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Metal Nitride Coatings by Physical Vapor Deposition (PVD) for a Wear Resistant Aluminum Extrusion Die

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The purpose of this study is to investigate the friction and wear behaviors of CrN, TiN, CrAlN, and TiAlN coated onto SKD61 for application to Al 7000 series extrusion dies. On the wear test, the experimental parameters are the load and the counter material's temperature. The results showed that the friction coefficient increased with load but decreased with the counter material's temperature, and the friction coefficients of CrN and CrAlN were lower than the friction coefficients of TiAlN and TiN, especially at a higher temperature. The wear track with different coatings identified different wear behaviors; the wear behavior of CrAlN was found to be abrasive, but the wear behavior of TiN, CrN, and TiAlN was adhesive. Therefore, CrAlN showed the least wear loss with a lower friction coefficient and less adhesion with counter materials at the highest range of wear load and temperature. This resulted in the easy formation of aluminum oxide in the wear track and less Al adhesion; moreover during the hard second phase, AlN dispersed in the film during deposition.

Keywords: Wear Test, SKD61, Al 7000 Series, TiN, CrN, CrAlN, TiAlN.

1. INTRODUCTION

Hard ceramic coatings have been widely used on cutting tools and mechanical components to prolong their lifetime and to improve their working efficiency. Nitride coatings compound by various physical vapor deposition processes are found increasing applications for almost demand.[17] Metal (Ti and Cr) nitride-based coatings were the first type of ceramic system to be developed and they are the most popular materials for commercial wear-resistant coating applications. There are numerous studies on the friction of Ti and Cr coatings under various conditions. Different elements, such as Al, Si, and C, have been added to TiN and CrN coatings in order to improve their corrosion resistance, hardness, and oxidation resistance.[1–4]

The CrN, TiN, CrAlN, and TiAlN coatings have a high hardness ranging from 2000–3400 HV and high oxidation resistance. These coatings have also extended the tool life of a variety of machines. The CrN, TiN, CrAlN, and TiAlN coatings by using ion plating are one of the physical vapor deposition (PVD) techniques that has been widely applied to improve the lifetime and performance of diverse tool materials, due to its advantageous properties such as high hardness, good wear, and chemical stability.[5–7] Recently, a new ternary nitride, CrAlN, which contains a higher percentage of aluminum, has become the subject of ever-increasing interest for coating due to its excellent properties, particularly under high temperature conditions.[8] The tribological behavior of the CrN, TiN, CrAlN, and TiAlN coatings have been investigated using reciprocating sliding and pin-on-disc test methods. The friction coefficients and the wear resistance against varied counter materials were studied as a function of the coating composition and the test parameters. Although, promising results in cutting and oxidation tests have been reported for the CrN, TiN, CrAlN, and TiAlN coatings against steel alloys, until now, insufficient efforts have been made to investigate the wear of those coatings against aluminum alloys, especially for the high-strength 7000 series. In this work, the tribological behaviors of the four commercially available CrN, TiN, CrAlN, and TiAlN coatings were comparatively investigated with a focus on their friction behaviors and their wear mechanisms against the Al 7000 series alloy.

2. EXPERIMENTAL DETAILS

In this experiment, the upper side testing part (pin) of the die was made of SKD61, which is the most widely used

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Table I. Chemical composition of SKD61.

Element (wt%)								
C	Si	Mn	P	S	Cr	Mo	V	Fe
0.42	1.20	0.50	0.03	0.03	5.50	1.50	1.20	Val.

Table II. Deposition condition for the CrN TiN, CrAlN, and TiAlN coatings.

Deposition condition	
Target	Ti, Cr, AlN (99.9%),
Working pressure	1×10^{-2} mbar
Gas	$Ar + N_2$
Time	8–10 h
Sub-temp.	400–450 °C

Table III. Chemical composition of the Al BM76 alloy.

Element (wt%)									
Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr	Al
0.15	0.2	0.3–0.5	0.1–0.2	1–1.5	0.15	4–5.0	0.1	0.08–0.18	Val

material for an extrusion die, and the chemical composition is shown in Table I. An 8 mm diameter and 19 mm height pin was deposited by CrN, TiN, CrAlN, and TiAlN thin films using the arc ion plating method under the condition indicated in Table II. The sub test plate was made of BM76 aluminum alloy (Al BM76); the chemical composition is shown in Table III. The sub plate was manufactured on the basis of drawings, as shown in Figure 1. All the specimens that were sub plated and pinned were cleaned, ultrasonically, before the wear test was conducted in order to remove the surface impurities that resulted from contamination during machining and coating.

The reciprocating friction wear tester (108-RF, R&B, Inc. Korea) that is a pin-on-disc type of tester, as shown in Figure 2, was used for sliding the straight pin side against the sub plate surface with reciprocating movement. The wear test was conducted under atmospheric pressure in an unlubricated condition by reciprocating the pin at a constant frequency of 1 Hz. The test load applied to the pin and the temperature controlled by heating the sub plate varied as follows: 11, 15, and 19 kgf/m^2 and RT, 120 °C, respectively (Table IV). The friction coefficient was measured *in situ* during the wear test, and the wear depth was determined from the depth changes after the wear test was completed.

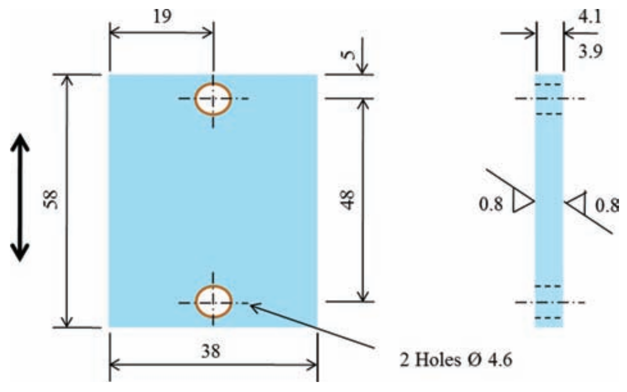

Figure 1. Drawing of the sub plate made of Al BM76 for the wear test.

Figure 2. Pin-on-disc type of reciprocating friction wear test.

Table IV. Wear test conditions.

Parameter	
Load	11, 15, 19 kgf
Temperature	RT, 120 °C
Time	12 h
Frequency	1 Hz
Others	Atmospheric pressure, Unlubrication

Four types of commercially available coatings were deposited using arc ion plating PVD equipment and Oerlikon Balzers (Korea) coatings. Customized Ti, Cr, and AlN targets were used.

After coating the upper side pin, the Vickers hardness was measured by using an indentation tester (Mitutoyo, HM-200 series) on a load of 1 kgf. The X-ray diffraction (XRD, Rigaku, RU200B) patterns of the coatings were obtained in 2θ, ranging from 20–90° with Cu K_α radiation. The cross-section of the CrN, TiN, CrAlN, and TiAlN films was observed using a field emission scanning electron microscope (FE-SEM, JEOL, JSM7000F), and energy dispersive X-ray spectroscopy (EDS) was used to analyze the chemical composition of the powder that collected from the wear trails.

3. RESULTS AND DISCUSSION

Figure 3 shows the FE-SEM surface images of CrN, TiN, CrAlN, and TiAlN coated on the SKD61 upper pin using ion plating techniques. Surface scratches were generated during the machining of the pins. The coating surfaces show only an effective difference with Al alloying, and the surfaces with no Al alloying are relatively smooth. By incorporating Al, the second phase consisted of a high concentration of Al possibly mixed into the base of the CrAlN and TiAlN films, resulting in tiny inclusions in the surface.

Figure 4 shows the FE-SEM cross-sectional images of the Al-deposited CrN, TiN, CrAlN, and TiAlN films. The coating thickness varies from 2.63 μm to 6.03 μm with the same deposition time. This means that the deposition

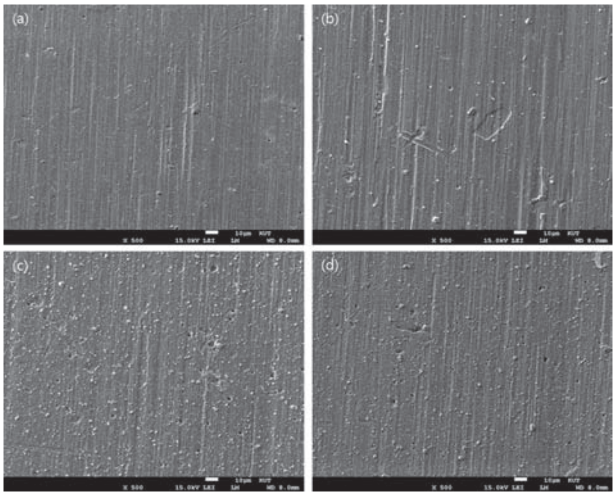

Figure 3. FE-SEM surface images of the CrN, TiN, CrAlN, and TiAlN coatings.

rate decreased nearly 50% or lower with the incorporation of Al. The Vickers micro-hardness measured in the 50 g load is listed in Table V. As shown, the CrN, TiN films and the CrAlN and TiAlN films have a similar hardness, but the hardness of the Al-incorporated film is about 1.5-times higher in comparison to the films that did not incorporate Al, in spite of the thinness.

Figure 5 presents the XRD patterns of the CrN, TiN, CrAlN, and TiAlN films. In Figure 5(a), CrN has an intense peak at 44°, which can be designated to (2 0 0) diffraction. While the TiN coating grew with (1 1 1) and (2 0 0) as its preferred orientation as shown in Figure 5(b). On the other hand, the CrAlN film shows an intense AlN (0 0 0 2) peak and weak CrAlN (2 0 0), (2 2 0), and (2 2 2) peaks, and the TiAlN film drove the (2 0 0) preference.[7, 10] A peculiar thing to note about the XRD patterns is the differences between the Al alloying in the CrAlN and TiAlN films; in the TiAlN film, incorporating Al creates a compound, whereas for the CrAlN film, incorporating the Al creates a compound plus a mixture. Therefore, the CrAlN film seems to include the AlN phase as the second phase in the film.

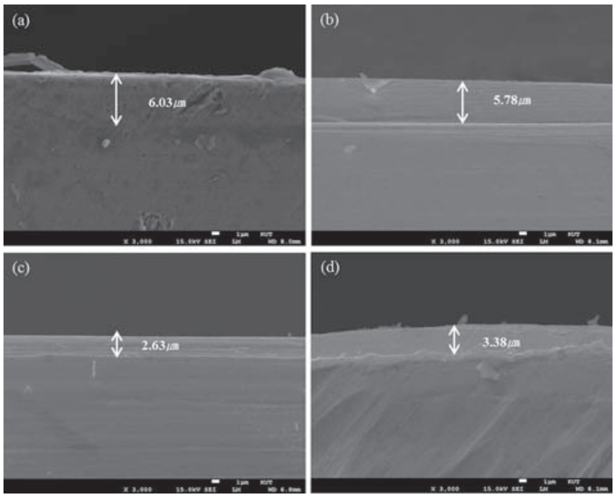

Figure 4. FE-SEM cross-sectional images of the CrN, TiN, CrAlN, and TiAlN coatings.

Table V. Physical properties of the CrN, TiN, CrAlN, and TiAlN coatings.

Material	Thickness (μm)	Hardness (Hv/50 g)
CrN	6.03	2074
TiN	5.78	2135
CrAlN	2.63	3041
TiAlN	3.38	3190

Figure 6 demonstrates the friction coefficient of each coating achieved from the reciprocating wear test. The applied load and sub plate temperature were changed. In Figure 6, the friction coefficient between the upper pin and the sub plate is the average load ratio for horizontal-to-vertical movement for full reciprocating, ranging from 2 hours to 12 hours. For every coating, the friction coefficients increase with time, which means that the contact surfaces-to-counterparts increase as the test proceeds. As the load increases, the friction coefficient increases in all the samples. However, the friction coefficient is different for each coating. The friction coefficient of the non-coated SKD61, shown in Figure 1(a), is as high as 0.78, while the friction coefficients for the CrN, TiN, CrAlN, and TiAlN films at 11 kgf are 0.35, 0.34, 0.19, and 0.23, respectively. In addition, the friction coefficients for CrAlN and TiAlN are less than 70% of the friction coefficients for CrN and TiN, and this trend is the same when the high load is applied. When the samples are compared by the plate temperature at 15 kgf, every sample had a lower friction coefficient at a high temperature. This signifies that the wear behavior shifts from adhesion to abrasion with increasing temperature.[11–13]

Figure 7 exhibits the sub plate wear depth 12 hours after the wear test with a 15 kgf load. The result indicates that the wear depth for CrAlN, TiAlN, CrN, and TiN is 3.55 mm, 4.89 mm, 5.33 mm, and 7.45 mm, respectively; these values are less than the wear depth of the non-coated SKD61, which is 9.88 mm. On the other hand, the wear depths for CrAlN, TiAlN, CrN, and TiN decrease to 1.88 mm, 3.12 mm, 4.11 mm, and 5.3 mm, respectively, by heating the sub plate to 120 °C. Those values are in exact agreement with the friction coefficients shown in Figure 6.

Figure 8 illustrates the wear track surface of the Al BM76 sub plate observed by FE-SEM 12 hours after the wear test. In the 11 kgf load, the wear in all the samples likely progresses due to abrasive friction, but as the load increases to 15 kgf, the wear behavior changes to adhesive in the CrN, TiN, and TiAlN films, whereas, the CrAlN film still shows abrasive intensive wear until the load increases to 19 Kgf. However, all the samples resume abrasive wear behavior at high temperature. This matches well with the

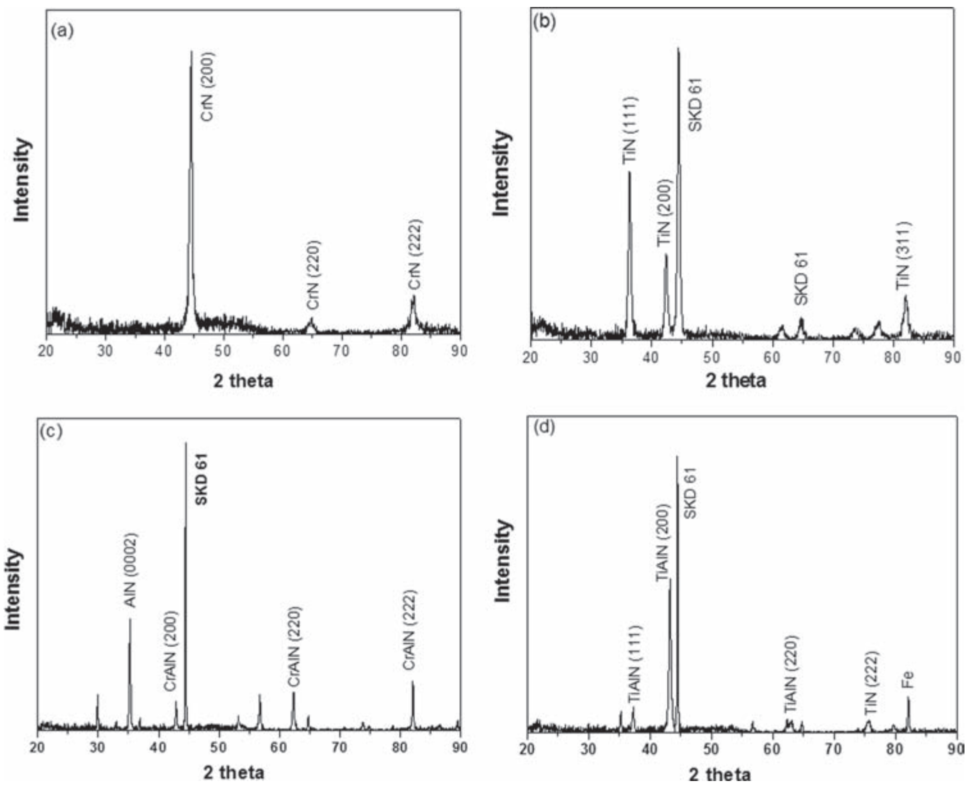

Figure 5. XRD patterns of the CrN, TiN, CrAlN, and TiAlN coatings.

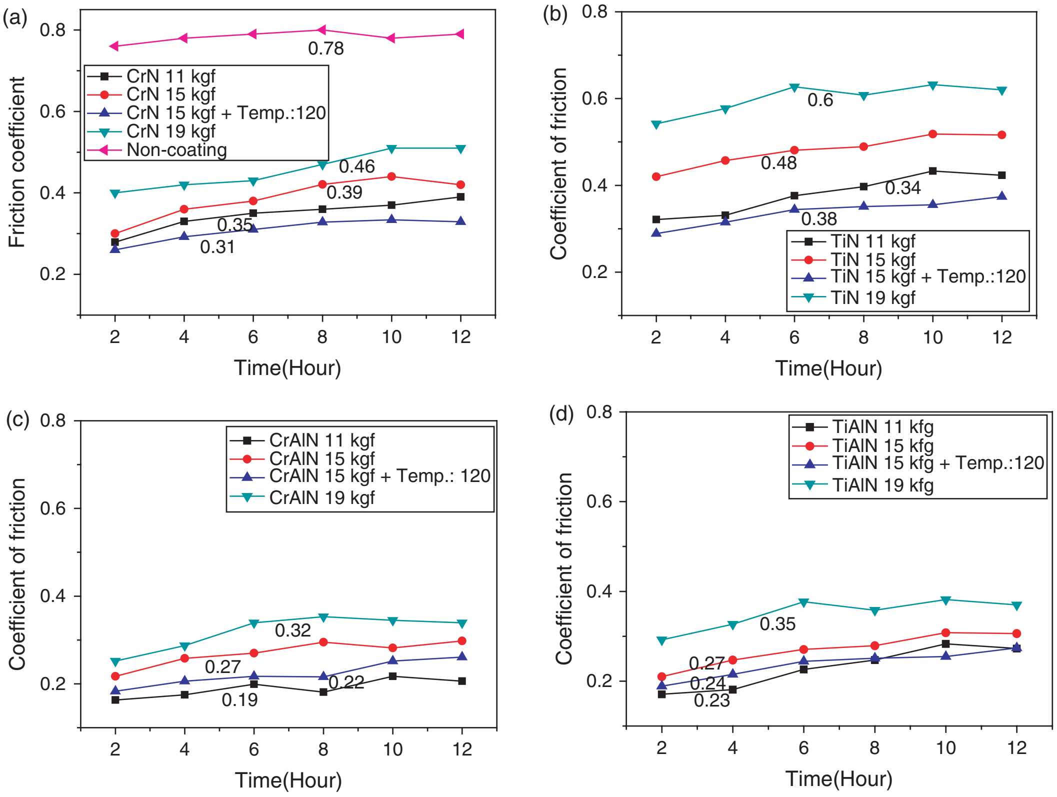

Figure 6. Friction coefficients with different loads and temperatures: (a) CrN, (b) TiN, (c) CrAlN, and (d) TiAlN.

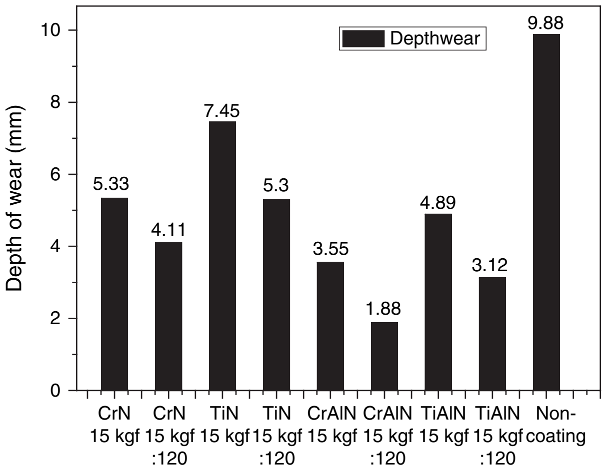

Figure 7. Wear depth of disc 12 hours after the wear test for the CrN, TiN, CrAlN, and TiAlN coatings and the non-coated sample at 15 kgf.

friction coefficient and wear depth findings, which increase with load but decrease drastically at 120 °C. The reason for this can be found in the easy formation of aluminum oxide in the CrAlN film. The Al content in the powder obtained from the wear track is listed in Table VI. This shows the especially high oxygen content in the CrAlN film, which implies that CrAlN is harder and less sticky, making it easy for small debris to oxidize, which induces abrasive intensive wear behavior and makes the wear track smooth.[14–16] As seen in Figure 5, the AlN in the CrAlN film also seems to play an important role in making the film hard and keeping the amount of debris small.

Table VI. EDS chemical composition of powder obtained from the wear track 12 hours after the wear test (weight %).

	CrN 15 kgf	CrN 15 kgf 120 °C	TiN 15 kgf	TiN 15 kgf, 120 °C	CrAlN 15 kgf	CrAlN 15 kgf 120 °C	TiAlN 15 kgf	TiAlN 15 kgf, 120 °C
Mg	1.43	0.94	1.30	1.28	1.25	1.14	1.30	1.18
Al	92.4	65.83	93.37	88.19	92.65	58.19	93.37	71.38
Zn	6.17	4.40	5.33	4.93	6.10	4.02	5.33	4.51
O		28.84		5.60		33.66		22.93
Total	100	100	100	100	100	100	100	100

Figure 9 depicts the FE-SEM cross-sectional image of the films after the wear test, showing the Al adhesion to the pin surface. Figure 9(a) shows that the CrN wears out at room temperature and the thickness increases from 8.79 μm to 5.78 μm (as seen in Fig. 4); but, at 120 °C, the thickness is reduced to 5.18 μm as can be seen in Figure 9(b). The TiN, CrAlN, and TiAlN films do not show dissimilar results in Figure 9. This suggests wear behavior with less adhesion at high temperature, which was

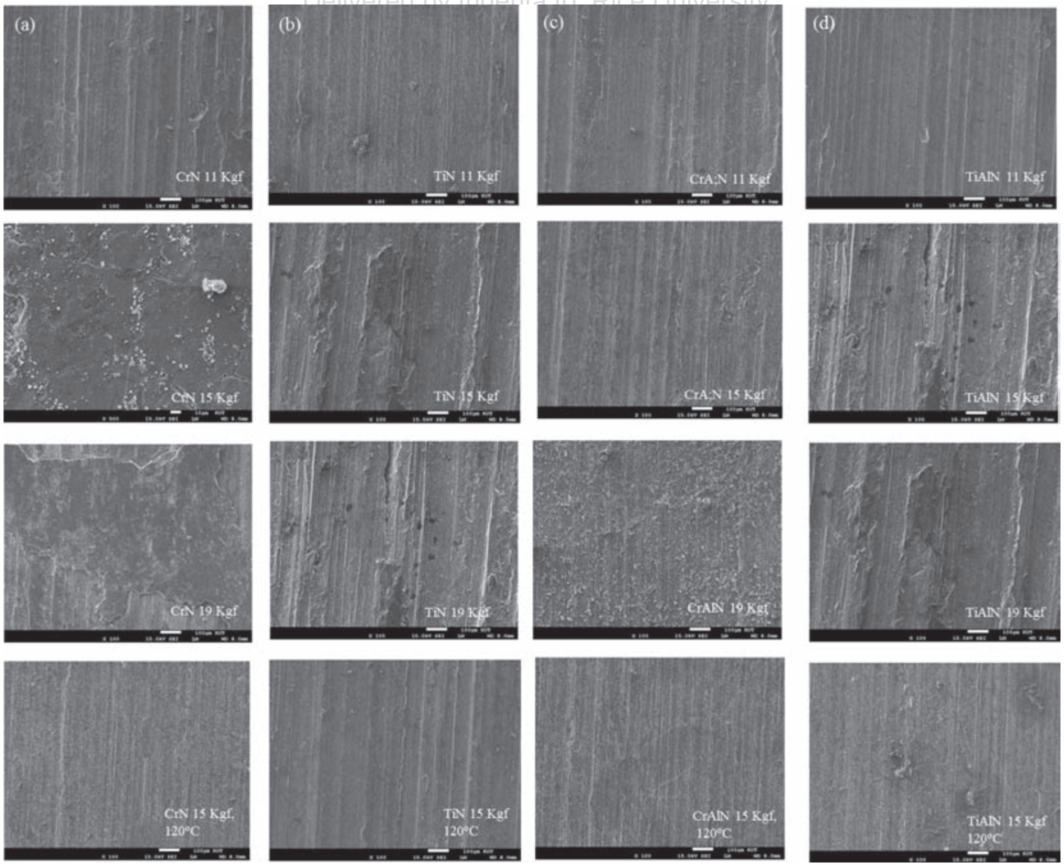

Figure 8. Surface of Al BM76 observed by FE-SEM after the wear test: (a) CrN, (b) TiN, (c) CrAlN, (d) TiAlN.

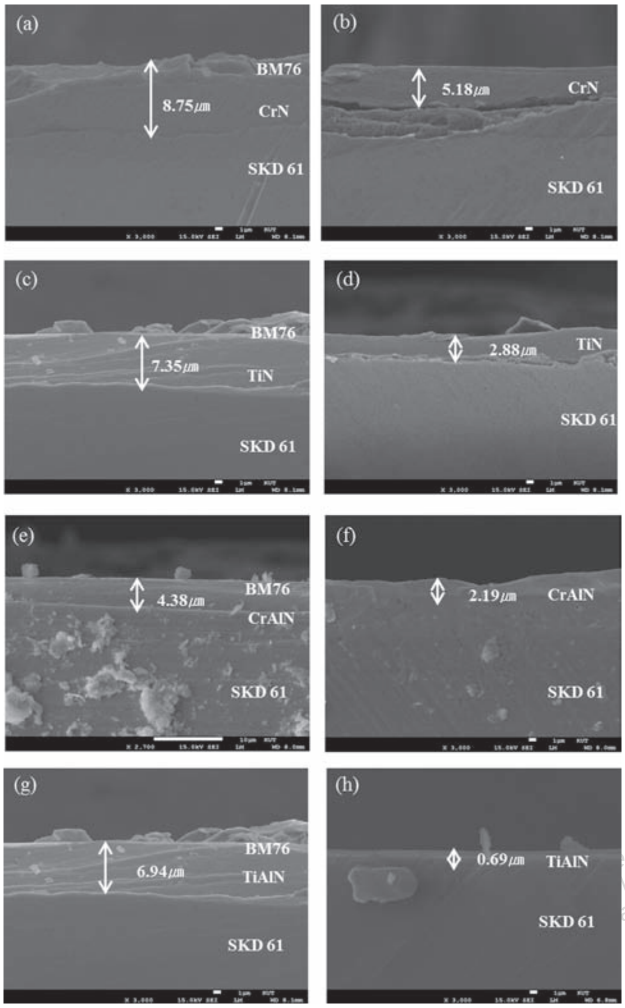

Figure 9. FE-SEM cross-sectional images after the wear test (a) CrN/15 kgf, (b) CrN/15 kgf/120 °C, (c) TiN/15 kgf, (d) TiN/15 kgf/120 °C, (e) CrAlN/15 kgf, (f) CrAlN/15 kgf/120 °C, (g) TiAlN/15 kgf, (h) TiAlN/15 kgf/120 °C.

previously anticipated from the data presented in Figure 8. From these results, we can know that the oxide formed by the tribochemical reaction at high temperature creates an anti-wear and anti-friction advantage due to its high oxidation resistance and thermal stability.[7]

4. CONCLUSION

This study compared the wear behavior of CrN, TiN, CrAlN, and TiAlN films on SKD61 against an Al 7000 series alloy for extrusion die application. For the wear test, load and temperature are the examined parameters. The friction coefficient increased with load but decreased with temperature for all the samples, which means that the wear behavior is in transition from adhesion to abrasion. The friction coefficients of the CrN and CrAlN coatings were lower than the friction coefficients of the TiN and TiAlN coatings. The wear depths were also low at high temperature, and they were lower in decreasing order ranging from CrAlN, TiAlN, CrN, to TiN. In particular, the CrAlN film showed abrasive wear for high loads and high temperature, and that type of film coating offered the lowest friction coefficient and the least wear loss. This was due to the easy formation of hard aluminum oxide in the wear track and the lower Al adhesion on that track; it was also due to the role played by the hard second phase of AlN that was dispersed in the film during deposition.

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