Queen's University
Belfast
Q

Oxidation-induced Cu coating on steel surface

Published in:
Materials Science Forum

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Oxidation-induced Cu Coating on Steel Surface

Na Li [1,a], Ning Wang[1,b], Minghong Sha[1,c], Wei Sha[2,d] and Junwei Zhang[1,e]

1. Laser Advanced Manufacturing Technology R & D Center, School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan, 114051, China

2. School of Planning, Architecture and Civil Engineering, Queen's University Belfast, Belfast, BT9 5AG, UK

[a]huatsing2006@163.com, [b]babening@126.com, [c]hongsmh_116@163.com, [d]lnkdzjw@163.com

Abstract. Copper is accumulated in recycled steels and is difficult to be removed during steelmaking processes when steel scrap is used as steel sources. Meanwhile, copper characteristics are of importance both to human beings and to animals and plants. In this paper, integrated copper coating was observed on the surface of copper-containing steels when the steels were heated at around 1150 ℃. However, the copper was separately scattered in and under the surface rust after heating at 1000 ℃. The forming mechanisms of copper coating are discussed in detail. By choosing a proper descaling reagent, self-generated oxidation-induced copper coating appeared on the steel surface. The method proposed in this work is environmentally friendly for nontoxic chemicals being used. In addition, this provides a new concept for producing protective composite by oxidizing from the substrate directly and there is no bonding problem.

Introduction

Steel recycling is important from the environmental point of view. Copper is accumulated in steels when steel scrap is used as steel sources because it is difficult to be removed during steelmaking processes. Copper can cause hot shortness problem in steels. On the other hand, copper is widely used in weathering steels, antibacterial stainless steels [1-3], biological steel materials [4] and some other steels such as HSLA [5-7], super 304H austenitic heat-resistant steel [8-10] and stainless steels [11-13] for its strengthening, corrosion resistance and antibacterial properties.

With the development of composite materials and its manufacturing technique, researchers have developed Cu-clad steel composite materials. These kinds of materials can achieve both high corrosion resistance, high electrical conductivity of copper and high mechanical strength of steel with low cost [14]. A higher use value of copper/steel composite materials is reflected from its good plasticity, weldability and magnetic characteristics [15]. Copper, with its noble potential and its red colour, has been used in countless applications both as an intermediate or undercoating, and as a top coat. There are more difficulties in producing clad composite materials, which are combination of different materials, than in producing single materials due to their different material characteristics. In this paper, a new method to gain copper coating on the surface of steels with copper addition is introduced.

Materials and Experimental Work

In the present work, low carbon steels with different copper contents were prepared in a high-frequency vacuum induction furnace. The chemical compositions of the steels are given in Table 1.

The samples with the size of about $10cm \times 10cm \times 10cm$ were used for the investigation. The cast samples were reheated at 1100℃ and 1150℃, respectively, for 2h in a normal furnace, in air, followed by furnace cooling.

For samples heated at 1150℃, the rusts were removed from the surface with the descaling reagent, where sodium dihydrogen phosphate anhydrous 50g and citric acid 30g were dissolved in 1L deionized water. The pH value of the descaling solution was about 1.6 (with digital pH tester) and the descaling process lasted 24 hours at room temperature.

Table1 Compositions of the test steels [wt%]

Steel	C	**Cu**	Si	Mn	Fe
1	0.014	**6.80**	0.030	0.037	Bal
2	0.001	**12.64**	0.056	0.064	Bal

The cross sections of the samples were ground and polished but not etched. The microstructures were observed by using an optical microscope (OM). A scanning electron microscope (Quanta FEG250) equipped with energy dispersive X-ray spectroscopy (EDS) was employed, to obtain elemental composition at different areas of the coating microstructure.

Results and Discussion

Thick rusts appeared on all the samples after being heated at high temperature, 1000℃ and 1150℃ in current work. Fig.1 shows the back scattered electron images of the inclined cross section of the test steels heated at 1000℃ for 2h. Oxidation of iron happened rapidlly during heating process, and the oxides appear in black in Fig.1. On the other hand, the oxidation of copper at these temperatures was slow comparing with iron. Both samples show that separately scattered copper particles, the brighter parts in back scattered electron images in Fig.1 with more than 95% copper according to EDX results, distributed near the substrate in the rusts. The copper in the rusts have little or nothing to do with the development of the oxidation. In other words, the rusts connect directly to the substrate and it can be deduced that if the sample heating continued, the rust would keep growing.
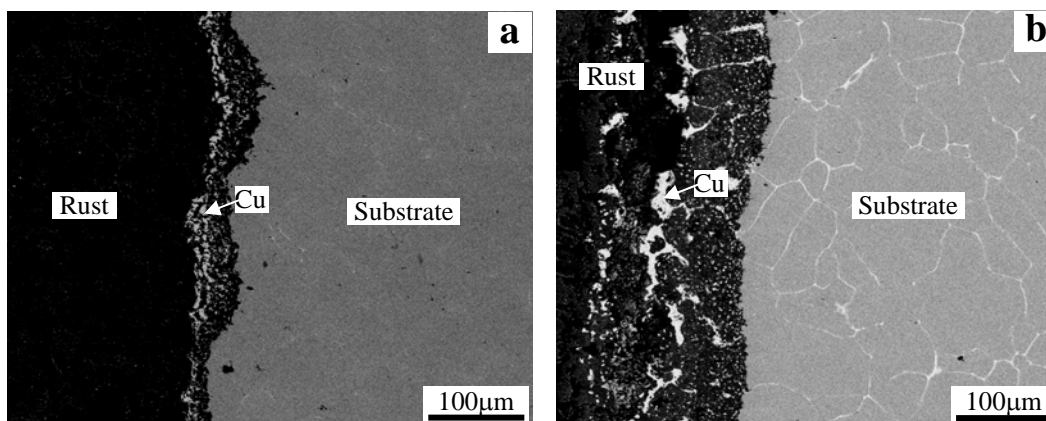

Fig.1 Back scattered electron images of the inclined cross sections of the steel samples with 6.8%Cu (a) and 12.6%Cu (b) after heating at 1000℃ for 2h.

For the steels with 6.8% copper (Fig.1a), the copper particles in the rust are much finer than those in the steels with 12.6% copper (Fig.1b). For the latter, in the substrate, a copper-rich phase precipitated at the grain boundaries because of the rather high copper content. At the same time, it is likely that a certain amount of copper dissolved in the steel as solid solution uniformly, and no copper-rich precipitation appeared in the steel with 6.8% copper as shown in Fig.1a. Under the temperature of 1000℃, the copper particles in the rusts cannot connect with each other even though the copper content is high enough to form copper-rich phases.

After heating at 1150℃, both steels show an integrated copper layer beneath the thick rusts. Fig.2 shows the morphology of the inclined cross section of steel with 6.8% copper after heating at 1150 ℃ for 2h. The copper layer appears between rust and substrate, which was the perfect position of copper coating.
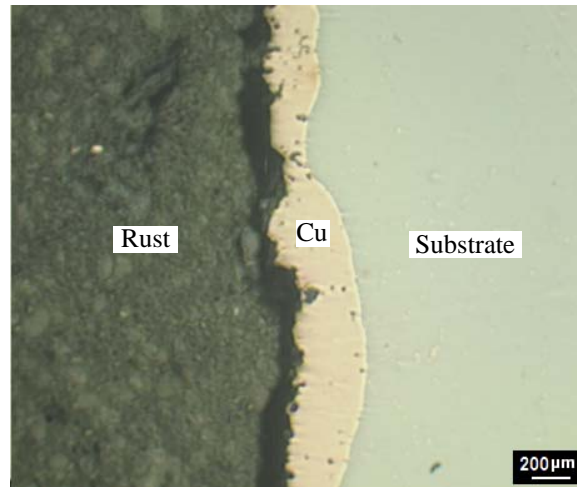

Fig.2 Optical microscope image of the inclined cross section of steel with 6.8%Cu after heating at 1150℃ for 2h.

By observing the interface between the copper layer and substrate, as shown in Fig.3, a fine line can be seen at the interface. The brighter part above the line in Fig.3 is copper layer with copper content of higher than 97% according to EDX results, and the less bright part under the line is substrate with the copper content of 7.4%, close to the copper content of the bulk steel. The dark particles in the copper layer are mainly oxides of iron with small amount of copper. The copper coating and substrate connected perfectly and there is not any slight void between them, which usually can be seen in other composite materials, even though the interface is not so straight.
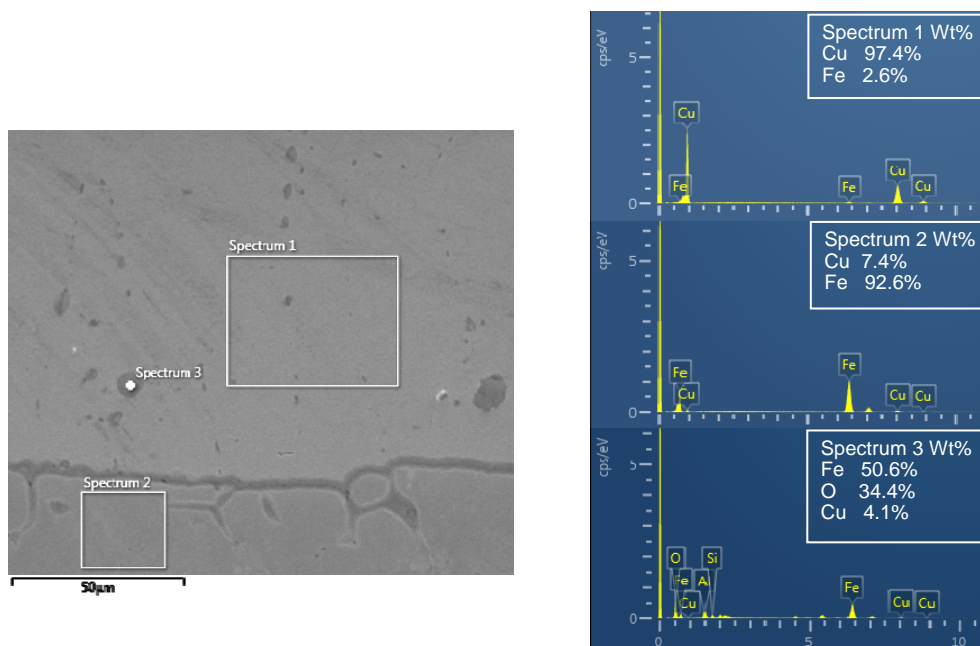

Fig.3 SEM morphology and EDX spectra of the substrate and Cu layer on the inclined cross section of steel with 6.8%Cu after heating at 1150℃ for 2h.

The thickness of copper coating changes from a few microns to tens of microns with some small oxide particles scattered in the layer. Major oxides were pushed away from the substrate and gathered at the outer layer as shown in Fig.2, and there were no copper particles scattered in the rusts either.

According to the above observation results, the forming of integrated copper layer on the surface of steels with copper addition depends on the heating temperature. It is considered that this temperature is associated with the melting temperature of pure copper, 1085℃, because the content of the copper-rich layer is around 95% Cu or 97% Cu, and its melting point must be very close to that of pure copper. At a higher temperature, e.g. 1150℃, both copper and iron atoms are active, especially copper atoms. It is easy for the small copper particles formed during oxidation to coalesce. The melted or quasi-melted particles should be able to penetrate through the oxide to connect with the substrate steel. On the other hand, at a lower temperature, such as 1000℃ in this work, the copper atoms are not so active for the copper particles to coalesce to form an integral film. It can be deduced that the formation of copper coating is thermally activated.

By choosing a proper descaling reagent, the rusts could be removed while keeping the copper layers, which can be judged by naked eyes because of copper's noble colour. The microstructure of the "copper coating" after descaling was observed with SEM, as shown in Fig.4. It shows that some irregular holes appeared on sample's surface after descaling. There are some oxide patches left on the surface as well, which are shown in white. Under the hole, EDX test result shows that the copper content decreased and the iron content increased correspondingly, though this analysis result is subjected to error, as EDX composition calculation is accurate only for flat surfaces.
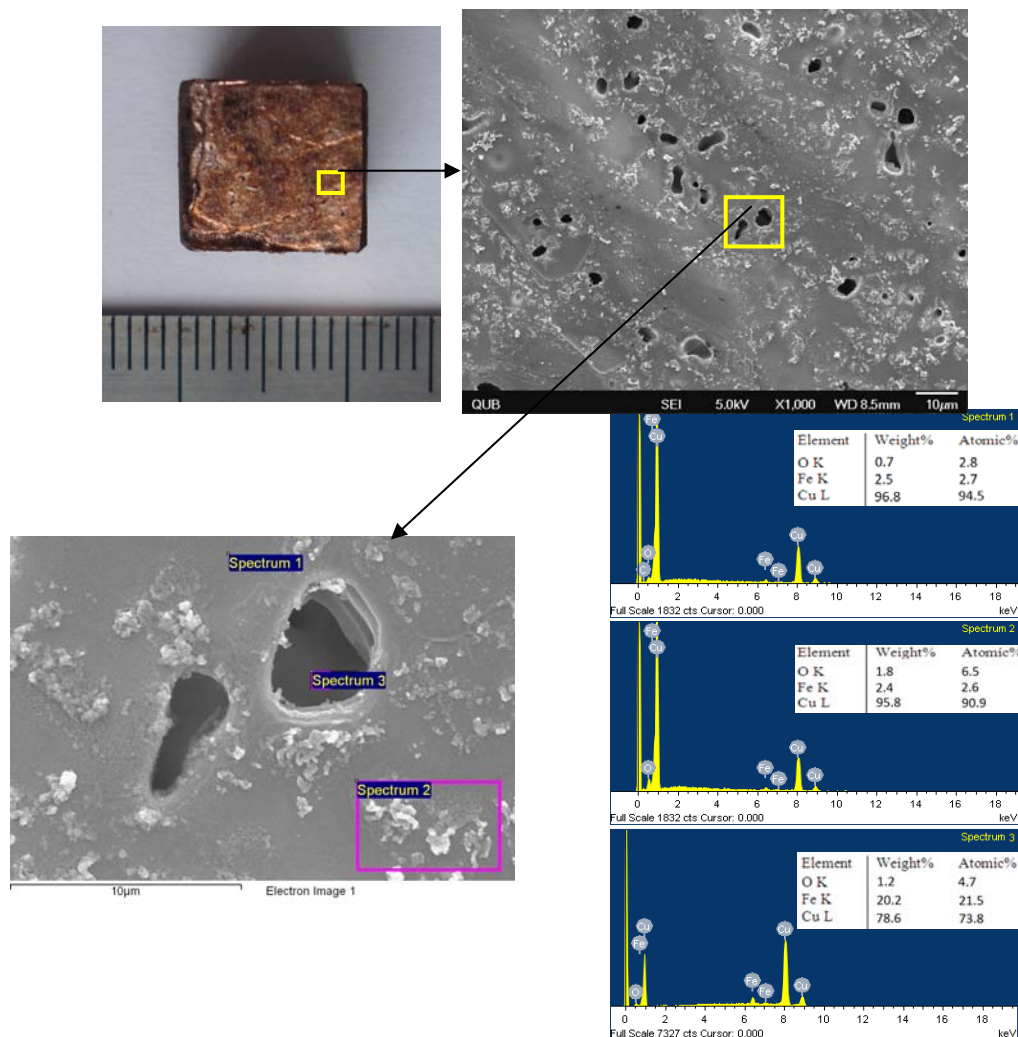

Fig.4 Macro-photograph, SEM morphology and EDX spectra of the surface of the steel with 12.6%Cu after descaling.

In Fig.2 and Fig.3, there is not any hole in the copper layer of the samples before descaling, so the holes in Fig.4 must be formed during the descaling process. From both Fig.2 and Fig.3, it can be observed that there are some dark particles with different sizes within the copper layer area, and they may have the same composition as spectrum 3 in Fig.3. In other words, there are some oxide particles in the copper, which were formed during heating and oxidation. These small oxide particles near the surface reacted with the descaling reagent and were dissolved in the solution, leaving small holes behind; then the solution reacted with other small oxide particles near these holes. These holes might become deeper or larger after the reaction, thus forming many holes with different depths and shapes. Therefore, further research should aim at achieving a clean surface without holes.

Conclusions

Copper accumulations on the surface of steels with copper addition after being heated at high temperature were studied in this work. The following conclusions can be made:

An integrated copper coating was observed on the surface of steels heated at 1150℃, but not on the steels heated at 1000℃. Therefore, likely, the forming of an integrated copper coating is thermal-activated.

By choosing a proper descaling reagent, the copper coatings were made on the steel surface while removing the rust. Some holes in the copper coating were formed, possibly from the reaction between the descaling solution and the oxides in the copper layer.

Acknowledgement

References

[1] L. Nan, K. Yang: J. Mater. Sci. Technol. Vol. 26 (2010), p. 941.

[2] X. Zhang, X. Huang, L. Jiang, Y. Ma, A. Fan, B. Tang: Appl. Surf. Sci. Vol. 258 (2011) , p. 1399.

[3] O. Sharifahmadian, H.R. Salimijazi, M.H. Fathi, J. Mostaghimi, L. Pershin: Surf. Coat. Technol. Vol. 233 (2013), p. 74.

[4] P.L. Fox, in: *The copper-iron chronicles: The story of an intimate relationship*. Biometals, Department of Cell Biology, The Lerner Research Institute, The Cleveland Clinic Foundation, Cleveland, OH 44195, USA, 16(1) (2003).

[5] S.K. Dhua, A. Ray, D.S. Sarma: Mater. Sci. Eng. A Vol. 318 (2001), p. 197.

[6] A. Fatehi, J. Calvo, A.M. Elwazri, S. Yue: Mater. Sci. Eng. A Vol. 527 (2010), p. 4233.

[7] A.A. Gornia, P.R. Mei: J. Mater. Process. Technol. Vol. 197(2008), p. 374.

[8] M. Tsujikawa, M. Egawa, N. Ueda, A. Okamoto, T. Sone, K. Nakata: Surf. Coat. Technol. Vol. 202 (2008), p. 5488.

[9] C. Chi, H. Yu, J. Dong, W. Liu, S. Cheng, Z. Liu, X. Xie: Progress in Natural Science: Materials International, Vol. 22 (2012), p. 175.

[10] Y. Sawaragi, N. Otsuka, H. Senba, S.Yamamoto: Sumitomo Search Vol. 56 (1994), p. 34.

[11] Z.X. Zhang, G. Lin, Z. Xu: J. Mater. Process. Technol. Vol. 205 (2008), p. 419.

[12] B. Soylu, R.W.K. Honeycombe, in: *Microstructural refinement of duplex stainless steels. Future developments of metals and ceramics*, The Institute of Materials, Maney Materials Science: London, 1992, p. 325.

[13] D.M. Nicholas, E.A. Wilson, W. Sha: Microscopy and Analysis Vol. 26 (2012), p. 19.

[14] O. Sharifahmadian, H.R. Salimijazi, M.H. Fathi, J. Mostaghimi, L. Pershin: Surf. Coat. Technol. Vol. 233 (2013), p. 74.

[15] D.B. McDonald, P. D. Krauss: Corrosion-resistant reinforcing steel. Second International Conference on Concrete under Severe Conditions. Norway: E & FN Spon, 1998. p. 382.