Carbide fragmentation and dissolution in a high-carbon high-chromium steel using hot rolling process: microstructure evolution, wear, high temperature oxidation and chloride induced corrosion properties

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Abstract

A series of hot rolling processes with different reduction percentages (10, 30 and 50 %) were applied to a high-carbon high-chromium tool steel (2HCTS). Microstructural evolutions, wear behavior, high temperature oxidation, and aqueous corrosion properties were investigated. The results revealed the breakage and dissolution of primary carbides and a uniform carbide distribution after the hot rolling process. It was proposed that the presence of higher amounts of dissolved chromium in the hot rolled samples leads to the formation of Cr-rich oxides with more protection and less porosity at high temperatures as well as an improved corrosion behavior in 3.5 wt.% NaCl solution. This improvement in the corrosion behavior is not at the expense of the degradation of wear resistance. Probable mechanisms for carbides dissolution are also discussed.

Keywords: Steel; Carbides; Wear; Oxidation; Corrosion resistance

1. Introduction

Directly or indirectly, dry and wet corrosion processes have an important role on the costs and reliability of industrial facilities, environment and human safety [1]. Using corrosion resistant alloys with modified microstructures is a common method to control these phenomena in a wide variety of harsh environments [2]. The corrosion resistance of these alloys is usually determined by formation of a protective surface oxide layer. The formation of this layer is completely dependent on the presence of scale former elements such as Cr, Al and Si in the base alloy [3,4].

High-carbon high-chromium tool steels (2HCTSs) are a class of steels with extraordinary resistance to wear, abrasion and heavy pressure loads which are extensively used for making dies, extrusion mandrels, plastic molds, cores, die holder blocks and hot work punches [5,6]. In these applications, both wear and corrosion resistance properties at room as well as at high temperatures are needed. However, even though 2HCTSs contain considerable amounts of chromium (a scale former element), enhanced formation of chromium carbides as a result of high concentration of carbon and therefore lack of an ideal surface oxide layer (such as Cr_2O_3) leads to poor corrosion resistance during their service [7,8]. In addition, formation of micro-galvanic cell between carbides and/or chromium-depleted zones around them and matrix can accelerate preferred dissolution of the matrix [9].

In different types of ferrous and non-ferrous alloys, carbide re-dissolution has been recognized as an effective method to increase the amount of alloying elements (especially chromium) in the matrix and to obtain a more homogeneous microstructure. As a result of these microstructural changes, mechanical, tribological and/or corrosion properties can also improve [10]. Various methods have been applied to break and/or dissolve carbides in the alloy matrix. Clare et al. [11] improved the corrosion performance of a composite material (Spherotene/Inconel 625) by optimizing the amount of tungsten carbide dissolution through laser processing. Ivanisenko et al. [12] studied the microstructure homogeneity and carbide dissolution of a pearlitic steel during high pressure torsion in shear stresses up to 430 MPa and reported a complete dissolution of the cementite. They postulated that wear of cementite at ferrite/cementite interface, followed by drag of carbon atoms by the ferrite matrix, plays a key role in the cementite dissolution. Liu et al. [13] showed that cold rolling of 347H austenitic heat-resistant steel with a deformation degree of 90 % can dissolve primary NbC particles in the austenitic matrix. After NbC dissolution, secondary NbC nanoparticles are formed and niobium concentration increases throughout the matrix. In addition to the mentioned methods, carbide dissolution may also occur during high temperature phenomena [14,15]. Imparting high energy to a given alloy (common feature of the mentioned works) is considered as an essential prerequisite to dissolve existing carbides in the matrix and reach a more homogeneous microstructure [16–18].

There are few reports on the carbide dissolution of 2HCTSs and its impacts on the microstructure and corrosion properties [19,20]; however, a better understanding of the effects of microstructure on corrosion resistance of 2HCTS is needed. In the present work, hot rolling, as a treatment which is able to break/dissolve carbides in the alloy steels [21], was applied to improve the microstructure homogeneity and consequently the dry/wet corrosion performance of 2HTCSs. For this purpose, a series of hot rolling treatments were introduced on a 2HCTS. Optical (OM) and electron microscopies (TEM/EDS and SEM/EDS) were employed to characterize the microstructural evolutions. In addition, wet and dry corrosion tests were performed in 3.5 wt.% NaCl solution (at room temperature) and in air atmosphere (at 700 and 900 °C), respectively. Since wear resistance is the most important characteristic of 2HCTSs, the variations of this property during the hot rolling process were also examined.

2. Material and methods

2.1. Materials and rolling process

The chemical composition of 2HCTS used in this study is given in Table 1. This steel is known as the K100 Bohler tool steel which is similar to D3 tool steel in the AISI designation system. As received 2HCTS slabs (165 × 50 × 5 mm) were homogenized at 950 °C for 5 h prior to hot rolling passes. Hot rolling process was conducted by a laboratory mill. The roller diameter and mill width were 200 mm and 1000 mm, respectively. The rollers were preheated to about 250 °C by a flame and kept at this temperature during the rolling process. This preheating can minimize potentially detrimental surface quenching effects that would reduce the effectiveness of high temperature deformation. The rolling speed was set at 21 rotations per min. Three rolled slabs with 10 %, 30 % and 50 % reduction in thickness were prepared (see table 2 for abbreviations of samples discussed in this paper). Before starting each pass, rolled samples were re-heated at rolling temperature (950 °C) for 15 min to maintain formability. After the final rolling pass, the hot rolled plates were water quenched. Apart from the slight edge cracks, no severe cracking was observed on the surface of rolled slabs.

*2.2. Sample preparation and microstructure characterization before oxidation/*corrosion tests

Samples for microstructural analyses (10 × 10 × 2.5 mm), wear (Φ 30 × 2.5 mm), high temperature oxidation (3 × 2.5 × 2.5 mm) and wet corrosion (10 × 10 × 2.5 mm) tests were cut from the middle of each rolled slab by electro-discharge machining. All samples were mechanically ground to 1200 grit emery paper and then polished with 6-, 3- and 1-micron water-based diamond suspensions (DP-Suspension P, Struers) to get a mirror-like surface. Subsequently, these samples were first washed in deionized water and then in ethanol and immediately dried with hot air. Microstructure observations were carried out using optical (OM, Nikon Eclipse LV150), scanning electron (SEM/EDS, LEO 1450 VP) and transmission electron (TEM/EDS, Tecnai G2 operating at 200 kV) microscopies. Optical images were achieved by etching the samples with Vilella’s reagent (1 g picric acid, 5 ml HCl and 100 ml ethanol). The TEM specimens were prepared by wet micro-grinding/polishing to get an overall thickness of about 50 µm, afterward prepared foils were perforated by dimpling and finally ion-milled. For each system (Ref, HR1, HR2, and HR3, see Table 2) a minimum of three samples were considered for OM and SEM. A Philips Analytical X-ray (X'Pert) instrument with Cu-K$_\alpha$ radiation ($\lambda = 0.1542$ nm) under a voltage of 40 kV and a current of 30 mA was also applied for phase analysis of 2HCTS samples after hot rolling.

2.3. Wear resistance

Wear tests were conducted via a pin-on-disk wear testing machine with steel pins with the hardness of ≈ 68 HRC. The tests were carried out at 35 ± 2 °C with 50 ± 5 % humidity and the applied load of 100 N in sliding speed of 0.15 m/s. The sliding distance was 1000 m and the samples weight loss was calculated by an electronic balance with an accuracy of 1 µg. The wear rates were calculated using following equation [22]:

$$Wr = \left(\frac{\Delta m}{\rho L F_{\mathrm{N}}} \right) \times 10^{3} \qquad (1)$$

where Wr is the wear rate (mm^3/N·m), Δm is the weight loss (g), ρ is the steel density (g/cm^3), L is the wear distance (m), and F_{N} is the applied load (N). The worn-out surface of the samples was analyzed using SEM to observe the severity of wear damage and clarify the wear mechanism of the samples.

2.4. High temperature oxidation and wet corrosion studies

High temperature oxidation kinetics under isothermal conditions (700 °C and 900 °C) was recorded by means of a LINSEIS TG-DTA (Selb, Germany) microthermobalance for 360 minutes in artificial air (80 % N_2 + 20 % O_2 in vol.%). Samples obtained from the isothermal tests were firstly mounted in epoxy resin, ground and subsequently polished to investigate the phase and morphology of cross section of oxide layers similar to previous section. Mirror polished samples with a 10 × 10 mm^2 surface were subjected to potentiodynamic polarization experiment in a 3.5 wt.% NaCl solution at room temperature. This solution is commonly used to characterize the corrosion resistance in saline environments [23]. A ZAHNER potentiostat (Model IM6ex) was employed to run the corrosion tests in a conventional three electrode configuration. 2HCTS samples as the working electrode (WE), a saturated calomel reference electrode (RE) and a platinum counter electrode (CE) were used to run this test. Additionally, weight loss of square samples in 3.5 wt.% NaCl solution was determined after 24 h of immersion period in air. Since corrosion products were quite loose, they were detached from the surface during washing in deionized water. After potentiodynamic polarization experiment, corroded samples were analyzed through SEM observations to characterize the degree and morphology of attack. In each high temperature oxidation or wet corrosion examination, at least three tests were applied to evaluate the performance of sample under study. It should be noted that in order to highlight the effect of hot rolling on the microstructure and consequently oxidation/corrosion properties of 2HCTSs, the results of hot rolled samples were compared to an as-received sample (Ref, annealed at 950 °C for 5 h).

3. Results and discussion

3.1. Microstructure and phase characterization

The optical and SEM micrographs of 2HCTS samples hot rolled with different reduction percentages are shown in Figs. 1 and 2. The microstructure of 2HCTS samples mainly consists of disconnected carbides distributed in a martensitic matrix. Depending on the rolling reduction, the amount, kind and shape of carbides are variable. Figs. 1a and 2a depict the microstructure of 2HCTS before hot rolling (Ref sample). As one can see, primary carbides are irregular polygonal blocks distributed in the matrix. Some are paralleled to each other; some are round distributed around the large carbides. Figs. 2b and 2c are related to the samples that have undergone 10 % (HR1) and 30 % reduction (HR2). Comparing with the Fig. 2a, large primary carbides have been broken and dissolved in the martensitic matrix.

Transverse cracks are obvious through the large primary carbides in Figs. 2b and 2c. As a result of the dissolution of primary carbides, the chromium concentration of matrix is gradually increased (see mean values of chromium concentrations (wt.%)) and secondary carbides as very fine white grains are formed as well. Since the reference sample experiences a severe deformation after 50 % reduction (HR3), a considerable carbide breakage/dissolution has occurred and consequently lower amounts of primary carbides are observed in Fig. 2d. As long as more primary carbides are broken/dissolved, the concentration of chromium in the matrix is remarkably increased so that this amount for HR3 sample is several times more than for the Ref one. This claim is evidenced by higher concentrations of chromium in EDS results, severe breakage of primary carbides, and enhanced formation of secondary carbides compared with other samples (as can be seen in Fig. 2d). The results of Microstructure Image Processing (MIP) software also displayed a considerable decrease in the amount and size of primary carbides. Based on MIP results, the mean fraction of primary carbide is decreased from 18.9 % of whole microstructure for Ref sample to 17.2 %, 14.6 % and 10.5 % for HR1, HR2 and HR3 ones, respectively. Additionally, carbide particle's average size is remarkably decreased from 29.6 µm for Ref sample to 8.7 µm for HR3 one. These results were calculated by averaging obtained values of five random images with 200× magnification.

X-ray diffraction was applied to characterize the existing phases in the studied samples (Fig. 3). As can be seen in Fig. 3a, microstructures of hot rolled samples include M_7C3 (JCPDS 05-0720) and $M_{23}C_6$ (JCPDS 01-078-1500) carbides and martensite matrix (JCPDS 00-050-1275) as main phases along with some traces of retained austenite (JCPDS 00-03-0397) and Cr_3C_2 (JCPD 03-065-2427) carbide. Some minor deviations from reference peaks can be attributed to the carbide dissolution during hot rolling [24]. Martensite was identified with data for ferrite because of the small differences in lattice constants while retained austenite was determined using crystallographic data for austenite. In the Ref sample, M_7C_3 is the main carbide which is none-uniformly dispersed in the matrix. During the hot rolling process, M_7C_3

is gradually transformed to stable $M_{23}C_6$ which is evident with comparing the XRD patterns of Ref and HR3 samples. It is noteworthy that the chemical composition of Cr_3C_2 is very close to that of the M_7C_3 which is formed as a by-product of the decomposed M_7C_3 carbides [25]. In order to investigate the lattice expansion of the matrix phase, martensite diffraction peaks of different samples are separately presented in Fig. 3b. Comparison of these peaks (solid solution phase) obviously shows that the peaks shifted to the left for the HR2 and HR3 samples, suggesting in these cases the lattice constant of matrix is increased and probably some carbon/chromium atoms are dissolved into the martensite phase [26,27] though carbon has a very negative mixing enthalpy with other constituent elements (namely Fe and Cr).

3.2. Fragmentation of carbides during the hot rolling process

Since carbides are very brittle phases and cannot undergo severe plastic deformation [28] it is easy to crack them during the hot rolling process. In this kind of deformation, the matrix first undergoes plastic deformation. After that, a frictional force (*F*) is created between the matrix and the carbides which can be calculated as follows [29]:

$$F = f.P.A \tag{1}$$

where *f*, *P*, and *A* are friction coefficient of matrix and carbides, pressure perpendicular to the interface of matrix and carbides and area of the interface, respectively. Based on the slip-line field theory of rolling, *P* can be calculated using Eq. 2 [30].

$$P = K\left(a + \frac{bl}{\sqrt{Hh}}\right).A \tag{2}$$

where a and b are hot rolling constants which are respectively equal to 1.31 and 0.53 for thick plates [31]. *K*, *l*, *H*, and *h* are rolling constant, length of contact arc, thickness before hot rolling and thickness after hot rolling, respectively. With considering strain (ε) equation, Eq. 2 can be rearranged as follows:

$$F = f.K.\mathrm{A}^2\left(a + \frac{bl}{H\sqrt{1-\varepsilon}}\right) \tag{3}$$

Thus, as ε or reduction during hot rolling increases, F increases. When the reduction reaches the tensile strength of carbide, it will break. Suppose that the tensile strength of carbides is S_u and its cross-section area is A_u, the minimum condition for carbides breakage is:

$$F_\mathrm{min} = S_\mathrm{u}.A_\mathrm{u} \tag{4}$$

So, the minimum strain for carbide breakage is as follows:

$$\varepsilon_\mathrm{min} = 1 - \left[\frac{blfKA^2}{\left(S_\mathrm{u}.A_\mathrm{u} - afKA^2\right)H}\right]^2 \tag{5}$$

In this way, ε_min is remarkably affected by A_u. That is to say, necks in each carbide (shown in Fig. 1), i.e. cross-sections with minimum area, formed during hot rolling deformation, play a key role in the carbide breakage. Additionally, since H reduces and l increases after each pass, P increases. So, the effect of carbide breakage will be more obvious after each pass.

3.3. Dissolution of carbides during the hot rolling process

Before hot rolling, the mean content of chromium in the matrix is 1.57 wt.% while this value reaches 2.76 wt.%, 3.95 wt.% and 4.85 wt.% for HR1, HR2 and HR3 samples, respectively (see EDS results in Fig. 2). This increment can clearly prove the carbide dissolution phenomenon. Here, the mechanism of carbide dissolution during hot rolling is the main question. When 2HCTS is heated to austenite temperature, carbides start to dissolve in the matrix, as the actual carbon content in the matrix (CM) is less than the solubility of carbon (CT) at the corresponding temperature. In fact, the driving force for this kind of solubility is proportional to ΔC = CT – CM. In the presence of hot rolling force and carbide fragmentation, following issues should also be considered which can remarkably affect the carbide dissolution process:

(i) Interfacial energy: After carbide fragmentation, increase in the matrix/carbide interfacial energy is caused by the surface to volume ratio increase. Accordingly, the overall interfacial energy increases and leads the carbide to be unstable. Since HR3 experiences more carbide fragmentation, these conditions are more severe in the case of this sample. Blavette et al. [32] modelled the effect of interfacial energy on carbide dissolution in a heavily deformed pearlitic steel through atomic-scale observations. They also reported that the dramatic increase in interface areas during deformation can serve as the driving force for carbide dissolution.

(ii) Carbon solubility: The second mechanism for dissolution is based on the increase of carbon solubility in the matrix under the rolling force. For comparison, Fig. 4 shows the TEM images corresponding to the interface of carbide/matrix in Ref and HR3 samples. Presence of parallel sliding lines in primary carbides (Fig. 4b) is an indication of the occurrence of plastic deformation (dislocation slipping) for carbides during hot rolling. Similar observations have also been reported elsewhere [30]. Kang et al. [33] claimed that the presence of crystallographic defects (e.g. stacking faults, dislocations, etc.) causes carbon activity increase in the carbide and its dissolution. In fact, carbon diffusion is assisted by a high density of defects generated during hot rolling. From this point of view, it can be claimed that since HR3 meets a high degree of deformation during hot rolling, its carbides are more prone to dissolution.

(iii) Binding energy of carbon and dislocations: The third contribution focuses on the interaction of dislocations and carbon atoms. Since the binding energy of a dislocation with carbon atoms exceeds that of iron and/or chromium atoms with a carbon atom in carbide [10,34,35], carbon atoms tend to reside in dislocation strain fields rather than within carbide. In other words, when a high dislocation density region is adjacent to a matrix/carbide interface, dislocations show this tendency to draw carbon atoms from the carbide until the dislocations become saturated. Fig. 4 can also support this claim. As can be seen from Fig. 4b, some tiny precipitates have been trapped among dislocations which surrounded the carbide. EDS analysis shows that they are mainly composed of carbon.

3.4. Wear behavior

Fig. 5 shows the wear rate of different samples at sliding speed of 0.15 m/s under 100 N normal load in pin-on-disk wear test. The results show that the hot rolling process first degrades the wear resistance so that the wear rate increases from ≈ 0.011 $mm^3/N\cdot m$ (Ref) to ≈ 0.020 $mm^3/N\cdot m$; however, with increasing the hot rolling reduction, wear resistance gradually increases and wear rate reaches the values of ≈ 0.017 and ≈ 0.012 $mm^3/N\cdot m$ for HR2 and HR3 samples, respectively (Fig. 5). The HR3 sample shows a wear behavior similar to the Ref one. In the case of HR3 sample, it was shown that two important phenomena take place (Fig. 2):

(i) Severe breakage/dissolution of the primary carbides which in turn reduces the wear resistance [36].

(ii) Enhanced formation of the secondary carbides and uniform distribution of carbides which favor the wear resistance increment [37].

So, it can be claimed that for the HR3 sample, above phenomena counteract each other and its wear rate is almost the same as the Ref one. Fig. 6 presents the SEM images of the worn-out surface of the samples after this test. The micrographs show that the predominant wear mechanism is adhesive wear and that the surface damages are fewer in the samples with lower wear rates (Ref and HR3 samples).

3.5. High temperature oxidation behavior and oxide layers microstructures

Figs. 7a and 7b show the weight gain curves of different samples exposed to 700 °C and 900 °C up to 360 min. Based on the Wagner theory of oxidation (thick films), this phenomenon is a diffusion-controlled reaction and highly dependent on the time and temperature [38]. As can be seen from Fig. 7a, there are only minor changes in the weight gain and its trend for oxidized samples even after 360 min at 700 °C. In order to take into account a more accurate evaluation on the effect of hot rolling on the high temperature oxidation behavior of 2HCTS in the mentioned exposure time, all samples were also oxidized at 900 °C. A clear difference between oxidation behaviors of different samples can be seen at this temperature (Fig. 7b). In this case, as the reduction is increased from 10 % to 50 %, two different behaviors are observed for each sample. At the initial stages of oxidation (exposure times less than about 2 h), weight gain of hot rolled samples, especially HR3, is higher than Ref one. This can be attributed to the higher contents of dissolved chromium as a scale former element in their microstructure and fast formation of oxide scales on the hot rolled samples. For the rest of the exposure time, weight gain of Ref sample gradually surpasses hot rolled ones, so that its weight gain is about two times more than HR3 sample after 360 min. Formation of more protective oxide scales on hot rolled samples (particularly HR3) can be a reason for such behavior [39]. The oxidation kinetics of different samples can also be quantitatively described as a form of polynomial equation as [40]:

$$\left(\frac{\Delta m}{A}\right)^2 = k_\mathrm{p} t \qquad (6)$$

where Δm is the weight change, A is the surface area of the sample, t is the exposure time, and k_p is the parabolic rate constant (kg^2/m^4·s). The k_p values, acquired through the slope of $\left(\frac{\Delta m}{A}\right)^2$ - t plot (Figs. 7c and 7d), are given in Table 3. In all cases, the oxidation of free surface of each sample, i. e. initial stages of oxidation, experiences high oxidation rate. In line with Fig. 7a, the k_p values are comparable for different samples oxidized at 700 °C. After two hours of exposure at this temperature, k_p values are between $6.61 \pm 0.01 \times 10^{-9}$ kg^2/m^4·s and $1.11 \pm 0.03 \times 10^{-8}$ kg^2/m^4·s for different samples, indicating a similar time dependence of the growth rate of oxide film (Fig. 7c). On the other hand, these conditions are completely different at 900 °C. As can be seen from Table 3, in the case of Ref sample, k_p value is $5.61 \pm 0.05 \times 10^{-6}$ kg^2/m^4·s which in turn shows that the alloy-oxide and oxide-atmosphere interfaces are not in thermodynamic equilibrium and no protective oxide film forms on the alloy surface [41]. With increasing the hot rolling reduction, k_p values gradually decrease so that its value reaches about 1.99×10^{-7} $kg^2/m^4 \cdot s$ for HR3, indicating the formation of an oxide film with more protection compared with other samples.

Since the rate of oxidation and its difference between various samples are extraordinary at 900 °C, cross sectional morphology and corresponding EDS lines of samples oxidized at 900 °C for 360 min are presented in Fig. 8 for further illustration of the obtained results. With comparing the elemental line scans and corresponding SEM images, it can be seen that the oxide layers on all samples are composed of two parts: outer part with higher amounts of porosities and the inner one which is nearly free of porosity. In addition, the outer and the inner parts predominantly consist of Fe-O and Fe-Cr-O mixed oxides, respectively. As rolling reduction increases, the total amount of porosities in the upper part significantly decreases and consequently the protectiveness of oxide scales increases. By considering Figs. 7 and 8, this behavior can be attributed to the formation of chromium-enriched oxides with a higher level of protection on hot rolled samples (especially on HR3). On the other hand, a breakaway oxidation mode due to the formation of less-protective Fe-O oxides and enhanced diffusion of oxygen can serve as a reason for the rapid kinetics of oxidation of Ref sample at 900 °C.

3.6. Chloride induced corrosion behavior

Fig. 9 and Table 4 present the potentiodynamic polarization curves and main corrosion parameters derived from corrosion tests (polarization and weight loss measurements), respectively. Polarization curves of different samples in 3.5 wt.% NaCl solution (pH ≈ 6.8) were obtained at a scan rate of 1 mV/s. Nearly parallel cathodic Tafel curves in Fig. 9 (comparable β_c values in Table 4) suggest that the oxygen reduction mechanism is not significantly affected by the hot rolling process. Assessment of Fig. 9 and Table 4 reveals that the net anodic current density remarkably decreases and β_a value increases by increasing the hot rolling reduction. In addition, the corrosion potential (E_{corr}) shifted towards more noble values for hot rolled samples (from -501 mV SCE for HR1 to -421 mV SCE for HR3) compared with the Ref one (-557 mV SCE). Comparison of the corrosion current densities also shows that the maximum decrease in the corrosion rate is achieved for the sample hot rolled with 50 % reduction (HR3). To further interpret these results, examination of the surface morphology of corroded samples is essential. Therefore, Fig. 10 shows SEM images of different samples after polarization tests. As expected, corrosion attack has taken place only for the matrix phase in all samples and the carbides do not dissolve under these conditions. As can be seen in Fig. 10, corrosion of the matrix phase surrounding the carbides plays a key role in the corrosion resistance of the whole microstructure, as matrix corrosion can lead to disbanding of the carbides and hence render them mechanically unstable in the system.

Based on these findings, improved wet corrosion behavior of severely hot rolled samples (especially HR3) compared with Ref one can be discussed from two points of view:

(i) More homogeneous microstructures (presence of smaller primary carbides in fewer amounts): Comparison of Fig. 10a and Fig. 10g reveals that as the size and amount of primary carbides decrease (i.e. more carbide fragmentation and carbide dissolution), the corrosion attack becomes more uniform. In addition, less primary carbides are exposed to unstable conditions in the microstructure. Resultantly, corrosion potential shifts towards more noble values, corrosion resistance of the whole microstructure increases, and corresponding weight loss decreases (see Table 4). This argument is in agreement with the study on laser treatment of 2HCTS by Manna et al. [6].

(ii) Higher concentrations of dissolved chromium in the matrix phase: Actually, the possible presence of chromium as solid solution element in matrix phase might block the active sites of crystal lattice structure of iron and increase the corrosion potential through the formation of surface oxide/hydroxide layers containing more chromium on the matrix phase. This fact can be reflected in lower corrosion current density and weight loss for hot rolled samples, especially HR3. This argument is in full agreement with the reports by Jinlong et al. [42] and Junhua et al. [43].

4. Conclusions

Based on the findings of this study, following conclusions can be made.

(1) Hot rolling of 2HCTS at 950 °C can severely affect its microstructure. With increasing the hot rolling reduction up to 50 %, the fraction of primary carbides decreases from 18.9 % to 10.5 % of the microstructure. The average size of primary carbides is also dropped from 29.6 µm (untreated sample) to 8.7 µm (50 % reduction).

(2) During hot rolling process, primary carbides which are mainly composed of M_7C_3 carbides may experience one of these physical/chemical changes: (a) breaking up into smaller carbides, (b) transformation to fine secondary carbides (mainly $M_{23}C_6$) and (c) dissolution in martensitic matrix and consequently increasing its dissolved chromium concentration.

(3) Primary carbide dissolution is attributed to the synergistic effect of interfacial energy increase during carbide fragmentation, increase of carbon solubility in the matrix phase, and lower energy state of carbon atoms in dislocations compared with within carbides.

(3) There is a significant difference in the oxidation behavior of different samples at 900 °C. At this temperature, due to fast formation of an oxide layer in the hot rolled samples (especially HR3), their weight gain is initially more than for the untreated one. With elapsing time, enhanced diffusion of ionic species leads to a poor oxidation resistance for untreated sample and its weight gain surpasses the hot rolled ones, so that its oxidation rate is about thirty times more than the sample with 50 % reduction.

(4) Oxide layers on different samples are composed of two parts: the outer porous part which mostly consists of Fe-O oxides and the inner part which is mainly made up of Cr-rich oxides. As the hot rolling reduction increased, due to the formation of more protective oxides, total amount of porosity is decreased.

(5) Microstructure homogeneity and higher concentration of solid solution chromium can be reasons why the hot rolled 2HCTS (especially HR3) possess improved chloride induced corrosion behavior.

(6) Improved corrosion behavior of the HR3 sample is not at the expense of losing its wear properties. Both Ref and HR3 samples show similar were rates (0.0118 ± 0.001 $mm^3/N \cdot m$).

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Table captions

Table 1. Chemical composition of the high-carbon high-chromium tool steel (2HCTS), wt.%.

Table 2. Abbreviations for sample denotation.

Table 3. The parabolic rate constants of isothermal oxidation of different samples at 700 °C and 900 °C.

Table 4. Polarization parameters and weight loss data for corrosion of 2HCTS samples in 3.5 wt.% NaCl solution.

Figure captions

Fig. 1. Micrographs of the 2HCTS samples: (a) Ref, (b) HR1, (c) HR2, and (d) HR3.

Fig. 2. SEM/EDS results of experimental samples: (a) Ref, (b) HR1, (c) HR2 and (d) HR3.

Fig. 3. (a) XRD patterns of the as-received and hot rolled samples and (b) matrix peak of different samples showing a minor left shift for HR2 and HR3.

Fig. 4. TEM analysis of carbide/matrix interface for (a) Ref and (b) HR3 samples. Sliding lines (arrows begin with diamond) and carbon clusters (arrows begin with oval) are obvious in the right image.

Fig. 5. Variation of wear rate of different samples under 100 N load.

Fig. 6. SEM images of worn-out surfaces of 2HCTS samples at 100 N load, 0.15 m/s sliding speed and sliding distance of 1000 m: (a) Ref, (b) HR1, (c) HR2, and (3) HR3.

Fig. 7. Isothermal oxidation kinetics of different samples: weight gain data at (a) 700 °C and (b) 900 °C. The square variation of weight per surface area $(kg/m^2)^2$ versus oxidation time at (c) 700 °C and (d) 900 °C.

Fig. 8. Cross sections and EDS line scanning element analyses of oxidized samples at 900 °C: (a) Ref, (b) HR1, (c) HR2, and (d) HR3. As highlighted in this figure, oxide layers are composed of an outer porous part and an inner dense one. 1, 2, and 3 line scans are corresponded to Fe, Cr, and O, respectively.

Fig. 9. Potentiodynamic polarization curves of as-received and hot rolled samples in 3.5 wt.% solution.

Fig. 10. Surface morphology of different samples after polarization test: (a and b) Ref, (b and c) HR1, (e and f) HR2 and (g and h) HR3. Mechanical instability of carbides after matrix corrosion is obvious