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Effect of CrTiAlN Coatings on High-Temperature Oxidation Behavior of H13 Steel

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Abstract. CrTiAlN hard coatings have been deposited on H13 steel for improving the oxidation resistance by Closed Field Unbalanced Magnetron Sputter Ion Plating (CFUMSIP). The phase components, surface and section morphology of H13 steel before and after oxidation were analyzed by XRD and SEM. The results showed that the columnar crystal film possesses three major parts, i.e., the internal Cr bonding layer, the intermediate CrN transition layer, the external CrTiAlN gradient coating. The selective oxidation of Cr element was found on the surface of uncoated H13 steel while oxidation, but a continuous protective layer was not formed because of low Cr content, finally a lot of alpha Fe_2O_3 particles took place on the surface of H13 steel owing to the oxidation of the matrix element. O element can diffuse much more easily through the coating and oxide scales at 800 ^oC, and spallation and cracks were not found during the oxidation. These results indicated that the CrTiAlN coating have excellent high-temperature oxidation resistance at 800 ^oC.

Introduction

H13 steel (4Cr5MoSiV1), which is widely used in hot extrusion, forging and non-ferrous metal die-casting mould manufacturing [1, 2] and is one of the most representative hot work die steels, possess high hot strength, hardness, toughness and good heat fatigue resistance and other advantages. But its maximum working temperature is 600 ^oC [3], which particularly limits the application range of H13 steel at a high-temperature environment. Preparing the protective coatings on H13 steel is a better way to improve its high temperature oxidation performance. TiAlN film fabricated on H13 steel by PAPVD pulse arc technology by Jimenez et al. showed excellent thermal denaturation resistance [4]. An Al coating as thick as 10 μm have been produced on H13 by arc deposition, then post-treated with high current pulsed electron beam (HCPEB). The oxidation results indicated that high temperature oxidation resistance of coated H13 steel was improved by approximately 40 times as compared to the untreated sample at 750 ^oC [5].

CrTiAlN coatings have attracted more and more interest because of their high hardness and high temperature oxidation resistance, which make it have good abrasion resistance combined with thermal stability. CrTiAlN gradient coating produced by Bai et al. had good thermostability at less than 900 ^oC [6]. The high temperature oxidation resistance of CrTiAlN coatings, which have been deposited by Zhou et al., was better than TiN, TiAlN and other traditional coatings [7]. Improved oxidation resistance of CrTiAlN coatings is mainly due to the formation of dense protective Al_2O_3 and Cr_2O_3 oxide scales on the surface while high temperature oxidation, which prevent further diffusion and penetration of O_2 to the internal of coatings. CrTiAlN composite coating prepared on 65Mn steel by arc ion plating technology by Cai et al. possessed excellent high-temperature oxidation behavior at 900 ^oC, whose oxidation mechanism was internal diffusion oxidation of O element to coating [8]. Therefore, CrTiAlN coatings are potential oxidation candidates for oxidation resistant coatings. Based on these, H13 steel was the research object in our present work, and CrTiAlN hard coatings have been fabricated on H13 steel for improving the oxidation resistance by CFUMSIP. The micro-morphology, phase structure and high temperature oxidation resistance of CrTiAlN coating

were analyzed by XRD and SEM. The oxidation mechanism of CrTiAlN coatings on high-temperature oxidation behavior of H13 steel was also discussed in this paper.

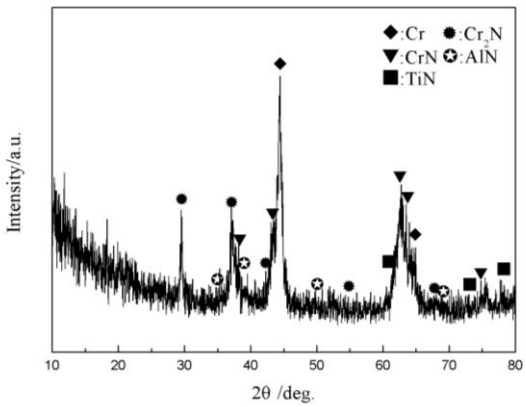

Fig.1. XRD spectrum of CrTiAlN coating

Experimental

The martensitic hot die steel H13 steel (4Cr5MoSiV1) was chosen as the substrate in the present work. Before coating deposion, the specimens cut into slices of the dimensions of $15\times10\times2$ mm^3 by Wire cut Electrical Discharge Machining(WEDM) were ground to 2000 grit SiC paper, then degreased ultrasonically in acetone, cleaned by ethanol and dried in air.

CrTiAlN coatings were prepared using the UDP 650 CFUMSIP system (Teer Coatings Ltd, UK). The deposition process was given as follow: vacuumize → heat(the inert Ar gas was introduced into the sputtering chamber, glow discharge) → high-energy plasma bombardment for removing the surface oxides and other dirties of H13 steel → the deposition of Cr bonding layer → the introduction of reactive gas N_2, preparing the CrN transition layer and CrTiAlN gradient coating → taking out of samples after fully cooling.

The oxidation experiments of H13 steel before and after coated were performed in high temperature heat treatment furnace at 800 for 10 h respectively.

The phase components, surface and section morphology of H13 steel before and after oxidation were investigated by XRD (Shimadzu XRD-6100, Japan) and FESEM (Carl Zeiss Sigma, Germany). The composition of coatings and oxide layers was also analyzed by EDS.

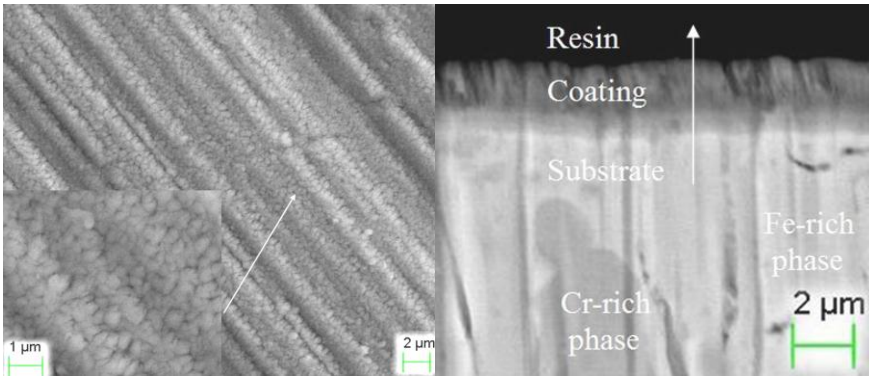

Fig.2. Surface morphology (a) and section morphology (b) of CrTiAlN coating

Results and Discussion

Characteristics of CrTiAlN coating before oxidation. The phases in CrTiAlN coating are mainly metal Cr, Cr_2N and CrN, and also a small amount of TiN and AlN (Fig.1).

The surface and section morphology of CrTiAlN coating are showed in Fig.2. As is shown in Fig.2 (a), the coating is the dense columnar crystal, whose crystal column outcrops are small averagely. Besides, its color is even and presents the silvery white metal color. Still could be observed parallel furrows. It is clear from the Fig.2 (b) that H13 steel is mainly composed of Fe-rich phase and Cr-rich phase; the thickness of coating is about 2.5 μm; defects such as microcrack and pinhole were not found in its cross-section morphology; the interface of coating and matrix is level off and clearly visible, which could guarantee good adhesion strength between the coating and matrix ; but the columnar crystal structure was loose. The composition of CrTiAlN coating along the direction of the arrow in Fig.2 (b) by EDS is as follow: the very thin Cr bonding layer, 0.5μm CrN transition layer and

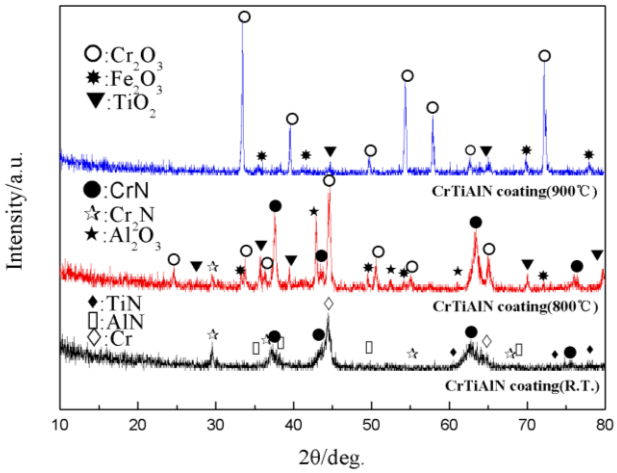

Fig.3. XRD spectra of CrTiAlN coating before and after oxidation

the external about 2μm CrTiAlN gradient coating, which was consistent with the design train of thought of CrTiAlN coating.

High-temperature oxidation resistance performance of CrTiAlN coating. After oxidation at 800 and 900 ^{o}C for 10 h respectively, the crystalline phases in H13 steel are mainly alpha Fe_2O_3, and a little of Cr_2O_3.

Fig.3 presents the XRD spectra of CrTiAlN coating before and after oxidation. The results showed that the phases in CrTiAlN coating after oxidation at 800 ^{o}C for 10 h are mainly Cr_2O_3 and CrN, which is very good for the high temperature oxidation resistance of coating. At the same time are there a small number of TiO_2 and Al_2O_3, also a small amount of microcrystalline alpha Fe_2O_3. The phases in CrTiAlN coating at 900 ^{o}C contain mainly Cr_2O_3, alpha Fe_2O_3 and little of TiO_2.

Only is the surface morphology of CrTiAlN coating after oxidation at 800 ^{o}C for 10 h demonstrated because of the basically same morphologies of coating after oxidation (Fig.4). From Fig.4, we can see that furrows on the surface of CrTiAlN coating were apparent. A few of Fe_2O_3 micro-particles grown up on the coating, but it was dense between the coating and substrate, and warping was not found.

As can be seen from the Fig.5, the CrTiAlN coating still existed after oxidation at 800 ^{o}C for 10 h (the elliptical area shown in Fig.5), and the total thickness of oxides layer was not more than 10μm, but the external and internal Oxidation layers (the "1" and "2" zones shown in Fig.5 respectively) were observed in the coating. Each element of CrTiAlN coating still existed in the oxides layer, which proved the existence of the coating after oxidation at 800 ^{o}C. Fe element of low content was also found in the coating. Therefore, the coating had a very good protection effect for H13 steel and improved the performance of high temperature resistant of the matrix obviously.

The oxidation process of CrTiAlN coating at 800 ^{o}C for 10 h can be as follows: The CrTiAlN coating reacted with oxygen at the beginning of oxidation; Cr_2O_3, TiO_2 and Al_2O_3 were concurrently produced on the surface of the coating. After the surface of the coating was completely covered by thin oxides scales, a continuous $(Cr,Al)_2O_3$ protective layer was not formed and the open cell TiO_2

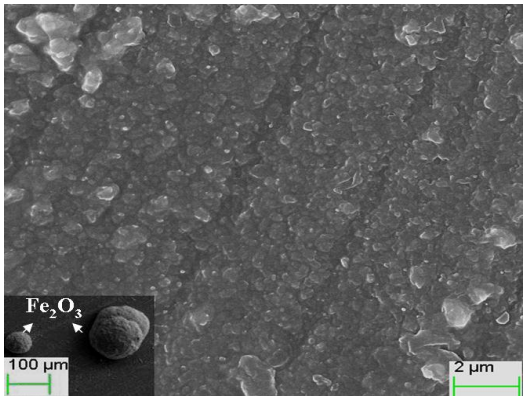

Fig.4. Surface morphologies of CrTiAlN coating after oxidation at 800 ^{o}C for 10 h

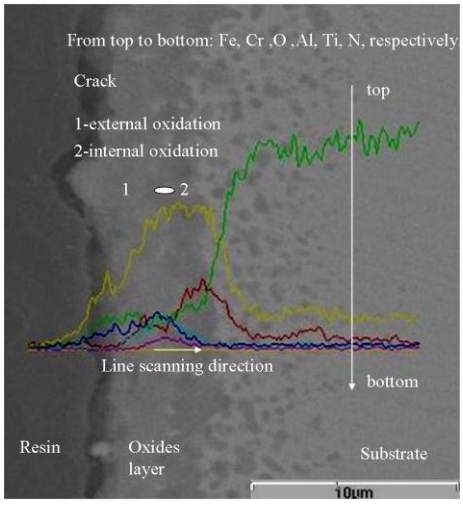

Fig.5. Section morphologies and line scanning results of CrTiAlN coating after oxidation at 800 ^{o}C for 10 h

provided the fast track to the metal ions and O atoms. The inward diffusion of O atoms holded the advantage because the external diffusion of metal ion was obstructed by the $(Cr,Al)_2O_3$ oxide and the content of TiO_2 was little. The content of Cr_2O_3 is more and more with the further oxidation and finally the continuous layer, which can prevent further the external diffusion of metal ions, formed on the surface of the coating. Oxygen would diffuse inwardly unceasingly to react with coating and go through the coating. Although Al has a higher affinity to oxygen and a lower free energy of formation than Cr and Ti elements and Al will also be oxidized preferentially, the concentration of Al in the coating was not high enough to form a continuous Al_2O_3 film. Therefore, the "nail wedge" shaped Al_2O_3 generated in the inside of the coating.

Summary

The columnar crystal CrTiAlN coating mainly possesses three parts, i.e., the internal Cr bonding layer, the intermediate CrN transition layer, the external CrTiAlN gradient coating. The phases in coating are chiefly metal Cr, Cr_2N and CrN, also a small amount of TiN and AlN.Although the selective oxidation of Cr on the surface of uncoated H13 steel while oxidation, a continuous protective layer was not formed because of low Cr content, finally a lot of alpha Fe_2O_3 particles generated on the surface of H13 steel owing to the oxidation of the matrix element Fe. The inward diffusion of O was dominant at 800 ^oC, and spallation and cracks were not found during the oxidation of the coating. The CrTiAlN coating have excellent high-temperature oxidation resistance at 800 ^oC.

Acknowledgments

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