriate amount of Cu element can be added to steel in order to solve problems that will normally arise from an increase in Mn. As a austenite stabilizing element, Cu can change the austenitic phase transformation kinetics while improving the thermal stability of austensite by reducing the martensite critical transformation temperature. It has been found that Cu diffuses from ferrite to austenite, improving the strength and toughness of the steel^[18-21]. Meanwhile, Cu addition can refine welding metal microstructure, while improving machinability and impact toughness. Because of this, Cu is being used more and more in special steel, though it is not often used in advanced high strength steel for automobiles^[22-27].

Therefore, this work seeks to optimize the alloy composition design. Cu element partitioning behavior was researched under the intercritical annealing then quenching process (I&Q). In addition, intercritical annealing, subsequent austenitizing, then quenching and partitioning process (I&Q&P) were used to study the influence of Cu partitioning on the microstructure and mechanical properties.

2 Experimental

The chemical composition of the studied steel was: Fe-0.12C-1.34Si-1.33Mn-0.55Cu-0.35Ni. The steel was prepared using a vacuum melting furnace and then forged in a casting billet with an 80 mm thickness.

The billet was heated to 1 200 °C in a box furnace and homogenized for 1 h. The bloom rolling temperature was 1 100 °C, and the finishing rolling temperature was 860 °C. The steel was rolled to a thickness of 5 mm after 7 passes. The steel plate was air cooled to room temperature. The critical temperatures as measured by dilatometer analyses were Ac₃=885 °C, Ac₁=767 °C, *M*s=430 °C.

Fig.1 shows the three heat treatment processes. In the I&Q process (shown in Fig. 1(a)), the samples were intercritically annealed at 800 °C for 10, 20, 30, and 40 min, respectively. I&Q heat treatment was employed to observe the alloving elements' partitioning behavior. The I&Q&P process is shown in Fig.1(b), in which specimens were intercritically annealed at 800 °C for 20 min, subsequently austenitized at 950 °C for 5 min, then quenched and partitioned at 320 °C for 100 s and finally water-cooled to room temperature. The Q&P process is shown in Fig.1(c), in which specimens were first austenitized at 950 °C for 5 min, then quenched and partitioned at 320 °C for 100 s and finally watercooled to room temperature. The I&Q&P and Q&P heat treatments were performed to compare their mechanical properties.





Microstructures in the cross section perpendicular to the transverse direction etched with 0.3 % Nital were observed by scanning electron microscopy (SEM). Alloying elements partitioning behavior was investigated using an electron probe micro analyzer (EPMA). The EPMA was operated at 20 kV with a LaB6 electron gun, and the secondary electron resolution was 5 nm. The volume fraction of the retained austenite was measured by X-ray diffraction (XRD) with a Cu tube (operated at 40 kV, 150 mA). During the XRD experiment, a 2θ range from 40° to 100°, containing the 200, 220, and 311 austenite peaks and the 200, 211, and 220 ferrite peaks was step-scanned at a scanning speed of 0.3°/s. Tensile specimens with a 25 mm gauge portion length were cut with their longitudinal axes parallel to the rolling direction. The tensile test was carried out on an INSTRON5969 machine at room temperature.

3 Results and discussion

3.1 Alloying element partitioning influence on microstructure

When the samples were intercritically annealed, austenite primarily nucleated in the original pearlite until the pearlite dissolved completely. Then, austenite annexed surrounding ferrite and slowly grew up. In this process, when C was partitioned from ferrite to austenite until equilibrium, alloying elements such as Cu and Mn barely were partitioned, indicating that the formation of austenite occurs more efficiently with C partitioning. Cu and Mn were partitioned slowly from ferrite to austenite when the heat preservation time was extended. Austenite continuously grew up during the



Fig.2 SEM images of the tested steel treated by intercritical annealing and quenching(I&Q) process at IT=800 °C for (a) 10 min; (b) 20 min; (c) 30 min; (d) 40 min

extended time. Austenite transformation equilibrium was reached before the alloying element partitioning was finished.

Fig.2 shows the SEM micrographs of specimens after the I&Q process. It could be observed that the microstructure after I&Q process was mainly ferrite and Martensite. When the sample was intercritically annealed for only 10 min, the austenite content was relatively small and transformed mainly with C partitioning. A small amount of martensite was gained after quenching. The martensite morphology of the sample appeared blocky, meanwhile, the grain size was relatively small, and martensite lath was not obvious. After intercritically annealed at 800 °C for 20 min, austenite slowly grew up with partitioning of Cu and Mn. The grain size of Martensite became larger, and the blocky martensite edge appeared to be thick lath. When intercritical annealing time was further extended, austenite content reached saturation, and the quenched martensite displayed more thick lath.

3.2 Alloying element partitioning behavior

As is known from Fick's law, diffusion coefficient has a great effect on diffusion in addition to concentration gradient. The diffusion coefficient D was calculated using the Arrhenius type relation, where D_0 = frequency factor and Q = activation energy:

$$D = D_0 \exp\left(\frac{-Q}{RT}\right)$$

Enter $R=8.314 \text{ J}\cdot\text{mol}^{-1}$, thermodynamic temperature T, and D_0 , Q (shown in Table 1) into the formula, and the diffusion coefficient of allaying element in austenite and ferrite at 800 °C would be calculated (shown in Table 1). The calculated results showed that the diffusion coefficients of C, Cu and Mn in ferrite were much larger than those in austenite, while diffusion abilities of allaying elements in ferrite were stronger than those in austenite. Moreover, ferrite was a body-centered cubic structure, and austenite was a face-centered cubic structure. The ability of austenite to accommodate alloying elements towers over ferrite's potential. Therefore, during the intercritical annealing process, the driving force formed by the chemical potential promoted the diffusion of C, Cu and Mn,

Alloying element -	Austenite			Ferrite		
	$D_0/({ m m}^2/{ m s})$	Q/(kJ/mol)	$D/(m^2/s)$	$D_0/({\rm m^2/s})$	Q/(kJ/mol)	$D/(m^2/s)$
С	0.738×10^{-4}	159.0	1.34×10^{-12}	0.008×10^{-4}	82.5	7.70×10^{-11}
Cu	0.160×10^{-4}	261.7	5.16×10 ⁻¹⁹	1.490×10^{-4}	233.6	2.91×10^{-18}
Mn	4.16×10 ⁻⁴	306.2	5.94×10^{-17}	0.47×10^{-4}	244.4	6.32×10^{-16}

Table 1 Diffution coefficient alloying element in austenite and ferrite

resulting in the enriching of the elements in austenite. Fig.3 shows the EPMA images of the C, Cu and Mn distribution in the steel after IQ process at 800 $^{\circ}$ C for 20 min. It was clearly seen that the three alloying elements were enriched in martensite compared with the microstructure. This was due to the partition of the alloying elements from ferrite to austenite during the intercritically annealing process. As C partitioning was a result of interstitial diffusion, C partitioning could be done in a short time. Meanwhile, Cu and Mn partitioning was a result of substitutional diffusion, indicating that Cu and Mn partitioning could be done in



Fig.3 EPMA images of C, Mn and Cu distribution in the steel in IQ treated steel: (a) Microstructure; (b) EPMA images of C; (c) EPMA images of Mn; (d) EPMA images of Cu



Fig.4 Curves of the content of C and Cu element in the two phases of IQ treated steel: (a) The position of the line; (b) The curves of C and Cu element

a larger amount of time.

Fig.4 shows the curves of the content of C and Cu element in the two phases of IQ treated steel. Line scanning position in Fig.4(a) from left to right was ferrite- Martensite (original austenite)- ferrite in turn. The quantitative calculated results are shown in Fig. 4(b). In the early stages of austenite nucleation and growth, C was partitioned to austenite and controlled phase transformation until sub-equilibrium, the average contents of C in austenite and ferrite were about 0.22% and 0.07%, respectively. In the late stage of austenite growth, the rate of austenite transformation slowed down. Cu was also partitioned from ferrite to austenite, resulting in the grown of the austenite, the average contents of C u in austenite and ferrite were about 1.2% and 0.3%, respectively.

3.3 Cu partitioning behavior

Fig.5 shows the SEM images and EMPA images of the tested steel treated by I&Q process at 800 °C. The sample intercritically annealed for 10 min had already exhibited an uneven distribution of Cu. The Cu in martensite was also higher than that in ferrite, indicating that the Cu had already been partitioned from ferrite to austenite. As the intercritical annealing time was short, the partitioning amount was relatively small. As the time of intercritical annealing was extended, Cu in ferrite was partition to austenite gradually. Hence, the percentage of Cu-rich martensite areas kept increasing until it reached its chemical potential equilibrium. Overall, the mass fraction of Cu had a trend of increasing. However, it declined at 30 min. This could be explained by the fact that the Cu was enriched on the edge of austenite boundaries first. The diffusion coefficient of Cu in austenite was relatively small, and Cu would be partitioned to the interior of austenite grains after it was intercritically annealed for a long period of time. Fig.6 shows the highest mass fraction of Cu and percentage of Cu-rich areas of the steel as the time of intercritical annealing at 800 °C was varied.

3.4 Alloying elements distribution after I&Q&P process

Fig.7 shows the EPMA images of C, Cu and Mn distribution in the steel after the steel samples were subjected to I&Q&P treatment. It was clearly seen that the microstructure in Fig.7 was typical of Q&P treated steel, *i e*, martensite and small amount of retained austenite. Alloying elements were partitioned from ferrite to austenite during the intercritically annealing process. The resulting distribution was the same as in Fig.4. The microstructure was turned into one-phase austenite after austenitizing, leading to the



Fig.5 SEM images and EMPA images of the tested steel treated by intercritical annealing and quenching (I&Q) process at 800 °C for (a) 10 min; (b) 20 min; (c) 30 min; (d) 40 min

concentration gradient of the alloying element in onephase austenite. Therefore, downhill diffusion took place as the elements alloyed. The diffusion ability of C was shown to be strong, and C became homogenized after austenitizing. Because of the short austenitizing time, Cu and Mn were heterogeneous due to their small diffusion coefficients. However, they did exhibit downhill diffusion, and had an observable enrichment effect. In the last quenching and C partitioning stage, the temperature was low, and Cu and Mn didn't diffuse any more. Austenite with enriched Cu and Mn was easier to retain, and it provided more austenite for C partitioning process. As shown in area A in Fig.7, C, Cu and Mn were all enriched, causing retained



Fig.6 Most mass fraction of Cu and percent of Cu-rich areas of the steel after intercritical annealing at 800 ℃ for different times and quenching



Fig.7 EPMA images of C and Mn distribution in I&Q&P treated steel: (a) Microstructure; (b) EPMA images of C; (c) EPMA images of Mn; (d) EPMA images of Cu

austenite more easily reserved at room temperature. In area B, the effect of Cu and Mn enrichment was not obvious, but the effect of C partitioning was obvious, as austenite in this area was controlled by C partitioning. In area C, the three alloying elements were not enriched; retained austenite was barely reserved at room temperature in this area.

3.5 Effects of alloying elements on retained austenite and mechanical properties

The volume fraction of the retained austenite was measured using XRD, as shown in Fig.8. Three austenite diffraction peaks could be observed from 40° to 100°, at 200, 220, and 311. The austenite peaks of the steel after I&Q&P process were higher than those after Q&P process. The volume fraction of retained austenite for Q&P process was about 8.5%, while the volume fraction of retained austenite for I&Q&P process was about 11.2%.

Fig.9 shows the stress-strain curves of the experimental steels treated by Q&P and IQ&P processes,



Fig.9 Stress-strain curves of the experimental steels treated by Q&P and IQ&P processes

Table 2 Mechanical properties of steel after Q&P and I&Q&P

pro	10035				
Process	<i>R</i> _m /MPa	A/%	RA/%	$R_{\rm m}$ ·A/ MPa·%	
QP	986	19.8	8.5	19 522	
I&Q&P	944	26.3	11.2	24 827	

respectively. Compared with Q&P process, the strength of the steel after I&Q&P process was declined from 986 to 944 MPa, while the elongation was increased from 19.8% to 26.3%. The strength and elongation of the products was increased by 27.2%. The volume fraction of retained austenite and the products of strength and elongation of the steel for I&Q&P were both higher than those of the steel that underwent the Q&P process. Therefore, it could be seen that Cu and Mn partitioning had a noteworthy effect on the mechanical properties of the steel treated by Q&P process. Table 2 shows the mechanical properties of the steel samples after the two processes, as well as their volume fractions of retained austenite.

4 Conclusions

A low carbon Si-Mn steel containing Cu was treated by I&Q process and martensite+ferrite microstructure was obtained. When the sample was intercritically annealed, the effect of Cu partitioning was obvious, and the C and Mn partitioning effect did not occur. When the steel was intercritically annealed at 800 °C, C partitioning reached equilibrium in a short time. As a result, austenite transformation was mainly controlled by C partitioning. When the annealing time was extended, the Cu and Mn partitioning effect was increased gradually. Consequently, austenite slowly grew up until equilibrium was reached. When the steel was treated with the I&Q&P process, the Cu and Mn partitioning effects during intercritical annealing could be reserved. These effects provided more austenite for C partitioning in the quenching and partitioning stage.

After the I&Q&P process, the strength of the steel was 944 MPa, and the elongation reached 26.3%. This showed an increase of 5 305 MPa% in the strength and elongation compared with the steel that was subjected to the Q&P process. The volume fraction of retained austenite was also increased from 8.5% to 11.2%.

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