A Comparative Study of Fish-scaling Resistance of Low Carbon Non-microalloyed and Boron-microalloyed Steels for Enameling

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Abstract. TH values of low carbon non-microalloyed and boron-microalloyed steels before and after baking were measured and microstructures of low carbon non-microalloyed and boron-microalloyed steels before and after baking were observed by scanning electron microscope as well as transmission electron microscope in order to study fish-scaling resistance of steels for enameling. Results show that cementite is the important hydrogen storage trap in low carbon steels and cementite at ferrite grain boundary is the most important hydrogen storage trap. TH value of non-microalloyed steels before baking is highest because all cementites distribute along ferrite grain boundaries. TH value of non-microalloyed steels after baking decreases due to a decrease in cementite-ferrite interfaces when cementites grow up. TH value of boron-microalloyed steels before baking is lowest because most cementites disperse in ferrite grains. TH value of boron-microalloyed steels after baking increases because cementites in ferrite grains are pushed to ferrite grain boundaries by migratory grain boundaries when ferrite grains grow up.

Introduction

Low carbon steel sheets for enameling are widely used in industry of home appliances, metallurgy, chemistry and building. It can be made into kitchen utensils, sanitary wares, ovens, liners of water heaters, chemical reaction pots and so on [1]. Fish scaling is the most terrible defect for low carbon steel sheets for enameling [2]. The cause of fish scaling is hydrogen which generated in steel sheet during acid pickling and enameling process [3]. Ability of fish-scaling resistance directly depends on hydrogen storage capacity of steel sheet. Grain boundaries, dislocations, vacancies, inclusions and precipitates are hydrogen storage traps in steel [4,5]. Low carbon steel has not enough hydrogen storage traps due to its high purity, so fish scaling often occurs in it. Many studies on improvement of fish-scaling resistance using precipitates have been done [6,7], but researches about effect of cementite on fish-scaling resistance are few.

In this paper boron-microalloyed steel sheets were made by adding boron in low carbon steel. TH values of low carbon boron-microalloyed and non-microalloyed steels before and after baking were measured. Relation between fish-scaling resistance (TH value) and the amount, morphology and distribution of cementites was analyzed by observing microstructures of boron-microalloyed and non-microalloyed steels.

Materials and experimental method

Table 1 Chemical composition of tested steel (wt%)

	C≤	Si≤	Mn	P≤	S≤	Alt	B
non-microalloyed steel	0.05	0.05	0.12-0.35	0.010	0.030	0.02-0.07	-
boron-microalloyed steel	0.05	0.05	0.12-0.35	0.010	0.030	0.02-0.07	0.0015-0.005

Chemical compositions of non-microalloyed steel and boron-microalloyed steel are shown in Table 1. After smelting, hot rolling, cold rolling and annealing, non-microalloyed steel and boron-microalloyed steel sheets with 1mm thickness were obtained. Test samples for hydrogen permeation, scanning electron microscope (SEM) and transmission electron microscope (TEM) were cut out at 1/4 sheet width position. Size of sample for hydrogen permeation is 25mm×25mm×1mm. Hydrogen permeation test was carried out at electrochemical workstation 2273 using some samples which were cleaned with acetone and ethanol and other samples which were baked at above 800□ for 5 minutes. Microstructures were observed by JSM-7001F SEM and JEM-2100F(HR) TEM.

Experiment results and discussion

Fish-scaling resistance of non-microalloyed steel and boron-microalloyed steel. Hydrogen permeation time t_b of non-microalloyed steel as well as boron-microalloyed steel was measured at electrochemical workstation. Fish-scaling resistance sensitivity TH can be calculated out with Eq. (1).

$$TH = t_b / d^2 \quad (1)$$

Where TH is fish-scaling resistance sensitivity, t_b is hydrogen permeation time, d is thickness of sample. The calculated TH values of non-microalloyed steel and boron-microalloyed steel are shown in Table 2.

Table 2 TH values of non-microalloyed steel and boron-microalloyed steel, min/mm^2

	before baking	after baking
non-microalloyed steel	82.6	58.0
boron-microalloyed steel	44.5	63.5

It can be seen from Table 2 that after baking TH value of non-microalloyed steel decreases from 82.6 min/mm^2 to 58.0 min/mm^2 whereas TH value of boron-microalloyed steel increases from 44.5 min/mm^2 to 63.5 min/mm^2. Fish scaling does not occur in cold rolled steel sheets with TH>6.7 according to research of T. Okuyamas and G. Papp [8,9]. TH value of steel for enameling must be above 6.7 in European standard [2]. Then we can know two kinds of tested steel sheets both have excellent ability of fish-scaling resistance. In addition, the fish-scaling resistance ability of boron-microalloyed steel is better than non-microalloyed steel. In order to analyze reasons for changes of TH value of non-microalloyed steel and boron-microalloyed steel after baking, microstructures of two kinds of steel sheets before and after baking have been observed by SEM and TEM.

Microstructures of non-microalloyed steel and boron-microalloyed steel. Microstructures of non-microalloyed steel before baking and after baking are shown in Fig. 1. It can be seen from Fig.1 that microstructure of non-microalloyed steel before baking consists of ferrite and cementite. Fine cementites distribute almost along ferrite grain boundaries and few cementites distribute in ferrite grains. After baking cementites distributing along ferrite grain boundaries grow up. Sizes of cementites increase but amount of cementites decreases obviously.

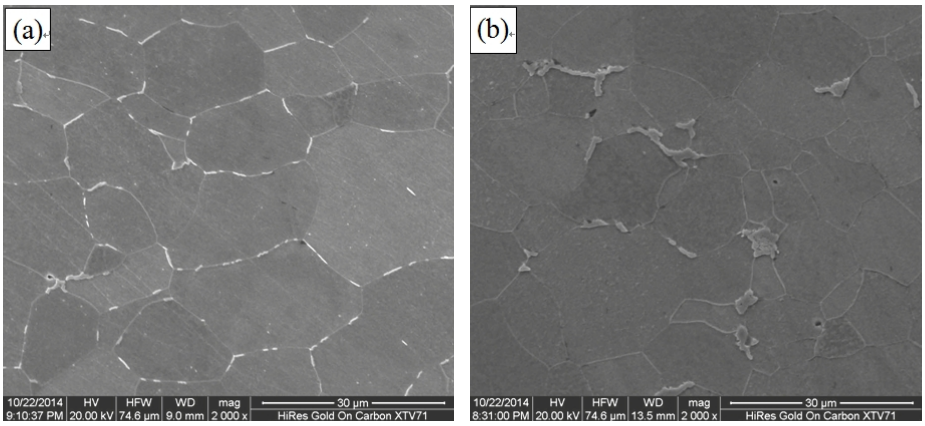

Fig.1 Microstructures of non-microalloyed steel before baking (a) and after baking (b) by SEM

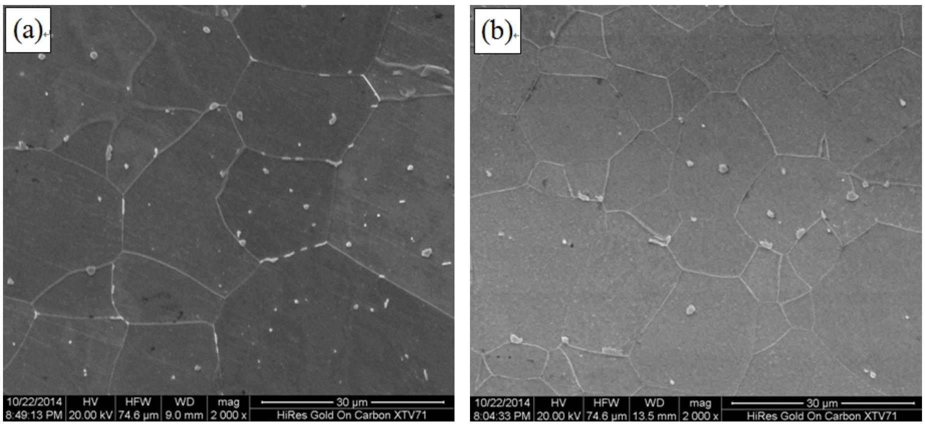

Fig.2 Microstructures of boron-microalloyed steel before baking (a) and after baking (b) by SEM

Microstructures of boron-microalloyed steel before baking and after baking are shown in Fig. 2. It can be seen from Fig.2(a) that microstructure of boron-microalloyed steel before baking consists of ferrite and cementite. Most cementites disperse in ferrite grains and a few cementites distribute along ferrite grain boundaries, which is different than non-microalloyed steel. It can be seen from Fig.2(b) that cementites in steel after baking grow up but size increase of cementites is not obvious. Amount of cementites in ferrite grains decreases. There are more cementites distributing along ferrite grain boundaries than dispersing in ferrite grains. From Fig.2(b) and Fig.1(b) we can know growth velocity of cementites distributing along ferrite grain boundaries in non-microalloyed steel is higher than that of cementites dispersing in ferrite grains in boron-microalloyed steel when the two kinds of steel sheets are baked at same temperature for same time.

Microstructures of boron-microalloyed steel after baking by TEM are shown in Fig. 3. It can be seen from Fig.3(a) that microstructure of boron-microalloyed steel consists of ferrites, cementites and a large amount of particles. These fine particles disperse in ferrite grains. In Fig.3(b) boron nitride (BN) about 100um, Cu_2S about 20nm and other particles are observed by TEM.

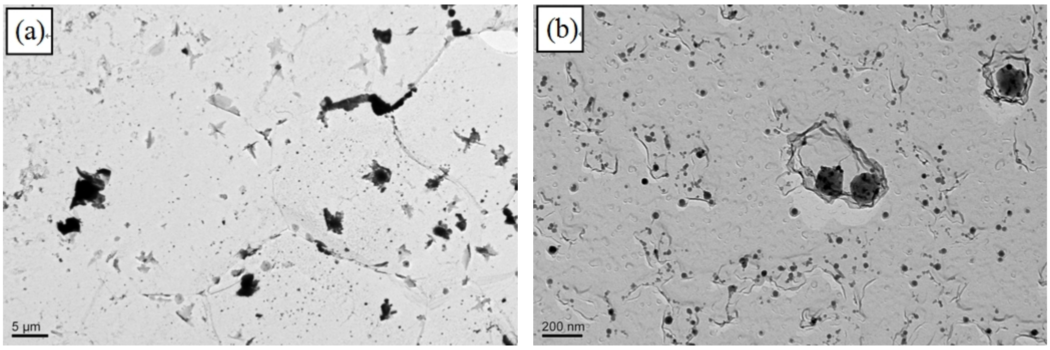

Fig.3 Microstructures of boron-microalloyed steel after baking by TEM

Analysis of fish-scaling resistance of boron-microalloyed steel and non-microalloyed steel. Microstructures of boron-microalloyed steel and non-microalloyed steel show that cementite is the important irreversible hydrogen trap in low carbon steel for enameling. Fish-scaling resistance (TH value) of low carbon steel depends on the amount, morphology and distribution of cementites. Hydrogen traps mainly locate at cementite-ferrite interfaces. More cementite-ferrite interfaces, more higher TH value.

Cementites grow following three-dimensional mode after nucleating in ferrite grains during transformation from austenite to ferrite. Cementites nucleating along ferrite grain boundaries are restricted by neighboring ferrite grains so they can only grow following two-dimensional mode. With the same cementite volume fraction, more cementite-ferrite interfaces can be obtained when cementites distribute along ferrite grain boundaries rather than disperse in ferrite grains. Cementites distributing along ferrite grain boundaries become hydrogen traps more easily than dispersing in ferrite grains.

Cementites distribute almost along ferrite grain boundaries from Fig.1(a) so non-microalloyed steel before baking has the highest TH value. Most cementites disperse in ferrite grains and a few cementites distribute along ferrite grain boundaries from Fig.2(a) so TH value of boron-microalloyed steel before baking is lower than that of non-microalloyed steel.

Volume of cementite distributing along ferrite grain boundaries increases and amount of cementite decreases when non-microalloyed steel is baked. Cementite-ferrite interfaces decrease. So TH value of non-microalloyed steel decreases. Cementites in ferrite grains in boron-microalloyed steel during baking are pushed to ferrite grain boundaries by migratory grain boundaries when ferrite grains grow up. Amount of cementites dispersing in ferrite grains of boron-microalloyed steel after baking reduces and amount of cementites distributing along ferrite grain boundaries increases. So TH value of boron-microalloyed steel after baking is higher that before baking. Cementites dispersing in ferrite grains and distributing along ferrite grain boundaries in boron-microalloyed steel after baking grow slightly and their size is much smaller than size of cementites in non-microalloyed steel after baking. So TH value of boron-microalloyed steel after baking is higher than TH value of non-microalloyed steel after baking.

Majority cementites in boron-microalloyed steel nucleate in ferrite grain during transformation from austenite to ferrite which may be relate to second phase particles dispersing in ferrite grains, such as BN.

Conclusions

(1) Higher TH value of non-microalloyed steel and boron-microalloyed steel indicates fish-scaling resistance ability of tested steel sheets for enameling is perfect and the fish-scaling resistance ability of boron-microalloyed steel is better than non-microalloyed steel.

(2) Cementite is the important hydrogen storage trap in low carbon steels and cementite at ferrite grain boundary is the most important hydrogen storage trap. Fish-scaling resistance of low carbon steel depends on the amount, morphology and distribution of cementites.

(3) TH value of non-microalloyed steels before baking is highest because all cementites distribute along ferrite grain boundaries. TH value of non-microalloyed steels after baking decreases due to a decrease in cementite-ferrite interfaces when cementite grow up.

(4) TH value of boron-microalloyed steels before baking is lowest because most cementites disperse in ferrite grains. TH value of boron-microalloyed steels after baking increases because cementites in ferrite grains are pushed to ferrite grain boundaries by migratory grain boundaries when ferrite grains grow up.

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