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Morphology, orientation relationships and formation mechanism of TiN in Fe-17Cr steel during solidification

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ABSTRACT

Morphology, orientation relationships, and formation mechanism of TiN in Fe-17Cr ferritic stainless steel were investigated theoretically and experimentally by scanning electron microscopy, X-ray diffractometer, and electron backscatter diffraction. Two types of structures of TiN, without cores and with cores, were observed in the solidified microstructure. The dimensionless entropy of fusion ($\Delta S_m/R$) of TiN is calculated as 2.5, which suggests that TiN will exhibit regular faceted morphology. The planar disregistry between (111) plane of TiN and (110) plane of ferrite is calculated as 17.1%, which indicates that it is not sure if TiN can act as the heterogeneous site for ferrite nucleation during solidification. Pole figures of TiN and ferrite by EBSD show that Kurdjumov-Sachs orientation relationship between TiN and ferrite exists, which confirms that TiN can act as the heterogeneous site for ferrite. In addition, based the EDS mapping, TiN in the microstructure should form during solidification rather than solid-state transformation.

1. Introduction

Compared with austenitic stainless steels, ferritic stainless steels are attracting more and more attention due to their high thermal conductivity, low linear expansion, good resistance to chloride stress-corrosion cracking and pitting corrosion, high temperature resistance to oxidation, and low cost [1–6,7,8]. For ferritic stainless steels, it is inevitable that some non-metallic elements, such as carbon, nitrogen, and oxygen, are contained during metallurgy operation. These non-metallic elements occupy interstitial sites in the steels due to smaller atomic size compared with the metallic elements. In order to minimize the energy of the system, the carbon or nitrogen atoms in the interstitial sites tend to segregate to the dislocation line to form atmospheres or segregate at the grain boundary to form chromium carbides or chromium nitrides. The atmospheres can hinder dislocation motion and impair the surface quality during subsequent deformation [6] and the chromium carbides or nitrides at the grain boundaries may result in intergranular corrosion (IGC) [9]. In order to reduce or eliminate the harmful effect of the non-metallic elements in ferritic stainless steels, the general approach is to reduce the content of carbon or nitrogen and add the stabilizing elements such as, Ti and/or Nb [7]. When the content of carbon or nitrogen is sufficiently low in ferritic stainless steels, further reduction of the contents is extremely difficult and the cost of this metallurgy operation is very high. Thus, addition of Ti and/or Nb is considered as an effective approach during the metallurgy of ferritic stainless steels.

For 436 stainless steel, Ti is added to stabilize carbon and nitrogen, and as a result, titanium carbides or nitrides tend to form due to the affinity of N and C with Ti is much stronger than that of Fe, Cr and other metal elements [9,10]. Both TiN and TiC are with rock salt type structure (space group $Fm\bar{3}m$) and their lattice parameters are $a_{TiN} = 4.27$ Å and $a_{TiC} = 4.32$ Å, respectively [11,12]. Compared with carbon, nitrogen has a higher affinity with titanium and therefore TiN will form prior to TiC [11,13,14].

For ferritic stainless steels, it is known that the grain size of ferrite matrix has a determining influence on the mechanical properties and corrosion resistance of the steels [2,15–17]. Besides ferrite, TiN precipitates also have a significant effect on the microstructure and properties of the class of steels [8,15,18–21]. The solutes Ti and N will be rejected into the liquid at/ahead of the solid/liquid interface during solidification since the equilibrium distribution coefficients of both Ti and N in Fe melts are less than unity [22]. Thus, the concentration of Ti and N reaches the highest value at the grain boundary, where TiN tend to precipitate. TiN precipitates, especially coarse TiN at the grain boundary, will deteriorate the properties of the steels greatly since TiN is brittle and it is hard to deform. TiN stripe may occur at the surface of

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the stainless steel sheet during subsequent rolling, which impairs the surface quality greatly. However, if fine TiN can precipitate dispersedly, it can act as the heterogeneous site and refine the solidified microstructure of the stainless steels [15,23–24].

In order to understand the formation mechanism of TiN in ferritic stainless steels, great efforts have been made. Firstly, formation thermodynamics of TiN was investigated [22,25–28]. The activity coefficient and first-order interaction coefficient, which was used to calculate the formation thermodynamics of TiN, in Fe-Cr-Ti-N alloys [25–26], Fe-Cr melts [27], and liquid iron [28] were determined using calculation and experiments. In our previous work, TiN precipitation in AISI 439 stainless steel was discussed by using thermodynamics, and the non-equilibrium effect is also considered [22]. It was found that TiN forms during solidification rather than from the melts directly. High cooling rate can promote the formation and can refine the grain size of TiN during solidification. In terms of the formation of TiN during solidification in steels, one important consideration is grain refinement by heterogeneous nucleation. Mu et al. [18] developed a model to calculate the critical diameter of TiN for heterogeneous nucleation of ferrite on TiN in steels, and the calculated critical diameter of TiN is 0.355 μm, which suggests that TiN less than 0.355 μm cannot act as the heterogeneous site of ferrite during solidification.

Experimental works were also carried out to examine the nucleation behavior of ferrite on TiN in steels [15,24]. Kang et al. [15] investigated the effect of Ti content on the microstructure and mechanical properties of UNS S44100 stainless steel. It was shown that the average grain size of the as-cast steel was decreased with increasing Ti content due to the formation of TiN precipitates. Meanwhile, significant grain refinement was also observed in 430 stainless steel [24] with the increase of Ti content. They attributed this refinement effect to heterogeneous nucleation of ferrite on TiN. To achieve heterogeneous nucleation, a certain orientation relationship between the nucleation phase and the substrate is required to minimize the interface energy. The frequent orientation relationship between the ferrite matrix and the nitrides with B1 crystal structure is Baker–Nutting when the nitrides precipitate from ferrite in steels [12]. Besides, using TEM, Tirumalasetty et al. [11] observed that the (Nb, Ti)N precipitates, in the size range 10–150 nm, have a Nishiyama–Wassermann [29–30] orientation relationship with the ferrite matrix in TRIP assisted multiphase steels, when (Nb, Ti)N precipitates from ferrite.

However, no evidence about the orientation relationship between TiN and ferrite during solidification can be found until now, although grain refinement of ferrite can be achieved with Ti addition in the steels. The grain refinement mechanism in ferritic steels with Ti addition remained unclear.

The aim of the present work is to examine the orientation relationship between TiN and the ferrite matrix in 436 stainless steels using electron backscatter diffraction (EBSD) technique. The grain refinement mechanism of ferrite and the formation mechanism of TiN are discussed according to the obtained orientation relationship.

2. Experimental Procedure

The chemical composition (wt%) of the Fe-17Cr stainless steel used in the present work was 0.009C, 17.50Cr, 0.30Si, 0.25Ti, 0.27Mn, 0.86Mo, 0.023P, 0.001S, 0.008N, and Fe the balance. In the experiments, the stainless steels were first heated to1873 K in a vacuum induction furnace, and then cast into magnesia molds with the dimension of 50 mm inner diameter, and 100 mm height, after stabilization at 1873 K for about 20 min. SEM samples were ground successively with 800, 1000 and 2000 grade SiC paper and then carefully polished with 2.5, 1.5 and 0.5 μm polishing pastes. Then, the samples were electrolytically etched with 10% oxalic acid reagent. The EBSD samples were mechanically polished followed by the electro-polishing in the solution of 10% perchloric acid and 90% alcohol at approximately − 25 °C for 60 s with an applied potential of 16 V. The microstructures were observed by JSM-6490LV tungsten filament scanning electron microscopy (SEM) [31–32]. The analytical method of energy dispersive X-ray spectroscopy (EDS) was employed to investigate chemical compositions. Phase identification was carried out by Rigaku D/max-2400 PC X-ray diffractometer using Cu Kα working at a voltage of 56 kV and current of 182 mA. An Oxford-S-3400N SEM operating at a voltage of 200 kV and current of 120 μA, equipped with HKL channel 5 software, was used for EBSD data acquisition and analysis.

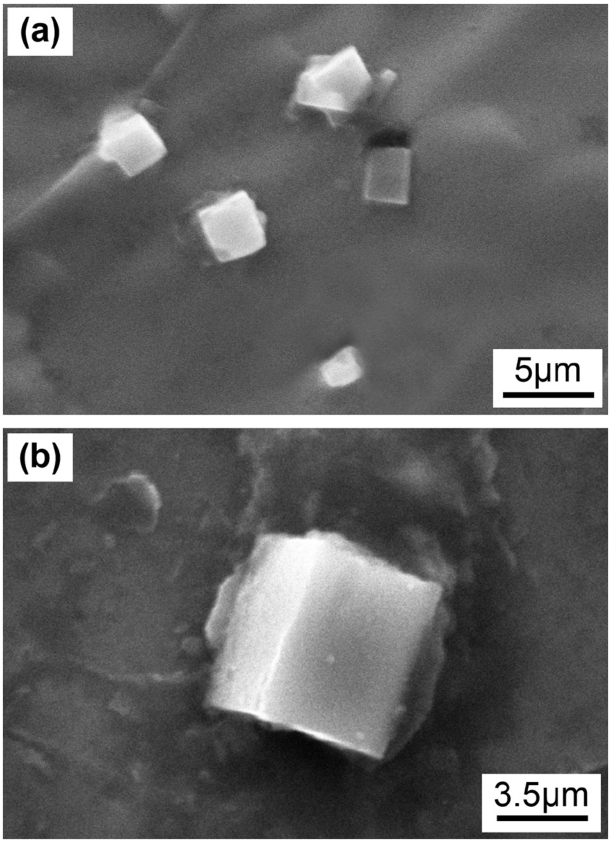

Fig. 1. SEM image of the distribution and dimensional morphology of TiN in the solidified microstructure. (a) distribution of TiN in the solidified microstructure; (b) dimensional structure of the cubic TiN.

3. Results and Discussion

3.1. The Type and Growth Morphology of TiN

In the experiments, two types of TiN were observed in the as-cast samples of the steel. The first type is the TiN without heterogeneous core and the second one is the TiN with heterogeneous cores. The dimensional morphology of TiN in the solidified microstructure usually exhibits a cubic shape, as shown in Fig. 1 (a) and (b). It is known that an anisotropy of the interface energy exists during crystal growth, especially for faceted phase. For crystals with FCC structure, the close-packed plane (111) has the lowest interface energy during solidification. Thus, the final shape of the FCC crystal in the solidified microstructure should be octahedral. However, other factors, such as impurities in the melts and solidification parameters, often affect the growth behavior of specific planes and change the final appearance of the crystal [33]. When the interface is bounded by the secondary close-packed plane (100), the crystal will exhibit cubic appearance, which is also the frequently observed shape in the solidified microstructure for FCC crystals, as shown in Fig. 1.

In general, the substances can be divided into faceted and non-faceted types based on their growth morphology. From Fig. 1, it can be