O artigo a seguir apresenta a influência da adição de cobre e fósforo como elementos de liga de um aço bainítico de baixo-carbono.

Responda as seguintes questões considerando o conteúdo do artigo e das aulas da disciplina:

1) Segundo os autores, quais os objetivos da adição de cobre e fósforo nesse aço? Como esses elementos beneficiam ou prejudicam as propriedades mecânicas em função das porcentagens adicionadas?

2) Qual foi o procedimento experimental para a obtenção das chapas e como elas foram analisadas?

3) Os autores conseguiram demonstrar as modificações de propriedades previstas com a adição dos elementos de liga?

4) Quais foram os mecanismos de amaciamento observados?

5) Como os átomos de cobre e fósforo afetaram os mecanismos de amaciamento, particularmente a ocorrência de recuperação estática?

6) Associe o formato, o tamanho e a orientação das partículas de Nb(C,N) aos mecanismos de endurecimento do aço.
Mechanical properties and hot-rolled microstructures of a low carbon bainitic steel with Cu–P alloying

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Abstract

A low carbon bainitic steel with Cu–P alloying was developed. The new steel aims to meet the demand of high strength, high toughness and resistance to chloride ion corrosion for the components used in the environment of sea water and oceanic atmosphere. Mechanical properties of the steel were tested and strengthening and toughening mechanisms were analyzed by comparing hot-rolled microstructures of the low carbon bainitic steels with and without Cu–P alloying. The results show that Cu–P alloying provided strong solution strengthening with weak effect on ductility. The toughness loss caused by Cu–P alloying could be balanced by increasing the amount of martensite/remaining austenite (M/A island) at lower finishing temperature. The static recovery process during rolling interval was delayed by the interaction of phosphorous, copper atoms with dislocations, which was favorable to the formation of bainitic plates. Super-fine Nb(C, N) particles precipitated on dislocations had coherency with bainite ferrite at 830 °C finishing temperature. Raising finishing temperature to 880 °C, Nb(C, N) particles were prone to coarsening and losing coherency. It was also found that no accurate lattice match relationship among retained austenite, martensite and bainite in granular bainitic microstructure.

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1. Introduction

Traditional weathering steels represented by 09CuPcCrNi steel have been widely used in the area of buildings, bridges and vehicles. However, the mechanical properties and corrosion resistance of the weathering steels have no special advantages in Cl− containing environment such as sea water or oceanic atmosphere [1,2]. The main reason is that the carbides in steel act as role of micro-cathodes which accelerates corrosion of ferrite matrix [3,4]. Also massive pearlite is extremely adverse to the fracture toughness of the steel. Recently, an ultra low carbon bainitic (ULCB) steel was developed based on ultra low carbon component and granular bainitic microstructure. ULCB steel has higher tensile strength, impact toughness and equivalent corrosion resistance in comparison with 09CuPcCrNi steel [5,6]. It will be a potential new-type weathering steel. Nevertheless, the corrosion resistance of ULCB steel in Cl− containing environment still needs to be further improved. It has been found that copper and phosphorus ions as catalysts accelerate the air-oxidation of Fe2O3 at low pH, leading to the self-repair of the protective rust film [7]. Phosphorus also promotes the formation of protective amorphous oxide [8,9]. Thus, ULCB steel with Cu–P alloying is expected to have combination properties of high strength, high toughness and good resistance to oceanic atmosphere corrosion.

Phosphorus is an effective strengthening element in low carbon low alloying steel [10]. In some cases phosphorus behaves a good balance of yield strength and ductility in ultra-fine low carbon steels [9] because the strong interaction between solute phosphorus atoms and dislocations increases working hardening rate. But in other cases phosphorus is a harmful element because excessive phosphorous content in steels causes cold embrittlement phenomenon after quenching or tempering [11–14]. Up to date, the different roles of phosphorus in different steels have been attracting researcher’s attention [15,16].

The present paper investigated the effects of Cu–P alloying on the mechanical properties and microstructure of low carbon bainitic steel. The hot-rolled microstructures at different finishing temperatures were observed and the mechanisms of strengthening and toughening of the steel were analyzed. For comparison, the mechanical properties and microstructure of low carbon bainitic steel without Cu–P alloying was also studied.

2. Experimental procedures

The chemical compositions (wt.%) of low carbon bainitic steel with Cu–P alloying (LCB-CuP steel) and the comparative steel
without Cu–P alloying (LCB steel) are shown in Table 1. The two steels were prepared by melting in vacuum induction furnace. The forged slabs were austenitized at 1200 °C for 2 h and then hot-rolled into plates by TMCP process. Rolling temperatures started at 1100 °C and finished at 830 °C and 880 °C, respectively. After rolling finished, the steel plates were immediately cooled by spraying water in order to avoid the appearance of ferrite and pearlite phase. The microstructures of steel plates were observed by Olympus GX71 optical microscope and Philips CM200 transmission electron microscope (TEM). The φ3 mm thin foils for TEM observation were ground mechanically to 50 μm thickness and then electrolytically polished at −20 °C in a solution containing perchloric (5 vol.%) + ethanol (95 vol.%). The tensile specimens were taken from the plates along rolling direction and machined into 50 mm gauge length and 12 mm gauge width. The tensile tests were performed at constant cross-head speed of 1.8 mm/min. Charpy impact tests were carried out at room temperature and −40 °C, respectively.

3. Results and analysis

3.1. Mechanical properties and microstructures of rolled-plates

Table 2 lists the mechanical properties and impact toughness of the two experimental steels. LCB-CuP steel has the higher yield strength, higher ultimate strength and the same ductility at 880 °C and 830 °C finishing temperatures in comparison with LCB steel. This proves that phosphorus and copper resulted in strong solution strengthening as well as more uniform plastic deformation. Although the impact toughness of LCB-CuP steel was lower than LCB steel, but when finishing temperature decreased to 830 °C, the impact toughness of LCB-CuP steel still reached 112 J at −40 °C. The value can completely meet the engineering demand of structural steels. The result indicates that the toughness loss of LCB-CuP steel can be covered by reducing finishing temperature.

It is known that phosphorus in steel increases the sensibility of cold embrittlement because of segregation phenomenon at grain boundary. However, in present investigation, the special component design and the particular microstructural morphology of LCB-CuP steel balanced the detrimental effect of high phosphorus content on the low temperature toughness. Firstly, trace boron atoms in the steel preferentially occupied the positions at prior austenite grain boundary through a competition system, which led to that the segregation tendency of phosphorus atoms at grain boundary was weakened [17]. Secondly, Boron element effectively delayed ferrite transformation and promoted the formation of granular bainitic microstructure under moderate cooling rate, as seen in Fig. 1. Large numbers of martensite/retained austenite phase (M/A small islands) randomly distributed on bainite ferrite and acted as roles of complex phase strengthening and toughening. The volume fraction of M/A islands in LCB-CuP steel looked to be more than LCB steel. This is because phosphorus decreased the starting temperature of bainite transformation by inhibiting carbon diffusion, which caused the increase of amount of untransformed austenite [9].

3.2. TEM observation of the hot-rolled microstructures

3.2.1. Microstructures at 830 °C finishing temperature

By TEM observation, the details of hot-rolled microstructure can be examined clearly. Fig. 2 is TEM images of hot-rolled microstructures of LCB-CuP steel at 830 °C finishing temperature. Bainitic plates with 0.4–1.0 μm width and 3–6 μm length were frequently observed (Fig. 2(a)). M/A film in between bainitic plates and ran-

![Fig. 1. Metallographs of hot-rolled steel plates: (a) LCB steel; (b) LCB-CuP steel.](image_url)
domly distributed massive M/A islands are indicated by black arrows. Fig. 2(b) displays a strong strain contrast at plate interfaces. The image reflects that bainitic plates were formed by shear transformation mechanism. The shear stress produced by one bainitic plate transformation agitated another bainitic plate transformation. The asynchronous transformation of bainitic plates caused higher orientation angle difference between adjacent plates. Actually, the bainitic plate interfaces with lattice misorientation and
M/A film at interface increased the impact absorption work by deflecting the direction of crack propagation [18]. In addition to this, the massive M/A islands also increased the crack propagation energy because the stress concentration at the crack tip was weakened due to the “stress induction phase transformation” effect [19–21]. Therefore, both bainitic plates and M/A islands contributed to toughening of the steel.

It was found that accumulated deformation induced a lot of super-fine Nb(C, N) precipitations on dislocations. Fig. 2(c) is a dark field image of Nb(C, N) particles. These spherical or spheroid particles were only 5–15 nm long and had the coherent orientation relationship with bainite ferrite: (0 1 1)½///(0 2 2)Nb(C,N), [0 0 1]½/|[1 1 1]Nb(C,N). Apparently, dislocations were the best sites for Nb(C, N) precipitations. At the same time, the precipitations produced strong pinning effect to dislocation movement, which stabilized dislocation structure and strengthened bainite matrix.

Contrast to LCB-CuP steel, many substructures were observed in LCB steel besides bainitic plates (Fig. 3(a)). Since spraying water cooling was used immediately after the last rolling pass, there was no enough time to bring about recovery process during cooling. The formation of subgrains resulted from static recovery or static recrystallization between rolling pass at the stage of finish rolling. The high-density dislocations within subgrains were produced by the subsequent rolling deformation. Since the size of subgrain was too small (ranging from 0.5 to 1.5 μm) to form bainitic plates within subgrains. Thus, we seldom observed bainitic plates in the area of substructures. Fig. 3(b) and (c) are TEM images of dislocation structure, Nb(C, N) precipitation and M/A islands in LCB steel. They had similar features to LCB-CuP steel. But one important phenomenon is that no accurate lattice match relationships were found among retained austenite, martensite and bainite. Fig. 3(d) is selected area diffraction (SAD) patterns of M/A island and bainite ferrite and their corresponding analyzing results. It is seen that (0 1 1)M and (0 1 1)BF crystal plane deviates 1–2° relative to (1 1 1), plane as electron beam directions exist [0 1 1]L//|[1 1 1]M//[0 0 1]BF. The results are not in agreement with K–S or G–T relationship. It is possible that the existence of high-density dislocations distorted the lattice of austenite or bainite ferrite phase, resulting in measurement error of crystal plane direction by using SAD technology. Nevertheless, it is indeed reported that there is the orientation relationships deviating classical theory in some alloys even measured by using Kikuchi pattern [22]. Further investigation is needed to clarify accurate orientation relationship between different phases in granular bainitic microstructure.

3.2.2. Microstructures at 880 °C finishing temperature

At 880 °C finishing temperature bainitic plates can still be observed, but dislocation structures displays some difference in the two steels. Straight and parallel dislocation arrangement was seen in LCB-CuP steel (Fig. 4(a) and (b)), while the tangled and zigzagged dislocation structure in LCB steel (Fig. 4(a) and (b)). Obviously, the cross slip and climb movement of dislocation appeared in LCB steel, and mainly planar slip movement of dislocation in LCB-CuP steel. The result shows that the way of dislocation movement in LCB-CuP steel was affected by small size solute atoms, e.g. phosphorous and copper atom. Some investigations revealed that copper atoms are prone to segregate around the dislocations forming ε-Cu precipitations [23,24]. Likewise, phosphorous atoms are often captured by dislocation core forming so-called “Cottrell atmosphere”. The interaction between dislocation kink and phosphorous atoms strongly affects the property of dislocations [25–27]. At the stage of finish rolling, the diffusion of phosphorous and copper atoms were accelerated by high-density dislocations, which promoted to form phosphorous-rich or copper-rich atmospheres. The segregation of
phosphorus and copper around dislocations also promoted Nb(C, N) precipitations on dislocations. The early precipitated Nb(C, N) particles were prone to coarsen and lose coherency, as seen in Fig. 4(a). The interactions of phosphorous and copper atoms with dislocations and Nb(C, N) precipitations on dislocations remarkably increased the resistance to cross slip and climb of dislocation and thus delayed static recovery process of LCB-CuP steel. This is beneficial to the formation of more bainitic plates during cooling after rolling.

Fig. 5(c) displays the internal details of M/A island. Retained austenite lath and transformed martensite arranged alternatively. It is not clear why retained austenite and martensite arranged in such a way, but it is presumed that the morphology related to the short-distance diffusion of carbon. In the process of cooling, the alternatively arranged carbon-rich and carbon-poor areas gradually formed within prior austenite. Then the carbon-rich areas were stabilized to room temperature to become retained austenite and the carbon-poor areas transformed into martensite. The alternative arrangement way of retained austenite and martensite was considered to be good for balancing plastic deformation between hard martensite phase and soft austenite phase and avoiding microvoid nucleation and propagation in local regions. The SAD pattern of M/A island in Fig. 5(d) proved again that retained austenite has no accurate lattice match relationship with bainite ferrite.

4. Conclusions

In this paper, the mechanical properties and hot-rolled microstructures of low carbon bainite steel with and without Cu–P alloying at different finishing temperatures were investigated. The strengthening and toughening mechanisms of the steels were clarified by analyzing microstructural characteristics. The conclusions are summarized as follows:

1. Cu–P alloying in low carbon bainitic steel produced obvious solution strengthening together with the decreased of impact toughness as compared with the steel without Cu–P alloying. However, the loss of toughness due to Cu–P alloying could be recovered by decreasing finishing temperature because the more M/A islands and bainitic plates formed at lower finishing temperature. Both retained austenite and bainitic plate interfaces were beneficial to inhibiting crack propagation.

2. Phosphorus-rich or copper-rich atmospheres formed by interaction of phosphorous and copper atoms with dislocations inhibited cross slip and climb of dislocation, and thus delayed static recovery process at the stage of finish rolling.

3. At 830 °C finishing temperature, disperse super–fine Nb(C, N) particles precipitated on dislocations produced strong precipitation strengthening because of the complete coherent relationship of Nb(C, N) particles with bainite ferrite. But at 880 °C finishing temperature Nb(C, N) particles tended to coarsen and lose coherency, which lead to the weakening of strengthening effect.

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