The Properties of Cr–Al–N Based Coatings Formed on AISI D2 Steel by Thermo-Reactive Diffusion Technique

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In this study, chromium aluminum nitride coating was applied on pre-nitrided AISI D2 steel by the thermo-reactive deposition technique in a powder mixture consisting of ferrochromium, aluminum, ammonium chloride, and alumina at 1000 °C for 2 h. Steels were gas nitrided for the purpose to enrich the surfaces with nitrogen of the steels in a nitrogen and ammonia atmosphere at 560 °C for 8 h. The effect of aluminum content in the powder mixture on the Cr–Al–N layer properties was investigated. The coated samples were characterized by X-ray diffraction analysis, scanning electron microscope, and micro-hardness tests. Chromium aluminum nitride layer formed on the pre-nitrided AISI D2 steel was compact and homogeneous. Electron dispersive spectrometer results showed that coating layer includes chromium, aluminum, and nitrogen. X-ray studies showed that the phases formed in the coating layers on the steel surfaces are Cr_2N, $(Cr,Fe)_2N_{1-x}$, AlN, and Fe_2N. The depth of the Cr–Al–N layer ranged from 10.01 ± 1.2 to 13.2 ± 1.7 μm, depending on the aluminum content. The hardness of the coated layers produced on AISI D2 steel are changing from 1743 ± 150 $HV_{0.01}$ to 2067 ± 160 $HV_{0.01}$ depending on bath compositions.

1. Introduction

Recently, research in ternary nitrides has been extended to other coating materials. Similar to TiN, chromium nitride (CrN) has been successfully applied to the molding dies, wear components, and cutting tools. As the addition of Al improves the mechanical properties and oxidation resistance of TiN coatings, a similar effect of Al in CrN coatings could also be expected. CrN is known to be superior to TiN in corrosion and wear resistance, friction behavior, and toughness [1, 2]. For example, the applications on the various kinds of sliding materials are used car parts, machine parts, and molding dies [3]. CrAlN coatings have been deposited by different physical vapor deposition (PVD) techniques: magnetron sputtering [2, 4], arc ion plating [5–7], cathodic arc evaporation [8, 9] and pulsed laser deposition [6]. CrN coating with high hardness, good wear resistance and corrosion resistance and is widely used in die casting, metal forming, and tool machining applications to increase productivity and tool life. $Cr_{1-x}AlN$ films can be obtained in a wide range of compositions due to the high solubility of CrN for AlN [1, 8]. The need for an improved tool life has led to the exploration of the performance of CrN coatings by the addition of ternary elements such as Al, Si, V, Nb or Cu. Cr–Al–N ternary films are of interest due to the formation of chromium and aluminum

oxides which suppress further diffusion of oxygen to the bulk. Increasing the Al content in the coatings has been shown to improve the oxidation resistances and hardness [10, 11]. As compared to CrN, CrAlN coatings exhibit high hardness and their properties are greatly affected by the aluminum content in the coatings. The Al content also controls the structure of CrAlN coatings [7, 12]. Therefore, CrAlN can be a promising candidate for high speed machining and other high temperature wear applications [13]. In addition, CrAlN also exhibits lower thermal conductivity than CrN, good tribological properties, and high hardness [14, 15]. The objective of this work is to develop Cr–Al–N coatings by thermo-reactive deposition (TRD) process, and to investigate the properties of the as-deposited Cr–Al–N coatings as a function of aluminum content.

2. Experimental procedure

The steel substrates used in the study was AISI D2 steel with chemical composition of 1.56% C, 0.27% Si, 0.30% Mn, 0.020% P, 0.001% S, 11.2% Cr, 0.75% Mo, 0.93% V and iron. Test pieces of AISI D2 were sectioned into the dimensions of 20 mm in diameter and 5 mm in thickness and prepared metallographically. Steels were gas nitrided for the purpose to enrich the surfaces with nitrogen of the steels in a nitrogen and ammonia atmosphere at 560 °C for 8 h. Then Cr–Al–N coating was performed on the pre-nitrided steel samples by the TRD technique in a powder mixture consisting of fer-

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rochromium, aluminum (by wt% 1, 2, 3, 4, 5, 7, 10), ammonium chloride and alumina at 1000 °C for 2 h.

The morphological details and layer thickness measurements of samples were carried out by optical microscope and scanning electron microscope. XRD analysis was performed on the sample surface. The hardness of uncoated steel, nitride layer and Cr–Al–N coating layer were measured with 10 g loads.

3. Results and discussion

Both of optical and scanning electron microscope (SEM) cross-sectional examinations of Cr–Al–N coated steel revealed that Cr–Al–N layer formed on the steel substrate has a compact, smooth and laminar morphology, as shown in Fig. 1a and b. Energy dispersive spectroscopy (EDS) analysis showed that the laminar structures of the coating layers include different iron content in the different layer content. Sen et al. realized the TiN coatings using similar technique and explained that the plain low carbon steels have a denticular morphology in the coating layer, while the TiN coating layer formed on the high alloy steels were of smooth morphology [16, 17]. Ozdemir et al. explained that CrN coating layers formed on the AISI 1010 steels produced by TRD technique exhibited homogeneous morphology with significant regularities in their thickness and presented a smooth interface with the substrate [18]. Coating layer formed on the steel sample consists of Cr_2N, $(Cr,Fe)_2N_{1-x}$, AlN, and Fe_2N phases which were confirmed by X-ray diffraction analysis as shown in Fig. 1c.
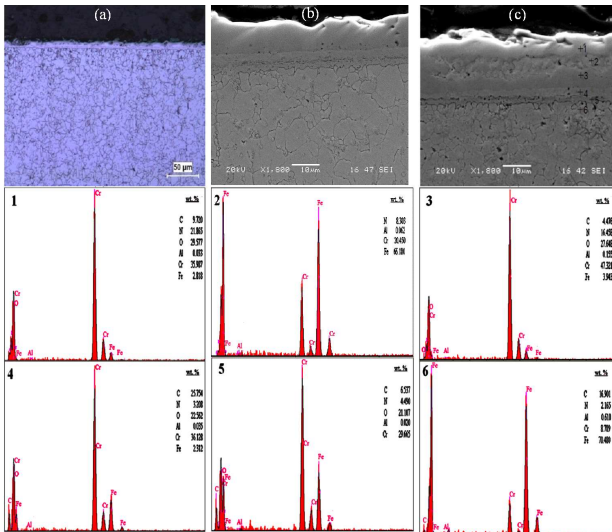

Fig. 1. (a) Optical, (b) SEM micrographs of the Cr–Al–N coated (5 wt% Al in pack) steel and (c) EDS analysis of the Cr–Al–N coated (3 wt% Al in pack) steel.

EDS analysis of Cr–Al–N coated steel on the cross--section from surface to interior showed that chromium, aluminum, and nitrogen concentrations are higher than that of the matrix and chromium concentration of the

coated sample decreases towards the matrix, and top of the coating layer has higher chromium concentration than the matrix, as shown in Fig. 2.
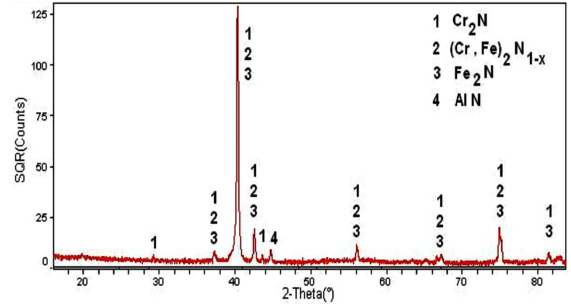

Fig. 2. XRD pattern of the Cr–Al–N coated (5 wt% Al in pack) steel.

TABLE

The thickness and hardness of the nitride and Cr–Al–N coating layer on steel samples.

Coating type	Al [wt%]	Layer thickness [μm]	Hardness [$HV_{0.01}$]
nitrided AISI D2	–	79.92 ± 2.2	920 ± 20
Cr–Al–N coated AISI D2	1	13.2 ± 1.7	1891 ± 120
	2	12.4 ± 1.3	1676 ± 160
	3	12.2 ± 0.4	1870 ± 130
	4	11.9 ± 1.1	1743 ± 150
	5	11.8 ± 1.3	2067 ± 160
	7	10.01 ± 1.2	1752 ± 180
	10	10.4 ± 0.6	1933 ± 110

As seen in Table, the thickness of Cr–Al–N layer formed on the pre-nitrided steel decrease with increasing Al content in the coating bath. The thickness of the coating layer is changing between 10.01 ± 1.2 to 13.2 ± 1.7 μm, depending on Al content. It is assumed that (i) the growth rate of Cr–Al–N layer is controlled by chromium diffusion rate in the coating layer and nitrogen diffusion rate from the pre-nitrided steel sample to Cr–Al–N layer, (ii) Cr–Al–N layer growth occurs as a consequence of chromium diffusion perpendicular to the pre-nitrided steel sample. The hardness of the surface of Cr–Al–N coated steel is much higher than that of the matrix due to the presence of hard Cr_2N, $(Cr,Fe)_2N_{1-x}$, AlN phases formed on matrix. The hardness of Cr–Al–N layer is between 1743 ± 150 $HV_{0.01}$ to 2067 ± 160 $HV_{0.01}$, whereas the hardness of steel matrix and nitrided steel are 550 ± 14 $HV_{0.01}$ and 920 ± 20 $HV_{0.01}$, respectively (as seen in Table). The hardness of the Cr–Al–N coating layer formed on the AISI D2 steel is higher than that of chromium nitride layer formed on the AISI 1020 steel [18]. The hardness results agree with Ding and Zeng studies [1, 13].

References

[1] X.Z. Ding, X.T. Zeng, *Surf. Coat. Technol.* **200**, 1372 (2005).

[2] S.R. Pulugurtha, D.G. Bhat, *Surf. Coat. Technol.* **201**, 4411 (2006).

[3] M. Uchida, N. Nihira, A. Mitsuo, K. Toyoda, K. Kubota, T. Aizawa, *Surf. Coat. Technol.* **177-178**, 627 (2004).

[4] C. Nouveau, C. Labidi, J.P.F. Martin, R. Collet, A. Djouadi, *Wear* **263**, 1291 (2007).

[5] A. Kimura, M. Kawate, H. Hasegawa, T. Suzuki, *Surf. Coat. Technol.* **169-170**, 367 (2003).

[6] J. Romero, M.A. Gomez, J. Esteve, F. Montala, L. Carreras, M. Grifol, A. Lousa, *Thin Solid Films* **515**, 113 (2006).

[7] H.C. Barshilia, N. Selvakumar, B. Deepthi, K.S. Rajam, *Surf. Coat. Technol.* **201**, 2193 (2006).

[8] C. Yu, S. Wang, L. Tian, T. Li, B. Xu, *J. Mater. Sci.* **44**, 300 (2009).

[9] X.Z. Ding, A.L.K. Tan, X.T. Zeng, C. Wang, T. Yue, C.Q. Sun, *Thin Solid Films* **516**, 5716 (2008).

[10] T.M. Brizuel, G.A. Luisa, I. Braceras, J.I. Onate, S.J.C. Lopez, M.D. Martıne, L.C. Cartes, A. Fernandez, *Surf. Coat. Technol.* **200**, 192 (2005).

[11] S.R. Pulugurtha, D.G. Bhat, M.H. Gordon, J. Shultz, M. Staia, S.V. Joshi, S. Govindarajan, *Surf. Coat. Technol.* **202**, 1160 (2007).

[12] T. Ghrib, B. Tlili, C. Nouveau, Y. Benlatreche, M. Lambertin, N. Yacoubi, M. Ennasri, *Physics Procedia* **2**, 1327 (2009).

[13] X.Z. Ding, X.T. Zeng, *SIMTech Technical Reports* **6**, No. 3 (2005).

[14] C. Yu, L. Tian, W. Yinghui, S. Wang, T. Li, B. Xu, *Appl. Surf. Sci.* **255**, 40 (2009).

[15] J. Lin, B. Mishra, J.J. Moorea, W.D. Sprou, *Surf. Coat. Technol.* **202**, 3272 (2008).

[16] G. Deniz, S. Şen, U. Şen, *Sci. Forum* **554**, 219 (2007).

[17] U. Şen, *Vacuum* **75**, 339 (2004).

[18] O. Ozdemir, S. Şen, U. Şen, *Vacuum* **81**, 567 (2007).