

Oxidation of The Arc Ion-plated CrN Coatings at Elevated Temperatures

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以陰極電弧離子鍍著氮化鉻鍍膜之高溫氧化行爲

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摘 要

本研究是以 X 光繞射分析儀(XRD)、掃描式電子顯微鏡(SEM)、穿透式電子顯微鏡(TEM)和歐傑電子能譜儀(AES)探討CrN薄膜在300°C到800°C的溫度範圍於空氣中氧化60分鐘的特性。CrN薄膜是利用陰極電弧沈積技術沈積在具有鉻中間層的304不銹鋼上。XRD結果顯示CrN薄膜鍍著的不銹鋼在高於500°C溫度以上會產生Cr₂O₃和β-Cr₂N兩個相，且兩者的含量隨著氧化溫度升高而增加。氧化溫度在600°C以上的試片，經由SEM觀察出薄膜表面形貌有顯著的變化。橫截面TEM影像顯示出鍍著氮化鉻的試片，經高溫氧化後於鍍膜表面生成一氧化鉻層，其下方為CrN與β-Cr₂N兩相混合層。與剛鍍著的試片不同的是，氧化後試片中的混合層具有等軸晶結構，且晶粒尺寸亦隨氧化溫度升高而成長。由不同氧化溫度之歐傑電子縱深分析得知元素分佈，且利用其結果換算出不同溫度之氧化鉻厚度，亦由此計算出氧化鉻氧化的活化能為1.63eV。

關鍵詞：氮化鉻；氧化；微觀分析；穿透式電子顯微鏡；歐傑電子能譜儀。

ABSTRACT

Characterization of the CrN coatings oxidized in air at temperatures ranging from 300°C to 800°C for 60 min was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Auger electron spectroscopy (AES). The CrN coatings were prepared by cathodic arc ion plating deposition on a type 304 stainless steel with a Cr interlayer. The XRD results show that oxidation of the CrN-coated steel above 500°C produces two new phases, Cr₂O₃ and β-Cr₂N, and the amount of both phases increases with the oxidation temperature. A noticeable change in the surface morphology of the coatings were observed by SEM in the specimens oxidized at temperature above 600°C. Cross-section TEM

reveals that oxidation of the CrN-coated steel at high temperatures produces an oxide layer, Cr_2O_3 , on the coating surface, and the underlayer is a mixture of CrN and β - Cr_2N phases. Unlike the as-deposited specimen, the dual phase layer in the oxidized specimens has an equiaxed grain structure and the average grain size of the layer increases with the oxidation temperature. Depth profiling of the oxidized CrN coatings at various temperatures by AES gives the elemental distributions near the free surface, and the activation energy for oxidation of the CrN coatings was calculated to be 1.63 eV.

Keywords: Chromium nitride; Oxidation; Microanalysis; TEM, AES.

1. Introduction

Transition metal nitrides have successfully applied as diffusion barrier in microelectronics, hard wear resistant coatings on cutting tools, or as a corrosion and abrasion resistant layer on optical and mechanical components [1]. Applications of metal nitride-coated components often require good mechanical and tribological properties in ambient environments, and also good oxidation resistance at elevated temperatures. There is a growing interest placed on thermal stability of metal nitrides hard coating due to the fact that oxidation is an important mechanism leading to degradation of mechanical properties and performance at elevated temperature [1-2]. Among the wide variety of metal nitrides, chromium nitride has drawn great interest over the years and is considered to be a promising alternative to both electroplated Cr and TiN coatings for forming tools and as protective layers for moulds and dies to improve the performance and to extend the service life while operating at elevated temperatures [3-5].

Over the past several years, the engineering aspects of the coating technology including process optimization such as partial pressure of nitrogen [5-6] and substrate bias [7], and the resulting coating properties such as hardness, wear and corrosion resistance [8], have been studied extensively. In contrast, our knowledge of the microstructure and chemistry of as-deposited and

heat-treated CrN coatings, and its relationships to the coating properties and environment stability, is still relatively limited.

2. Experimental

In this study, CrN films on a type 304-stainless steel were produced by a cathodic arc ion plating deposition system. The microstructure and chemistry of the as-deposited coatings and those oxidized at elevated temperatures in the range of 300-800°C are characterized by X-ray diffraction (XRD), Auger electron spectroscopy (AES), scanning electron microscopy (SEM) and both cross-section and plan-view transmission electron microscopy (TEM). The evolution of layer structure and phase transformation in the CrN coating as well as activation energy of oxide scale growth is discussed.

3. Results and Discussion

3.1. X-ray diffraction analysis

Fig.1 show the X-ray diffraction spectra of the CrN-coated steel oxidized in air at various temperatures ranging from 300 to 800°C. A new crystalline phase, β - Cr_2N , is observed at 500°C-heated specimen, which indicates that phase transformation has occurred in the

CrN coating upon heat treatment. Similar crystalline phase are detected for the specimen oxidized at 600°C, except the small bump located at 33.60°, which corresponds to the Cr₂O₃ phase. This oxide peak is easily discerned for the specimen oxidized at 700°C and 800°C. It is also noted from the XRD spectra that the diffraction peaks of the CrN phase become sharper as the oxidation temperature increases because the crystallinity of the coating is improved. The content of the Cr₂O₃ and β-Cr₂N phase reflected from the integrated peak intensity increases with increasing oxidation temperature, and vice versa for the CrN and the steel substrate. The decrease in the peak intensity of the steel substrate illustrates that the coating including the oxide scale grows thicker as the oxidation temperature.

3.2 Plan-view TEM

Since the performance of a component is usually determined by the microstructure and chemistry of its surface during service, it is worth making a further investigation of the surface coating layer using plan-view transmission electron microscopy. Fig. 2(a) and (b) shows the bright field image and selected area diffraction pattern, respectively, of the as-deposited CrN surface layer. Analysis of the SAD pattern in Fig. 2(b) reveals that the only phase present is the face-centered cubic CrN. The BF image and diffraction pattern of the specimen oxidized at 300°C are shown in Fig. 2(c) and (d), respectively. It can be seen that the microstructure of the CrN coating upon heat treatment is similar to the as-deposited specimen. The void with a diameter about 200nm present on the left side of Fig. 2(c) is the locus of a macroparticle, which was sputtered off during ion milling. The bright field image of the specimen oxidized at 600°C for 60 min is shown in Fig. 2(e), where small particles of size about 90 nm are dispersed

in a large grains is clearly resolved in the right-hand side of the micrograph in Fig. 2(e). The diffraction analysis of Fig. 2(f) reveals the presence of CrN, β-Cr₂N and Cr₂O₃ phases. Fig. 2(g) and (h) gives the BF image and SAD pattern, respectively, of the CrN-coated specimen oxidized at 800°C for 60 min. The electron diffraction result indicates that the surface layer is only composed of the Cr₂O₃ phase. The average grain size of the oxide layer is measured to be ~150 nm, which is similar to that observed in the cross-sectional TEM micrograph of Fig. 3(a).

3.3 Cross-section TEM

The microstructure of the CrN-coated specimen oxidized at 800°C shown in Fig. 3(a). It is noted that extensive grain growth has occurred in the original CrN coating layer. Strictly speaking it is a mixture of CrN and β-Cr₂N phases. The Oxide layer with equiaxed grains is right next to the CrN coating layer. And its thickness was measured to be approximately 300nm. A high dislocation density can be observed in the large grains next to the oxide layer as a result of the coefficient of thermal expansion between the oxide and the nitrides. The variation of the grain size in the nitride layer with distance away from the steel substrate is tremendous.

Since the grain size of the nitride coating near the layer is as large as 1.5 μm, it is possible tilt the specimen to have the grains in a zone axis. The SAD pattern of the strongly diffracted grain appeared as the dark one in the upper-left corner of Fig. 3(b), is given in Fig. 3(d). Analysis of the diffraction pattern indicates that the incident beam is along the ^[011] direction of a cubic CrN grain. A similar tilting produce was applied to the grain, as shown in Fig.3 (c), next to the one above. The SAD pattern shown in Fig. 3(e) indicates that the grain is oriented along the ^[01-11] zone axis of a

hexagonal β -Cr₂N crystallite. This result further confirms that the nitride layer upon oxidation treatment consists of a mixture of CrN and β -Cr₂N phase.

3.4. Depth profiling analysis by AES

Figure 4 shows the Auger depth profiles of the as-deposited CrN coating and the specimens oxidized at 600°C, 700°C and 800°C. The presence of oxygen on the coating surface of the as-deposited CrN specimen is clearly demonstrated. The profile of the 600°C-oxidized specimen illustrates the formation of an oxide layer on the coating surface. The thickness of the oxide is estimated to be approximately 40nm. From the in-depth information of the 700°C-oxidized specimen, the thickness of the oxide layer is about four times that in the 600°C oxidized one. The thickness of the oxide layer in the 800°C oxidized specimen is about two times that in the 700°C oxidized one, i.e. about 300nm, which is in good agreement with the thin layer in the cross-section TEM observation in Fig. 3(a). Unlike that of the 600°C oxidized CrN specimen, which has a sharp oxide/nitride transition, the concentration profile in the 700 and 800°C specimens have lower slope and shows irregularity near the oxide/nitride interface. This is likely due to that the oxide/nitride interface in the 600°C oxidized specimen is much smoother than that in the 700°C and 800°C oxidized specimens.

Using the AES information in Fig. 4 and the Arrhenius plot, i.e. plotting $\ln Kp(T)$ as a function of $1/T$, the activation energy (E_a) can be calculated to be about 1.63eV by determined the slope of the fitting line as shown in Fig. 5. Comparing the activation energy in this study with published researches^[9-10] where give the values of 1.92 eV for CrN and 1.27 eV for Cr₂N, it is believed that the activation energy was a contribution from both CrN and β -Cr₂N phases at elevated temperature, consistent with the cross-sectional TEM

analytic results.

4. Conclusions

Characterization of the arc ion-plated CrN coatings oxidized at elevated temperatures shows that oxidation of the CrN coatings at elevated temperatures ranging from 300 to 800°C for 60 min produces a chromium oxide, Cr₂O₃, on the coating surface and an underlayer composed of CrN and β -Cr₂N phases. Both the thickness of the Cr₂O₃ layer and the proportion of the β -Cr₂N phase in the nitride layer, increase with the oxidation temperature. Unlike the as-deposited coating that has columnar structure, the nitride layer in the oxidized specimens has an equiaxed grain and the average grain size of the nitride layer also increases with the oxidation temperature. By investigating the thickness of oxide scales underwent various temperatures using the AES depth profiles compared with the cross-section TEM image, the activation energy of oxidation was calculated to be 1.63eV.

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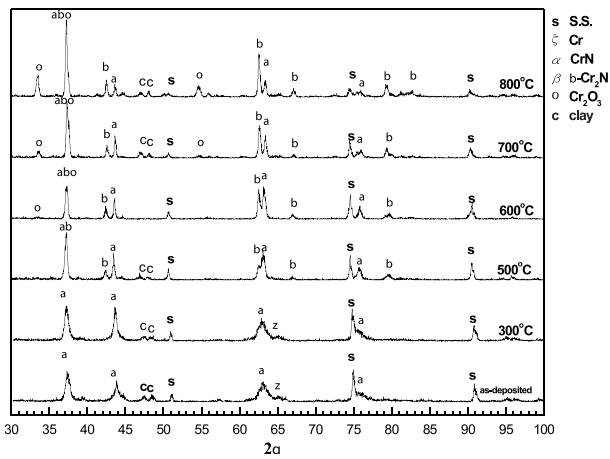


圖 1. 氮化鉻鍍著之不鏽鋼在空氣氣氛下氧化 60 分鐘之 X 光繞射圖。

Fig.1 X-ray diffraction spectra of the CrN-coated steel oxidized in air at various temperatures for 60min.

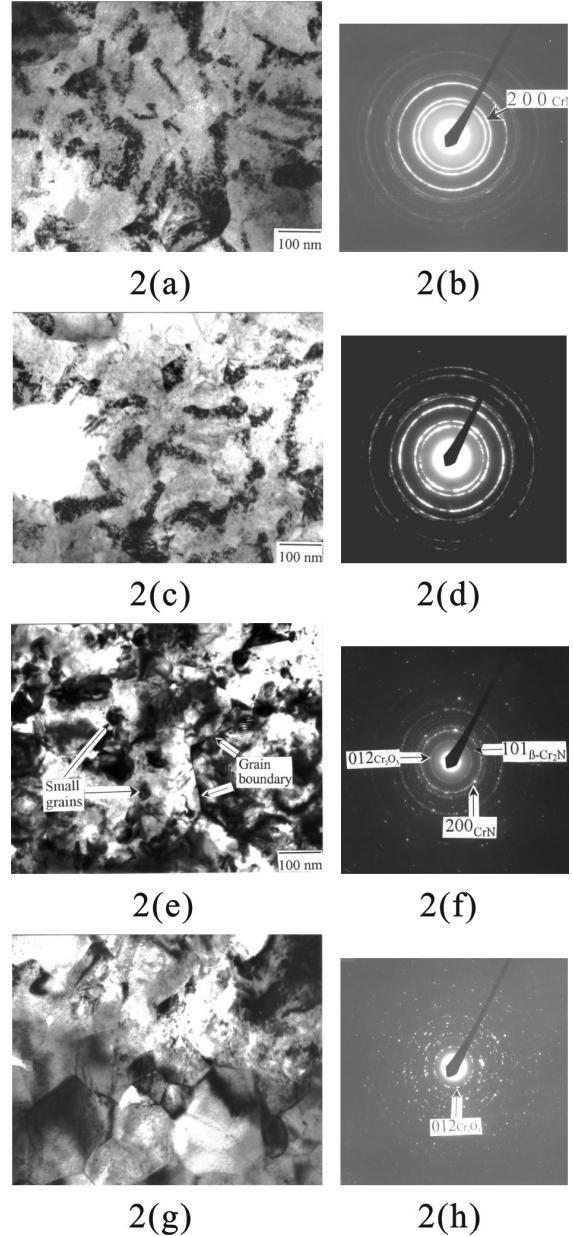


圖 2. (a,b). 剛鍍著，(c,d) 300°C，(e,f) 600°C，(g,h) 800°C 氧化之氮化鉻薄膜之 TEM 表面微觀及擇區繞射圖。

Fig. 2. (a,b). The plan-view TEM micrographs and the SAD patterns of (a,b) the as-deposited, (c,d) the 300°C, (e,f) 600°C and (g,h) 800°C oxidized CrN-coated specimen

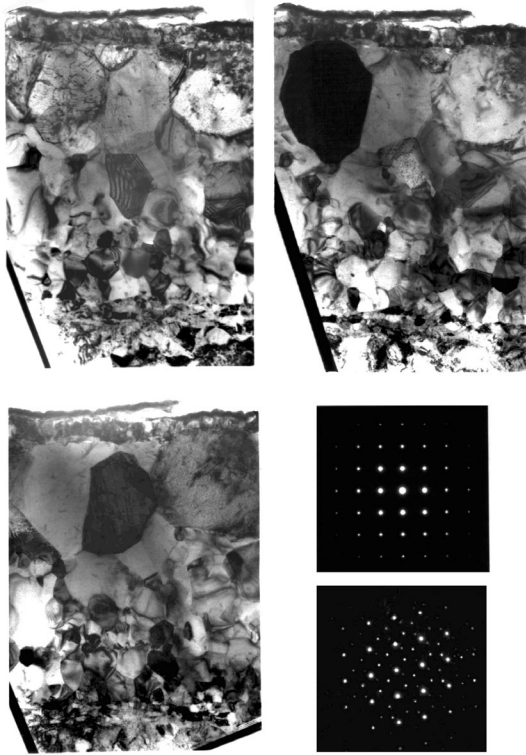


圖3. 800°C 氧化之氮化鉻薄膜之TEM截面微觀及擇區繞射圖。
Fig. 3 Cross-sectional TEM micrograph of the 800°C oxidized CrN-coated specimen.

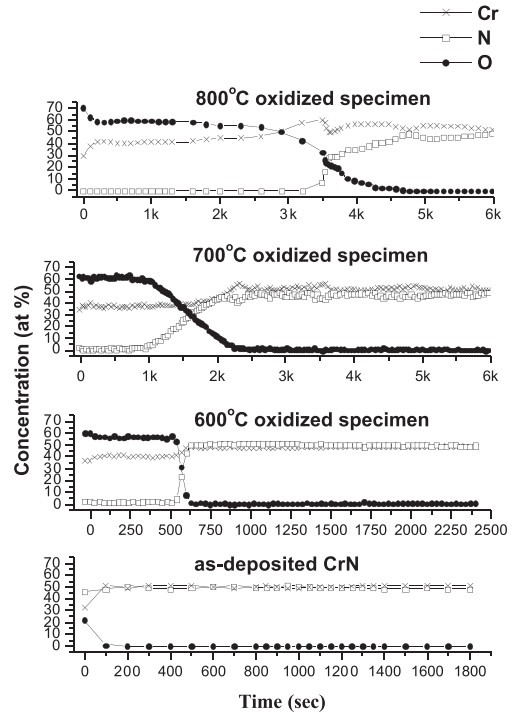


圖4. 剛鍍著，300°C，600°C，及800°C 氧化之氮化鉻薄膜之歐傑縱深曲線圖。
Fig. 4 Auger depth profiles of the as-deposited CrN coating and the specimens oxidized at 600°C, 700°C and 800°C.

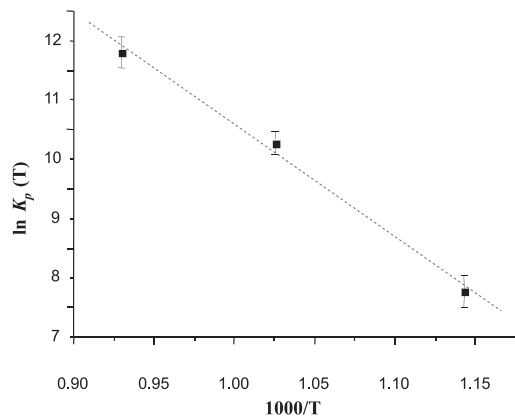


圖5. 600°C，700°C，及800°C 之 $\ln K_p(T)$ 與 $1/T$ 之關係圖。
Fig. 5 $\ln K_p(T)$ as a function of $1/T$ at 600°C, 700°C and 800°C.