JTTEE5 5:139-144
©ASM International

Chromium-Nitride in situ Composites with a Compositional Gradient Formed by Reactive DC Plasma Spraying

Y. Tsunekawa, M. Okumiya, T. Kobayashi, M. Okuda, and M. Fukumoto

Nitrides of transition metals have good wear- and corrosion-resistant properties because of their high hardness and chemical stability. Chromium-nitride coatings can be deposited by ion plating; however, the thin thickness due to the slow deposition rate must be improved for severe wear-resistant applications. The main objective in this paper is to realize good structural control in the processing of chromium-nitride in situ composite coatings formed at a high deposition rate. They were synthesized by reactive low-pressure plasma spraying using elemental chromium powder as a spray material. The transferred arc between the gun electrode and the substrate was used to accelerate the nitriding reaction. The sprayed coatings consist of chromium, Cr_2N, and CrN, which have a composition gradient from the substrate interface to the surface. The volume fraction of Cr_2N increases with transferred arc current, and nonreacted chromium concurrently decreases, except close to the substrate. The CrN phase, however, only exists as a surface layer of 20 to 30 μm because it is decomposed to Cr_2N above 1420 K. The hardness of the composite coatings depends on the volume fraction of Cr_2N, and it increases to 1300 HV at a Cr_2N volume fraction of 0.98. The seizure stress with lubricant depends on the coating hardness. The maximum seizure stress of 24.9 MPa is obtained at a hardness of 1300 HV. The composite coatings also show a superior wear resistance. Hence, the Cr_2N in situ composite coatings synthesized by reactive plasma spraying with transferred arc are expected to be good candidates for wear-resistant applications.

1. Introduction

NITRIDE coatings of transition metals with high hardness have been used for wear-resistant applications (Ref 1-5). They are also expected to have corrosion- (Ref 4-6) and oxidation-resistant properties up to medium temperatures (Ref 3, 7) because of their chemical stability. The existence of CrN and Cr_2N is known as a nitride in the Cr-N system (Ref 8, 9). The friction and wear properties of the coatings may change due to the difference in decomposition temperature of each nitride. The adhesive strengths may also differ from each other because of the difference in thermal expansion coefficient (Ref 3). For example, cracking or peeling of the CrN coatings on steel substrates may appear (Ref 3, 10). The chromium-nitride coatings are usually produced by reactive ion plating and, recently, by ion beam enhanced deposition (Ref 11). The coating thickness prepared by ion plating is normally less than 10 μm, and the low deposition rate is the major problem for severe wear-resistant applications.

Plasma spray processing is a well-developed technique that has been used to produce protective coatings and advanced metal and intermetallic matrix composites. The direct syntheses of $Ti_2AlN/TiAl$ (Ref 12, 13) and AlN/FeAl composite coatings (Ref 14) from the premixed elemental powders were reported.

In the present paper, the synthesis of chromium-nitride in situ composite coatings with a composition gradient was performed by a method of reactive low-pressure direct current (DC) plasma spraying using pure chromium powder as a spray material. The application of the transferred arc is aimed at accelerating the nitriding reaction in the spray process. In addition to examining the nitriding reaction of liquid chromium droplets in flight, we also identified constituents and element distribution, investigated the possibility of structural control, and determined the beneficial hardness and friction characteristics of the coatings.

Keywords chromium-nitride, chromium powder, composition gradient, in situ composites, reactive low-pressure plasma spraying, transferred arc

Y. Tsunekawa, M. Okumiya, T. Kobayashi, and **M. Okuda,** Toyota Technological Institute, Nagoya, Japan; **M. Fukumoto,** Toyohashi University of Technology, Toyohashi, Japan

2. Experimental Procedure

Pure chromium (99.8 wt% in purity) powder was supplied as a spray material for the direct fabrication of in situ composites by reactive low-pressure plasma spraying (RLPPS) with a nitrogen plasma gas. The chromium powder was sieved to give particles less than 44 μm, unless otherwise mentioned.

The sprayed coatings were formed by the RLPPS system as schematically shown in Fig. 1, in which the transferred arc circuit was connected between the gun electrode and the substrate. The spray gun and the substrate were then insulated from the vacuum chamber. In addition to the conventional RLPPS, some spraying was performed with a transferred arc current below 38 A. The substrate temperature was continuously recorded by in-

Nomenclature

I_t	Transferred arc current
P_c	Chamber pressure
P_m	Main plasma power
T_s	Maximum substrate temperature
V_{CrN}	Volume fraction of CrN
V_{Cr_2N}	Volume fraction of Cr_2N
σ_s	Seizure stress

serting a thermocouple into the center of the substrate; that is, 2.5 mm from the substrate surface. A nitrogen atmosphere in the vacuum chamber was then maintained at a given low pressure during the spray process. Low carbon steel (SS400) plates of 30 by 30 by 5 mm were used as a substrate. Standard spray parameters are listed in Table 1.

Several tens of impinged chromium particles having homogeneous temperature and velocity were collected by installing a fixed slit with a circular hole of 10 mm diameter and a moving graphite shutter of 46 mm diameter between the spray gun and the substrate (Ref 15). The flattened particles were collected on the substrate by opening the shutter system for 93 ms. There was no temperature rise of the substrate during this particle sampling period. The particles were examined for elemental distribution by electron probe microanalysis (EPMA) and Auger electron spectroscopy, and phase analysis was performed by x-ray diffraction (XRD) at a spot size of 100 µm with copper Kα radiation.

Spectroscopic analyses of chemical composition of the sprayed coatings, optical and scanning electron microscopy observations of the cross sections, analyses of XRD with cobalt Kα radiation, and EPMA were then carried out to characterize the constituents of the matrices and nitrides in the sprayed coatings. Average Vickers microhardness of 7 tests was measured under a 4.9 N load for 15 s at room and high temperatures. Friction and wear tests were also performed using a ring on a disk-type apparatus with lubricant (engine oil; SAE 30).

3. Results and Discussion

3.1 *Chromium-Nitride Composite Coatings by RLPPS*

Figure 2 shows a typical optical micrograph of the cross section of the sprayed coating formed by RLPPS without transferred arc at a chamber pressure (P_c) of 3.1 kPa. A distinctive wavy microstructure is observed in the vicinity of the interface; however, this becomes less distinctive at regions far from the interface. It is expected that the constituents of the sprayed coatings change gradually along the thickness direction because there is a difference in the extent of etching. The XRD pattern using cobalt Kα radiation is shown in Fig. 3, which is taken from the same coating surface as shown in Fig. 2. The coating is composed of Cr_2N, CrN, and small amounts of chromium.

Table 1 Standard spray parameters used in RLPPS

Plasma gas flow, m^3/s	Nitrogen: 0.89×10^{-3}
Plasma current, A	500
Plasma voltage, V	46 - 51
Powder feed rate, g/s	0.08 - 0.11
Chamber pressure, kPa	3.1
Spray distance, mm	300
Transferred arc current, A	0 - 38

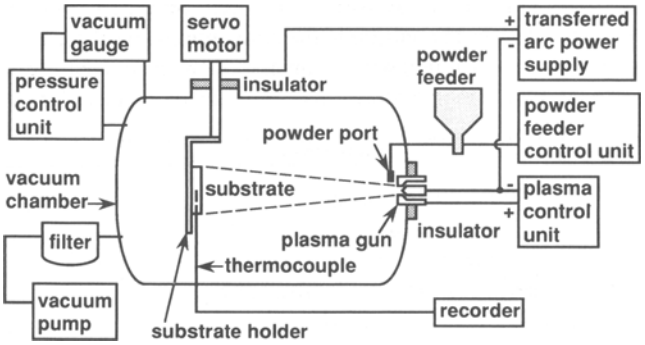

Fig. 1 Schematic of RLPPS system with a transferred arc circuit for the direct fabrication of chromium-nitride composites

The effect of P_c on the chromium-nitride formation in the composite coatings was examined. The intensity ratio of the sum of Cr_2N and CrN to all the constituents at the coating surfaces is shown in Fig. 4 as a function of P_c and with the maximum substrate temperature (T_s) during the spray process. This indicates that the total amount of Cr_2N and CrN at the surface decreases with increasing P_c. The T_s tends to decrease with increasing P_c and is lower than 1183 K, except $T_s = 1273$ K at P_c of 3.1 kPa. The formation of CrN is fairly appreciable at P_c of 3.1 kPa; however, this reduces at P_c above 4.9 kPa. The formation of Cr_2N is dominant in all the coating surfaces sprayed at P_c below 15.6 kPa. With the highest P_c of 19.8 kPa, the formation of Cr_2N decreases, and chromium becomes the principal constituent instead of Cr_2N. Since the low P_c satisfies the process conditions for large amounts of nitride formation, mainly due to the temperature hysteresis of substrate, all the following spray processes were performed at P_c of 3.1 kPa.

3.2 *Nitriding Reaction of Liquid Chromium Droplets*

The chromium-nitride in situ composite coatings are formed through the impingement and deposition of each liquid chromium droplet on a substrate. Although the maximum substrate temperature (T_s) significantly affects the formation of nitrides, a fundamental question is whether or not the nitriding reaction takes place at the droplet surfaces during their flight in the plasma flame. The impinged chromium droplets on the substrate

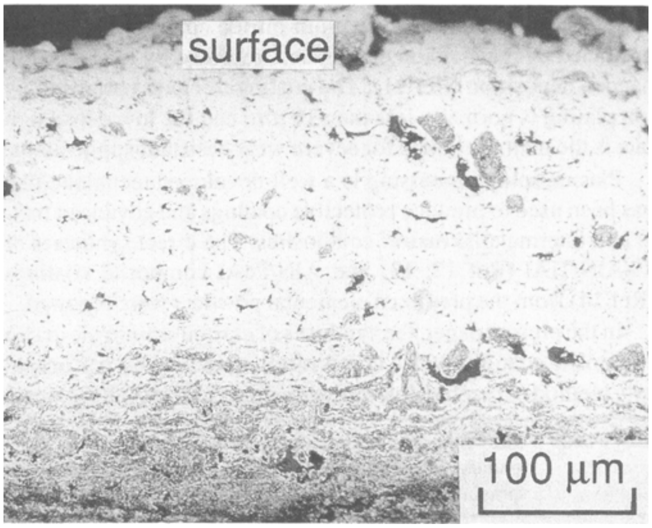

Fig. 2 Optical micrograph of the cross section of a typical sprayed coating (chemically etched by 5% hydrofluoric acid aqueous solution for 1.8 ks)

were collected by sampling the plasma flame containing chromium droplets for 93 ms. Typical impinged chromium particles have circular shape with an average diameter of 107 μm, as shown in Fig. 5, and 3.5 μm in thickness measured by laser microscopy. Then the flattening ratio, which is the value of an average impinged droplet diameter divided by an original particle diameter, is approximately 2.6 with a particle velocity of 170 m/s because the diameter of chromium powder is 38 to 44 μm in this particular spraying. A comparison of Fig. 6(a) and (b) of the characteristic x-ray image shows that the intensity distributions of chromium Kα and nitrogen Kα are consistent with each other.

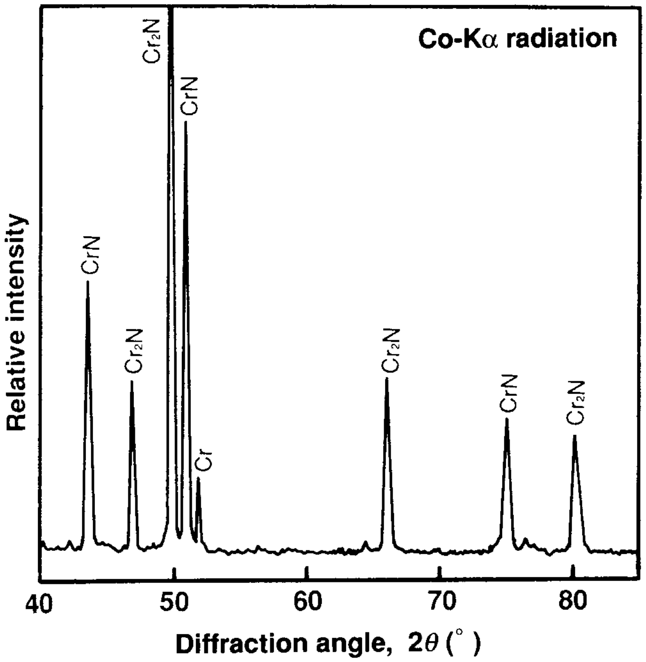

Fig. 3 XRD pattern of a typical coating surface sprayed without transferred arc

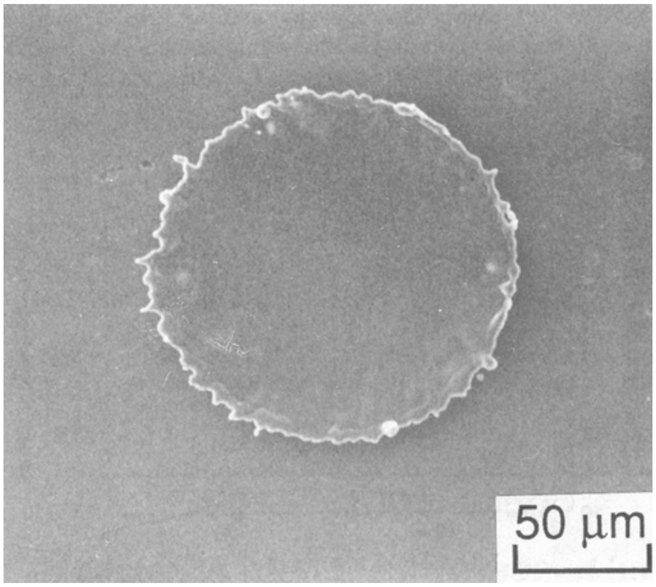

Fig. 5 Scanning electron micrograph showing a typical impinged chromium droplet

The existence of nitrogen is recognized in chromium particles. The flight time of droplets in the plasma flame is approximately 2 ms in this spray condition.

Figure 7 shows typical depth profiles of Auger electron intensity on an impinged chromium particle. Sputtering time has the same meaning as a distance from the particle surface. The appearance of an iron intensity indicates that the steel substrate is revealed at a sputtering time over 17 ks. At times less than 17 ks, the existence of nitrogen is recognized. The intensities of chromium and nitrogen are nearly constant within the impinged chromium particle. However, there are no chromium-nitride diffraction peaks on the XRD pattern with copper Kα taken from the same impinged particle. The nitriding reaction does not occur at particle surfaces while in flight for 2 ms. Nitrogen seems to be simply absorbed into the liquid chromium droplets. Since the nitriding reaction does not occur at room temperature, it must take place at the deposited chromium droplets on the substrate in the spray process because of exposure to the nitrogen atmosphere at high temperature. Therefore, most of the chromium-nitride formation proceeds on the substrate.

3.3 *Acceleration of Nitriding Reaction by Transferred Arc*

Increasing the flame temperature would seem to accelerate the nitriding reaction of chromium on a substrate and to elimi-

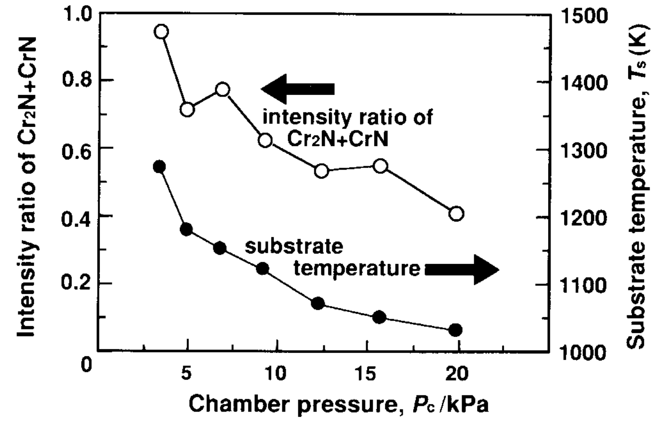

Fig. 4 Intensity ratio of the sum of Cr_2N and CrN to all the constituents and substrate temperature (T_S) as a function of chamber pressure (P_C)

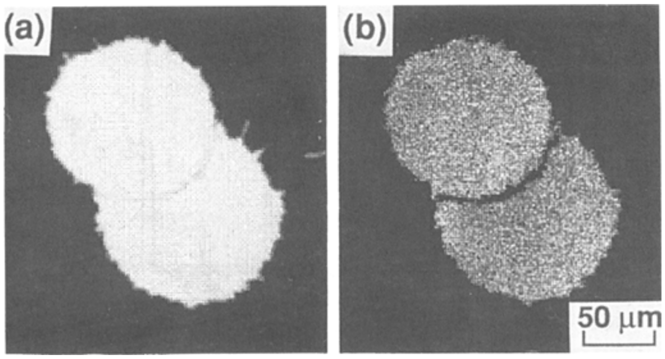

Fig. 6 Element mappings due to characteristic x-ray of impinged chromium droplets: (a) chromium Kα image and (b) nitrogen Kα image

nate the nonreacted chromium. In the present research, a transferred arc was used to accelerate the nitride formation. Changes in substrate temperature during the spray process were examined as a function of transferred arc currents (I_t). The T_s increases with I_t. It is approximately 1280 K without the transferred arc, but it becomes more than 1400 K with the transferred arc.

Figure 8 shows a typical XRD pattern of the coating surface sprayed at I_t = 25 A. The stronger diffracted intensity of CrN at 2θ is 44°, 51°, and 75° as compared with that in Fig. 3. This is partially due to nonreacted chromium that has completely disappeared. According to the calibration curve of the volume fraction of CrN (V_{CrN}), the V_{CrN} of the coating surface in Fig. 3 is only 0.36. By contrast, that in the coating surface of Fig. 8 increases to 0.71 so that the nitride formation is accelerated by applying a transferred arc.

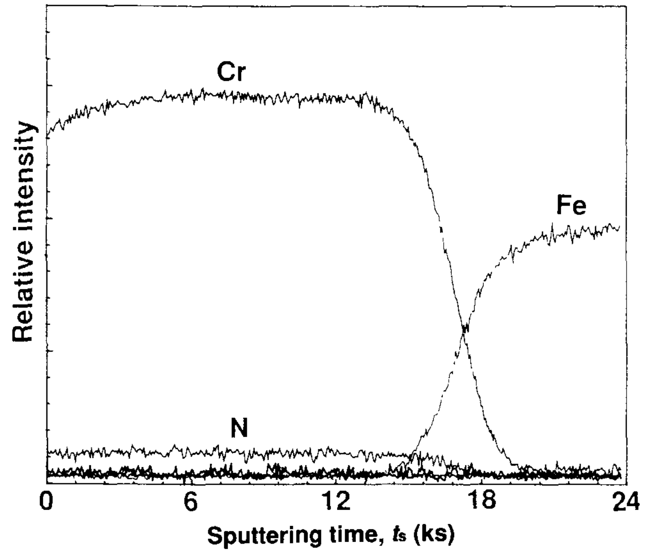

Fig. 7 Depth profiles of Auger electron intensity on an impinged chromium particle in reactive plasma spraying

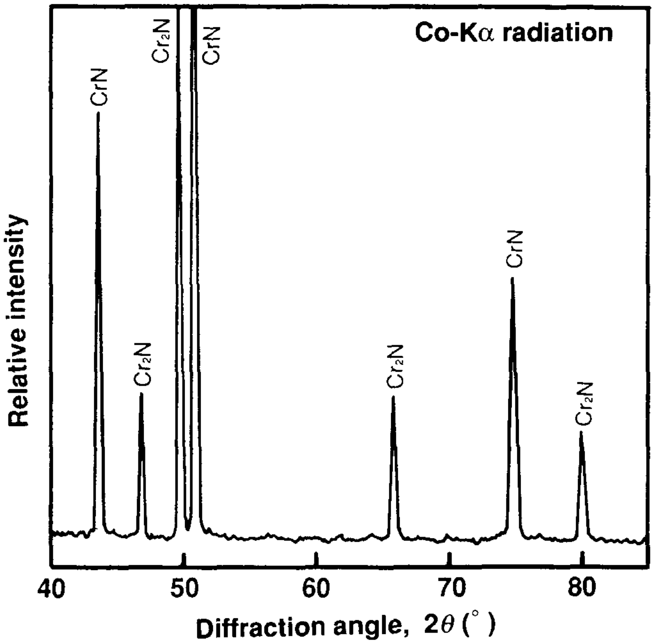

Fig. 8 XRD pattern of a typical coating surface sprayed with a transferred arc current (I_t) of 25 A

The nitrogen content at the coating surface gradually increases with I_t of up to 25 A, as shown in Fig. 9 because of the increase in V_{CrN}. It is expected that the nitriding reaction of chromium proceeds as follows.

$$4Cr + N_2 \rightarrow 2Cr_2N \tag{1}$$

$$2Cr_2N + N_2 \rightarrow 4CrN \tag{2}$$

The nitriding of reaction 1 proceeds first, then CrN forms at higher temperatures of the substrate. With I_t above 30 A, a decrease in nitrogen content occurs due to the increase in T_s. According to the Cr-N equilibrium phase diagram (Ref 9), CrN decomposes to Cr_2N at above 1323 K. Although it is necessary to attain T_s above 1300 K to form a coating with higher V_{CrN}, the decomposition of formed CrN to Cr_2N occurs quickly above 1420 K; that is, the opposite of reaction 2. The maximum nitrogen content is obtained at I_t of about 25 A because of the balance between the formation and the decomposition of CrN based on the reaction dynamics.

3.4 *Elements Distribution of Cross Section of Composite Coatings*

Elements distribution was observed by EPMA along the thickness direction of the coatings, as shown in Fig. 10. As expected from the optical microscopy observations of the cross sections without transferred arc, nitrogen Kα intensity is weak close to the interface, chromium Kα intensity is complementally strong as shown in Fig. 10(a). On the other hand, nitrogen Kα intensity becomes stronger at about 80 μm away from the interface. It is expected that Cr_2N is the dominant phase in this area. As shown in Fig. 10(b) with I_t of 25 A, the existence of nonreacted chromium is limited at up to 25 μm from the interface. The nitrogen Kα intensity becomes strong at about 20 to 30 μm from the surface; CrN exists only at the coating surface. The intensity ratio of CrN or Cr_2N is shown in Fig. 11 as a function of the main

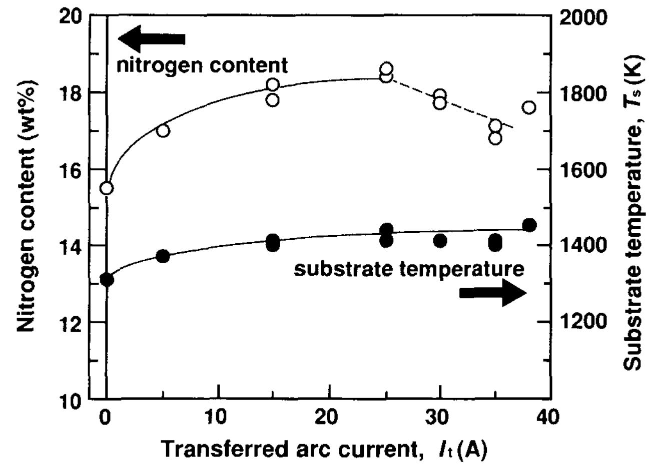

Fig. 9 Changes in nitrogen content at the coating surface and substrate temperature (T_s) as a function of transferred arc current (I_t)

plasma power (P_m), where that of Cr_2N is analyzed at 70 μm away from the surface. The T_s is also shown in Fig. 11. The CrN intensity at the coating surface increases with P_m. However, no CrN exists at 70 μm away from the surface due to decomposition. Hence, the chromium-nitride in situ composite coatings have a composition gradient.

3.5 *Friction and Wear Characteristics of Composite Coatings*

The hardness measurements were carried out at 100 μm from the interface on the cross section of composite coatings. Hardness results are shown in Fig. 12 as a function of the volume fraction of Cr_2N (V_{Cr_2N}). The hardness may be low even if sprayed with a transferred arc because a low P_m leads to the coatings with low V_{Cr_2N}. The hardness of the coatings increases linearly with V_{Cr_2N}; the coatings with V_{Cr_2N} of 0.98 have a hardness above 1300 HV. The coating hardness can be controlled by selecting the appropriate spray parameters. Although the Cr_2N/Cr composites have two or more times higher hardness than that of Ti_2AlN/TiAl composites at room temperature (Ref 12, 13), it drops at medium temperatures, unlike that of the TiAl matrix composites (Ref 13).

The seizure tests in the presence of lubricant (SAE 30) of 160 mm^3/s were performed through loading step by step every 120 s using the coatings with various V_{Cr_2N} and gas-nitrided steel (SACM645) as a counter body. Seventy micrometers of the coating surface was removed from the surface by polishing prior to the tests. The seizure stress (σ_s) of the composite coatings is shown in Fig. 13 as a function of hardness. All the friction surfaces do not contain CrN, but are composed of Cr_2N and chromium. The σ_s increases rapidly with hardness, namely with increasing V_{Cr_2N}. The σ_s of 24.9 MPa is obtained for a coating with a hardness of 1344 HV, which is approximately 1.9 times higher than that of precipitation hardened Ni-P electroless plating found by the authors.

Wear tests were also performed at 12.5 MPa for a friction distance of up to 5.4 km using the same experimental setup as the seizure tests. A wear depth greater than 20 μm is observed on the Ni-P platings; however, wear loss is not appreciable on either the composite coatings or the counter bodies. Hence, the sprayed Cr_2N/Cr in situ composites demonstrated excellent wear resistance.

4. Conclusions

Chromium-nitride composite coatings were synthesized by RLPPS using pure chromium powder as a spray material. The nitriding reaction was accelerated by applying a transferred arc during the spray process. The following results were obtained.

- Coatings consist of chromium, Cr_2N, and CrN, which have a composition gradient from the substrate interface to the surface. The maximum amount of chromium-nitride is formed at a low chamber pressure of 3.1 kPa due to a temperature rise of substrate.
- Although nitrogen is recognized on sprayed particles that collided with a substrate, the nitride formation does not proceed at surfaces of liquid chromium droplets in flight, but does proceed on a substrate.

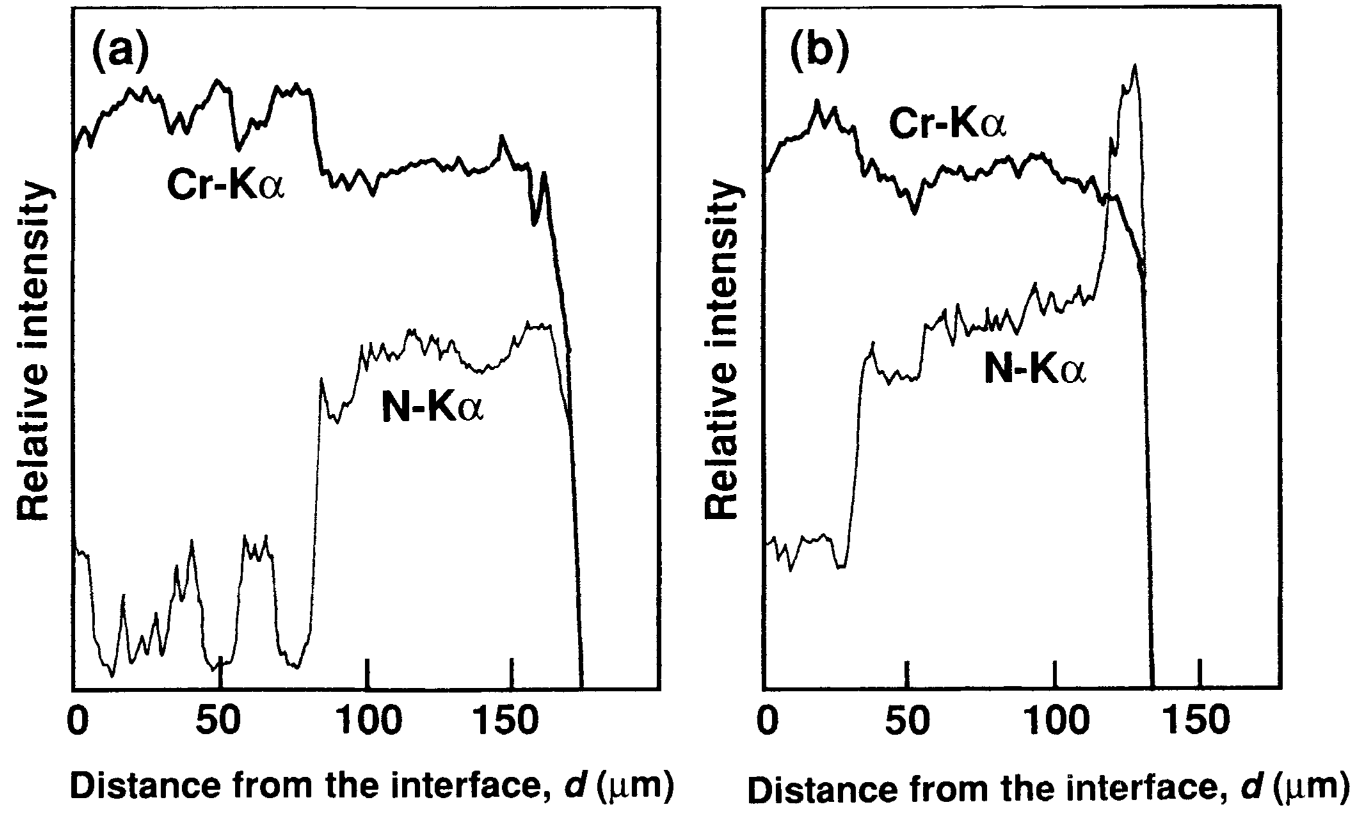

Fig. 10 Intensity profiles of characteristic x-ray obtained on the cross section of chromium-nitride composite coatings: (a) I_t = 0 A and (b) I_t = 25 A

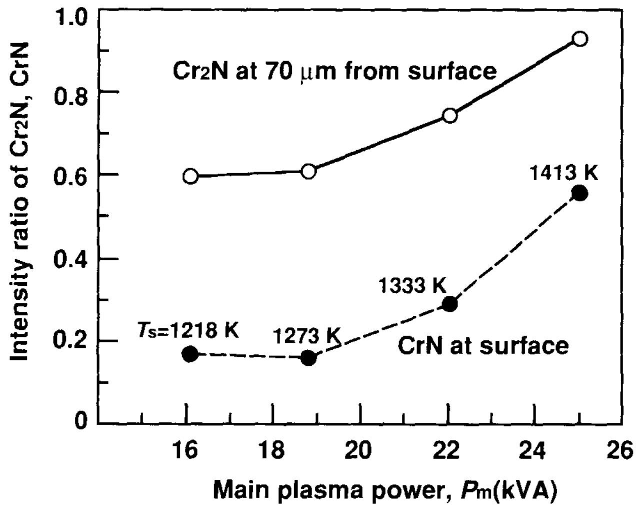

Fig. 11 Influence of main plasma power (P_m) on the formation of CrN at the coating surface and Cr_2N at 70 μm away from the surface

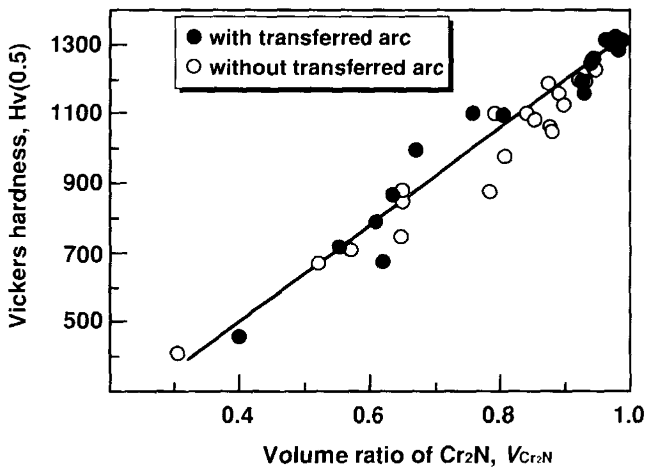

Fig. 12 Influence of Cr_2N volume fraction (V_{Cr_2N}) on the hardness at 100 μm away from the interface

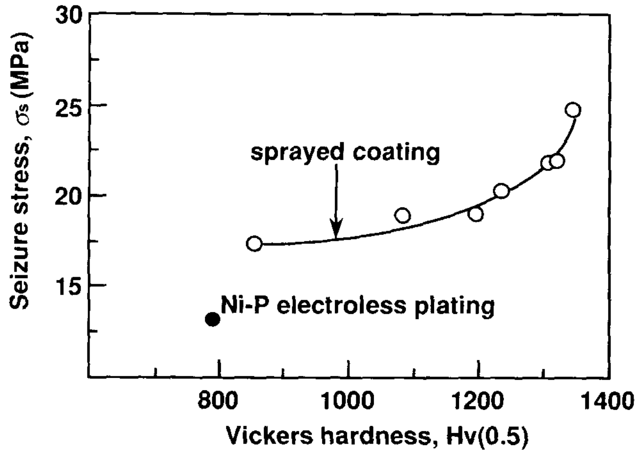

Fig. 13 Change in seizure stress of the composite coatings as a function of surface hardness: friction speed, 1 m/s; counter body, gas-nitrided steel (1150 HV), lubricant, engine oil (SAE 30) of 160 mm^3/s

- The substrate temperature increases by applying a transferred arc. Although the maximum nitrogen content in the coatings is attained with a transferred arc current of 25 A, CrN is available to decompose to Cr_2N. Then the existence of CrN is limited to 20 to 30 μm from the surface.
- The hardness of the coatings depends on the volume fraction of Cr_2N. It is 1300 HV with a Cr_2N volume fraction of 0.98.
- The seizure stress with lubricant increases rapidly with the coating hardness; it becomes 24.9 MPa at 1300 HV, which is 1.9 times higher than that of precipitation hardened Ni-P electroless platings. Wear characteristics of the sprayed coatings are also superior when compared with Ni-P platings.

References

1 S Komiya, S. Ono, N Umezu, and T. Narusawa, Characterization of Thick Chromium-Carbon and Chromium-Nitrogen Films Deposited by Hollow Cathode Discharge, *Thin Solid Films*, Vol 45, 1977, p 433-445

2. T. Sato, M. Tada, Y C. Huang, and H Takei, Physical Vapor Deposition of Chromium and Titanium Nitrides by the Hollow Cathode Discharge Process, *Thin Solid Films*, Vol 54, 1978, p 61-65

3. O Knotek, W. Bosch, M. Atzor, W -D Munz, D. Hoffmann, and J. Goebel, Properties of Chromium Nitrides Deposited by Reactive Sputtering, *High Temp.—High Press.*, Vol 18, 1986, p 435-442

4. O. Knotek, F. Loffler, and H.J. Scholl, Properties of Arc-Evaporated CrN and (Cr,Al)N Coatings, *Surf. Coat. Technol.*, Vol 45, 1991, p 53-58

5. M. Taguchi and H Takahashi, Corrosion Behaviour of Chromium Nitride Films Produced by Reactive Ion Plating in Sulfuric Acid Solution, *J. Jpn. Inst. Met.*, Vol 56, 1992, p 1221-1227 (in English and Japanese)

6. P Ballhause, H Hensel, A. Rost, and H. Schssler, CrN$_x$—A Hard Coating for Corrosion and Wear Resistance, *Mater. Sci. Eng. A*, Vol 163, 1993, p 193-196

7 J. Goebel, Some Examples for the Application of Surface Analysis Techniques in Thin Film Technology, *Z. Anal. Chem.*, Vol 319, 1984, p 771-776 (in English and German)

8 T Mills, Pressure-Temperature Relations in the Chromium-Nitrogen System, *J. Less-Common Met.*, Vol 22, 1970, p 373-381

9. H Holleck, *Binary and Ternary Carbide and Nitride Systems of Transition Metals*, Gebruder Borntraeger, 1984, p 45

10. Y.L. Su and J S Lin, An Investigation of the Tribological Potential of TiN, CrN and TiN+CrN Physical Vapor Deposited Coatings in Machine Element Applications, *Wear*, Vol 170, 1993, p 45-53

11 E Takasaka and S Iwamoto, Preferential Crystal Orientation of Chromium Nitrided Films Prepared by IBED Method, *J. Jpn. Inst. Met.*, Vol 57, 1993, p 417-420 (in English and Japanese)

12. Y Tsunekawa, K Gotoh, M Okumiya, and N. Mohri, High-Temperature Stability of Titanium Aluminide Matrix Composites Fabricated by Reactive Low Pressure Plasma Spraying, *Thermal Spray: International Advances in Coatings Technology*, C.C Berndt, Ed., ASM International, 1992, p 189-194

13. Y Tsunekawa, K. Gotoh, M Okumiya, and N. Mohri, Synthesis and High-Temperature Stability of Titanium Aluminide Matrix in situ Composites, *J. Therm. Spray Technol*, Vol 1, 1992, p 223-230

14 Y. Tsunekawa, M Okumiya, K. Gotoh, T Nakamura, and I. Niimi, Synthesis of Iron Aluminide Matrix in situ Composites from Elemental Powders by Reactive Low Pressure Plasma Spraying, *Mater. Sci. Eng. A*, Vol 159, 1992, p 253-259

15 M. Fukumoto, S Katoh, and I Okane, Splat Behavior of Plasma Sprayed Particles on Flat Substrate Surface, *Thermal Spraying: Current Status and Future Trends*, A. Ohmori, Ed , High Temperature Society of Japan, 1995, p 353-358