Research on the New Low Temperature Self-Protective Paste Boronizing Processes of Thermal Power Plant Economizer Pipe

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Abstract: Power plant boiler economizer pipe tend to crack rapidly due to the erosion of high temperature flue gas. In this paper, the power plant boiler economizer pipe (annealing 20 steel) was chosen as the research materials, three new formulations of self-protective paste in which quartz powder, fly ash and coal gangue were as the main ingredients were investigated,what's more,the low temperature self-protective paste boronizing technology with the rare earth added was studied. The experimental results show that the quartz powder, fly ash and coal gangue protective layer sintered at the boride temperature have the virtues of high strength, good sealing and easier peeling off, and these protective layers also brought good boronizing effect. 9wt% rare earth addition can bring good boronizing effect, when the boronizing temperature down to 700 ℃, the rare earth added self-protection paste boronizing process can still achieve boronizing layer. The wear-resisting and corrosion resistant performance of the economizer pipe after boronizing process obviously improved.

Keywords Self-protective paste boronizing, Protective coating, rare earth, economizer pipe, low temperature

1 Introduction

Economizer is an important heat-absorbing surface in the power plant boiler. It is usually equipped in the flue and absorbs the quantity of heat of flue gas in order to heat the boiler. But the existence of the large number of solid particles and corrosive gases in flue gas will cause the high temperature erosion wear and hot corrosion to the economizer tube and even leads to abnormal tube wall thinning and premature failure, frequent detonation tube leakage thus become serious threat to the safe and economic operation of boilers [1]. In coal-fired power plants, boiler accidents accounted for more than half of the power plant accident, while economizer of boiler tube blasting accidents accounted for 45% ~ 50%, among those economizer abrasions leakage is a main reason [2, 3]. So the improvement on the operational process of economizer pipe outer surface erosion and hot corrosion resistance is of great significance to improve the service life of the power plant boiler economizer, boost the reliability of boiler and prolong average trouble-free operation time of the boiler.

Boronizing is a kind of important chemical heat treatment technology. Take steel material for an example, after dealing with boron, its wear resistance, corrosion resistance, and the rigid and high oxidation resistance can be improved. Paste boronizing is a technological method in which the boron agent, activator, and filler are mixed through the use of the binder paste to be applied to the clean metal surface, and then sealed, packed, heated and preserved heat to achieve the boronizing layer [4,5]. Self-protection paste boron which overcomes the shortcomings that the traditional medicinal extract boron needs seal packing or the protection of the atmosphere, adapts the paste outer take cover [6,7],then in boronizing temperature a glaze shell generates on the paste coating surface to achieve self protection in the process of boronizing. The technology has the characteristics of simple process, fast boron permeability speed, good effect and low cost [8-10], which is suitable various shapes of the workpiece. It is a promising surface treatment technology [8]. The paste boronizing temperature of boron treatment is commonly in 800 ~ 1000 ℃, in such a high temperature, the traditional boronizing agent generates active boron atom which is essential to the boronizing process. But generally such a high temperature may reach to the austenitic temperature of steel tube. what's more, considerable changes in the organization of the original material took place, affected the performance of the matrix, then restricted the development and application of self-protection paste boronizing technology. Therefore, the research and development of new low-temperature self-protection paste boronizing technology is of important engineering application value.

2 Experimental details

Thermal power plant boiler economizer tube blasting operation pipe (20 steel annealing states) was used as boron material. B_4C 、KBF_4 、 the activated carbon,、SiC 、Al_2O_3 (filler), sodium silicate solution (adhesive) and a certain amount of lanthanum rare earth were prepared for boron paste, then the prepared cream boron paste was evenly coated on the surface of the sample, thickness is 3 ~ 5 mm, as is shown in Fig.1. The coated boron sample was dried in the drying oven at 160℃, and then moved into carbon silicon rod furnace to be heated for boronizing. The boronizing experiments were made in a series of set temperature. After a certain period of boron heat preservation time, electric power supply were turned off. When the samples in the furnace were cooled to 100 ~ 200 ℃, they were removed to cool in the air. Then the protective layer and paste layer were removed to prepare metallographic specimen which was to be corroded with nitric acid of 5% alcohol. Then the 200 MAT inverted metallographic microscopes was used to observe the microstructure of the boron samples, and the HBRV 187.5 hardness tester was used to test the hardness of the boron samples.

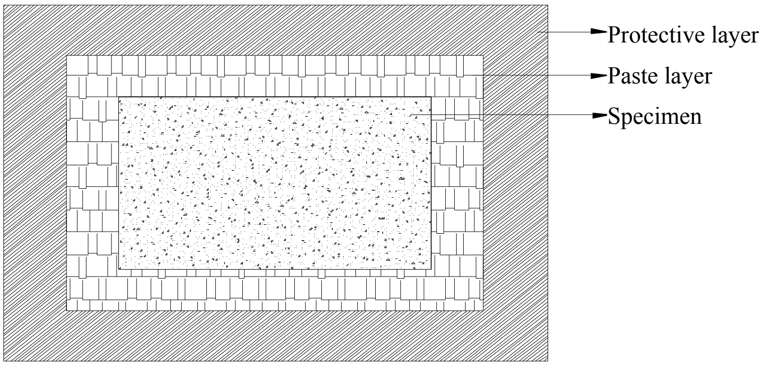
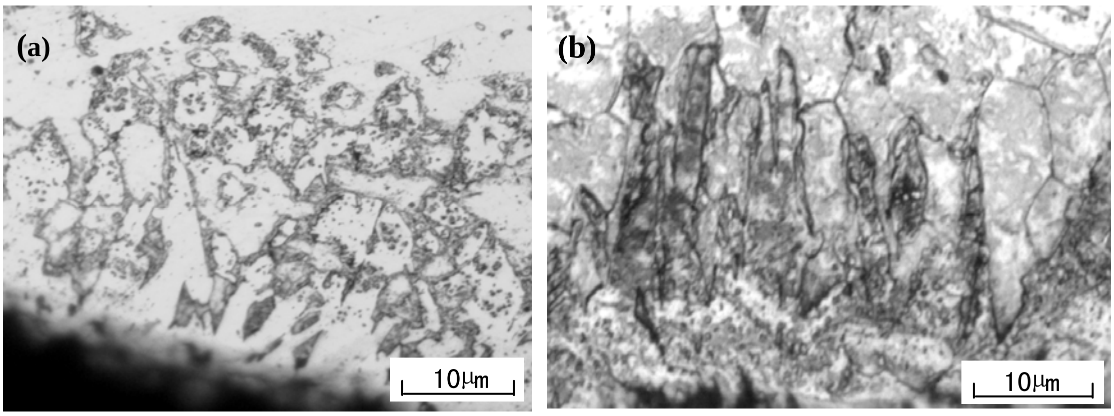


Fig.1 Schematic diagram of the specimen surface coating

3 Results and discussion

3.1 Temperature's influence on the boron effect without the rare earth

With no rare earth added, the microstructures of the self-protective paste boron sample are shown in Fig.2.



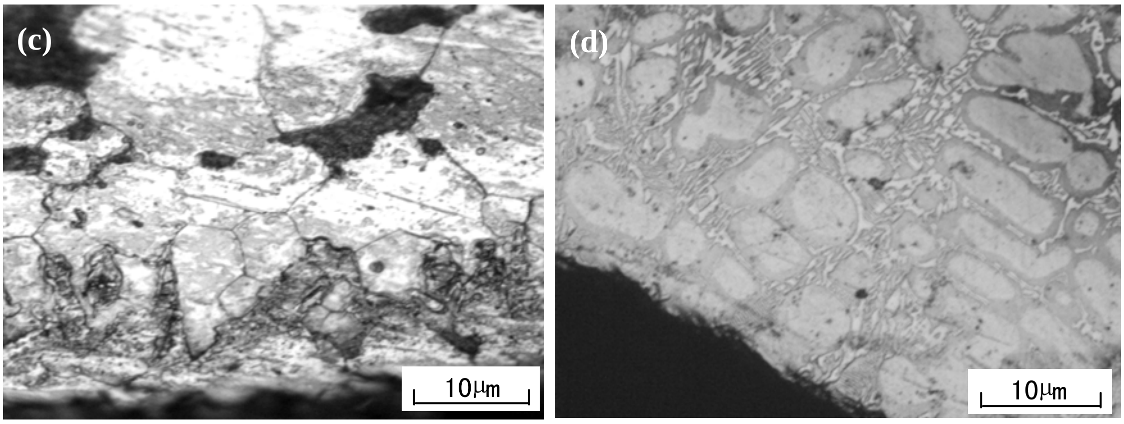


Fig.2 Microstructures of self-protective paste boronizing specimens at different boronizing temperature with no rare earth added (a) 960℃, (b) 900℃, (c) 850℃,(d) 800℃

It can be seen from Fig.2 that with the increase of boronizing temperature, boronizing layer thickness has a trend of increase. When the temperature is at 850℃, the boronizing layer of the sample is very thin, and discontinuous, the leading end of the sample has the trend of expansion along the steel matrix grain boundary; when the temperature is at 900℃, the ideal boronizing layer which was closely integrated like fingers and continuous on the surface of the whole sample can be obtained; when the temperature is at 960℃, the hardness of the boron sample increased, the appearance also changed, and fragmentation occurred in the boronizing layer which was in block or granular form. The main reason is related to boron carbide of nucleation characteristics and the obstacles that boron carbide suffered in the process of growing up. When the crystal nucleus formed on the surface grain boundary grew up, the distortion of the crystal nucleus formed in the crystal lattice lead to the increase of local stress which may cause the slight deviation of the growth of boride. 20G steel has the characteristics of small austenitic grain size, multi-grain boundary, multi-crystal nucleus formed on the surface grain boundary, all sorts of oblique nucleation. As for the economizer, the steel pipe carbon content is low and diffusion resistance is not big, which results in the irregular tooth structure.

When the temperature is decreased to 850 ℃, the boronizing layer was very shallow and boron effect was not obvious; when the temperature is at 800℃, no boron boronizing layer was found (as shown in Fig.2 (d)). Therefore, in the experiment, self-protective paste boronizing process can only be achieved when the temperature is over 800℃.

3.2 The influence of adding rare earth on the boron temperature

For the study of the influence of the addition of rare earth on the boron temperature in low temperature, protective paste in which fly ash and coal gangue are the main components was adopted. 7wt% rare earth was added into the original Boronizing agent formula, and then the same self-protective paste boronizing was employed. Heat preservation boron were adopted at 850℃、800℃、750℃、700℃ and 680℃ respectively, then it could be seen that the protective layer showed brick-red and on the surface there was a thin enamel layer, boron paste and sample were bonded but easy to clean up. Parts of boron sample microstructures at boronizing temperature are shown in Fig.3. The experiment results showed that when the temperature was over 700℃, boronizing layer could be achieved effectively; when the temperature was decreased to 680℃, no boron boronizing layer was found(as shown in Fig.3(c)).With higher boron temperature, the boronizing layer was deeper and the boron effects were better(as shown in Fig.3(a)).

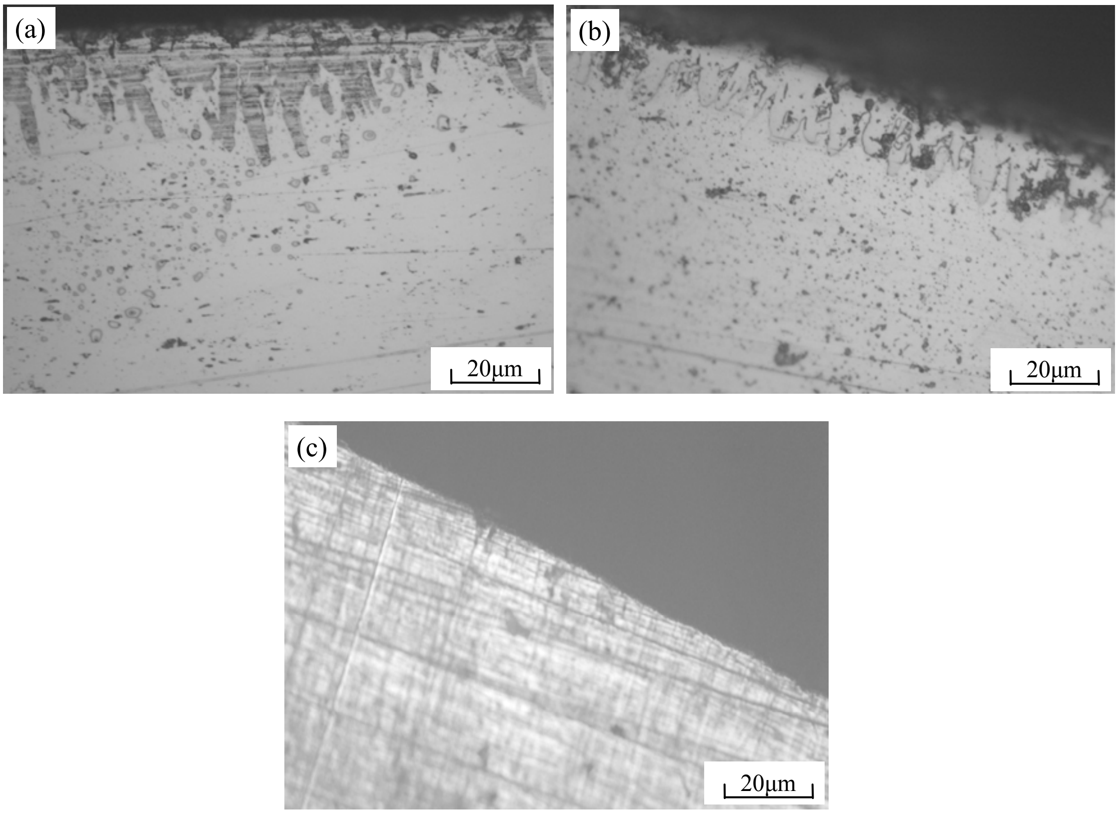
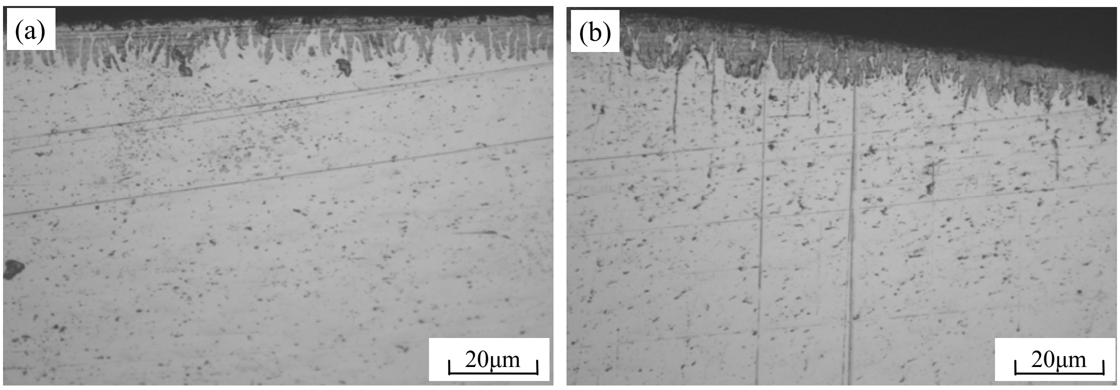


Fig.3 Microstructures of self-protective paste boronizing specimens at different boronizing temperature with rare earth added （a）850℃,（b）700℃,（c）680℃

3.3 The influence of the amount of rare earth added on the boron effect

To study the influence of the amount of rare earth added on the boron effect, 7wt%、8wt%、9wt% and 10wt% rare earth were chosen to add into the boron paste respectively, the addition of the amount of KBF4 and that of B4C were the same in each boron experiment, the same self-protective paste and the same boronizing processes were adopted, when the boron temperature was at 800℃, the microstructures of the self-protective paste boron samples with different amount of rare earth added were shown in Fig.4.



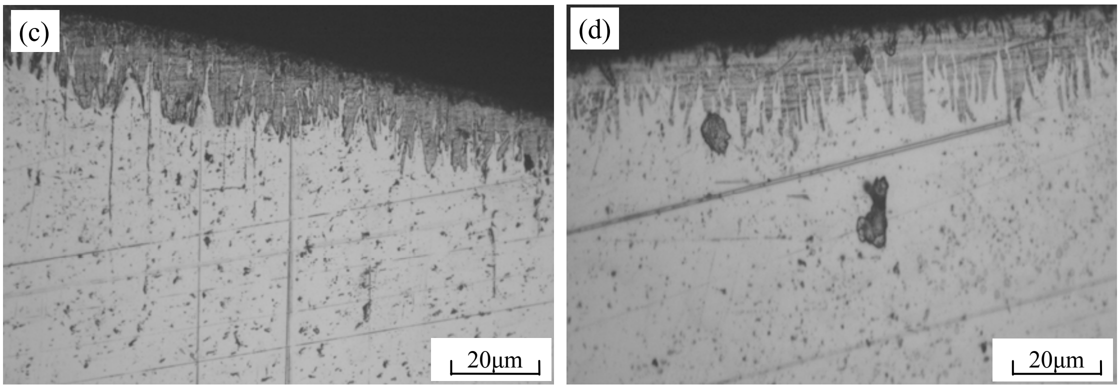


Fig.4 Microstructures of self-protective paste boronizing specimens with different rare earth addition
(a) 7wt%, (a) 7wt%, (b) 8wt%, (c) 9wt%, (d) 10wt%

It can be seen from Fig.4 that on the surface of the self-protective paste boron samples with rare earth added, a certain boronizing layer occurred. Under the circumstances of 8% rare earth addition and 9wt% rare earth respectively, boronizing layer was regular and closely integrated, which brought good boron effect. However, with the increase of the amount of rare earth added (as shown in Fig.4(d)), boronizing layer expanded further towards the sample, and the structure of which was irregular and its uniformity fell. From the hardness data of the boron samples (as shown in Fig.5), it can be seen that the hardness achieved the maxi value when the rare earth addition was 9wt%. Therefore, it can be drawn that in the current boronizing conditions and in the process of low-temperature boronisation, the optimum amount of rare earth added is 9wt%.

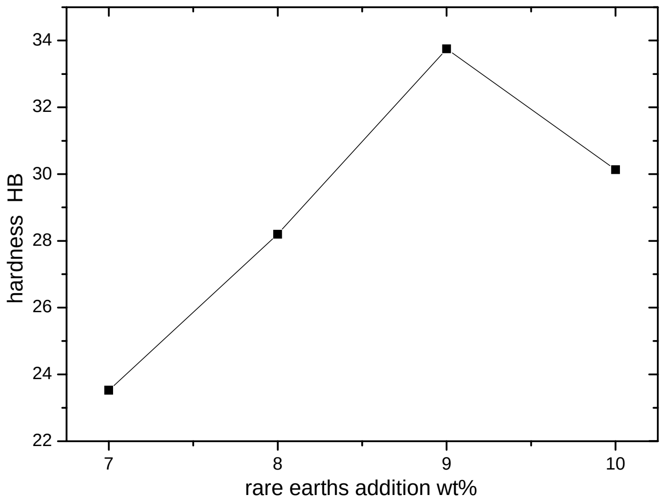


Fig.5 Hardness of self-protective paste boronizing specimens at different rare earth addition

3.4 Discussion

In the process of boronisation, the boron agent supplier in the paste had reaction and generated activate B atoms which had been absorbed by the iron and steel sample surface and were segregated and enriched on crystal defects such as grain boundary and the surface phase boundary and space [11], Then had a short-range diffusion in the direction of the internal lattice and matrix. With the continuous migration of B atoms, in the lattice when the conditions of concentration and fluctuation of energy were ready, Fe2B crystal nucleus formed. Then with the crystal grain's growing up, Fe2B-γ phase boundary propeled toward the inner matrix [12]. The protective paste in which quartz powder, the covering layer of fly ash and coal gangue were as the main ingredients, has the characteristics of high strength, good sealing and easy peeling in boronizing temperature, could achieve good boron effect.

Due to the intro protection layer, in the process of the self-protective paste boronizing,parts local boronisation can be achieved. When the boron temperature decreased effectively, the economizer steel pipe’s online instant boronisation could be achieved and this technology can be applied to the strengthening treatment of the surface of other boiler heat pipes and other high- temperature resistant and corrosion resistant parts.

4 conclusion

With no rare earth added, self-protective paste boronizing can only be carried out when the temperature was over 800℃. Within a certain range, rare earth could speed up the boronisation and make the boronizing layer be well-distributed and closely integrated. Therefore, the binding force between the boronizing layer and matrix was increased and the performance of the steel pipe was improved. Rare earth was used to assist boron, when the boriding technology was properly handled, the temperature of the economizer self-protective paste borinisation can be decreased to 700℃, the addition of 9wt％ rare earth could achieve good boron effect. The protective paste in which quartz powder, the covering layer of fly ash and coal gangue were as the main ingredients, has the characteristics of high strength, good sealing and easy peeling in boronizing temperature, could also achieve good boron effect.

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References

[1] W.L. Cheng, Y. Zhou, A Model to be Used for Monitoring the Wear of Boiler Economers, Power Engineering, 26（2006）646–649.

[2] J.M. Ye, Power plant boilers principle and equipment, China Electric Power Press, Beijing, 2004.

[3] W.P. Yan, Y.Z. Liu, Y.H. Gao, Comparing Study on Styles of Exetended Heating Surfaces of Economizers in Utility Boilers, Boiler Technology, 37(2006) 26-30

[4] X.H. Yi, F.H. Li, Z.G. Fan, Technology for Solid- State Pack Boronizing of Q235 Steel and Kinetic Study of Boron Diffusion in Steel, MATERIALS PROTECTION,42（2009）13-16.

[5] J.S. Hu, Z.Y. Li, J.M. Hao et al., Development and applications of self-protective boronising paste based on thermodynamic analysis, Ordnance Material Science and Engineering, 25（2002）38-40.

[6] S.Roumiana, Petrova, S. Naruemon., S. Veljko, The Effect of Boronizing on Metallic Alloys for Automotive Applications, Journal of Materials Engineering and Performance, 17(2008) 340-345.

[7] D.C. Loua, J.K. Solbergb, O.M. Akselsena, N. Dahlc, Microstructure and Property Investigation of Paste Boronized Pure Nickel and Nimonic 90 Superalloy, Materials Chemistry and Physics, 115 (2009) 239-244.

[8] X.M. Ou, Z.Y. Ni, Study and Analysis on Process of Paste Boronization Without Boxing, Journal of China University of Mining & Technology, 27(1998)200-203.

[9] Y.Z Gong, L.D. Zhang Research on Self-protective Rare Earth-Boronizing Pasty Agent[J]. ELECTRONICS PROCESS TECHNOLOGY, 7(2001) 161-165.

[10] J.S. Hu, Z.Y. LI, J.M. Hao, et al. Application and Thermodynamic Analysis on Self-Shield Boronizing Pasty, HEAT TREATMENT OF METALS, 27(2007) 26-28.

[11] Z.S. Ji, Multivariate Boronizing Technology and Applications, Metallurgical Industry Press, Beijing,2004.

[12] I. Campos, M. Islas, E. González, et al.. Use of fuzzy logic for modeling the growth of Fe_2B boride layers during boronizing, Surface & Coatings Technology, 201(2006)2717-2723.