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Effect of Zr-Ti combined deoxidation on the microstructure and mechanical properties of high-strength low-alloy steels

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Abstract

Effect of Zr-Ti combined deoxidation on the microstructures and mechanical properties of high-strength low-alloy steels was investigated by means of microstructure analysis, tensile- and Charpy impact-tests. Experimental results showed the addition of Zr-Ti based deoxidizing agent resulted in the formation of fine Zr-Ti complex oxides, and atom Mn entered into Ti_2O_3 but MnS precipitated on the surface of ZrO_2 . First-principle calculations revealed that Ti_2O_3 has cation vacancy and ZrO_2 has little misfit with MnS in lattice. Owing to abundant finely oxides dispersed in the matrix uniformly, the microstructures deoxidized using Zr-Ti was uniform and the strength was enhanced comparing against the steels deoxidized using Al based deoxidizer. The ductility and toughness of the thick steel plates deoxidized

using Zr-Ti were also considerably improved, apparently due to the formation of manganese depleted zone (MDZ) which embraced the uniform dispersed oxides.

Keywords: steel; deoxidation; microstructure; mechanical property; first-principles calculation

1. Introduction

High-strength low-alloy (HSLA) steels are essentially low-carbon steels which contain small amounts of alloying elements such as Nb, V and Ti [1, 2]. These steels have been widely used to fabricate large engineering structures such as oil storage tanks, ships and pressure vessels because of their desirable combination of mechanical properties, such as high strength and toughness, as well as good weldability. Although carbides and nitrides play a very important role in precipitation strengthening and particle pinning in most steels [3, 4], oxides have additional advantages mainly because they tend to be more stable than the carbides and nitrides, particularly at high temperatures [5], they have strong pinning effect to retard austenite grain growth in coarse-grained heat-affected zone [6]. The oxides also can act as nucleating sites for the formation of grain during solidification and the eventual formation of acicular ferrite in intermediate temperature transformation [7, 8].

Grain size and the resulting microstructure of steel play an important role in the final mechanical properties [9]. Acicular ferrite is recognized as a desirable microstructural constituent in HSLA steels, not only for increasing strength but also for improving the toughness, by virtue of effective grain refinement [10, 11]. For the ferrite formation, not only the ferrite forming ability of oxide particles but the distribution of the nucleation sites is also important [8]. Extensive studies have been conducted on the Ti oxides working as an inclusion with high ferrite forming ability [12]. Former works showed that the application of Zr in steels on dispersion and spheroidization of inclusion [8]. The effect of oxides is in relation to their structural

and electrical properties, such as vacancy, density of states (DOS), etc. These properties will be first-principle calculated in the study and used to interpret the results.

The present investigation was undertaken with the objective of determining the effect of small combined addition of Zr and Ti, as deoxidizer, on the size, distribution and composition of inclusions. A secondary objective was to study the uniformity of the microstructure and stability of mechanical properties in HSLA heavy plates.

2. Experimental and calculation

Two HSLA steel plates, one deoxidized using Zr-Ti based agents with an overall composition of 0.01-0.02 wt% and the other deoxidized by adding 0.025wt% Al, were made in an industrial scale. Ca treatment was carried out at the final stage of liquid steel for both steels. The basic chemical composition of these two steels in tundish is listed in Table 1. The processing condition during the steelmaking, continuous casting, rolling and tempering were virtually identical for both two 30 mm thick steel plates.

A number of tensile test specimens with a dimension of 30 mm×10 mm×6 mm were cut from the plates and perpendicular to the rolling direction. The tensile tests were performed at room temperature with a constant strain rate of 1 mm/min using a universal tensile testing machine. The yield strength was determined using a 0.2% offset. At least three Charpy impact test specimens from each plate, with V-notch in the transverse direction, were prepared. The toughness measurements were carried out at -60°C and the average values are reported in this article.

The fracture surface of all Charpy test were examined by scanning electron microscope (SEM). Metallographic specimens were taken from the center of steel plates paralleled, 45° and perpendicular to the rolling direction, as illustrated in Fig. 1. The crystallographic grain size and misorientation of microstructures were measured using electron backscatter diffraction (EBSD) with a resolution of 0.15 μm on a SEM. The size and distribution of the precipitates were estimated by examining and image analysis of 30 SEM micrographs.

The vacancy energies and DOS of oxides were calculated by the first-principles [13]. The formation energy of vacancy was performed within the Density Functional Theory (DFT) framework. The calculations were made by using the Full Potential Augmented Plane Wave (FPLAPW) method implemented in the Wien2k code [14]. The generalized gradient approximation (GGA) derived by Perdew-Burke-Ernzerhof (PBE) scheme was used for the exchange-correlation potential [15]. The energy was calculated on a mesh of 1000 k-points in the irreducible Brillouin zone. All crystal cells were optimized with relaxation of both lattice parameters and atomic positions.

3. Results

3.1 Microstructures and EBSD analysis

The SEM micrographs in Fig. 2 show that both specimens taken from the 1/4-thickness of steel plate perpendicular to the rolling direction deoxidized using Zr-Ti and Al has a similar mixed microstructure of predominantly bainite and a small

proportion of acicular ferrite in the rolled-tempered condition. It is indicated that the addition of Zr-Ti has no adverse effect on the overall microstructure of the HSLA steel.

Because the effective grain size of the intermediate temperature transformed mixed microstructures of bainite and acicular ferrite is difficult to determine by traditional metallographic method, the microstructures of specimens were analyzed through EBSD. Fig. 3 shows the orientation images for specimens taken from the center of two steel plates paralleled, 45° and perpendicular to the rolling direction. The acicular ferrite laths or plates (indicated by black arrow) have different orientations with neighboring bainite packets. The parallel bainitic ferrite laths in individual bainite packets have the same or similar color, indicating that the bainitic ferrite plates occur in bundles or packets with low angle grain boundaries between the plates, whereas larger misorientations occur across bainite packet boundaries. The large angle grain boundary threshold is estimated to be 15° in the present work. The grains were assumed to be spherical in shape to evaluate the grain size. The size for crystallographic grain smaller than 2 μm was deleted as error. Table 2 shows the crystallographic grain size for the specimens paralleled, 45° and perpendicular to the rolling direction. The maximum, mean, and standard deviation equivalent diameters of grains in Zr-Ti-killed steel from different directions were smaller than that in Al-killed steel, respectively. It is seen that the microstructures in Zr-Ti-killed steel are slightly finer and more uniform.

The angles between neighboring grains were examined by EBSD. The typical

EBSD analysis map and statistical distribution of the grain angles between adjacent grains for specimens paralleled the rolling direction with different deoxidizations are presented in Figs. 4 and 5, respectively. In Fig. 4, different colors represent different grain boundary angles, purple stands for angles of 10-15°, and blue for larger than 15°. It demonstrates in Fig. 5 that most of the neighbouring grains are characterised as low angle grain boundaries, with angles smaller than 15°. However, one of the peaks occurs at the angles from 50 to 60°, indicating that some high angle grain boundaries exist in the specimen. Those high angle grain boundaries are the boundaries between ferrite and bainite or the boundaries between bainite packets. Comparing with two specimens, the obviously different characteristic of the two micro-structures is that the frequency of high angles ($>15^\circ$) grain boundaries in specimen deoxidized using Zr-Ti than using Al. The summary of the proportion of grain boundaries with different grain boundary angles is presented in Table 3. It demonstrates that most of neighboring grain angles are smaller than 15°. Comparing with Al-killed steel, larger angle was existed in the specimens deoxidized using Zr-Ti measured from sections with different angles to the rolling direction. It also indicate indirectly that more acicular ferrite formed in the specimens, deoxidized using Zr-Ti due to the acicular ferrite laths or plates keeping large angle boundary with neighboring microstructures.

3.2 Mechanical properties

Table 4 illustrates the outcome of the numerous tensile and Charpy tests carried out on steels deoxidized using Zr-Ti and Al. The average yield strengths of steel deoxidized using Zr-Ti and Al were 807 MPa and 801 MPa, respectively. However,

steel deoxidized using Zr-Ti had a smaller standard deviation than steel deoxidized using Al (*i.e.* 28 MPa as to 66 MPa, respectively). The average tensile strengths of these steels were also comparable (*i.e.* 845 MPa as to 839 MPa for steels deoxidized using Zr-Ti and Al, respectively). Meanwhile, the samples made in steel deoxidized using Zr-Ti had a much lower variation (*i.e.* 15 MPa) in tensile strength as compared to steel deoxidized using Al (*i.e.* 50 MPa). This is somehow consistent with the above-mentioned differences observed in the microstructures of these steels.

The elongation and impact toughness of steel deoxidized using Zr-Ti and Al are also presented in Table 4. The average elongation of steel deoxidized using Zr-Ti was 35.2% with a standard deviation of 2.0%, and that of steel deoxidized using Al was 26.9% with a standard deviation of 2.4%. Hence, it is determined that the use of Zr-Ti deoxidizer had a positive effect on the ductility of the HSLA steel. The average Charpy absorbed energy of steel deoxidized using Zr-Ti was 136 J at -60°C with a standard deviation of 11.5 J, whereas that of steel deoxidized using Al was 122 J at same temperature with a standard deviation of 59.2 J. It is noticeable that the impact toughness of steel deoxidized using Zr-Ti is substantially higher with a less variation than those of steel deoxidized using Al.

3.3 Analysis of particles

The fractured surface of steels deoxidized using Zr-Ti and Al and particles were analyzed by SEM and electron dispersed spectroscopy (EDS). Figs. 6a and 6b showed that the fractured surface of steels deoxidized using Zr-Ti which contains a complex inclusion in the centre of a dimple. The inclusion consists of a Zr-Ti deoxidized oxide

and a MnS precipitate. Figs. 6c and 6d revealed that the fractured surfaces of steel deoxidized using Al consist of dimples with lot of particles, which were Al deoxidized oxide, some of particles were large abnormally. The SEM and EDS analysis of particles in the matrix steels in Figs. 7a and 7b also indicated that the inclusion in steel deoxidized using Zr-Ti and Al consisted of Zr-Ti deoxidized oxide with MnS precipitate and Al deoxidized oxide, respectively. However, the individual MnS clusters were observed in the matrix with Al deoxidation, as shown in Fig. 7c. MnS precipitated and then be broken into clusters due to the rolling process.

The sizes of the particles were estimated by examining and image analysis of 30 SEM micrographs. Fig. 8 shows the size distribution of inclusions in the specimens of the steel deoxidized using Zr-Ti and Al, respectively. It should be noted that the nanoscale inclusions are not included in the statistics. Approximately 65% of the oxides are smaller than 1 μm in the steel deoxidized using Zr-Ti whereas only about 47% of them are in the same range in the steel deoxidized using Al. It can be seen that there are more amounts of fine inclusions in the steel deoxidized using Zr-Ti than those in the steel deoxidized using Al.

3.4 Calculation results

The mole cation and anion vacancy energies for Ti_2O_3 , ZrO_2 and Al_2O_3 are 0.029 Ry, 0.106 Ry, 0.141 Ry and 0.045 Ry, 0.039 Ry, 0.110 Ry, respectively. It is obvious that Ti_2O_3 is the only oxide with cation vacancy, while the others, have lower anion vacancy energies. These results are in good agreement with previous work [16-23]. The formation energy of MnTi_3O_6 (formation product of diffusion) is -0.531 Ry and

negative energy suggests that the formation of MDZ is a spontaneous process. For anion vacancy oxides (ZrO_2 and Al_2O_3), the atom of Sulphur (S) can take over the vacancy left by Oxygen. The formation energies of $\text{Zr}_4\text{O}_7\text{S}$ and $\text{Al}_4\text{O}_5\text{S}$ are 0.139 Ry and 0.347 Ry, respectively. Positive formation energy does not mean that it is impossible to introduce atom into ZrO_2 with vacancy [24]. But it is obvious that the possibility of formation of $\text{Zr}_4\text{O}_7\text{S}$ is more than that of $\text{Al}_4\text{O}_5\text{S}$. The density of states (DOS) as a function of the energy is useful in analyzing the electronic structure of the solids. The DOS of the oxides are shown in figure 9. There are no energy gaps near to the Fermi level for Ti_2O_3 , indicating the metallic nature for it. But for ZrO_2 and Al_2O_3 , the energy gaps are 3.5 eV and 6.3 eV in the Fermi level, respectively. Large energy gap means the insulator, and all these accord with the literatures that the electrical conductivity ($\Omega^{-1}\text{m}^{-1}$) above 1273 K of Ti_2O_3 , ZrO_2 and Al_2O_3 are 10^2 , 10^{-1} and 10^{-2} [25], respectively.

4. Discussion

4.1 Inclusion formation controlled by the combined deoxidization by Zr-Ti

It is well known that Zr, likewise Ti, is a strong oxide-forming element. The combined oxidation by Zr and Ti contributed to the uniform distribution of Zr and Ti complex oxides. Firstly, the densities of Ti_2O_3 (4.486 g/cm^3) and ZrO_2 (5.68 g/cm^3) are larger than that of Al_2O_3 (3.97 g/cm^3) and are closer to that of liquid steel (7.15 g/cm^3) [26], and thus, once oxides are formed, Ti_2O_3 and ZrO_2 are not easy to float up in the liquid steel [27]. Secondly, the electrical conductivity is the key factor in the motion of particles. It can conclude that the driving force for the motion of Al_2O_3 is

higher than those of ZrO_2 and Ti_2O_3 in molten metal according to their electric conductivities [25]. ZrO_2 and Ti_2O_3 tend to be mutually exclusive and more difficult to form clusters than Al_2O_3 during electric refining process [28]. Therefore, abundant finely Zr and Ti complex oxides are uniformly dispersed in the steel deoxidized using Zr-Ti, as testified through Figs. 6-8.

The formation of ferrite arises from MDZ. There are two models of formations of MDZ. For cation vacancy oxide (Ti_2O_3), the Mn can diffuse into the cation vacancy of Ti_2O_3 and a manganese depleted zone (MDZ) will be formed in the vicinity of Ti_2O_3 . For the anion vacancy oxide (ZrO_2), the S can take over the vacancy and it will attract Mn by the formation of MnS around oxide because the manganese and sulphur have strong affinity. It has been reported that both MnS particle and ZrO_2 have similar lattice parameters [8], as shown in Table 5. First, the lattice parameter of fcc MnS is 5.224 Å, close to those of monoclinic ZrO_2 , where a, b and c parameters range from 5.145 to 5.311 Å. Secondly, there is only a 9-degree difference in β . Moreover, MnS and ZrO_2 have exactly the same interplanar distances of 1.847 Å and 1.509 Å at the reciprocal planes of MnS [220] / ZrO_2 [022] and MnS [222]/ ZrO_2 [113], respectively. In addition, MnS and ZrO_2 have very similar interplanar distances of 2.612 Å and 2.621 Å, respectively, at the reciprocal plane of MnS [111] and ZrO_2 [002]. Noticeably, there are at least two exactly the same and one very similar interplanar distances between MnS and ZrO_2 . (整段去掉) Thus it can be concluded that MnS and ZrO_2 exhibit a very good coherency relationship, which greatly reduces the interfacial energy. Lower interfacial energy results in more intensely contact between different

surfaces. This explains why MnS tends to precipitate on the preformed ZrO₂. As a result, many fine sulphides were precipitated on the oxides in the steel deoxidized by Zr-Ti (Figs. 6 and 7). For anion vacancy oxide (Al₂O₃), there is no MDZ in the vicinity of it because of the large formation energy of Al₄O₅S and greater oddity of lattice between MnS and Al₂O₃.

4.2 Effect of microstructure uniformity on the stability of strength

The oxides are more stable than carbides and nitrides in liquid steels, those stable particles existed in steels could be regarded as nucleation sites of grains during solidification. Because Zr-Ti complex oxides are more difficult to form clusters, the number of particles in Zr-Ti-killed steel was more than that in Al-killed steel and provided more sites for grain nucleation during solidification. Meanwhile, the particles in the Zr-Ti-killed steel were uniformly dispersed. They effectively restrict the growth of grain, especially for abnormal growth of grain at high temperature. Thirdly, Ti oxide is known to be one of the most effective inclusions for acicular ferrite formation [29]. It is often accompanied with other precipitates, such as MnS [30]. MnS precipitation and Mn diffusion into oxide by means of cation vacancies can cause the Mn depletion zone around Ti oxides [31]. MnS tends to precipitate on the pre-formed ZrO₂ due to strong interaction and similar crystal structure, as shown in Table 5. Therefore, the complex Zr-Ti oxide can promote the formation of acicular ferrite by Mn depletion zone. The lath-like or plate-like acicular ferrite grains can partition a large austenite grain into smaller separate regions [10]. The bainite transformed at lower temperatures is thus confined in the smaller regions, resulting in

the formation of fine-grained mixed microstructures [32]. The mean and standard deviation equivalent diameters of grains in Zr-Ti-killed steel were smaller than that in Al-killed steel (Table 2). It means that the grain in Zr-Ti-killed steel was smaller and uniform due to the uniformly dispersed fine particles.

The strengthening mechanisms include solid solution strengthening, grain refinement (fine-grain strengthening), precipitation strengthening, and dislocation strengthening. These factors are closely related to processing of steel. Fine-grain strengthening can be calculated under empirical equation [33], which is given by,

$$\sigma = k(d_z)^{-1/2} \quad (1)$$

where σ is the strength improved by grain refinement, d_z is the effective diameter of grain, and k is parameter (usually seen as $17.4 \text{ N/mm}^{-3/2}$ in high strength low alloy steels[33]).

It was shown in Table 2 that the mean diameters of grains for specimens taken from Zr-Ti-killed and Al-killed steel plates paralleled to the rolling direction were 2.66, and 2.88 μm , respectively. The calculations of σ in Zr-Ti-killed and Al-killed steel plates were 338 and 325 MPa, respectively. The difference of strength by grain refinement between Zr-Ti-killed steel and Al-killed steel is in agreement with the result of measured strength shown in Table 4. However, the maximum grain size was larger than usual due to the abnormal grain growth. When the d_z was seen as the maximum crystallographic grain size (7.36 μm in Zr-Ti-killed steel and 10.9 μm in Al-killed steel), the calculations of σ in Zr-Ti-killed and Al-killed steel plates were 203 and 167 MPa, respectively. The scatter and difference of yield and tensile

strength would due to the abnormal grain. The stability of strength in Zr-Ti-killed steel was better with smaller and uniform grain due to the uniformly dispersed fine particles.

4.3 Improvement of toughness by spheroidization and dispersion of MnS

Clusters and large-sized MnS inclusions considerably reduce the toughness, ductility and fatigue strength of steels. As a secondary phase in steel, MnS inclusions can cause damage to the continuity of the steel matrix, decreasing the uniformity and thereby exerting a deleterious effect on its mechanical properties. It has been reported, and is generally known, that cracks may nucleate from clusters of MnS and large inclusions [33]. Inclusions are harder than the surrounding matrix, which can lead to a concentration of stress and strain during matrix deformation. Matrix-inclusion decohesion or fracture of inclusion particles can occur, ultimately resulting in the formation of voids [34]. However, if MnS inclusions are small particles, and are evenly dispersed in the matrix, they can improve the mechanical properties of steels, especially the transverse impact toughness and fracture resistance. MnS can be formed during the solidification of HSLA steels and preferentially precipitated on the Zr-Ti oxides. Consequently, many fine sulphides were formed with a spheroidized morphology and more uniform distribution in the steel deoxidized by Zr-Ti (as shown in Figs. 6 and 7), and this resulted in a higher toughness as seen in Table 4. Because MnS was precipitated on the Zr-Ti oxides, the Mn depletion zone was formed around inclusions and promoted formation of acicular ferrite (indicated indirectly in Table 3). Acicular ferrite is recognized as a desirable microstructural constituent for improving

the toughness by virtue of effectively grain refinement [11].

5. Conclusions

(1) The finely dispersed oxides in the steel matrix were identified as Zr and Ti complex oxides when the steel was deoxidized with Zr and Ti. Atom Mn entered into Ti_2O_3 but MnS precipitated on the surface of ZrO_2 during solidification, meanwhile MDZ was formed in the vicinity of them.

(2) Because of abundant finely oxides dispersed in the matrix uniformly, the microstructures was uniform and stability of strengthen was enhanced. The ductility and toughness of the thick steel plates deoxidized using Zr-Ti was considerably improved, apparently due to the formation of MDZ which embraced the uniform dispersed oxides.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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Table 1 Chemical composition of the investigated steel (wt.%)

C	Mn	Si	Ni+Cr+Nb+Mo	B	Ca	N	P	S
0.04-0.07	1.55-1.68	0.20-0.30	0.50-0.80	0.0012-0.0020	0.0008-0.0035	≤0.006	≤0.015	≤0.002

Table 2 Crystallographic grain size of microstructure observed under different directions.

Crystallographic grain size		Max, μm	Min, μm	Average, μm	Standard deviation
Zr-killed	0° to the rolling direction	7.36	2.00	2.66	0.76
	45° to the rolling direction	12.9	2.00	2.81	1.00
	90° to the rolling direction	10.6	2.00	2.74	0.90
Al-killed	0° to the rolling direction	10.9	2.00	2.88	1.06
	45° to the rolling direction	15.2	2.00	2.94	1.12
	90° to the rolling direction	21.0	2.00	2.92	1.13

Table 3 Misorientations of microstructure observed under different directions.

	Steel	>3° (%)	>10° (%)	>15° (%)	>30° (%)	>40° (%)
	0° to the rolling direction	38.4	18.3	14.5	12.9	12.0
Zr-killed	45° to the rolling direction	38.2	18.1	14.5	12.5	11.7
	90° to the rolling direction	38.9	18.7	15.2	13.6	12.8
	0° to the rolling direction	36.4	17.6	14.0	12.1	11.3
Al-killed	45° to the rolling direction	35.1	16.3	12.7	10.3	9.3
	90° to the rolling direction	35.3	17.0	13.6	11.7	11.0

Table 4 Mechanical properties of base metals.

Steel	Yield strength, MPa				Tensile strength, MPa				Elongation, %				Impact toughness, J (-60°C)			
	Max	Min	Mean	σ	Max	Min	Mean	σ	Max	Min	Mean	σ	Max	Min	Mean	σ
Zr-Ti-killed	835	750	807	28	865	820	845	15	39.0	31.0	35.2	2.0	167	114	136	11.5
Al-killed	880	725	801	66	900	745	839	50	32.5	23.0	26.9	2.4	279	38	122	59.2

Table 5 Lattice parameters of MnS and ZrO₂.

Category	Crystal structure	Planes (hkl)	Plane distance	β	int	h	k	l	a	b	c
ZrO ₂	Monoclinic	002	2.621		20	0	0	2			
		022	1.847	99.23	14	0	2	2	5.145	5.207	5.311
		113	1.509		4	1	1	3			
		111	2.612		100	1	1	1			
MnS	Fcc	220	1.847	90	50	2	2	0	5.224	5.224	5.224
		222	1.509		20	2	2	2

Fig. 1 Schematic illustration of metallographic specimens obtained from heavy steel plate.

Fig. 2 Optical micrographs of specimens taken from the 1/4-thickness of steel plates deoxidized using (a) Zr-Ti and (b) Al perpendicular to the rolling direction.

Fig. 3 Orientation image maps of the specimens taken from the center of steel plates

(a, b) parallel, (c, d) 45° and (e, f) perpendicular to the rolling direction. (a, c, e) Zr-Ti
killed steel, (b, d, f) Al killed steel.

Fig. 4 EBSD maps of grain angles between adjacent grains for the specimens deoxidized using (a) Zr-Ti and (b) Al. The specimens are parallel to the rolling direction.

Fig. 5 Statistical distribution of the grain angles between adjacent grains for the specimens deoxidized using (a) Zr-Ti and (b) Al. The specimens are parallel to the rolling direction.

Fig. 6 SEM images of fracture surface and the EDS analysis of the steel deoxidized using (a, b) Zr-Ti and (c, d) Al.

Fig. 7 SEM micrographs and EDS analysis of particles in the specimens taken from (a)

Zr-Ti-killed, and (b) and (c) Al-killed steels.

Fig. 6. Line analysis of a typical Zr-Ti complex inclusion. (a) Morphology and (b)-(f) spectra of O, Zr, Ti, S and Mn, respectively.

Fig. 8 The size distributions of inclusions in the specimens deoxidized using (a) Zr-Ti and (b) Al.