JOURNALOF

Ceramic Processing Research

Effect of carbon presence in the substrate and salt bath on the formation of chromium coating layers on steel through TRD process

Ali Akbar Ghadi and Mansour Soltanieh

Centre of Excellence for Advanced Materials & Processing, School of Metallurgy and Materials Science, Iran University of Science and Technology, Tehran, 16844, Iran

Thermo-reactive diffusion (TRD) process is used to produce hard, wear-resistant, oxidation and corrosion-resistant coating layers on steel substrates. In this research, molten salt bath method was used for the formation of chromium coating in which, low- and high-ferrochromium powder was separately dissolved in molten borax as the source of chromium. The purpose of this research is to investigate the effect of the carbon content in the substrate and the salt bath on the formation of chromium-based coating layers on sample surfaces. Coating thickness and microstructure formed in the baths were studied using scanning electron microscope (SEM) and optical microscope (OM). The coating thickness of the samples treated in low-carbon ferrochromium baths ($38 \pm 2 \mu$ m) was 5 times greater than those treated in the high-carbon ferrochromium baths ($8 \pm 2 \mu$ m). The sample surface, the final baths residue, and the initial ferrochromium powders were examined by X-ray diffractometer (XRD). Results showed that, no chromium carbide phases (Cr₇C₃ or Cr₂₃C₆) were formed on the pure iron samples which comes to the point that, the presence of carbon in the samples plays a major role on the formation of carbide coating layers. In comparison, the carbon content of bath has no positive effect on the chromium carbide formation and even reduces the chromium diffusion into the surface of the samples.

Key words: Thermo-reactive diffusion process, Borax salt bath, Ferrochromium, Chromium carbide.

Introduction

In order to fabricate thin hard coatings, three major kinds of processes namely Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD) and Thermo-Reactive Diffusion (TRD) techniques were put into practical application by a number of worldwide industries [1-3]. TRD is one of these processes which are used for making hard and wear-resistant coating layers such as carbides, nitrides, or carbonitrides on ferrous alloys [4-6]. These coatings are used to improve the wear and corrosion behavior of the surfaces of ferrous materials such as steels, in addition to increasing their hardness [4, 7, 8]. The TRD process is carried out by molten salt bath [9] and fluidized bed [10] methods. Molten salt bath method involves immersion of materials in a molten borax bath that contains the relevant carbide forming elements (CFE) such as vanadium, niobium, or chromium [4, 11].

Chromium is one of the elements which have been successfully diffused into ferrous alloys by TRD process especially using the salt bath method. A bath composed of an appropriate salt and a chromium containing agent is used for successful salt bath chromizing [9, 12, 13].

Different salts such as: borax, boric acid or sodium

chloride may be used as baths in the salt bath method. However, Arai et al. reported that using borax causes better quality coatings [9, 13-15]. This is why the borax was used as the base of bath in the present study.

Chromium metal powder, ferrochromium, chromium halides and chromium oxide have been used as the chromium sources. According to literature survey, ferrochromium is the most economically-available source of chromium for the TRD process. Two kinds of ferrochromium are available, namely, low-carbon ferrochromium that contains maximum 0.1 wt% carbon and high-carbon ferrochromium that contains 4-7 wt% carbon. The chromium content of both groups lies in the range of 60-70 wt% [6, 14, 15].

Different sources of chromium with dissimilar percentages of carbon were used as starting materials. Different phases of chromium coating layer and the coatings thickness were achieved [13-16]. A summary of these results prepared by TRD method is listed in Table 1. Nevertheless, no attention was reported on the carbon content of this material and its effects on the type and thickness of coating layers. In current study, an attempt was made out to survey the aforementioned results and also to investigate the effect of carbon in both substrate and bath during the formation of the chromium coating layer on steel samples.

Experimental

In this research, as substrates, pure iron (99.99%) plates with $10 \times 10 \text{ mm}^2$ and half of a millimeter thickness were prepared using precise cutting tools. As

^{*}Corresponding author:

Tel : +989368833024, +982177240500

E-mail: a_ghadi@iust.ac.ir, mansour_soltanieh@iust.ac.ir

 Table 1. Results of using ferrochromium powder as the carbide-forming agents for the formation of chromium coating layer in molten salt bath [13-15].

Substrate	Salt	Chromium source	T (hrs)	T (°C)	Thickness (µm)	Coating phase	Ref.
Plain carbon steel JIS S10C			4	1000	20	Solid solution of Fe-Cr	13
Plain carbon steel JIS S45C		150 g ferrochromium powder	8	1000	30	$Cr_{23}C_6 + Cr_7C_3 +$ solid solution of Fe-Cr	14
Tool carbon steel JIS SK2	300 g Borax		24	800	15	$Cr_{23}C_6+Cr_7C_3+$ solid solution of Fe-Cr	15
Plain carbon steel		40 g Low carbon ferrochromium powder	14	1000	32 ± 8	$Cr_{23}C_6+Cr_7C_3+$ solid solution of Fe-Cr	16
Plain carbon steel	Plain carbon steel	40 g High carbon ferrochromium powder	14	1000	6.8±1.2	Cr ₇ C ₃	16

Table 2. Chemical composition of the LCFC and HCFC powders (wt%).

Element (wt%)	С	Cr	Si	S	Р	Fe
LCFC	0.1	68	0.7	0.005	0.02	Balance
HCFC	7.5	68	0.7	0.004	0.04	Balance

solution media for coating, two salt baths with the same amount of barox salt and relatively different carbon content was used. Bath No.1 constitutes 12 wt% of low-carbon ferrochromium (LCFC) powder and the latter (bath No.2), high-carbon ferrochromium (HCFC) with identical weight percent. Table 2 illustrates the detailed chemical compositions of baths used in this work. The iron plates were ground and polished. The samples were immersed into salt baths for 14 hours at 1000 °C. Subsequently, coated dragged out samples were air-quenched and washed with distilled water and finally desiccated.

Optical and scanning electron microscope (SEM) micrographs were used to study the morphology and the thickness of the coating layers. X-ray diffractometer (XRD) (model: JEOL JDX-5030) was utilized to characterize the surface of the samples, the final baths residue and the initial ferrochromium powders, as well.

Results and Discussion

Investigation of the chromium coating layer

Based on the experiments performed, it is believed that the carbon content of both the substrate and the salt bath plays a major role in the chromium diffusion. The images of optical and scanning electron microscope (SEM) for samples coated in baths with low and high carbon content of ferrochromium are shown in Fig 1 and 2, respectively. In addition, X-ray diffraction



Fig. 1. Optical (a) and SEM (b) images of the pure iron sample coated in bath No. 1, at 1000 °C for 14 hrs (etched in nital 3% HNO₃ solution).

patterns were analyzed (Fig 3a and 3b) for bath No. 1 and 2, respectively.

As can be seen clearly in Fig 1 and 2, chromium has diffused into pure iron samples. The chromium coating layer formed in bath No. 1 possessed a uniform thickness of $38 \pm 2 \mu m$ (Fig 1). Based on XRD results in Fig 3a, this chromium coating layer consisted of an iron-chromium solid solution phase. Since there was no carbon in the substrate and the bath, neither of the chromium carbide phases was formed on the sample surface.

The chromium coating layer formed on the pure iron sample in bath No. 2 was non-uniform and had a thickness of $8 \pm 2 \mu m$ (Fig 2). As shown in this figure, the microstructure of the sample has changed. Based on XRD results indicated in Fig 3b, no chromium carbide phases were formed, but iron carbide (Fe₇C₃), ferrite and iron-chromium solid solution phases were detected. It is anticipated that some excess carbon has diffused from salt bath into pure iron substrate. Since,



Fig. 2. Optical (a) and SEM (b) images of the pure iron sample coated in bath No. 2, at 1000 °C for 14 hrs (etched in nital 3% HNO₃ solution).



Fig. 3. XRD patterns of the sample surface of the pure iron immersed into bath No. 1(a) and bath No. 2(b).



Fig. 4. Elemental point analysis at a point located 2 μ m under the sample surface of the pure iron treated in bath No. 1.

iron carbide is thermodynamically more stable than chromium carbide, neither of chromium carbide phases such as Cr_7C_3 and $Cr_{23}C_6$ was detected in the sample surface. Regarding the results from pure iron samples, it can be deduced that the carbon content of the samples plays an essential role in the formation of the



Fig. 5. Elemental line scan analysis from the sample surface of the pure iron treated in bath No.1.



Fig. 6. Elemental point analysis at a point located 2 μ m under the sample surface of the pure iron treated in bath No. 2.

chromium carbide phases. Chromium diffuses into the substrate and reacts with the carbon present in the steel and subsequently, chromium carbide is formed on the metallic surface [11, 17]. Furthermore, as claimed by X. Fan, as the activity of carbon in the substrate increases, more approving carbide phase is observed in the coating microstructure [18].

The EDS results of the elemental point analysis (Fig 4), conducted on the chromium coatings layer formed on the pure iron samples for bath No. 1, indicated that the chromium has diffused into the surface of the pure iron so that its amount reached to 15.6 wt% in a point which is 2 µm below the surface. In Fig 5, the SEM micrographs of the sample treated in bath No. 1 are shown. This figure is a line-scan analysis of the sheet sample. The linear elemental scan results, shown in Fig 5, indicate that chromium curve reaches a maximum of about 40 µm below the surface, then chromium content decreases and finally it increases again to the former value of approximately 40 µm below the surface of the other end of the sample. All in all, it can be concluded that a relatively high amount of chromium has diffused from bath No. 1 into the sample surface of the pure iron.



Fig. 7. Elemental line scan analysis from the sample surface of pure iron treated in bath No. 2.



Fig. 8. The XRD pattern of quenched bath No.1(a) and Low-carbon ferrochromium powder (b).

The EDS results of a point where is located $2 \mu m$ under the surface of the treated pure iron sample shown in Fig 6 indicate that the chromium and carbon has diffused into this sample while bath No. 2 is used. These results show that the carbon has increased to 3.5 wt% while the chromium has reached to 6.9 wt% in that point. As it is obviously seen, carbon has diffused into the plate and then, it has reacted with the pure iron sample resulting in the formation of iron carbide. As a consequence, the sample structure of the pure iron has altered. In Fig 7, the SEM micrograph of end to end analysis of the sample treated in bath No. 2 is shown which indicates that, a small amount of the chromium has diffused into the sample surface of the pure iron.

The analysis of the baths and the additive powders

As previously discussed, the thickness of the chromium coating layer using bath No. 1 is higher than that of bath No. 2. However the only difference between the two baths is the carbon content of the ferrochromium.



Fig. 9. XRD pattern of quenched bath No.2 (a) and high-carbon ferrochromium powder (b).

To address this phenomenon, the quenched bath and ferrochromium powders were investigated by XRD method. In Fig 8a, the diffraction pattern of bath No. 1 is shown. The crystalline phases such as iron-chromium solid solution and ferrite (iron-carbon solid solution) were detected just simultaneously with the amorphous background present due to the amorphous structure of borax. In Fig 8b, XRD pattern of the initial low-carbon ferrochromium powder (LCFC) is presented. Comparisons of these two patterns show that the same phases were detected in both samples.

In Fig 9a, the diffraction pattern of bath No. 2, chromium carbide phase (Cr_7C_3) , iron-chromium solid solution phase and carbon phase can be observed and also in Fig 9b, X-ray characterization of as received high-carbon ferrochromium powder (HCFC) is shown.

Comparing Figs 8a and 8b, and Figs 9a and 9b, it can be conceived that the phases present before and after addition of ferrochromium powder in the borax bath maintain their structure i.e. it seems that borax acts only as a medium for the dissolution of the ferrochromium powder and causes no considerable changes in the state of the ferrochromium powder.

According to the results obtained from X-ray diffraction patterns, it can be understood that the chromium in bath No. 1 only exists in iron-chromium solid solution phase. Therefore, the chromium will freely move within the bath and no atomic bond forms between the chromium and the other atoms (such as carbon or iron) in the bath. Consequently, a high amount of chromium diffuses into the pure iron sample and, as a result, a chromium coating layer with a thickness of $38 \pm 2 \ \mu m$ is formed.

Based on XRD results, in addition to iron-chromium solid solution, two other phases i.e. chromium carbide

and some carbon phases were detected in bath No. 2 due to the higher carbon content. This chromium carbide phase results in less free-chromium in this bath compared to bath No. 1. So the thickness of chromium coating layer in the sample surface is measured to be about $8 \pm 2 \,\mu$ m. Thus, the chromium coating layer formed using bath No. 1 is about five times thicker than that of the sample treated in bath No. 2.

Bath No. 2 including HCFC powders contains some stable chromium carbide phase which lowers down the chromium mobility and its diffusion into the sample. Furthermore, some free carbon has diffused in the sample and tends to form iron carbide phase in the sample surface and then, this phase acts as a chromium diffusion barrier. So all together, existence of carbon in the bath is not in favor of the formation of the chromium carbide coating, in contrast, the carbon presence in the substrate is favorable on the formation of the chromium carbide coating layers.

Conclusions

It can be concluded that the carbon content of the substrate acts the main role in the formation of the chromium carbide phase. Chromium in bath No. 1 (molten borax salt containing LCFC) only exists as a free atom in the iron-chromium solid solution phase. Therefore, chromium will freely diffuse into the sample surface. In bath No. 2 (molten borax salt containing HCFC), less free chromium atoms are available because of the existence of chromium carbide phase. Therefore in comparison with bath No. 1, less chromium diffuses into the pure iron substrate and as a result, the thickness of the chromium coating layers formed in bath No. 1 is five times higher than those formed in bath No. 2. High carbon content in the bath

may act as an inhibiting factor against diffusion of chromium element into the substrate and the formation of the chromium-containing coating layers on the sample surface will decrease drastically.

References

- M.A. Djouadi, C. Nouveau, et al., Surface and Coatings Technology. 133-134 (2000) 478-483.
- D.K. Merl, P. Panjan, et al., Electrochimica Acta. 49 [9-10] (2004) 1527-1533.
- H.R. Karimi Zarchi, M. Jalaly, et al., steel research international. 80 [11] (2009) 859-864.
- M. Aghaie-Khafri and F. Fazlalipour, Journal of Physics and Chemistry of Solids. 69 [10] (2008) 2465-2470.
- G. Khalaj, A. Nazari, et al., Surface and Coatings Technology. 225 (2013) 1-10.
- Z. Yuan, Z. Wang, et al., J. Wuhan Univ. Technol.-Mat. Sci. Edit. 25 [4] (2010) 596-599.
- 7. U. Sen, Materials & Design. 26 [2] (2005) 167-174.
- C.K.N. Oliveira, C.L. Benassi, et al., Surface and Coatings Technology. 20 [3-4] (2006) 1880-1885.
- 9. T. Arai, H. Fujita, et al., J. Mater. Eng. 9 [2] (1987) 183-189.
- C.-Y. Wei and F.-S. Chen, Materials Chemistry and Physics. 91 [1] (2005) 192-199.
- 11. T. Arai and S. Moriyama, Thin Solid Films. 259 [2] (1995) 174-180.
- 12. A.R. Castle and D.R. Gabe, International Materials Reviews. 44 [2] (1999) 37-58.
- 13. T. Arai, J. Heat Treating 1 [2] (1979) 15-22.
- N. Komatso, T. Arai, et al., Patent US3671297 A, United States, 1972.
- 15. N. Komatso, T. Arai, et al., Patent US3885064 A, United States, 1974.
- A. Ghadi, M. Soltanieh, et al., Defect and Diffusion Forum. 326-328 (2012) 377-382.
- 17. T. Arai and S. Moriyama, Thin Solid Films. 249 [1] (1994) 54-61.
- X.S. Fan, Z.G. Yang, et al., Journal of Alloys and Compounds. 505 [1] (2010) 15-18.