The effect of Cr interlayer on the microstructure of CrN coatings on steel

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Abstract

The effect of electroplated Cr interlayer on the microstructure of CrN coatings on AISI 4140 steel were investigated. Two types of CrN-coated specimens by cathodic arc plasmas were prepared with and without an intermediate layer deposited by electroplated hard chrome (CrN/steel and CrN/Cr/steel). The microstructure and crystallinity of chromium nitride have been investigated using X-ray diffraction (XRD), cross-sectional transmission electron microscopy (XTEM) and selected area diffraction (SAD). Both CrN/steel and CrN/Cr/steel coating assemblies exhibit microcolumnar morphologies. However, it is noted that the columnar structure of CrN coating directly on steel is less evident, strong, and upward in comparison with that deposited on electroplated chromium layer. For CrN/Cr/steel assembly, the preferred orientations of CrN(220) and Cr(200) are observed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hard chrome coatings deposited by electroplating are extensively used for wear resistant applications in a wide range of engineering fields such as automotive and tooling industries [1–6]. One of the advantages of this technique is that the worn coating can be repaired by stripping and REPLATING the surface. However, the emission of chromium contaminant will lead to environmental pollution. This work aims to investigate how the interface microstructure of AISI 4140 changes by using electroplated Cr with CrN coatings. If we can prolong the life span of electroplated Cr, then the problem of environmental pollution can be reduced. Furthermore, CrN coating assemblies were deposited by using a cathodic arc plasma deposition technique at an industrial scale [4–8]. Cross-sectional transmission electron microscopy (XTEM) and X-ray diffraction (XRD) are used to obtain detailed information about the coating microstructure of CrN with and without the electroplated Cr interlayer.

2. Experimental

The substrate material to be coated is an AISI 4140 steel comprising (wt.%) 0.39 C, 0.24 Si, 0.71 Mn, 0.029 P, 0.04 Ni, 0.18 Mo and 1.06 Cr. All specimens were ground with a series of emery papers of 120, 320, 600
and 1200 grit. To remove possible contamination from the surface, each specimen was ultrasonically cleaned in acetone, dried and stored in a desiccator prior to the coating operation.

An interlayer of chromium was introduced by optimal commercial electroplating with Atotech HEEF 25 as catalyst [9]. The thickness of the hard chrome was approximately 6 μm. A cathodic arc plasma deposition technique was used to prepare the CrN coatings. In the deposition, the substrate temperature was approximately 350°C at a substrate bias of −150 V. An arc current of 60 A, a N₂ partial pressure controlled at approximately 2.7 Pa, and a deposition time of 70 min were employed.

The coating phases were identified by X-ray diffraction (XRD) using Cu Kα radiation. The texture of the chromium nitride was determined by using a MAC Sci. MXP-18 with pole-figure attachment.

Cross-sectional specimens for TEM investigation were prepared as follows: two 5 × 5 mm² specimens were glued face to face using an epoxy resin of low viscosity, and then cut perpendicular to the coating-substrate interface into slices approximately 1 mm thick. After grinding and polishing down to ~50 μm, the thin specimen was attached to a Cu slot grid for ion milling. After dimpling from one side to 20 μm, final thinning was performed by ion milling with Ar⁺ in a BAL-TEC RES 010, operated at 6 kV at an incidence angle of 6°. TEM was carried out using a JEOL JEM-4000EX electron microscope operated at an acceleration voltage of 400 kV. The instrument is characterized by a spherical aberration constant of 1 mm, leading to a point-to-point resolving power of \( d = 0.17 \) nm at Schertz defocus (\( \Delta z = -48 \) nm).
3. Results and discussion

3.1. X-Ray diffraction

The diffraction patterns of CrN/steel and CrN/Cr/steel match that of CrN given in the JCPDS database (No. 11-0065) in the $\theta/2\theta$ mode which are shown in Fig. 1. For the CrN/steel, the peak of substrate still can be observed (tracer 2 of Fig. 1), whereas the peaks of substrate can not be seen in CrN/Cr/steel (tracer 1 of Fig. 1), because the X-ray cannot penetrate through such thick electroplated Cr layer (~6 μm). Furthermore, the peak of CrN(220) dominates in the trace 1 of Fig. 1, which shows a pronounced preferred orientation of CrN(220) in CrN/Cr/steel.

The spatial distribution of the CrN(220) reflection of the CrN/Cr/steel was analyzed by using the pole figure as shown in Fig. 2. The result of this indicates that a preferred orientation of the (220) planes is specially dominant.

3.2. Cross-sectional TEM investigation

Fig. 3a,b show the cross-sectional bright field (BF) images of CrN coatings on steel with and without an electroplated chromium layer, respectively. The CrN thickness of both specimens is approximately 1.2 μm and they exhibit strong columnar structure. The shape and the grain size in both coatings are approximately the same. However, it is noted that the columnar structure of the CrN coating directly on steel is less evident, straight, and upward in comparison with that deposited on an electroplated chromium layer.

To explore the differences of the orientated growth for the CrN coating possessing columnar structures on different substrates, SAD patterns obtained from CrN coating and electroplated chromium interlayer have been carefully taken near the interfaces. For the CrN coating deposited on chromium layer, strong texturing is detected, since only short CrN(220) and (200) arc, instead of rings, are observed in the SAD pattern (Fig. 4a). The growth direction of the columnar CrN structure is identified as (220), which agrees with the XRD results reported previously. On the other hand, the SAD pattern corresponding to CrN coating which was deposited directly on steel shows a rather random crystal orientation relationship with respect to the growth direction, as indicated by the ring characters (Fig. 4b). Surprisingly, the SAD pattern of the electroplated chromium layer strongly indicates that this layer is well-textured (Fig. 4c). The growth direction of the columnar chromium grain is identified as Cr(200). In the study of TiN/Ti system, Shieu et al. [10] reported the strong epitaxial relation between the TiN and Ti interlayer. In the present study, it is believed that the electroplated Cr layer plays an important role to induce a strong texturing effect on CrN coating. In contrast with the steel substrate, the well-aligned Cr grains offer sound bases for the subsequent CrN deposition. Furthermore, the chemistry of Cr is more favorable than steel for the CrN formation. Strong chemical
affinity in combination with definite crystallographic orientation of the electroplated Cr layer thus result in the strong texturing of the CrN coating on it. On the top surface of the electroplated Cr layer, the CrN coating establishes its epitaxial growth during the cathodic arc plasma deposition process. However, a transition interlayer of approximately 25 nm in thickness is observed between CrN and Cr phases (Fig. 5a). The phase of the transition interlayer is not fully identified since it is too thin to be characterized by SAD technique alone. Earlier researches of investigating chromium nitride films [11–13] pointed out the possibility of forming CrN$_x$ and Cr$_2$N phases. It is also possible that phases such as Cr$_2$N, CrN$_x$, or even some non-stoichiometrical phases are created before the stoichiometrical CrN is stably formed. Further investigations, such as energy dispersion spectroscopy (EDS) and nano-beam electron diffraction of TEM, are needed to clearly determine the chemistry and structure of this thin interlayer between CrN and Cr. For CrN directly deposited on steel, the formation of a transition interlayer is also noticeable (Fig. 5b). The interlayer is ~ 6

Fig. 4. SAD patterns for CrN and Cr taken near the interface, showing: (a) strong texturing near the CrN/Cr interface; (b) random orientations near the CrN/steel interface; and (c) strong tendency toward a single crystal near the CrN/Cr interface.
Fig. 5. Bright field (BF) micrographs taken at different interfaces at the same magnification, showing morphologies and thickness of the transition interlayer: (a) CrN/Cr; (b) CrN/steel; and (c) Cr/steel.

mm in thickness. Since steel does not form nitride with nitrogen easily, the new phase formation of intermetallic compound, such as Cr, Fe between CrN and steel, is suggested. The possible existence of intermetallic compounds of chromium and iron between CrN and steel can not be denied but a further and careful examination is needed.

To understand the interface quality and morphology of the electroplated Cr layer on steel, XTEM has also been performed. Again, a transition interlayer of approximately 20 nm in thickness between the electroplated Cr layer and steel is found (Fig. 5c). The diffraction contrast of this transition interlayer is quite different in comparison with the electroplated Cr and the substrate steel. Both Cr and steel exhibit sharp diffraction contrast, an important indication for crystalline materials. The blurring outlook and the diffused contrast of this interlayer imply the existence of amorphous phase in it. The subsequent high-resolution TEM (HRTEM) investigation further confirms this point.

To explore the details of the transition interlayers appearing in the interfaces of CrN/Cr, CrN/steel and Cr/steel discussed above, HRTEM investigations are employed. Fig. 6a shows the lattice image of the transition interlayer between the CrN coating and the electroplated Cr layer. There is no doubt that this interlayer is crystalline since strong lattice fringes resulting from phase contrast of electron wave are evidently present. In some areas in this interlayer, the lattice fringes of crystalline are weak but still distinguishable due to the deviation from exact zone axis with the incidence electron beam. The grains in this interlayer keep on forming the columnar structure of the electroplated Cr, bridge the succeeding CrN coating and result in well-textured forms. Fig. 6b is the HRTEM image taken at CrN/steel interfacial area. The thickness of the interlayer is smaller than that of CrN/Cr interface, only approximately 6 nm. This interlayer is crystalline but with a small amount of amorphous-like materials embedded in it. Fig. 6c is the interfacial HRTEM image of electroplated Cr on steel. The interlayer between Cr and steel exhibits an amorphous feature. However, little crystallites were also observed. A brief comparison of the three interfaces is presented in Table 1. Interestingly, it is noted that voids of approximately 1 nm in size are plentiful in the Cr interlayer near the interface as indicated by arrows in

<table>
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<tr>
<th>Interfacial region</th>
<th>Transition layer thickness (nm)</th>
<th>Feature</th>
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<tbody>
<tr>
<td>CrN/steel</td>
<td>6</td>
<td>Crystalline and amorphous</td>
</tr>
<tr>
<td>Cr/steel</td>
<td>20</td>
<td>Crystalline and amorphous</td>
</tr>
<tr>
<td>CrN/Cr</td>
<td>25</td>
<td>Crystalline</td>
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Fig. 6c, but not found on the top layer as compared with Fig. 6a. This phenomenon has never been reported before. A possible mechanism is the hydrogen formation at the beginning of electroplating due to local potential unbalance in the electrolytic bath. Since the process of electroplating is carried out near room temperature and the following CrN deposition temperature is only approximately 350°C for 70 min, void annihilation and inter-diffusion of Cr and Fe are not likely to form. Also, at the beginning of electroplating, no obvious recrystallization of the amorphous deposit of Cr forms.

4. Conclusions

In this study, characterization of the microstructure and chemistry of the cathodic arc plasma deposition CrN on AISI 4140 steel with and without an electroplated Cr intermediate layer have been investigated by XTEM, moreover, the phase identification is done by using XRD. Compared to the CrN-steel assembly, the introduction of an electroplated Cr layer between CrN and steel gives rise to the following effects:

1. The diffraction patterns of the coated specimens indicated the presence of CrN, furthermore, the spatial distribution of the CrN(220) reflection of the CrN/Cr/steel was analyzed by using the pole figure.
2. Both CrN/steel and CrN/Cr/steel exhibit strong columnar structures. The shape and the grain size in both coatings are approximately the same. However, it is noted that the columnar structure of CrN coating directly on steel (CrN/steel) is less evident, straight, and upward in comparison with that deposited on electroplated chromium layer (CrN/Cr/steel).
3. Based on SAD, the growth direction of the columnar CrN structure is identified as (220) and the growth direction of the columnar chromium grain is identified as Cr(200).

References