Effect of Nb on the As-cast Structure and Compactness Degree of Ferritic Stainless Steel Dual Stabilized by Ti and Nb

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The effect of Nb on the as-cast structure and compactness degree of ferritic stainless steel (FSS) dual stabilized by Ti and Nb are investigated. In this study, the as-cast structure of experimental ingots were almost composed of equiaxed grains and Ti-Mg-Al-oxide enveloped by Ti(C,N) or $(\text{Ti,Nb})_x(\text{N,C})_y$, namely complex nucleus, was found in the interior of FSS grain. When Nb was added to FSS, the as-cast grain size became smaller and the grain boundary precipitates (BP) became smaller and more dispersed. In addition, the composition of the outer layer of the complex nucleus and the BP both converted from Ti(C,N) to $(\text{Ti,Nb})_x(\text{N,C})_y$. Thermodynamics analysis showed that, the solidification region will be extended by Nb, which will be beneficial to the nucleation of complex nucleus. Complex nucleus is theoretically possible to form and exhibits good nucleation effect on $\delta\text{-Fe}$ as well as TiN according to the disregistry calculation. What's more, $(\text{Ti,Nb})_x(\text{N,C})_y$ particles in BP will be formed at the end of solidification and will prevent the grain merging by pinning effect.

KEY WORDS: Nb; ferritic stainless steel; as-cast structure; compactness degree; heterogeneous nucleation; pinning.

1. Introduction

Ridging is a typical surface defect of ferritic stainless steel (FSS) in the deformation process. Many efforts have been made to reduce the occurrence of ridging defect. Most studies conclude that the origin of ridging is strongly related to the columnar structure in the as-cast structure of FSS.^{1–8)} Equiaxed grain structure of FSS is desired to be obtained after the solidification process. Therefore, a lot of processes, such as electromagnetic stirring (EMS) technology, low-superheat casting, have been applied to improve the equiaxed grain ratio of as-cast structure of FSS.^{9,10)} However, low-superheat casting affects the smoothness of CC and the application of EMS increases the equipment and operating costs. Moreover, low-superheat casting and EMS have a limited effect in raising the equiaxed grain ratio of high-purity ferritic stainless steel.

Therefore, it has been paid more and more attention to refine the solidification structure by means of heterogeneous nucleation.^{9–11)} Bramfitt¹²⁾ found that TiN shows good coherency of crystal lattice parameters with $\delta\text{-Fe}$. The research of Villafuerte *et al.*¹³⁾ showed that the equiaxed grain ratio increased and the size of the equiaxed grains decreased in the weld structure when Ti was added in FSS gas-tungsten arc (GTA) welds. Itoh *et al.*¹⁴⁾ studies the effect of Ti, B, N, Zr and REM addition on the equiaxed ratio of SUS430 steel. However, in order to obtain a high equiaxed grain ratio, an

excessive Ti is added to the molten steel, which will cause nozzle clogging in the CC process conversely. What's more, in order to stabilize C, N element and decrease the addition of Ti, dual stabilization of FSS by Ti and Nb was proposed.

In the past two decades, dual stabilized FSS has developed rapidly. Most studies of Nb addition were focused on the high temperature and material performance of FSS,^{15,16)} while few researches were conducted on the effect and mechanism of Nb on the as-cast structure. Scheller *et al.*¹⁷⁾ observed the development of microstructure and precipitations in a simulated strip casting process of Nb-alloyed Cr-steel. Shan *et al.*¹⁸⁾ investigated the grain structures and the precipitates in the solidification microstructure of the ultra-pure 17 mass% Cr ferritic stainless steels with different Ti and Nb content.

To increase the equiaxed grain ratio of the as-cast FSS, it has been proved that heterogeneous nucleation by TiN or Oxide-TiN is a relatively effective method. However, with the development of dual stabilization of FSS, the requirements for ultra-pure ferritic stainless steel is increasing rapidly. It's become more and more important to obtain not only high equiaxed grain ratio but also high density and fine equiaxed grains.

In order to improve the quality of the high-carbon continuous-casting billet, Hou *et al.* investigated compactness degree (grain number per unit area) in outer columnar grain zone and central equiaxed grain zone.¹⁹⁾ Ohno *et al.*²⁰⁾ investigated the effects of Nb addition on as-cast γ -austenite grain structure in 0.2 mass% carbon steel. It was found that coarse columnar grain was suppressed and as-cast structure

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was refined owing to the pinning effect of Nb(C,N) particles. However, few researches have been reported on the improvement of grain density and refinement of FSS as-cast structures.

In this study, the effect of Nb addition on the as-cast structure of 18 mass% Cr ferritic stainless steel dual stabilized by Ti and Nb was investigated. The solidification characteristics of FSS with different Nb content and the corresponding formation of complex nucleus during solidification process were analyzed by equilibrium thermodynamic calculation. Composition evolution of precipitates during solidification process was further analyzed by Scheil model.

2. Experimental

Basic alloy with composition of Fe-18 mass% Cr-0.22 mass% Ti was firstly melted in a vacuum induction furnace. Temperature of molten steel was measured by Raytek Marathon MR1SB infrared thermometer. When the temperature of the molten steel reached 1 600°C, high-purity niobium blocks were added into the molten steel. For homogenization of the composition, the molten steel was held for 2 minutes, after which the molten steel was cast into mold at 1 570±15°C. The ingot was tapped 5 minutes later and quenched to the room temperature in water.

The laboratory samples consist of four ingots with different niobium content, named as S1, S2, S3, S4. The average composition of the four ingots are listed in **Table 1**. The shape of these ingots are cylinder with the height of 80 mm, the bottom diameter of 40 mm and the top diameter of 50 mm. The ingots were cut into two parts vertically through the centerline. One part was etched by aqua regia solution (HCl:HNO₃ = 3:1). to reveal the as-cast structure. And sample A was cut in the middle of these ingots from the mold side to the center in the other part. The outline dimensions and the sampling method of each ingot are shown in **Fig. 1**.

The sample A of each ingot was polished and etched by mixed solution of 2 g picric acid, 3 ml hydrochloric acid and 50 ml alcohol at room temperature. Afterwards, the microstructure was revealed and then examined by Leica DM4000 M optical microscope (OM).

The grain size and grain density were analyzed by MiVnt software statistically. The feature diameter of equiaxed grain is calculated by Eq. (1).

$$\bar{d}_g = \sqrt{\frac{4 \cdot S_E}{\pi}} \dots \dots \dots (1)$$

where $\bar{d}_g$ is the feature grain diameter (mm) of each equiaxed grain, S_E is the area (mm²) of each equiaxed grain.

The 3D morphology of particles existing in the steels

were revealed using potentiostatic electrolytic etching method. Sample A of each ingot was dissolved in 100 ml AA solution under a electric voltage ranging from 10 to 15 V for 45 seconds. In this paper, the 100 ml AA solution is composed of 1 g tetramethylammonium chloride, 10 ml acetylacetone solution, and the rest of methanol.^{21,22)} Then the 3D morphology was observed and analyzed using a field emission scanning electron microscope (FESEM-EDS, JSM-6701F, JEOL). Thermo-Calc software was applied to analyze the formation and evolution of these particles.

3. Results

3.1. As-cast Structure of the Ingots

Figure 2 shows the as-cast structures of the four ingots. The equiaxed grain ratio of these ingots all reached almost up to 100 percent. However, the average grain size and the grain density are different among these ingots. The corresponding statistical results were shown in **Figs. 3–4**.

Figure 3 shows the proportion of grain diameter distribu-

Fig. 1. Ingot outline dimensions and the sampling method.

Fig. 2. As-cast structure of four ingots. (a) S1 with no Nb addition, (b) S2 with 0.1 mass% Nb, (c) S3 with 0.3 mass% Nb and (d) S4 with 0.56 mass% Nb.

Table 1. Composition of the four ingots, mass percent.

Ingot	Cr	Ti	Nb	C	N	O	Si	Mn	Al	Ca	Mg
S1	17.98	0.20	0	0.0066	0.011	0.0018	0.27	0.087	0.0066	0.0008	0.0004
S2	17.81	0.24	0.10	0.0060	0.012	0.0022	0.28	0.097	0.0075	0.0008	0.0004
S3	17.63	0.19	0.30	0.0076	0.0077	0.0017	0.30	0.0081	0.0067	0.0013	0.0017
S4	17.68	0.13	0.56	0.0046	0.010	0.0022	0.30	0.030	0.0045	0.0008	0.0006

Fig. 3. Grain diameter distribution of each ingot.

Fig. 4. Grain quantity of each ingot.

tion of each ingot. The distribution of feature grain diameter is divided into four groups, which are 0 to 0.5 mm, 0.5 to 1.0 mm, 1.0 to 1.5 mm and 1.5 to 2.0 mm, respectively. Figure 4 shows the grain density and average grain diameter of each ingot. As can be obviously seen, the grain density and compactness degree increased and the average grain diameter decreased with the increasing niobium content. It can be concluded that the higher the niobium content, the smaller the grain size will be.

3.2. Microstructure and Precipitates

Microstructure of each ingot, observed by optical microscope, was shown in Fig. 5. The precipitates on grain boundary (BP) and in the grain interior (IP) were clearly revealed.

Optical microscope images shows that the size of IP decreases and the BP seems to become more apparent when the addition of Nb increases. More details of BP and IP were revealed in the following FESEM observation. Composition of precipitates located both in the grain interior and on the grain boundary were further revealed with EDS analysis. Most of the IPs were identified as complex nucleus in FESEM observation.

3.3. Precipitates in the Grain Interior

The morphology and composition of interior precipitates (IP) revealed by FESEM and EDS analysis were shown in Fig. 6. The majority of these interior precipitates were complex nucleus. As for sample S1 without niobium, titanium

Fig. 5. Microstructure observed by OM with 500X magnification after electropolishing. (a) S1, (b) S2, (c) S3 and (d) S4 (IP: Precipitates in grain interior; BP: Precipitates on grain boundary).

oxide was found in central part of the complex nucleus which was enveloped by Ti(C,N). In the Nb-added samples S2–S4, the titanium oxide was also found in the central. However, the enveloped layer turned into Ti-rich (Ti,Nb)(C,N), which contained little niobium element. Additionally, epitaxial tiny shape Nb-rich (Ti,Nb)(C,N) particles appear on the outside surface of Ti-rich (Ti,Nb)(C,N). Nb-rich (Ti,Nb)(C,N) particles might prevent interior precipitates from aggregation, in which way will reduce the size of interior precipitates.

According to the research by Bramfit⁽¹²⁾ and Villafuerte⁽¹³⁾ *et al.*, TiN is very effective for promoting the heterogeneous nucleation of δ -Fe. However, the supersaturation required for the formation of TiN leads to an excessive amount of Ti, which causes aggregation of TiN and formation of harmful inclusions. The study of Kimura *et al.*⁽²³⁾ showed that TiOx and Al–Mg–Ti–O will promote the formation of TiN, which promoted the nucleation of FSS hereafter. Shi *et al.*⁽²⁴⁾ proposed that the formation of Ti₂O₃–TiN complex nucleus during solidification will increase the equiaxed grain ratio of FSS slab in case of a lower Ti addition.

When FSS is alloyed with niobium, (Ti,Nb)_x(C,N)_y appears instead of Ti(C,N), which indicate that (Ti,Nb)_x(C,N)_y can be formed at the early stage of solidification and will promote the nucleation of FSS probably. Both the formation of (Ti,Nb)_x(C,N)_y and the heterogeneous nucleation effectiveness of TiC, NbC, NbN and NbC are further discussed in the following part.

3.4. Precipitates on the Grain Boundary

A large number of precipitates were found on the grain boundaries. Figure 7 shows the FESEM analysis of the precipitates presented on the FSS grain boundary.

For the sample S1 without Nb addition and the sample S2 with Nb content of 0.1 mass%, the precipitates on the grain boundary have a trunk shape and a branch-shape precipitates existed beside the trunk-shape precipitates. However, the branch-shape precipitates of S2 is smaller than that of S1. As for sample S3 and S4, when Nb content is further increased, the trunk-shape precipitates are dispersed, and the branch-shape precipitates are disappeared. Even in the

Fig. 6. Typical morphology and composition of complex nucleus in the grain interior. (a) S1, (b) S2, (c) S3 and (d) S4.

sample S4, the size of BPs decrease to several hundred nanometers.

According to the EDS analysis, the BP is mainly Fe, Cr, Nb, Ti carbonitride. However, on one hand, Fe, Cr element might come from the matrix because spatial resolution of the FESEM-EDS is beyond the size of the BPs. On the other hand, Fe, Cr element might also come from the chromium carbide at the grain boundaries due to the sensitization process of FSS (formation of chromium carbide and chromium-depleted zones at the grain boundaries). The precise chemical composition of BP could be identified by method of TEM-EDS, which had not been performed in this study. But it can be seen that the intensity of Nb increases in the order from S1 to S4 and the Ti, C, N composition of the BP is higher than that of matrix.

Figure 8 shows the normalized atomic distribution of Ti, Nb and C + N elements in the grain boundary precipitates of these four samples. To normalize the distribution, atomic ratio summation of Ti, Nb and C+N elements in each point

Fig. 7. Typical morphology and composition of precipitates on the grain boundary. (a) S1, (b) S2, (c) S3 and (d) S4.

was assumed to be one. Among them, the solid triangle mark, the hollow square mark, the solid square mark and the hollow circular mark represent the samples S1, S2, S3 and S4, respectively. The dash line represents the average Ti/Nb atomic ratio of BP in corresponding sample.

It can be seen that the Nb content in the BPs increases gradually, the Ti content decreases and the C + N content remains with the increase of Nb content in the ingots. Due to the presence of Fe and Cr elements, the carbon and nitrogen atomic content are high and widely distributed in the Fig. 8. However, the Ti and Nb atomic ratio in the BP are more concentrated.

4. Analysis

4.1. Solidification and Precipitation Characteristics

The effect of Nb on the solidification properties and the precipitation behavior were also analyzed thermodynamically. The complex nucleus formation during solidification

process was carried out by Thermo-Calc. The equilibrium phases existed in the range of 1 400–1 600°C were calculated using the TCFe7 database with the base component of 18 mass% Cr-0.20 mass% Ti-0.006 mass% C-0.01 mass% N-0.0020 mass% O. The calculated results are shown in Figs. 9 and 10.

It can be found that there are mainly four kinds of phases in the four ingots, which are Liquid, Ferrite, Ti_2O_3 and $\text{Ti}(\text{C},\text{N})$ or $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$ with a NaCl-type B1 type structure. The results show that Ti_2O_3 has already existed in the molten steel, and $\text{Ti}(\text{C},\text{N})$ or $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$ is generated during the solidification process.

In the course of the experiment, the raw material was

Fig. 8. Normalized atomic distribution of Ti, Nb and C + N in the grain boundary precipitates and the average Ti/Nb atomic ratio.

melted at about 1 570°C. Ti_2O_3 was able to form at this temperature theoretically. In the subsequent casting process, when temperature decreased, $\text{Ti}(\text{C},\text{N})$ or $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$ was generated during solidification. The calculation results correspond with the experimental phenomena, indicating the formation of IP (complex nucleus) is thermodynamically feasible.

It can be seen from Fig. 10 that the addition of Nb element slightly reduced the liquidus temperature of FSS and the precipitation temperature of $\text{MX}(\text{B1})$ type carbonitride, while obviously reducing the solidus temperature of FSS and increasing the solidification interval, which will contribute to the formation of $\text{Ti}(\text{C},\text{N})$ or $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$.

Fig. 10. Solidification characteristics of the four ingots with equilibrium model. (T_L -liquidus temperature, T_S -solidus temperature, $T_{\text{MX}(\text{B1})}$ -Precipitation temperature of $\text{Ti}(\text{C},\text{N})$ or $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$).

Fig. 9. Equilibrium thermodynamic analysis in solidification process of FSS. (a) S1, (b) S2, (c) S3 and (d) S4.

4.2. The Formation Possibility and Nucleation Effect of Complex Nucleus

Bramfitt¹²⁾ put forward the disregistry concept to measure the effectiveness of heterogeneous nucleation. The effective heterogeneous nucleation can reduce the nucleation energy of metals or alloys in the solidification process, thereby reducing the metal solidification nucleation undercooling.

With the help of the disregistry calculations, Bramfitt,¹²⁾ Park *et al.*²¹⁾ and Cheng *et al.*²⁵⁾ have reported the effective nucleation effect of TiN. However, few people have discussed the formation possibility and nucleation effect of complex nucleus (Ti-oxide with Ti(C,N) or (Ti,Nb)_x(C,N)_y). Due to the structural similarity of the TiN, TiC, NbC, NbN, the specific composition changes in (Ti,Nb)_x(C,N)_y during solidification. For the purpose of simplification, the lattice disregistry calculations involving Ti(C,N) or (Ti,Nb)_x(C,N)_y were replaced by TiN, TiC, NbC, NbN.

The lattice parameters of the relevant material are given in Table 2,²⁷⁾ the parameters at 1 500°C were used in the disregistry calculation. The orientation relationship between Ti₂O₃ and MX(B1) type carbide or nitride, which refers to TiN, TiC, NbN and NbC, is shown in Fig. 11.²¹⁾ The orientation relationship between δFe and MX(B1) type carbide or nitride is shown in Fig. 12.

The disregistry calculation model already proposed by Bramfitt is shown in Eq. (2),

$$\delta_{(hkl)_n}^{(hkl)_s} = \sum_{i=1}^3 \left(\frac{\left| d_{[uvw]_s} \cos \theta - d_{[uvw]_n} \right|}{3 \times d_{[uvw]_n}} \right) \times 100 \dots\dots (2)$$

where $\delta_{(hkl)_n}^{(hkl)_s}$, disregistry between the substrate and nucleated solid; $(hkl)_s$, a low-index plane of the substrate; $[uvw]_s$, a low-index direction in $(hkl)_s$; $(hkl)_n$, a low-index plane in the nucleated solid; $[uvw]_n$, a low-index direction in $(hkl)_n$; $d_{[uvw]_n}$, the distance between a nonmetallic element along $[uvw]_n$; $d_{[uvw]_s}$, the distance between the nonmetallic element along $[uvw]_s$, and θ , the angle between the $[uvw]_s$ and $[uvw]_n$.

The disregistry results between TiN, TiC, NbC, NbN and Ti₂O₃, δFe are shown in Table 3. When Nb was added to sample, the precipitate type changed and the disregistry varied due to differences in lattice parameters of TiN, TiC, NbC, NbN. It's easier for NbC and NbN to be formed when Ti₂O₃ exists, and the nucleation of δFe will be more likely to be promoted by TiN and TiC.

Bramfitt proposed that a nucleating agent is potent when the planar disregistry is less than about 12 pct. The disre-

gistry between Ti₂O₃ and TiN, TiC, NbC, NbN locate in the range of 12 to 14 pct, which are slightly beyond 12 pct. However, a lot of complex nucleus shown in Figs. 5 and 6 were found in the four samples. Therefore, it's considered that Ti₂O₃ will promote the formation of (Ti,Nb)_x(C,N)_y during the solidification process. The disregistry between TiN, TiC, NbC, NbN and δFe are all less than 9 pct, so (Ti,Nb)_x(C,N)_y is considered to be effective in promoting the nucleation of δFe. The heterogeneous nucleation of δFe will be promoted once the (Ti,Nb)_x(C,N)_y is formed. As a result, the growth of the columnar grains is suppressed, and the equiaxed grain ratio will be increased.

4.3. Precipitates on the Grain Boundary

The grain size of FSS became smaller when Nb was added. The morphology and composition of BP changed a lot in different ingots. Taking into account the great segregation of Nb elements during the solidification process,²⁸⁾ the Scheil model was induced to analyze the formation of grain boundary precipitates.

Table 4 is the basic composition used in the Scheil solidification calculation. The corresponding calculation results are shown in Fig. 13. In the figure, the left side represents

Fig. 11. The orientation relationship between Ti₂O₃ and MX(B1) type carbide or nitride (*i.e.*, TiN, TiC, NbN and NbC in this study). M represents Ti or Nb atoms and X represents C or N atoms respectively.

Fig. 12. The orientation relationship between δFe and MX(B1) type carbide or nitride (*i.e.*, TiN, TiC, NbN and NbC in this study). M represents Ti or Nb atoms and X represents C or N atoms respectively.

Table 2. Lattice parameters of the corresponding material in steel.

Substance	Lattice structure	a0 at 25°C/nm	a0 at 1 500°C/nm
δ-Fe	BCC-type	—	0.29396
Ti ₂ O ₃	Corundum-type	—	0.51251
NbC	NaCl-type B1	0.44702	0.45517
NbN	NaCl-type B1	0.43934	0.44474
TiC	NaCl-type B1	0.43257	0.43783
TiN	NaCl-type B1	0.42419	0.43055

Table 3. Misfit calculation results.

	(100) TiN	(100) TiC	(100) NbN	(100) NbC
(0001) Ti ₂ O ₃	13.61	12.83	12.25	12.73
(100) δ-Fe	3.57	5.32	6.98	8.69

Fig. 13. Scheil solidification calculation result and element content in precipitate phase. (a) S1, (b) S2, (c) S3 and (d) S4.

Table 4. Basic composition used in the Scheil solidification calculation, mass percent.

Element	Cr	Ti	C	N	O	Nb
Content	18	0.2	0.006	0.01	0.002	0, 0.1, 0.3, 0.56

the phases variation during solidification, the right side represents the composition change of precipitate having NaCl-type B1 type structure. It can be seen from Fig. 13 that the precipitate is $\text{Ti}(\text{C},\text{N})$ or $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$.

Since the composition in the precipitate phase changes a lot at the end of the solidification, the area where the solidification fraction above 0.95 is enlarged for ease of observation, and the dividing line is indicated by a dotted line in Fig. 13.

According to the calculation results, the phases in the Scheil solidification process are the same as that of the equilibrium precipitation. For the S1 sample without Nb, the precipitate is mainly $\text{Ti}(\text{C},\text{N})$. Due to the strong segregation of element C, the content of C gradually increases and N element content gradually decreases during the solidification process.

After the addition of Nb element in the sample, the precipitate is $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$. When the solidification comes to an end, the Nb content is rapidly increasing in the $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$. It is worth noting that when Nb content reached 0.56 mass%, the content of niobium exceed titanium in $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$ at the end of solidification.

The atomic distribution of Ti, Nb and C + N elements in $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$ calculated by Scheil model is shown in Fig. 14. The average Ti/Nb atomic ratio of BP obtained in the experimental ingots is also indicated by a dashed line in the Fig. 14.

Figure 14 shows that, the calculated Nb content increased and Ti decreased in $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$ when Nb content increases in FSS. Due to the little content of element Fe and Cr in the precipitate, the carbon and nitrogen content have a little change and the atomic content maintained at about 0.5. The calculation result shows the same law with the experimental process. However, the Nb content in the experiment is higher than that in the calculation, of which the reason might be attributed to a more intense segregation behavior of Nb during solidification or the further precipitation of NbC in the cooling process after solidification. With the help of Scheil calculation, it can be seen that the formation of BP will take place during solidification.

It's reported by Belyakov *et al.*⁽²⁷⁾ and Aksoy *et al.*⁽²⁸⁾ that the FSS grain will undergo a process of grain merging when solidification comes to end. DeArdo⁽²⁹⁾ pointed out that NbC would play an import role in the pinning effect. Grain merging phenomenon was also observed in the present study. The microstructure of Sample S1 without Nb revealed by etching is shown in Fig. 15.

It can be seen from Fig. 15 that the grain in the image center contains at least two sub-grains. There exists a crossline in the middle of this grain, namely the sub-grain boundary which had not been disappeared completely. The sub-grain boundary or merge line also exists in other grains. According to the calculation results of Scheil model, Nb-rich $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$ will precipitate in the residual liquid at the end of solidification, which probably play an important

Fig. 14. Calculated atomic Ti, Nb and C + N distribution in the $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$ compared with experimental data.

Fig. 15. Grain merging phenomenon in the FSS grains.

role in preventing the grain merging of FSS. The pinning effect of $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$ will be discussed in the following part.

4.4. The Pinning Effect of $(\text{Ti},\text{Nb})_x(\text{C},\text{N})_y$

The grain coarsening phenomenon will always be present in real steels, which can be slowed or eliminated by the presence of second phase particles.⁽²⁸⁾ The finely dispersed second-phase particles have a significant effect on the grain refinement. The pinning effect of second phase particles is analyzed by Gladman, which is expressed by Eq. (3)⁽³⁰⁾

$$D_c = \frac{\pi d}{6f} \left(\frac{3}{2} - \frac{2}{Z} \right) \dots \dots \dots (3)$$

where D_c is the calculated average diameter of the grain, d is the average diameter of second phase particles, f is the volume fraction of second phase particles, and Z is the ratio of diameter D_M/D_0 , which D_M is the maximum diameter of the measured grain, D_0 is the statistical average diameter of the measured grain.

According to the statistical analysis of grain size in the four ingots, D_M of each sample is 2.33 mm (S1), 1.76 mm (S2), 1.70 mm (S3) and 1.27 mm (S4), respectively. D_0 of each sample is 0.596 mm (S1), 0.526 mm (S2), 0.450 mm (S3) and 0.334 mm (S4) respectively. The corresponding Z of each sample is 3.91 (S1), 3.36 (S2), 3.78 (S3) and 3.83

mm (S4), respectively. We take average value of Z , which equals 3.7 to calculate the Gladman equation.

The precipitate $(\text{Ti,Nb})_x(\text{C,N})_y$ with NaCl-type B1 type structure is the major particle during the solidification process.

Table 5. Volume fraction of second phase particles at the solidification end of each ingot.

Content of Nb (mass percent)	0	0.1	0.3	0.56
Ts(K)	1 712.15	1 688.15	1 608.15	1 503.15
f	6.32E-04	6.67E-04	7.75E-04	9.35E-04

Fig. 16. Calculated grain size and the statistical average grain size of each ingot.

Fig. 17. Schematic illustration of solidification process in FSS (a) without and (b) with Nb addition.

cess in this study. The size of precipitates was performed with a software called INCA running on a SEM-EDS (EVO18 SEM, Carl Zeiss, Germany) and automatically finds and analyzes particles from a preselected area. According to the statistics analysis of INCA, the statistical average diameter of the second phase particles d is $1.47 \mu\text{m}$.

The volume fraction of second phase particles f is analyzed with the help of Thermo-Calc at the end of solidification. The results are shown in the following **Table 5**.

According to Gladman pinning model combined with the above data, the maximum grain size to which the grain could grow up can be obtained in theory. The calculated maximum grain size and the statistical average grain size are shown in the **Fig. 16**.

Both the statistical results and the calculated results show that the grain size of ferritic stainless steel exhibits a trend of refinement with the increasing content of Nb. However, the actual statistical result of grain size is lower than that of calculation, which may be due to the following two reasons. 1. The grain growth is limited due to the high cooling rate in a small mold. 2. At the end of solidification, the segregation of elements results in a large amount of precipitate in the residual liquid phase, which further hinders the growth and merging of grains.

In summary, for a more clearly understanding, the effect of Nb is sketched in **Fig. 17**. As can be seen in **Fig. 17**, Ti-Mg-Al-oxide will firstly form in the molten steel, which will promote the formation of $\text{Ti}(\text{C,N})$ or Ti-rich $(\text{Ti,Nb})_x(\text{C,N})_y$ in the solidification process and then the heterogeneous nucleation of $\delta\text{-Fe}$ will be facilitated. In the ingot without Nb addition, the solidification region is narrow and aggregation of $\text{Ti}(\text{C,N})$ particles might take place. Additionally, the FSS grains will exhibit grain merging after solidification.

When the Nb element is added to the FSS sample, the solidus temperature is obviously reduced, which will extend the solidification region. The extended region probably increase the formation opportunities for Ti-rich $(\text{Ti,Nb})_x(\text{C,N})_y$. The epitaxial tiny shape Nb-rich $(\text{Ti,Nb})_x(\text{C,N})_y$ particles appeared on the outside surface of Ti-rich $(\text{Ti,Nb})_x(\text{C,N})_y$ will avoid the occurrence of particles aggregation, which will offer more complex nucleus. The above-mentioned changes will increase the nucleation chance of $\delta\text{-Fe}$ during solidification.

When solidification comes to an end, small Nb-rich $(\text{Ti,Nb})_x(\text{C,N})_y$ particles formed in the residual liquid at the end of solidification will play a significant role in blocking the grain growth and pinning the grain boundaries. As a result, the as-cast structure of FSS is refined.

5. Conclusions

In this paper, the effect of Nb addition on the as-cast structure of ferritic stainless steel dual stabilized by Ti and Nb was studied, and the following conclusions are obtained.

(1) The addition of Nb element can reduce the size of equiaxed grains of FSS and improve the grain density, which exhibits strong effect of grain refinement.

(2) Complex nucleus were found in the interior grain of ferritic stainless steel. When Nb was added to FSS, the outer layer of the complex nucleus converted from $\text{Ti}(\text{C,N})$ to $(\text{Ti,Nb})_x(\text{C,N})_y$. The results of disregistry calculation show

that complex nucleus can be formed during solidification and promote the nucleation of δ -Fe.

(3) The solidification region will be extended when Nb is added to FSS, which will offer more opportunity for complex nucleus to form, and then promote the nucleation of δ -Fe.

(4) When Nb is added to FSS, The epitaxial tiny shape Nb-rich (Ti,Nb)(C,N) particles appeared on the outside surface of Ti-rich (Ti,Nb)(C,N) will suppress the aggregation and growth of Ti-rich (Ti,Nb)(C,N), making itself a smaller size and larger quantity, resulting in an increased nucleation chance of δ -Fe.

(5) With the addition of Nb, (Ti,Nb)_x(N,C)_y appeared in the grain boundary precipitates instead of Ti(C,N). The size of BP becomes small and the distribution becomes dispersed. Scheil calculation results indicate that the BP is mainly (Ti,Nb)_x(N,C)_y and forms at the end of solidification. What's more, (Ti,Nb)_x(N,C)_y exhibits an positive effect in preventing the grain merging of FSS grains after the solidification, according to the Gladman's pinning mechanism.

(6) The collective effect of nucleation and pinning on the grain formation and growth will play an important role in the refinement of the as-cast structure of dual stabilized FSS by addition of niobium.

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