Effect of ‘genetic’ rare earth on alloy dissolution behavior in micro-alloyed steel

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Abstract

The solid solubility of alloying elements and microstructures of insoluble second-phase particles of micro-alloyed steel containing genetic and additional rare earth were respectively investigated. Experimental results indicate that adding a rare earth can change the inclusion morphology and promote the formation of a core of composite inclusions with Al, Ca, Mg, S, and a small amount of Ti. The extremely small quantities of genetic rare earth in steel can promote the formation of a solid solution of Nb and Ti. Therefore, although the content of genetic rare earth in steel is negligible, the promotion effect on solid solubility is significant. The addition of a rare earth has no effect on the types of the insoluble second-phase particles; however, it has a distinct dissolution effect on the large particles in steel.

1. Introduction

The relentless search for lightweight and high-strength automobile steels and propulsion development using high-performance steel materials is at the forefront of materials science research [1]. Strength and toughness are important indexes of steel materials [2, 3]. In general, a high strength corresponds to a low toughness; it is necessary to avoid this trade-off and simultaneously ensure high strength and high toughness in automotive steel [4, 5]. Currently, the common composition design methods involve the use of a low carbon content, high manganese content, and micro-alloying [6–10]. There are several commonly used micro-alloying elements. Meyer et al [11] concluded that niobium easily formed niobium carbonitride, yet its tendency to form niobium sulfur oxide or sulfur oxide solid solution was quite negligible. On the contrary, the chemical activity of titanium was significantly high, and it was easy to combine titanium with carbon, nitrogen, oxygen, sulfur, and other elements to form compounds [12, 13]. The carbonitrides of niobium and titanium could enhance the strength of steel [11].

The use of rare earths to improve the properties of steel is a research focus. However, research in this field has mostly considered the properties of materials and ignored the utilisation of resources.

It is also well known that rare earth metals have high energy and chemical activity, among which La is the most active [14, 15]. Decades of research have revealed that rare earths can combine with several metal elements to form intermetallics [16]. Consequently, rare earths exist in the carbide solid solution, while the existent morphology of rare earths in steel determines the performance of the rare earths [17–20]. Accordingly, the existence state of rare earths in different phases significantly affects the properties of steel [21–25]. Most scholars mainly explored the micro-alloying effect of rare earths on steel, and few considered the role of trace rare earths in Bayan Obo ore.

Based on practical production experience, excess rare earth content will cause clogging of the water nozzle of the tundish. Therefore, most researchers controlled the target addition amount of rare earths at approximately 0.0010% [25]. Because the Bayan Obo ore contains rare earth elements, these elements will be retained in the
products. However, the influence of the rare earths that are retained in the ore on the properties of steel has been rarely investigated.

The primary goal of this study is to determine the effect of remnant and added rare earths on the state of micro-alloying elements niobium and titanium in a continuous casting slab. The findings can provide theoretical guidance on the development and application of automobile steel.

2. Materials and methods

Two groups of steel produced by a steel plant were selected as experimental materials, and their chemical compositions were detected. The chemical compositions (mass fraction %) of the studied steel are summarised in Table 1. There were no added rare earths in steel A. Because the ore raw material that was used to melt steel A contains a small amount of natural rare earth element, La, which is known as genetic rare earth, was used (0.0003% La). For comparison, a small amount of rare earth in the ore raw material that contained a small

| Tested steel | C   | Si  | Mn  | Al  | P   | S   | Ti+V + Nb | N   | La  |
|--------------|-----|-----|-----|-----|-----|-----|-----------|-----|-----|
| A            | 0.060 | 0.18 | 1.68 | 0.038 | 0.012 | 0.002 | ≤0.2 | 0.0034 | 0.0003 |
| B            | 0.067 | 0.19 | 1.66 | 0.037 | 0.014 | 0.002 | ≤0.2 | 0.0052 | 0.0008 |

Figure 1. Sampling plan of tested steel.

Table 1. Chemical composition of the studied steels/(wt%).
The detected amount of rare earth in steel B was 0.0008% La.

Considering that the relatively high temperatures used in flame cutting could affect the structure of the edge of the slab, a length of 15 mm should be cut off at the edge of the slab to eliminate the influence of flame temperatures. The heating and cooling rates during continuous casting were distinct on the surface and at the centre of the sample, which led to differences in the structures at the surface and centre. Therefore, samples with a size of 15 × 10 × 90 mm were collected from the upper surface and the centre of the slab and designated as 1# and 2#, respectively. The sampling methods for the tested steel containing the two different components were similar, as shown in figure 1.

The continuous casting slab exhibited distinct heating rates between the surface and centre in the soaking and heating sections. Therefore, two different heat treatment processes were established for simulating the actual heating process, as shown in figure 2. The tests were performed using a HTL1400-80 tube atmosphere furnace filled with nitrogen. Heat treatment was performed for samples 1# and 2# according to the surface and core heating processes, respectively. Sample 2# was mainly used as a reference to ensure accuracy of the results.

First, the oxide layer on the surface was completely polished and part of the sample was crushed into powder. The powder was then dissolved in 1:1 hydrochloric acid solution. Finally, the concentrations of niobium and titanium in the solution were measured using a Thermo Icap 6300 (ICP-MS), and the compositions of the undissolved second phase were measured using an x-ray diffractometer. The original specimens and heat-treated specimens were finely ground, mechanically polished, and subsequently electrolysed with AA solution for approximately 12s. The microstructure was observed through scanning electron microscopy (SEM). In this work, physicochemical methods were used to study the solid solution and precipitation; consequently, the experimental results were more statistical.

3. Results and discussion

3.1. Inclusion morphology

Various inclusions were generated from continuous casting owing to several chemical reactions in the molten steel. The change in the solubility of certain elements, as well as the shape and size of inclusions, have significant influence on the structures and properties of the steel [26]. During heating, a solid-state reaction between solid metal atoms and inclusions could have occurred in the steel matrix, resulting in the segregation of the steel matrix components, degeneration of the original inclusions, and precipitation of new inclusions. Therefore, it was necessary to study the microstructure of inclusions before heating.

Figure 3 shows the SEM images of the inclusion morphology of the steel with various components. There were very few inclusions in the steel after heat treatment. In this study, we analysed about 10–20 inclusions and found the following rules. The inclusion morphology, mutual position of elements in the inclusions, and
regional energy spectrum of these particles are visible in the picture. Figure 3(a) shows the SEM image of the inclusion morphology of the studied steel A. The inclusions comprise a composite precipitate that is made up of Ti, Ca, Al, and S in the interior, and Ti inclusions on the exterior. In contrast, the inclusions in steel B comprise a composite precipitate that is composed of Al, Ca, Mg, S, a minute quantity of Ti in the interior, and Ti inclusions on the exterior, as shown in figure 3(b). The analysis revealed that the genetic rare earth in steel can promote the combination of titanium and other elements, and form the composite core of Ti, Al, and Ca, whereas adding rare earths in steel can change the stage of inclusion nucleation.

### 3.2. Solid solubility of Nb and Ti

The different morphologies of niobium and titanium determine the outcome of steel alloying, which is chiefly achieved through manipulation of the solid solution atoms or precipitates to adjust the morphology of the hot-rolled austenite, and thereby obtain the desired structures and properties. Accordingly, niobium and titanium should be maximally dissolved into the steel substrate during heat treatment [27, 28].

Table 2 summarises the solid solubility of Nb and Ti with different types of steel. Considering the uneven distribution of elements in the steel, this experiment measured the total amounts of each position while measuring the solid solution content in order to ensure the reliability of the experimental results. I found that the niobium content of the central position is about 100 ppm lower than that of the surface location, and the titanium content is about 200 ppm lower than that of the surface location. The higher the total amount of alloying elements, the lower the solution percentage. Therefore, the overall solid solubility of Nb and Ti in the 2# samples is higher than that in the 1# samples. In the same heating process, the solid solubilities of the 1# samples of steel A and B were analysed. The results indicated that La in both amounts failed to affect the solid solubility of Nb and Ti. Moreover, the results for the 2# samples manifested the same observations. The total content of niobium and titanium in the sample with a low solution percentage was approximately 10%; the low solution percentage was likely due to the high total content. Compared with the data in [29], it is concluded that both, genetic rare earths and added rare earths, can promote the formation of the solid solution of niobium and titanium. Interestingly, although the content of genetic rare earth in the steel is less, the promotion effect on solid solubility is significant than that obtained with added rare earth.

| Test steel | Nb  | Ti  | Nb  | Ti  |
|------------|-----|-----|-----|-----|
| A          | 69.24 | 40.98 | 76.63 | 57.38 |
| B          | 61.45 | 35.89 | 78.74 | 55.35 |

Figure 4. X-ray spectrogram of the insoluble second phase after surface heating process (S_A) Steel A, (S_B) Steel B.
3.3. Microstructure analysis of the insoluble second-phase particles

The insoluble second-phase particles were filtered from the solution, and phase analysis was performed via X-ray diffraction. The results are presented in figure 4. The curves of S_A and S_B show the peaks of various types of particles in test steels A and B, respectively. Notably, the peaks of various types of particles in steel A and B are almost similar, although the rare earth contents are different. The main types of insoluble particles are Nb_2(CN), TiN, and NbVN_2.

Figure 5 shows the SEM images and energy-dispersive spectrum of the insoluble second-phase particles. We found that the insoluble second-phase particles in steel A were mainly long (square) with irregularly rounded corners, whereas those in steel B were mainly spherical and ellipsoidal (figures 5(a) and (b), respectively). Comprehensive analysis revealed that the second-phase particles are composite carbonitrides that contain Nb.
and Ti. When the morphology of the particles is elongated, the content of Ti is higher in the particles; however, when the morphology is nearly spherical, the content of Nb is higher. These results possibly arise due to the influence of the rare earth on the kinetics of the precipitation reaction. The formation modes of the second-phase particles vary according to temperature, resulting in the different morphologies of the second-phase particles [30]. Alternatively, there are numerous inclusions with high Ti content in steel A, as shown in figure 3(a), that are less susceptible to dissolution and provide nucleation conditions for nascent second-phase particles.

Figure 6 shows the particle size distribution of the second phase. In this study, approximately 150 precipitates were randomly selected and the sizes were measured using the intercept method. Figure 6(a) shows that the particle size distributions of the second phases of the 1# samples of steels A and B are mainly concentrated around <400 nm. The percentages of the second-phase particles larger than 400 nm in the rare earth-added steel are lower than those of the genetic rare earth steel. Figure 6(b) shows that the particle size distributions of the second phase of the 2# samples of steels A and B are mainly concentrated in 50–100 nm, and the proportions of the second-phase particles larger than 100 nm in the rare earth-added steel are also very small.

Figure 7 reveals the size changes and distribution characteristics of the insoluble second-phase particles. Comparing figures 7(a) and (b), the particle sizes of the insoluble second phase in steel B are smaller and the distribution is more dispersed. These observations also occur when comparing figures 7(c) and (d). Comprehensive analysis of the shape and size of the second-phase particles indicates that the addition of rare earths has a distinct dissolution effect on the large particles in steel.

4. Conclusions

The influences of genetic and added rare earth on the solid solubility of alloying elements and microstructure of the insoluble second-phase particles of the low-carbon micro-alloyed steel were studied. The following results were obtained.

(1) In comparison with the genetic rare earth, added rare earth can change the inclusion morphology and form a core of composite inclusions with Al, Ca, Mg, S, and a small amount Ti.
(2) Both, genetic and added rare earths, can promote the formation of a solid solution of Nb and Ti; however, comparison between the two revealed that their effect on solid solubility is not significant.

(3) The added rare earth in steel did not affect the types of the insoluble second-phase particles; however, it lowered the Nb/Ti ratio in the particles. The resultant morphologies of the particles were nearly ellipsoid and spherical. The insoluble second-phase particles became smaller and their distributions were more dispersed.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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