Corrosion Behavior of Low-Alloy Pipeline Steel with 1% Cr Under CO₂ Condition

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Received: 20 August 2014 / Revised: 18 November 2014 / Published online: 20 March 2015
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Abstract Carbon dioxide corrosion behavior of low-alloy pipeline steel with 1% Cr exposed to CO₂-saturated solution was investigated by immersion experiment. SEM, EDX, TEM, EPMA and XRD were utilized to investigate the microstructure, corrosion morphologies, corrosion phases and elements distribution of corrosion scale. The results demonstrate that the microstructure of tested steel consists of ferrite and carbides. During the corrosion process, ferrite dissolves preferentially, leaving carbide particles behind. The residual carbide particles may promote the nucleation of FeCO₃ crystal. The phase comprising of the inner layer is Cr compound, and the one of the outer layer is FeCO₃. The formation process of corrosion scale can be illustrated as follows: Firstly, a thin scale consisting of thin inner layer and outer layer is formed, which represents poor corrosion resistance; then, the inner layer changes little, once it has been formed, and the outer layer becomes thick and compact, which demonstrates that a fine corrosion resistance is obtained. The chemical elements of chromium and molybdenum accumulate in the inner layer of corrosion scale. The corrosion behavior of low-alloy steel based on microstructure and morphology characterization is also discussed.

KEY WORDS: Carbon dioxide; Low-alloy steel; Corrosion behavior; Microstructure

1 Introduction

As one of the most useful techniques in modern oil industry, CO₂-enhanced oil recovery has attracted many attentions owing to its positive contribution to geological

store of carbon [1–4]. Carbon dioxide corrosion (sweet corrosion) is an intractable problem when the dry CO₂ encounters water or saline in the process of producing and transporting oil and gas. The corrosion behavior could decrease the longevity of pipeline steel and even cause leakage failure incidents [5, 6]. Therefore, many research works have been carried out about carbon dioxide corrosion behavior, and the carbon dioxide corrosion mechanism of low-alloy pipeline steel has also been carried out [7–10]. The practical environment of some exploitation actions of oil and gas resource is harsher than that of the normal one. New kind of low-alloy pipeline steel with excellent carbon dioxide corrosion resistance and low cost is required to fill the gap between carbon steels and stainless steels, and the carbon dioxide corrosion behavior of the new steel is also expected to illustrate the corrosion phenomenon.

The behavior and mechanism of carbon dioxide corrosion are investigated by many specialists using surface morphology, electrochemical curve, corrosion rate and

Available online at <http://link.springer.com/journal/40195>

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corrosion phase. It was found that the corrosion phenomenon is affected by many factors, such as pH value of solution, microstructure of steel, experimental temperature, CO₂ partial pressure and strength of steel. [2, 9, 10]. Carbon dioxide corrosion behavior of low-alloy pipeline steels free of chromium was studied by many researchers [11–15]. It was found that experimental temperature plays a significant role on the carbon dioxide corrosion behavior in CO₂-contained water in the absence and presence of HAc, and high experimental temperature strengthens the dissolution of substrate steel and accelerates the FeCO₃ scale precipitation [11]. The carbon dioxide corrosion experiment of low-alloy pipeline steel free of chromium under turbulent flow condition in simulated stratum water was performed, and the results demonstrate that the extending of corrosion test time and the formation of complex carbonate contribute to the stability of surface film [12]. The carbon dioxide corrosion rate in distilled water for low-alloy pipeline steels free of chromium increases with temperature increasing from 50 to 80 °C, and then decreases with temperature increasing from 80 to 130 °C [13, 14]. A duplex structure film, comprising of an inner layer and an outer layer, was found on the coupon surface of low-alloy pipeline steels. The inner layer has a high corrosion resistance until the outer layer appears, and the outer layer presents adequate protection of the entire corrosion film [15]. Therefore, those experiments of low-alloy pipeline steels free of chromium showed that the corrosion rate of the tested steels exposed to CO₂ condition is high. Compared with low-alloy pipeline steels free of chromium, low-alloy steels containing chromium showed superior carbon dioxide corrosion resistance, and the corrosion rate is low [2, 16–18]. General corrosion of low-alloy steel with 1% Cr due to the formation of a compact and self-repairable Cr-rich scale is observed. The corrosion resistance of low-alloy steel with 1% Cr with ferrite–pearlite microstructure is better than that of tempered martensite microstructure [2]. In some cases, the corrosion rate of low-alloy steel with 1% Cr is similar with that of low-alloy steel with 13% Cr at 60 °C and under the pressure of 10 MPa [16]. The corrosion scale in low-alloy steel with 2% Cr showed that Cr can alter the crystalline state of corrosion scale by changing the local pH value, and the local corrosion appears when FeCO₃ stripes is formed on the amorphous scale [17]. For low-alloy steel with 3% Cr, the Cr-enriched inner layer enhances the protective ability of corrosion scale and improves localized corrosion resistance. Flow makes ions distribute evenly close to the specimen surface, leading to a uniform distribution of Cr compounds [9, 18]. The carbon dioxide corrosion experiment of low-alloy steel containing and free of Cr by using in situ synchrotron X-ray diffraction demonstrates that small amount of alloy element in steel decreases the local critical supersaturation of FeCO₃, which accelerates

the formation of an adherent and protective corrosion scale. With temperature increasing, the formation rate of corrosion scale increases, while the scale thickness and crystalline size decrease [19, 20].

It is no doubt that the carbon dioxide corrosion behavior of low-alloy pipeline steel has been investigated by many material scientists. The 1% Cr pipeline steel is studied by many researchers and entrepreneurs owing to its lower alloy content and the lower corrosion rate. So, it is essential to illustrate the carbon dioxide corrosion behavior of 1% Cr pipeline steel and exploit a new method to make corrosion rate lower. However, the carbon dioxide corrosion behavior, the distribution of Cr and the Fe-carbides of 1% Cr pipeline steel with ferrite microstructure were rarely studied. In this work, the carbon dioxide corrosion behavior of 1% Cr pipeline steel exposed to CO₂-saturated solution was investigated by using immersion experiment. The corrosion behavior was exhibited by using surface morphologies, cross-sectional morphologies, corrosion rate, corrosion phases and elements distribution. The relationship of those characterizations mentioned above was also discussed.

2 Experimental

2.1 Material and Solution

Low-alloy pipeline steel with chemical composition (wt%) of: 0.14 C, 0.26 Si, 0.84 Cr, 0.25 Mo, 0.025 Al, 0.84 Mn, 0.076 Ti and balanced of Fe, was melted in a vacuum furnace, and then casted into ingot. The obtained ingot hot rolled into thick plate from 80 to 10 mm, and then rolled into 4 mm thick sheet at room temperature to simulate the drawing process of the armor steel of flexible pipeline ('C' or 'Z' shapes). The steel was reheated to 620 °C and held for 30 min, and then air cooled to room temperature. For positioning, a hole of 3 mm diameter was machined. The size of tested coupons used in this experiment is 20 mm × 25 mm × 4 mm. Before experiment, all of the coupon surfaces were ground with silicon carbide papers up to 800 grit, cleaned by distilled water and acetone, respectively. The solution which contains 3.5 wt% NaCl was used in this experiment, and the chloride in solution is a bad case for corrosion rate [21]. Before immersion experiment, all the coupons were weighted (precision 0.1 mg) and stored in desiccator.

2.2 Mass Loss Experiment

The corrosion experiment was carried out in a 5 L autoclave under high temperature of 75 °C and high pressure of 1.2 MPa, and the partial pressures of CO₂ and N₂ are 0.64 and 0.56 MPa, respectively. Before experiment, N₂ was

purged into the solution to deoxygenate for 2 h, and then the mixture gas mentioned above was bubbled to saturate the solution for 1 h. The test durations in this experiment were 24, 48, 96 and 192 h. After corrosion, the corroded coupons were cleaned by distilled water and alcohol. To remove the corrosion products, a solution composed of 50 mL HCl (37 vol%), 5 g hexamethylenetetramine (urotropine) and 450 mL distilled water was used as cleaning solution. After removing the corrosion products, all the corroded coupons were weighted again to calculate the mass loss. The corrosion rate (R_c , mm/year) was obtained according to the following equation:

$$R_c = \frac{87,600 \Delta m}{t \rho A} \quad (1)$$

where Δm is mass loss, g; t is test duration, h; ρ is physical density of tested steel, g/cm^{-3} , A is area of coupon surface, cm^2 .

2.3 Morphology Observation and Analysis

The digital camera was utilized to photograph the macroscopic morphology. Scanning electron microscopy (SEM, FEI QUANTA 600) was used to investigate the surface morphology. SEM also performed on the corrosion coupons which were mounted into epoxy resin to show the cross-sectional morphology. Energy dispersive X-ray diffraction (EDX) was carried out to detect the chemical composition of corrosion scale. X-ray diffraction (XRD) was carried out with $\text{CuK}\alpha$ radiation and a step size of 0.04° to identify the corrosion phases. Corrosion phases were detected by matching peak position automatically using software MDI Jade equipped with PDF-2(2004). Electron probe micro analyzer (EPMA, JEOL JXA-8530F) was performed to show the element distribution of corrosion scale. The microstructure of corrosion scale was observed by field emission scanning electron microscopy (FE-SEM, ZEISS ULTRA55). Transmission electron microscopy (TEM, FEI Tecnai G²F20) was used to analyze the microstructure in detail.

3 Results and Discussion

3.1 Microstructure Morphology

Figure 1 shows the microstructure of tested steel revealed by FESEM and TEM. It can be seen from Fig. 1a that the microstructure consists of ferrite and precipitate particles, where the ferrite is elongated and parallel to rolling direction, and the precipitate particles are located in both grain substrate and grain boundary. The magnified microphotograph of the marked position in Fig. 1a

demonstrates that the size of precipitate particles ranges from 50 to 100 nm (Fig. 1b). EDX analysis result (see Fig. 1c) reveals that the precipitate particles are Cr- and Fe-rich carbides. Furthermore, the TEM image shown in Fig. 1d confirms the particles size, and those particles appear in the form of ellipse shape. As titanium is added to the tested steel, small particulate particles are observed in Fig. 1e, as evidenced later, they are Ti (C, N). The microstructure and precipitate particles morphology in tested steel may influence the corrosion behavior [2, 10, 22], which will be discussed in the following sections.

3.2 Surface Morphology

Figure 2 shows the macroscopic morphology of corrosion scale on coupons surface. After 24-h immersion, the coupon surface is covered with corrosion scale (Fig. 2a), which acts as the barrier between solution and substrate steel to resist corrosion. With corrosion time increasing, the coupon surface after 48-h immersion becomes more compact than that after 24-h immersion, that mean more corrosion products are formed on the coupon surface after 48-h immersion, and the porosity also decreases (Fig. 2b), while pitting corrosion is observed on the coupon surface after 48-h immersion. In Fig. 2c, the sparse clusters appear on the coupon surface, and those clusters may precipitate newly on the previous coupon surface. Some clusters have delaminated in drying coupon process, so it can be concluded that the stability of those clusters is low, and it is not beneficial to corrosion resistance. A compact and stable layer covers the whole coupon surface revealed in Fig. 2d, which acts as the shield to prevent the substrate from eroding further.

The microscopic morphology and EDX results of corrosion scale are shown in Fig. 3. It can be seen from Fig. 3b that Fe, C and O are found in the rhombohedral crystal, so it is siderite FeCO_3 . Cr is detected in Fig. 3c, that indicates the amorphous phase containing Cr is formed [17]. It is acknowledged that the cathodic reactions in CO_2 -saturated solution are [8, 9]

The anodic reactions are the dissolution of substrate steel described by the reactions as follows [23]:

Fig. 1 Microstructure morphologies of the tested steel: **a**, **b** FESEM image; **b** magnified image of the marked area in **a**; **c** EDX analysis result of the marked position in **a**; **d**, **e** TEM images

Fig. 2 Macroscopic morphologies of the surface of samples after immersion for different time: **a** 24 h; **b** 48 h; **c** 96 h; **d** 192 h

The formation process of siderite FeCO_3 can be described by [9, 24, 25]

In this experiment, chromium is added to the tested steel, so another anodic reaction could occur, which can be described as [2, 26]

Therefore, the corrosion product $\text{Cr}(\text{OH})_3$ would deposit on the coupon surface. As shown in reactions (2–5), HCO_3^- and CO_3^{2-} are produced due to the dissolution of H_2CO_3 . Meanwhile, Fe^{2+} is formed due to the dissolution of substrate steel, as shown by reactions (6–8). When the

Fig. 3 Microscopic morphology and EDX results of the corrosion products: **a** microscopic morphology; **b** EDX result of position A; **c** EDX result of position B

solubility $[\text{Fe}^{2+}][\text{CO}_3^{2-}]$ or $[\text{Fe}^{2+}][\text{HCO}_3^{2-}]$ exceeds the solubility limit of iron carbonate, FeCO_3 would precipitate on the substrate surface according to reactions (9) and (10), as shown in Fig. 3a.

The microscopic morphologies of the corrosion products of the sample after different time immersions are shown in Fig. 4. After 24-h immersion, the Cr-rich compound formed on the substrate surface and the unsystematic FeCO_3 with large gaps can also be observed (Fig. 4a). With immersion time increasing, more FeCO_3 is produced, and the coupon surface after 48-h immersion is more compact than that after 24-h immersion (Fig. 4b). The FeCO_3 clusters are observed in Fig. 4c, and those clusters are formed on the compact outer layer. Furthermore, the size of FeCO_3 crystal in Fig. 4c is smaller than that in Fig. 4b, as it is concluded from the insets. The pore on the coupon surface after 96-h immersion is also smaller than that after 48-h immersion. After 192-h immersion, the coupon surface is covered by compact and homogeneous layer, and the pore is smaller (Fig. 4d).

It is well acknowledged that crystal formation process consists of nucleation and growth. When the solubility $[\text{Fe}^{2+}][\text{CO}_3^{2-}]$ exceeds the solubility limit of FeCO_3 , FeCO_3 crystal would precipitate on the coupon surface.

FeCO_3 solubility limit is affected by ionic strength and temperature and can be expressed as [27]

$$\log K_{\text{sp}} = -59.3498 - 0.041377T - \frac{2.1963}{T} + 24.5724 \log(T) + 2.518I^{0.5} - 0.657I. \quad (13)$$

$$I = \frac{1}{2} \sum_i c_i z_i^2 = \frac{1}{2} (c_1 z_1^2 + c_2 z_2^2 + \dots). \quad (14)$$

where K_{sp} is the FeCO_3 solubility limit, mol^2/L^2 ; T represents temperature, K; I is the ionic strength, mol/L ; c_i is the concentration of the i th specie in aqueous solution, mol/L ; z_i is the charge of the i th specie.

In this experiment, T is constant. So, the FeCO_3 solubility limit K_{sp} increases with I increasing according to Eq. (13). The formation process and morphology characteristics of FeCO_3 crystal, such as compactness of corrosion scale, depend on the precipitation and growth kinetic of FeCO_3 . The precipitation rate (R_p) of iron carbonate is relative to the supersaturation (S_s) of FeCO_3 .

$$R_p = f(T)(S_s - 1)(1 - S_s^{-1}). \quad (15)$$

where $f(T)$ is the temperature impact factor.

Fig. 4 Surface microscopic morphologies of the corrosion products at different immersion time, and the insets are magnified images: **a** 24 h; **b** 48 h; **c** 96 h; **d** 192 h

$$S_s = \frac{[\text{Fe}^{2+}] \cdot [\text{CO}_3^{2-}]}{K_{sp}} \quad (16)$$

where $[\text{Fe}^{2+}]$ is the equilibrium concentration of Fe^{2+} , $[\text{CO}_3^{2-}]$ is the equilibrium concentration of CO_3^{2-} . At the initial stage, Cr is prior to the corrode than Fe, resulting Cr-rich compound deposits on the coupon surface (Fig. 4a). Meanwhile, Fe^{2+} produced by the dissolution of substrate steel is separated and enters into solution. However, the equilibrium concentration of Fe^{2+} in solution is low at that time. So, the solubility of $[\text{Fe}^{2+}][\text{CO}_3^{2-}]$ is low although the equilibrium carbonate ion concentration is high, resulting low R_p of FeCO_3 due to the low S_s of FeCO_3 . Therefore, few FeCO_3 are observed after 24-h immersion (Fig. 4a). As the immersion time increases to 48 h, the concentration of Fe^{2+} increases, while the CO_3^{2-} concentration becomes lower because the formation of FeCO_3 consumes CO_3^{2-} . So, the iron strength (I) is also smaller according to Eq. (14), which locally results into the lower K_{sp} . So, the S_s of FeCO_3 is larger according to Eq. (16). Finally, the higher R_p of FeCO_3 is obtained according to Eq. (15), which promotes the formation of FeCO_3 . Therefore, more FeCO_3 appear on the coupon surface after 48-h immersion (Fig. 4b). It is inevitable that Fe^{2+} will access into solution through the pore among the adjacent FeCO_3 crystals, and accumulates locally in the interface between solution and corrosion scale. This condition will accelerate the formation of FeCO_3 in local areas. So, the FeCO_3 clusters, which precipitate on the compact and homogeneous outer layer, are observed on coupon surface after 92-h immersion (Fig. 4c). After 192-h immersion, the process of nucleation and growth occurs uniformly, and a compact and thick layer is formed on the coupon surface (Fig. 4d).

After corrosion products are removed, the surface morphologies of tested coupons are revealed in Fig. 5. Small valleys are found in Fig. 5a, which may be the positions of distributed FeCO_3 crystals. From Fig. 5b, deep and large valleys can be observed, which indicate the pitting corrosion. The tested steel comprises ferrite and Cr-

rich compound (Fig. 1). Ferrite is eroded and dissolved preferentially due to its high energy and electric potential [28], and the Cr-rich compound can be the cathodic site as it is metallic conductor with low hydrogen overvoltage [15]. Therefore, the pitting corrosion is shown in the coupon surface after 48-h immersion due to the prior large dissolution of ferrite. Furthermore, the grain boundaries are also the possible positions for pit initiation due to their high carbide concentration in contrast to grains [29]. Because the coupon surface of sample is covered compact and homogeneous FeCO_3 layer, plain surface is shown after 96-h and 192-h immersions (see Fig. 5c, d).

3.3 Cross-Sectional Morphology

Figure 6 reveals the cross-sectional morphology of tested coupons. After 24-h immersion, a thin inner layer is observed, and the thickness of porous outer layer is about 7 μm , according to Fig. 4, it should be the Cr-rich compound; a outer layer of FeCO_3 is also found (Fig. 6a). After 48-h immersion, the duplex structure consisting of inner layer and outer layer is observed, the thickness of inner layer and outer layer are about 7 and 10 μm , respectively (see Fig. 6b.) The outer layer on the coupon surface after 48-h immersion is thicker than that after 24-h immersion, which ascribes to more FeCO_3 crystals. At the initial stage, Fe, Cr-carbide has a more positive potential than ferrite, which results in the preferential dissolution of ferrite [24]. That remained carbides could act as the nucleation sites of Cr-rich compounds and FeCO_3 crystals and anchor corrosion products to the substrate. So, the stable inner layer is formed on coupon surface after 48-h immersion (Fig. 6b). As the immersion time is prolonged further, the inner layer shown in Fig. 6c and d changes little. The bumps in Fig. 6c may be the FeCO_3 clusters. The interface between inner layer and outer layer is unclearly shown in Fig. 6d, so it can be concluded that the bond strength between inner layer and outer layer is strong. The compact structure in Fig. 6d can prevent ions, such as Fe^{2+} , CO_3^{2-} , HCO_3^- and Cl^- , penetrating into the corrosion products. The strong

Fig. 5 Microscopic morphologies of the corroded sample surface after the corrosion products removed with different immersion time: **a** 24 h; **b** 48 h; **c** 96 h; **d** 192 h

Fig. 6 Cross-sectional micrographs of the sample after different time immersions (*S* substrate, *E* epoxy, *I* inner layer, *O* outer layer): **a** 24 h; **b** 48 h; **c** 96 h; **d** 192 h

bond structure (Fig. 6d) could decrease the ions concentration at the interface between corrosion rust and substrate, inhibiting the formation of FeCO_3 . The cross-sectional morphology demonstrates that a stable inner layer has been formed on the coupons after 48-h immersion, and the outer layer indicates a significant improvement of the protective performance [15]. The outer layer becomes more and more compact with corrosion time increasing.

3.4 Element Distribution of Corrosion Scale

Figure 7 shows the elements distributions of the corrosion scales with different immersion time. From Fig. 7a, it can be found that Fe accumulates in the outer layer, and only a few Fe appears in the thin inner layer, while Cr and Mo are rich in the inner layer, but are not observed in the outer layer, these results are conformed to the results shown in Fig. 6. The elements distribution demonstrates that the outer layer consists of FeCO_3 and the thin inner layer comprises of major Cr-rich compound and minor FeCO_3 . Ti-containing particles are also detected in both inner layer

and outer layer. Those particles could change the nucleation style from homogeneous nucleation through pre-nucleation embryo of FeCO_3 to heterogeneous nucleation through the precipitated Ti-containing particles. Ti-containing particles in inner layer is located in the edge of pitting corrosion valley, which may be left owing to the ferrite dissolution preferentially, confirms the hypothesis that ferrite is prior to the corrosion than carbides. Ti-containing particles in outer layer may be separated from substrate.

As immersion time is prolonged to 48 and 96 h, similar results are obtained, as shown in Fig. 7b and c. The Cr and Mo are found in the inner layer, while Ti-containing particles can be found at the interface between inner and outer layers (see Fig. 7b), and in both outer layer and inner layer (see Fig. 7c). It should be noted that the inner layer can grow into the substrate (Fig. 7c), which was also observed by others [4]. Residual steel islands are found in the inner layer, which may be attributed to the preferentially dissolved carbides clusters, which can protect the surrounded ferrite from dissolution.

Fig. 7 Element distribution maps of the sample with different immersion time: **a** 24 h; **b** 48 h; **c** 192 h

3.5 Corrosion Phase

Figure 8 shows the XRD patterns took from the sample surfaces after immersion for different time. After 24-h immersion, the corrosion product is composed of FeCO_3 and FeOOH (Fig. 8a). FeCO_3 and Fe_3C are found on the coupon surface after 48-h immersion, the Fe_3C remains after the dissolution of substrate steel (Fig. 8b). Substrate steel is also detected after 24- and 48-h immersions, because of the coupon surfaces are not wholly covered with corrosion products. After 96-h immersion, the corrosion phase on coupon surface is only FeCO_3 (Fig. 8c). The corrosion phase on the coupon surface after 192-h immersion is FeCO_3 , and substrate Fe is also detected, which ascribes to the spalling of FeCO_3 layer (Fig. 8d). The XRD patterns are consistent with the microscopic morphologies.

3.6 Corrosion Kinetics

Figure 9 shows the corrosion kinetics curves which are obtained by revealing mass loss and corrosion rate versus corrosion time. As immersion time increases from 24 to 48 h, the mass loss increases sharply from 0.1766 to 0.2764 g, which represents this stage is a stage of acceleratory corrosion, because of the un-compact inner layer formed after 24-h immersion (Fig. 6a) could not prevent

ions in solution accessing into the substrate. The mass loss of the corrosion coupon changes slowly during 48–96-h immersion, which agree with the morphologies shown in Fig. 6b, c. After 192-h immersion, massive FeCO_3 crystal is formed on the coupon surface (Fig. 4d), so the mass loss increases mildly during 96–192 h. It can be seen in Fig. 9b that, at first, corrosion rate decreases rapidly at first, and then it decreased slowly, finally, a stable corrosion rate below 2 mm/year is obtained after 192-h immersion.

4 Conclusions

The low-alloy pipeline steel containing 1% Cr comprises of ferrite and carbides. When it was subjected to carbon dioxide corrosion, the ferrite dissolves preferentially and carbide particles are left. The carbide particles change the FeCO_3 crystal nucleation type from homogeneous nucleation through pre-nucleation embryo of FeCO_3 to heterogeneous nucleation through the precipitated particles. The corrosion products compose of inner and outer layers, which are identified as Cr-rich compound and FeCO_3 , respectively. As immersion time prolonged, the inner layer changes little once it is formed, which has a stable structure beneficial to corrosion resistance. The outer layer becomes thicker and compacter when immersion takes place for

Fig. 8 XRD patterns took from the surfaces of the sample after immersion for different time: **a** 24 h; **b** 48 h; **c** 96 h; **d** 192 h

Fig. 9 Corrosion kinetics curves of the sample: **a** mass loss versus time; **b** corrosion rate versus time

longer time, results better corrosion resistance. The Cr and Mo tend to accumulate in inner layer.

Acknowledgments This work was financially supported by National Key Technology Research and Development Program of the Ministry of Science and Technology of China during the “12th Five-Year Plan” (Grant No. 2011BAE25B03).

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