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STUDY ON WEAR AND CORROSION OF THE HVOF SPRAYED NiCr-Cr₃C₂ COATING AFTER ANNEALING

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Abstract. The crystallizer has a very limited operation without any surface treatment. The NiCr-Cr₃C₂ coating has been applied onto a CuCrZr plate by means of high-velocity air fuel spraying (HVOF) in order to improve its service life.

This paper presents the study of the microstructure, element distribution, and phase composition of the NiCr-Cr₃C₂ coating with the help of an X-ray spectrometer (EDS), X-ray diffractometer (XRD), MH-5LD microhardness tester, XMTD-7000 pin friction and wear tester, and CHI604C electrochemical analyzer. The wear resistance of the layer was analyzed. The results show that the strength of the adhesive NiCr coating layer annealed at 500 °C is higher than that of the non-adhesive layer due to the elimination of the residual stress. Due to the presence of a large amount of the hard ceramic phase of Cr₃C₂ in the coating, the melting point becomes high, resulting in a higher hardness of the entire NiCr-Cr₃C₂ coating. The adhesive layer NiCr is characterized with a more stable coefficient of friction after 500 °C annealing due to elimination of the residual stress within the coating. Combined with a higher strength, it suggests better wear resistance. According to the electrochemical test, the coating annealed at 500 °C tends to be less aggressive and exhibits better corrosion resistance.

Keywords: adhesive layer; HVOF; wear; corrosion.

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Problem statement. Crystallizer is the heart of the continuous casting machine. After the molten steel is drained rapidly into the system, it condenses to form a continuous scale and returns to the supporting part of the fan for cooling and condensation. The casting device is subject to temperature variation due to the cold and hot temperature difference of the molten steel [1-3]. The crystallizer is composed of a number of parts, such as the side guide, the foot roll, the mould frame, the

copper plate, the narrow side width and the wide side clamping structure [4]. The working conditions of the crystallizer are extremely harsh, and the steel drawing speed, casting efficiency and surface quality are directly affected by the crystallizer performance [5]. In addition, the mold performance has a direct impact on its production accuracy, reliability, and service life of the equipment. Such a phenomenon inevitably brings about high-efficiency means to the development of con-

tinuous casting technology in order to improve the quality of the mold, and puts forward higher technological requirements as for wear resistance, strength high thermal conductivity. These quantities have become a part of the standard in the measurement of the mold quality. This experiment is aimed at the study on the wear of mold copper plate in the Masteel continuous casting line.

As a new kind of hard alloy, Cr₃C₂ is referred to as “stainless steel in hard alloy”. Its hardness is similar to that of the WC-Co alloy and makes up 88-90 HRC. The alloy withstands temperatures up to 600 °C without much degradation. It has a good high-temperature oxidation resistance, corrosion resistance and wear resistance. The alloy’s density is low, generally making up half of that of the WC-Co alloy, and the thermal expansion coefficient is close to that of steel.

Because of its outstanding properties, NiCr-Cr₃C₂ is used as a thermal spraying material for metal surface protection (except for steel elements to avoid adverse reactions). It suitable to be used as a coating material for the mold plate in order to extend the service life of the crystallizer under consideration [7]. Therefore, the study of the mold of the CuCrZr plate covered with a NiCr-Cr₃C₂ coating with the help of high-velocity air fuel spraying (HVOF) and respective improvement of the mold’s surface properties and service life are associated with a great theoretical significance and practical value in the reduction of production costs.

BASIC MATERIAL

1. Experiment process and scheme

1.1. Experimental equipment

The test equipment mainly includes the following items: supersonic flame spray gun, tensile tester, micro hardness tester MH-5LD, pin plate friction and wear

tester XMTD-7000, X-ray diffractometer, EDS, electrochemical analyzer CHI604C, polishing machine, and sandpaper.

1.2. Experimental matrix material

The chemical composition of the chromium zirconium copper (CuCrZr) alloy is shown in Table 1. Its hardness is equal to HRB 78-83, and the conductivity is 43 ms/m.

1.3. Spraying material

The powders employed in the study are Cr₃C₂-25%NiCr (Sulzer Metco, 15-45 μm in diameter) and NiCr (Sulzer Metco, 15–45 μm), which are milled by means of a horizontal ball mill for 40 minutes.

The sprayed materials are divided into three groups: the Cr₃C₂-NiCr coating without the NiCr backing (group A), the Cr₃C₂-NiCr composite coating (group B), and the same coating annealed at (group C), which was annealed at 500 °C as group A.

1.4. Friction and wear test of the coating

As it has been mentioned, this experiment makes use of the XMTD-7000 pin plate friction and wear tester. The test has the following parameters: the speed of 318 r/min, the loading force of 10 N, the duration of 3600 s, the maximum friction force of 40 N, the grinding mark diameter of 7 mm, the temperature of 27 °C. The grinding medium is a hardened steel ball with the hardness of 60 HRC.

2. Experiment results and discussion

2.1. XRD analysis of the NiCr-Cr₃C₂ coating

The results of XRD inspection and analysis of coatings are presented in Fig. 1. The main component of the coating is the mixture of NiCr and Cr₃C₂. In the process of spraying, due to the high-velocity plasma flow, the mixture covers the spraying distance very quickly, avoid-

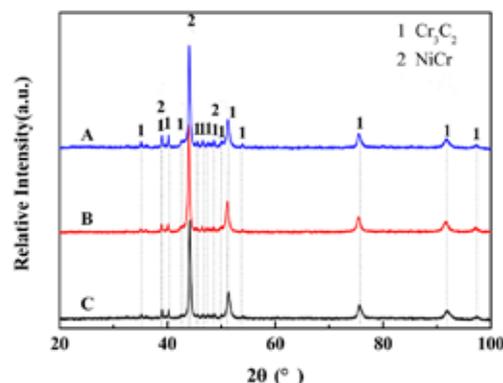


Fig. 1. XRD analysis of the coatings

Table 1. Composition of the CuCrZr alloy

Element	Al	Mg	Cr	Zr	Fe	Si	P	Total impurities
Content	0.1–0.25	0.1–0.25	0.1–0.8	0.3–0.6	0.5	0.5	0.1	0.5

ing oxidation. With the hard ceramic phase of Cr_3C_2 , the coating has high hardness and wear resistance and thus a very good protective effect on the substrate.

2.2. *Microstructure of the coating's cross section*

The cross-sectional morphology of the Cr_3C_2 -NiCr coating can be seen in Fig. 2. The black region begins to increase at the interface; the black areas are the pores. As can be seen from Fig. 2, *a-b*, the coating porosity at the interface is much higher without the NiCr backing, and sample *c* (with NiCr backing, annealed at 500 °C) assumes the intermediate level. Having compared the samples, we can see that the shape and distribution of pores are irregular, and sample *c* has the highest level of porosity.

The porosity of the coating is affected by many factors, with the size, shape, physical properties of the coating and spraying parameters among them. The size of pores is mainly affected by the spraying distance. The existence of pores has a very important influence on the properties of the coatings, such as hardness and wear resistance. Large pores are start to cause damage as wear proceeds. The particles at the pores lack the support of the edges and are easy to fall off, thus causing further wear failure. If there is a substantial porosity, the hardness will be collapsed when tested, so that the measured hardness would not match the actual result.

2.3. *Test results for the coating hardness*

Hardness is one of the important parameters reflecting the quality of the coating. It is the ability of a material to resist deformation or rupture in the local area of the surface. The hardness of the coating should take into account the characteristics of the sprayed coating structure and the spraying process, as well as high temperature of quenching, hardening, particles deformation, etc. A coating containing pores, oxides and structure heterogeneity will have different macro and micro hardness. Thus, the

macrohardness can only reflect the average hardness of the coating area, and microhardness can more accurately reflect the characteristic of a particular coating area and fix the change in its state.

The distribution of hardness in the coating cross section is shown in Fig. 3. It is clear that the hardness of the three groups of samples began to differentiate at the interface between the coating and the matrix. The hardness of the three groups of matrix is not big; the hardness of the coating annealed at 500 °C is obviously lower than that of the coating without annealing. Addition of the NiCr backing has little effect on the hardness of the coating, although the hardness of the coating without NiCr is still slightly inferior.

2.4. *Experiment results for the coating wear resistance*

Fig. 4 presents a diagram of friction coefficients of the coatings under study. The friction coefficient is mainly used to characterize the degree of wear of the coating. The coating without the NiCr backing and the coating annealed at 500 °C have similar friction coefficients, initially higher than that of the coating with the NiCr backing. However, after a period of time, the former starts to decrease, while the latter remains stable. The reason why the friction coefficient is unstable after annealing is that the precipitation of carbide in the coating aggravates the wear of the ball to the coating, and carbide is a wear-resistant phase, which causes the wear debris on the part of the ball to adhere to the surface of the coating. The adhesive debris interferes with the collection of pressure sensitive signals, leading to changes in the friction coefficient.

2.5. *Experiment results for the coating corrosion resistance*

The polarization curve analysis is one of the classical methods to study the electrochemical corrosion protec-

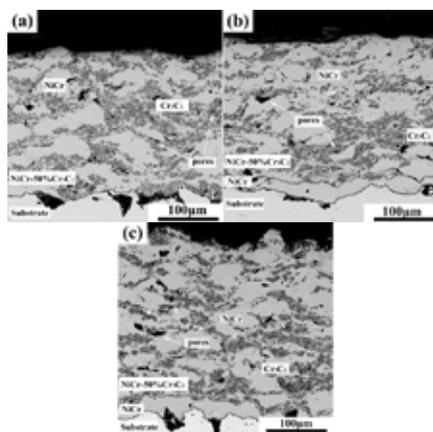


Fig. 2. Cross-section morphology of the Cr_3C_2 -NiCr coating *a* — without NiCr backing; *b* — with NiCr backing; *c* — with NiCr backing and annealed at 500 °C

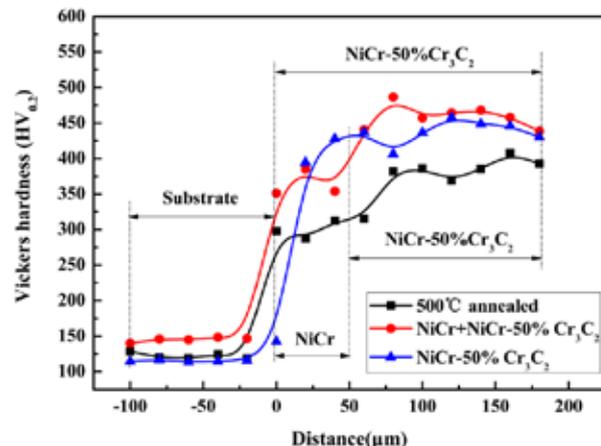


Fig. 3. Distribution of hardness in the coating cross section

tion of coatings. It is widely used in exploring the corrosion mechanism of coatings, determining the corrosion rate, judging the corrosion resistance of materials, and evaluating the best materials. Fig. 2.5 presents the coating polarization curve. It evidences that the NiCr backing offers a lower corrosion potential and a smaller corro-

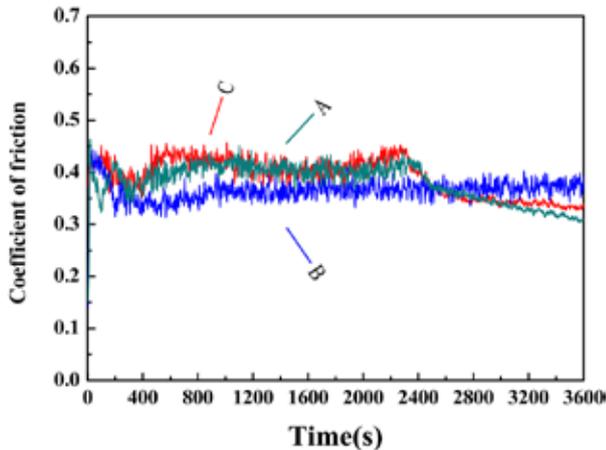


Fig. 4. Diagram of friction coefficients of coatings

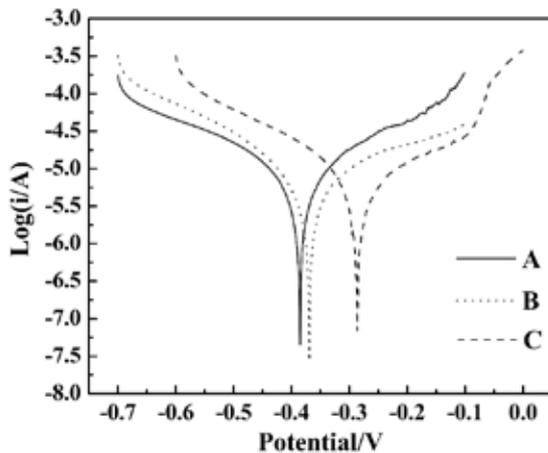


Fig. 5. Coating polarization curve:
A — Cr_3C_2 coating without NiCr backing; B — NiCr- Cr_3C_2 coating; C — NiCr- Cr_3C_2 base coating with NiCr addition and annealed at 500 degrees)

sivity. Besides, the corrosion tendency after annealing at 500 °C is much smaller. It follows from the comparison of the current density that the three corrosion rates are almost identical. In general, the annealed coatings have a better corrosion resistance.

CONCLUSIONS. In this paper, NiCr- Cr_3C_2 coatings were sprayed on CuCrZr plates by means of supersonic flame spraying – high-velocity air fuel spraying (HVOF). The samples under study were divided into 3 groups: a coating without the adhesive layer, a coating with the NiCr backing layer, and an annealed composite coating. The microstructure and properties of the coatings were analyzed with the help of special materials and instruments. The friction and wear behavior and corrosion resistance of the coating under different conditions were studied through friction and wear tests and electrochemical experiments, leading to the following conclusions.

1. The Cr_3C_2 alloy and the NiCr adhesive layer are subject to mechanical bonding, i.e. no chemical reaction occurs at their interface. There is a certain level of porosity in the coatings of all three groups within the coating and bond coating layer. However, it is minimized in composite and annealed coatings due to the elimination of residual stress and no adhesion.

2. Due to the existence of a large amount of the hard ceramic phase of Cr_3C_2 and its high melting point, the composite NiCr- Cr_3C_2 coating has the highest hardness.

3. The friction coefficient of the coating with the adhesive layer is more stable, but it is not the basis for judging the wear resistance.

The width of the upper and lower abrasion resistance can also be obtained. After annealing at 500 °C, the coating has a high strength and good abrasion resistance; the indicators are slightly worse for the coating without the adhesive layer. According to the electrochemical polarization curve of the coating, the corrosion tendency of the annealed coating is smaller; this sample manifests the highest resistance resistance.

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