Effects of Ca Addition on Formation Behavior of TiN Particles and HAZ Toughness in Large-Heat-Input Welding

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A new process technique, Kobe super toughness (KST), enables maintaining excellent toughness in heat affected zones (HAZs) formed by large heat input welding. In order to improve the KST treatment, the effect of Ca addition on HAZ toughness was studied with focus on TiN particles. It was found that Ca addition inhibits the crystallization of coarse TiN particles and increases the number of fine TiN particles precipitated. Consequently, a fine-grained microstructure of HAZ was achieved and HAZ toughness was improved significantly.

Introduction

Heavier gauge steel plates are more and more being used, with the recent increase in the size of steel structures such as container vessels and buildings. Welding such heavy gauge steel plates requires increased number of passes, making conventional multi-pass welding highly inefficient. Therefore, ultra-high-heat-input welding, such as electrogas arc welding and electroslag welding, which enable one-pass welding, is being increasingly used. The increased welding heat input, however, keeps the heat-affected zones (HAZs) of the welds at a high temperature for an extended period of time, as well as decreasing the cooling rate. This coarsens the microstructure and significantly decreases toughness.

To resolve such issues, Kobe Steel developed a process technique, Kobe Super Toughness (KST).[1] This technique enables the refinement of microstructure with a minor addition of Ti to disperse fine TiN particles, which suppress the coarsening of austenite (γ) grains in HAZs and serve as transformation nuclei for intragranular ferrite (α). This ensures favorable toughness in ultra-high-heat-input welded joints in HAZs, providing steel with a high degree of safety.

The requirement for HAZ toughness, on the other hand, is becoming increasingly stringent, which calls for further improvement of the KST technique. There are reports that HAZ toughness can be improved by utilizing CaO and CaS, along with TiN, as transformation nuclei for intragranular α[2, 3]. Kobe Steel has also confirmed that the addition of Ca improves HAZ toughness[4]. However, not much detailed study has been done on the effect of Ca addition on HAZ toughness and on TiN particles, leaving much unknown. Therefore, a detailed study was conducted to ascertain how Ca addition affects particle size and the number of TiN particles. Based on the knowledge obtained, the amount of Ca to be added was optimized for HAZ toughness and the improvement effect was verified. The following is an outline of this study.

1. Experimental procedure

Table 1 shows the chemical compositions of the steels tested in this study. Calcium mainly serves to form oxide. The addition of Al, another oxide-forming element, which is similar to Ca, was varied to vary the amount of dissolved oxygen which affects oxide formation. Each composition was melted in a 150kg vacuum melting furnace and was cast in an ingot having a diameter of 250mm and a height of 400mm. Each ingot was heated to 1,100℃ and hot rolled into a plate 50mm thick. The temperature at the completion of the hot rolling was adjusted so as to be 850℃.

Inclusions in each ingot were observed to study the effect of Ca addition on the crystallization of TiN. The observations were conducted at intermediate positions between the ingot surface and the center. A field emission electron probe micro-analyzer (FE-EPMA) was used to observe the inclusions, to analyze the composition of inclusions larger than 2μm and to determine the particle size of TiN. Each particle size of TiN was given by the diameter of a circle whose area is equal to the area occupied by the TiN in each inclusion.

To study the effect of Ca addition on the precipitation of TiN in a HAZ, a heat cycle test, called a synthetic weld thermal cycle, which reproduces and simulates ultra-high-heat-input welding, was conducted on rolled steels with the additive amount of Al fixed at 0.03%. The heat cycle was applied to specimens, each of which was taken from the mid-

Table 1 Chemical compositions of steels

(mass%)

C	Si	Mn	Al	Ti	Ca	N	others
0.08	0.35	1.55	0.013～0.058	0.015	0～0.0022	0.0060	Cu, Ni, B

plane between the rolled surface and the center plane of a plate. To reproduce the welding conditions, these specimens were heated to 1,400℃, held at that temperature for 30 seconds and then cooled in such a way that the temperature went from 800℃ to 500℃ in 730 seconds.

After the synthetic weld thermal cycle, inclusions larger than 2μm were measured for their TiN content by the FE-EPMA. The number density of TiN precipitates smaller than 300nm was determined using a transmission electron microscope (TEM).

2. Experimental results

2.1 Effect of Ca addition on crystallization of TiN in ingots

Fig. 1 shows typical inclusions observed by the FE-EPMA. Steel with no addition of Ca exhibits coarse TiN particles with sizes of around several microns, which have been nucleated from Al_2O_3. The steel with added Ca, on the other hand, exhibits complex oxides consisting of Al and Ca, with CaS surrounding the complex. Almost no crystallization of TiN was observed.

Fig. 2 shows the relation between the CaO content in the oxides and the size of TiN particles

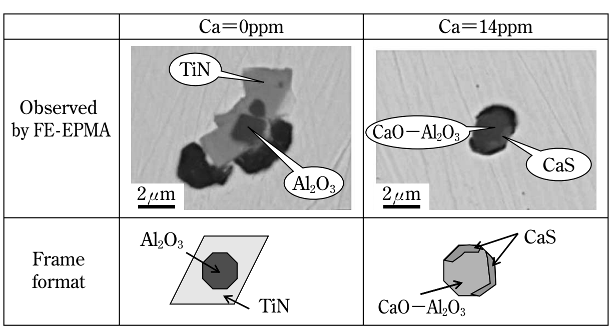

Fig. 1 Effect of Ca on inclusion morphology [5)]

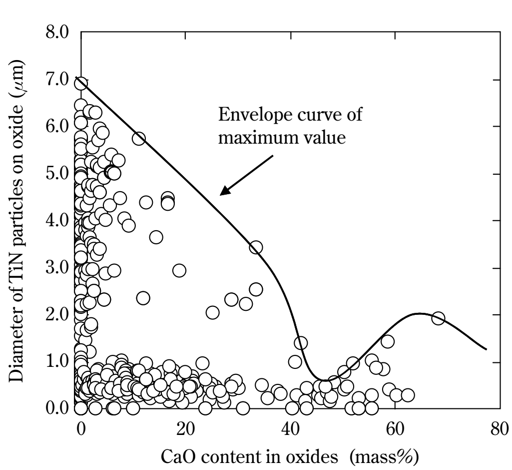

Fig. 2 Effect of CaO content in oxides on diameter of TiN particles

crystallized on these oxides. It should be noted that all the oxides in these compositions consist essentially of CaO and Al_2O_3, or in other words, the remainder of CaO is almost entirely Al_2O_3. As a whole, the particle size of TiN decreases with the increase in CaO content. The size of TiN particles rapidly decreases in the CaO concentration range of about 40-60% and reaches a minimum at about 50%.

Fig. 3 shows the relationship between the CaS content and the TiN content in the inclusions. The TiN content decreases rapidly with the increase in CaS content, and almost no TiN crystalizes out in the CaS content range higher than 20%.

2.2 Effect of Ca addition on TiN precipitation in HAZ

Fig. 4 shows the effect of Ca addition on the TiN content in the inclusions larger than 2μm and on the number density of fine TiN smaller than 300nm. With the increase in the amount of Ca added, the TiN content in the inclusions larger than 2μm decreases, while the number density of fine TiN increases. This is considered to be caused by the increased addition

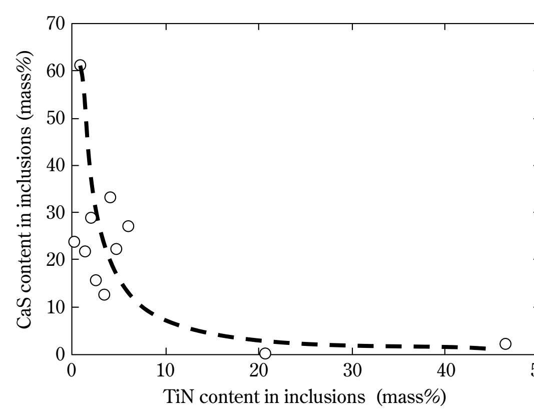

Fig. 3 Relationship between TiN content and CaS content in inclusions

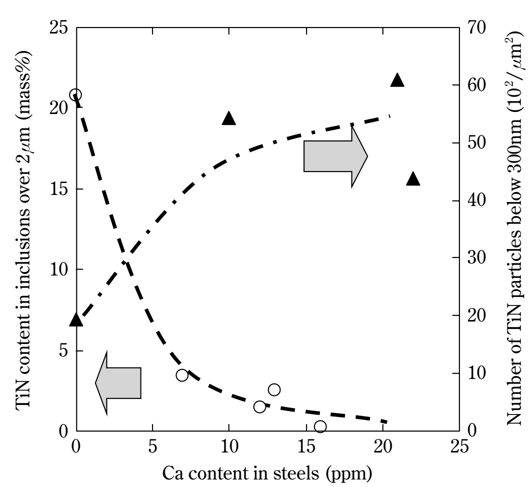

Fig. 4 Effect of Ca content in steels on coarse TiN particles and fine TiN particles

of Ca suppressing the crystallization of coarse TiN on the oxides, resulting in a large portion of TiN finely precipitated.

3. Discussion

As shown Fig. 1, TiN crystallizes out preferentially on Al_2O_3, but not on CaS or on $CaO-Al_2O_3$. In order to evaluate how easily TiN can crystallize out, the lattice misfits agsinst TiN and critical nucleus formation energies of CaO, CaS and Al_2O_3 were calculated according to the method proposed by Aaronson, J.H.Van Der Merwe, Jimbo and Morikage et al.[6)-8)] The results are shown in **Fig. 5** and **Fig. 6**. Here, the critical nucleus formation energy is standardized by the nucleus formation energy of Al_2O_3 for comparison. Moreover, for the calculation, the interface energy was assumed to be the same as the structural energy. The result indicates that CaS has the largest lattice misfit against TiN, while Al_2O_3 and CaO have almost the same level of lattice misfit. The critical nucleus formation energy was the largest for CaS and the smallest for CaO. Therefore, from the aspects of lattice misfit and critical nucleus formation energy, CaS is least likely to become the nucleus for the crystallization of TiN. This is

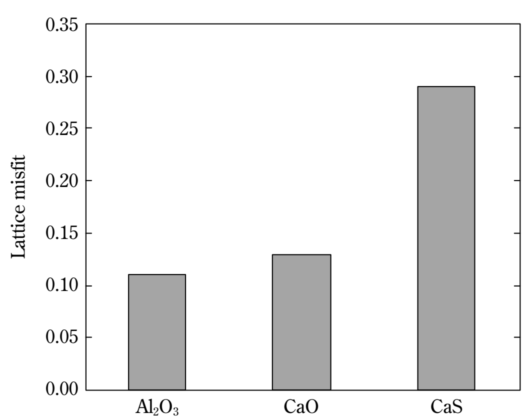

Fig. 5 Lattice misfit between TiN and inclusions

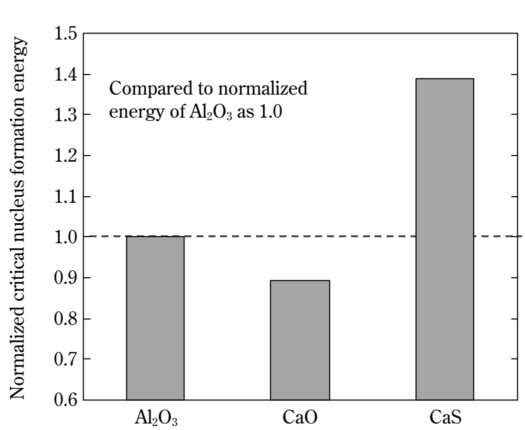

Fig. 6 Critical nucleus formation energy between TiN and inclusions

considered to have caused the rapid decrease of TiN content with the increase of CaS content, as shown in Fig. 3. Among the three compounds, CaO is the most likely to become the nucleus for the crystallization of TiN. However, as shown in Fig. 2, the particle size of TiN tends to decrease as the CaO content increases. This is considered to be caused by the increased addition of Ca, which not only increases the CaO content, but also increases the concentration of CaS, which is unlikely to become the nucleus for the crystallization of TiN. This is considered to have caused CaS, having critical nucleus formation energy smaller for CaO than for TiN, to be formed around the oxide as shown in Fig. 1, decreasing the area of contact between the molten steel and CaO.

The following discusses the phenomenon, as shown in Fig. 2, in which the particle size of TiN decreases rapidly in the CaO concentration range of 40-60%. In order for oxides to serve as the nuclei for the crystallization of TiN, it must exist as a solid in molten steel. Taking this into account, our research focused on the melting point of oxides. It is generally known that, when the CaO content in an oxide reaches 40-60%, the melting point of the oxide becomes 1,413-1,600℃ and is minimized at the CaO content of 49%[9)]. Assuming the temperature of molten steel during casting to be 1,600℃, the region where the content of CaO becomes 40-60% coincides with the region where the melting point of the oxide becomes lower than the temperature of the molten steel. In other words, as the CaO concentration approaches 49% in this region, the oxide in the molten steel remains as a liquid at lower temperatures, lowering the crystallization temperature of TiN and shortening the time from the start of crystallization until the completion of the solidification of molten steel. This is considered to have suppressed the coarsening of TiN.

4. Verification of improvement in HAZ toughness

Based on the above, the effect of Ca addition on TiN particles is summarized as follows. From the aspects of the melting point of oxides, lattice misfit and critical nucleus formation energy, an increase in Ca addition not only suppresses the formation of coarse TiN, which becomes the origin of brittle fracture, but increases the fine TiN which contributes to the refinement of γ grain and the generation of intragranular α. All of these are considered to be effective in improving the HAZ toughness of ultra-high heat-input welds.

In order to verify this, the chemical compositions shown in Table 1 were modified such that they have an additive amount of Al set at 0.03%. The steels were cast, rolled and subjected to the synthetic weld thermal cycle, as described previously; then Charpy tests were conducted to evaluate their HAZ toughness. The fracture surfaces of the specimens after the Charpy test were observed. Also observed were micro structures of the specimens etched by NITAL (an etching solution consisting of alcohol and nitric acid).

Fig. 7 shows the relationship between the amount of Ca added to the steel and the transition temperature at which fracture appears (*vTrs*). The increase in the amount of Ca has been verified to lower the *vTrs*, significantly improving the HAZ toughness of ultra-high heat input welds. The fracture surfaces of the Charpy test specimens clearly show that coarse TiN particles in steel without the Ca addition originate brittle fracture as shown in **Fig. 8**. Furthermore, the steel without Ca added exhibits coarse ferrite grains larger than 100 μm, as shown in **Fig. 9**, while the steel with Ca added exhibits a fine and homogeneous dispersion of ferrite with a grain size of around 20 μm, a result of the promotion of intragranular α generation. These results verify that the addition of Ca suppresses the formation of coarse TiN while increasing fine TiN, thus refining the microstructure in the HAZs of ultra-high heat input welds and improving their toughness.

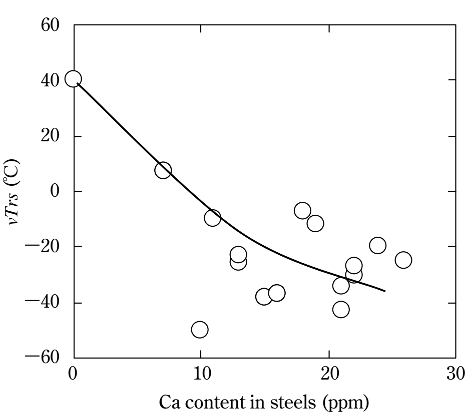

Fig. 7 Effect of Ca content on HAZ toughness

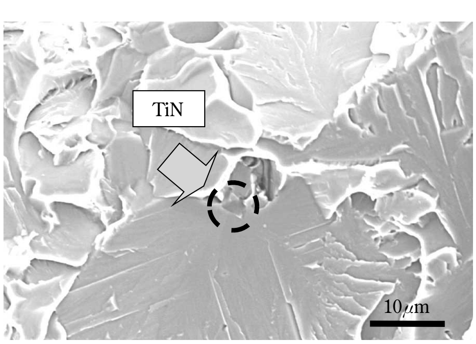

Fig. 8 Crystallized TiN at originating point of brittle fracture in Ca free steel

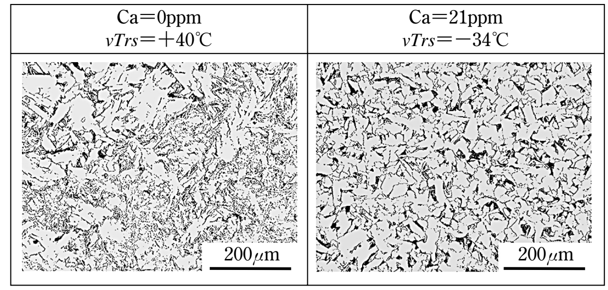

Fig. 9 Effect of Ca content on microstructure of HAZ

Conclusions

Kobe Super Toughness (KST), a process technique for finely dispersing TiN particles, was further improved by the addition of Ca. This technique is applicable to a wide variety of steel plates used in various fields including shipbuilding and construction, contributing not only to the improvement of welding efficiency, but also to the improvement of the safety of steel structures, and to the benefit of the entire society.

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