Yu Yan-chong*, Chen Wei-qing and Zheng Hong-guang

High-Temperature Oxidation Behavior and Formation Mechanism of Rolling Cracks of Fe-36Ni Invar Alloy

Abstract: The oxidation of Fe-36Ni invar alloy in 5%O₂-15%CO₂-80%N₂ atmosphere at 1200 °C for 4 h and the cause of rolling cracks have been investigated using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Gleeble thermal simulation machine. The result showed that the scales consisted of the external scale and the subscale. The external scale had stratified structures of Fe₂O₃/Fe₃O₄+NiO/Fe₃O₄+FeO+NiO from outside to inside. The subscale had a typical substructure of the intra-granular subscale and the inter-granular subscale. Oxidation particles of (Fe₃O₄+FeO) were isolated in FeNi₃ matrix in the intra-granular subscale zone. The grain boundary was the preferential short-circuit diffusion paths of the diffusing O and was first to be oxidized. The inter-granular subscale led to the subscale and was the origin of rolling cracks. The protective heating measure was put forward to prevent rolling cracks.

Keywords: Fe-36Ni invar alloy, the external scale, the subscale, rolling cracks

*Corresponding author: Yu Yan-chong: State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China, E-mail: yuyanchong0205@163.com
Chen Wei-qing: State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China
Zheng Hong-guang: Metallurgical Process Department, Baosteel Institute, Shanghai, 201900

1 Introduction

Fe-36Ni alloy consists of an austenite-single phase structure and is notable for its uniquely low thermal expansion coefficient (TEC) under its Curie temperature. Not only has it been employed in temperature-independent instruments, such as precision measuring devices, but it has also served as special structure materials [1–3]. However, Fe-36Ni alloy has a poor oxidation resistance because of the low amounts of Cr and Al in it, and serious subscales may lead to cracks in the hot-rolling process. It is therefore important to understand the oxidation behavior of Fe-36Ni invar alloy. To date, much work has been done on the oxidation of Fe-Ni systems in various atmospheres, such as pure oxygen, Ar-H₂O mixed gas, CO₂ atmosphere and air [4–9]. Furthermore, according to the type of scales formed, Fe-Ni systems have been divided into four major compositional ranges: 0–2%Ni, 2–35%Ni, 35–80%Ni and 80–100%Ni [10]. Previous studies have clarified the morphology and constituents of the external scales, but the characteristics of the subscale scale, especially the relationship of the inter-granular oxidation and rolling cracks have attracted relatively less attention. In addition, the oxidation behavior of Fe-36Ni alloy in 5%O₂-15%CO₂-80%N₂ atmosphere has not been reported yet. In this research, the high temperature oxidation behavior of Fe-36Ni alloy in 5%O₂-15%CO₂-80%N₂ atmosphere was investigated in detail. The cause and preventive measure against rolling cracks were also given.

2 Experimental procedures

The chemical composition of the Fe-36% Ni alloy is shown in Table 1. Specimens were cut from the cast slab with the dimensions of a 10 mm × 10 mm × 10 mm cube. Specimens were ground with SiC abrasive papers up to 2000#, polished and then cleaned in alcohol prior to being oxidized. The oxidation of the alloy was performed in a molybdenum wound furnace in 5%O₂-15%CO₂-80%N₂ atmosphere at 1200 °C for 4 h. High purity O₂, CO₂ and N₂ were prepared to form the experimental mixed gas. The temperature was measured with a B-type thermocouple placed just beneath the specimen and was controlled within ±5 °C of the set temperature. Two specimens were exposed in each oxidation experiment. The schematic diagram of the experimental apparatus is shown in Fig. 1. The external scales were stripped off mechanically and then the matrix specimen was compressed at a high-temperature using the Gleeble thermal simulation

The specimen was compressed with the deformation amount of 40% when it was heated to 1200 °C at a velocity of 10 °C/s and soaked for 2 minutes in the vacuum condition.

The microstructure, constituent and phase identification of the scale were analyzed by using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD) respectively.

### 3 Experimental results and discussions

#### 3.1 High temperature oxidation behavior of Fe-36% Ni invar alloy

##### 3.1.1 General morphology of the scale

The general morphology of the scale of the alloy oxidized in 5%O₂-15%CO₂-80%N₂ atmosphere at 1200 °C for 4 h is shown in Fig. 2. The oxidized microstructure can be divided into an external scale and a subscale. The symbol A denotes the external scale, which is subject to easy spallation from the specimen matrix surface due to the thermal stress in the cooling process. The symbols B and C denote the subscale, where B is the inter-granular oxidation zone, and C is the intra-granular oxidation zone. The frontier interface of the intra-granular subscale is severely undulated, and the inter-granular subscale extends beyond the intra-granular subscale. The symbol D represents the unoxidized metal matrix of the alloy.

##### 3.1.2 Morphological and phase analysis of the external scale

Fig. 3 shows the SEM morphology of the external scale of Fe-36Ni alloy. After being oxidized for 4 h, the external scale was evidently composed of three stratified layers, the thickness of which was approximately 455 um. The outermost layer seen in the external scale was of the gray phase and small pores existed in it. EDS analysis showed that the composition was 73.8 Fe and 26.2 O (wt.%) and that no Ni was present. XRD analysis further confirmed that the outermost layer was composed of Fe₂O₃, as shown in Fig. 5 (a). The middle layer which had big voids was of the...
ash-white phase and the composition was 72.33 Fe, 24.77 O and 2.99 Ni (wt.%). XRD analysis revealed that the middle layer consisted of Fe$_3$O$_4$ and a small amount of NiO, as shown in Fig. 5 (b). The innermost layer was of the white phase, with the composition of 72.98 Fe, 22.46 O and 4.46 Ni (wt.%). XRD analysis confirmed that the innermost layer was composed of Fe$_3$O$_4$, FeO and a small amount of NiO, as shown in Fig. 5 (c). Between the middle layer and the innermost layer was a transition zone, as shown in the rectangle frame of Fig. 3, and the SEM morphology of Fig. 4. Some white bands existed in the transition zone and it is noteworthy that the content of Ni is up to 14.6 wt.% determined by EDS. Therefore, we could assert that the white band is a Ni-enriched region.

3.1.3 Morphological and phase analysis of the subscale

The internal scale was observed and analyzed when the external scale of the specimen had been removed. Fig. 6 shows the SEM morphology of the intra-granular sub-scale. The symbol A represents the white phase. EDS analysis showed that the composition was 20.05 Fe, 79.95 Ni (wt.%) and no O was present. The symbols B and C denote the grey phase and light-grey phase respectively. The composition of B was 73.15 Fe, 23.50 O and 1.75 Ni (wt.%) and that of C was 78.26 Fe, 19.31 O and 1.20 Ni (wt.%) by EDS. XRD analysis revealed that the intra-granular subscale were composed of FeNi$_3$, Fe$_3$O$_4$ and FeO, as shown in Fig. 8. In combination with the analysis result of EDS and XRD, it could be seen that the white phase was FeNi$_3$ which was the metal matrix and the grey phase and light-grey phase were composed of Fe$_3$O$_4$ and FeO. However, NiO was not detected by XRD, which was probably because only a
small number of these oxides formed or they existed sporadically. Therefore, the intra-granular subscale is a mixed zone composed of oxides and the metal matrix, and oxides of (Fe$_3$O$_4$ + FeO) are isolated in the FeNi$_3$ matrix.

Fig. 7 shows the SEM frontier morphology of the inter-granular subscale. The subscale permeated into the metal matrix along the grain boundary which was severely oxidized and as a result the oxide in the inter-granular oxidation zone showed continuity. Therefore, we can conclude that the grain boundary is the preferential short-circuit diffusion path of the diffusing O and is first to be oxidized. The result is consistent with the previous reported results that the inter-granular oxidation zones always led to the subscales [5, 9]. In addition, islands of Fe$_3$O$_4$ and FeO partials become finer with the increasing distance of the matrix surface.

3.1.4 Formation process of the scales

Due to the larger affinity of Fe than Ni with oxygen, selective oxidation occurred, and the oxidation of Fe-36Ni invar alloy is thought to progress as follows. The Fe was oxidized initially and a thin surface scale formed during the initial stage of oxidation. However the internal scale had not yet formed. With the increase of the oxidation time the Ni which had a weak affinity with O would be enriched and O would then begin to permeate gradually into the alloy through grain boundaries and other short-circuit diffusion paths. Diffusing O reacted with Fe at the grain boundary and produced grain-boundary oxides, which caused local oxidation. Subsequently diffusing O permeated into grains though the oxides and the concentration of oxygen rose gradually with the increase of oxidation time. When the concentration of oxygen exceeded the threshold concentration for the formation of the oxide, selective oxidation in grains occurred, and Fe$_3$O$_4$ and FeO partials began to form and grow as well. In the meantime, the surrounding matrix was gradually enriched with Ni and eventually became stable. Therefore, the phase of the matrix changed from Fe$_3$Ni$_2$ to FeNi$_3$ because of the lack of Fe.

In contrast, Fe diffused outwards through the grain boundary, the inter-granular scale, and the consecutive oxide phase, and then reacted with O in the atmosphere on the surface to produce FeO. FeO is then oxidized by oxygen to form Fe$_3$O$_4$, and then Fe$_3$O$_4$ as external scales. Although Fe has a larger affinity than Ni with oxygen, it was inevitable that some NiO formed due to Ni diffusing and reacting with oxygen. Therefore, a little NiO existed in the subscale and external scale. The oxides of Si and Cr with a strong affinity for O were not detected by EDS and X-ray diffraction. This may be due to only a small number of these oxides being formed or their being finely dispersed. With the increase of oxidation time at this temperature, the thickness of the external scale and subscale increased.

3.2 Formation mechanism of the crack

Because of the size requirement of the Gleeble experiment, a specimen with dimensions of Φ8 mm × 12 mm was prepared and then oxidized on the same condition above. With the external scales stripped off, the macro-morphology of matrix specimen by high temperature compression using the Gleeble thermal simulation machine is shown in Fig. 9. It can be seen that obvious cracks occurred on the compressed surface and the fringe of the specimen.
also severely cracked. The cracks were similar to the case of roll cracks.

In order to determine the cause of the cracks, the compressed specimen was cut longitudinally, polished and then observed by SEM. Fig. 10 shows the SEM morphology of the longitudinal section. It can be seen that remarkable cracks occurred and propagated into the matrix along the oxidized grain boundary. However, it is noteworthy that no crack was observed in the intra-granular subscale. Therefore, the oxidized grain boundary, also named the inter-granular subscale, is the origin of the cracks.

The formation mechanism of the cracks is thought to be as follows. The grain boundary was the preferential short-circuit diffusion path of the diffusing O and was severely oxidized. Not only did the continuous oxides in the inter-granular oxidation zone destroy the integrity of the matrix, but it also weakened the grain boundary binding force. When the compressed stress exceeded the grain boundary binding force, a crack occurred and propagated to the matrix along the grain boundary. During the hot rolling process any crack source easily led to cracks, which deteriorated the surface quality and the hot ductility of the plate.

Based on the study above, it can be concluded that the inter-granular subscale led to the cracks during the hot rolling process. Therefore, a protective heating measure is proposed to prevent cracks.

The specimen was also prepared and oxidized in Ar atmosphere at the temperature of 1200 °C for 4 h and then compressed by the Gleeble thermal simulation machine on the same condition above. After oxidation, the specimen was cut longitudinally, polished and then observed by SEM. Fig. 11 shows the SEM morphology of the longitudinal section. Although there was a small amount of intra-granular subscale due to impure argon, the inter-granular subscale was not found; moreover no crack was observed. Therefore the protective heating measure is an effective measure to prevent rolling cracks.

4 Conclusions

1. The scales of Fe-36Ni invar alloy consisted of the external scale and the subscale when the alloy was oxidized in 5%O2-15%CO2-80%N2 atmosphere at the temperature of 1200 °C for 4 h.
2. The external scale had three stratified structures. The outermost layer was composed of Fe2O3; the middle layer consisted of Fe3O4 and a small amount of NiO; the innermost layer was composed of Fe3O4, FeO and a small amount of NiO.
3. The subscale had a typical substructure of the inter-granular oxidation and the intra-granular subscale which was composed of a metal/oxide mixed zone. Oxidation particles of (Fe₃O₄ + FeO) also permeated the FeNi₃ matrix with an island-like distribution.

4. The grain boundary was the preferential short-circuit diffusion path of the diffusing O and led to the subscales. The inter-granular subscale, rather than the intra-granular subscale, led to the rolling cracks. The protective heating measure was proposed to prevent rolling cracks.

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References


