Characteristic of AlCrN Hard Coatings Deposited with New AIP Evaporation Source and Evaluation on Actual Mold

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Abstract

Due to the growing concern about environmental issues, the use of oilless and cold working process is increasing in mold processing, and the operating environment is becoming more challenging each year. In order to extend the service life of molds, their surfaces are coated with metal nitride using the AIP (cathodic arc deposition) method, and AlCrN coatings are often used due to the requirement for high hardness. Additionally, the properties of the coating are greatly influenced by the properties of the evaporation source used for the deposition process. This paper evaluates the properties of AlCrN coatings deposited by varying the deposition conditions and Al content using a new evaporation source (hereinafter referred to as μ-ARC) while also assessing carbide punches coated with this coating and subjected to cold forging. AlCrN coatings deposited by μ-ARC demonstrated excellent durability due to the formation of a cubic structure with a high Al content and exceptional smoothness. In addition, reciprocating sliding tests were conducted, and the mold processing test results were examined from viewpoint of tribology.

Introduction

Physical vapor deposition (PVD) is a method in which a solid metal (hereafter, target) evaporates or sublimates in a vacuum and adheres to a substrate in the same vacuum chamber as a thin-film coating. PVD has been used as a surface treatment method to impart wear resistance to products such as cutting tools and dies since the 1980s. In 1986, Kobe Steel brought the foundational technology for cathodic arc deposition (arc ion plating, AIP), a type of PVD method, from the United States to Japan, initiating the production and sale of this equipment in Japan. The AIP method begins with an arc discharge in a vacuum chamber in which the target is the cathode. An arc spot, which has a diameter on the order of micrometers, forms on the surface of the target. Energy from the arc current concentrates at the arc spot, causing the target to evaporate and ionize and form a coating on the surface of the substrate. Introducing process gases such as nitrogen into the chamber during the process enables the formation of compound coatings (e.g., nitrides). A key characteristic of the AIP method is the extremely high ionization rate of the evaporated target material. A negative bias voltage applied to the surface of the substrate controls the ionization energy and enables the formation of a dense coating with excellent bonding properties.[1)] Since entering the PVD equipment market, Kobe Steel has focused not only on producing equipment but also improving and developing coatings to provide hard coatings suitable for cutting tools and dies. This paper introduces one of our developments in coatings for cold forging dies.

The operating environment for dies such as cold forging dies is becoming increasingly adverse. Metal nitride coatings applied via AIP are used to extend die life. These coatings must exhibit high hardness, wear resistance, and toughness alongside excellent frictional and anti-seizing properties. AlCrN coatings constitute one coating with these properties. The basic structure of AlCrN is the rock-salt cubic structure (B1) of CrN, with a mixture of CrN with Al substituted for Cr, and the cubic structure (B1) of AlN. Intrinsically, the stable phase of AlN is the hexagonal diamond structure (B4) of wurtzite, with the cubic structure being reported only under high-pressure conditions.[2), 3)] Therefore, AlCrN coatings are achieved by forming a solid solution of metastable cubic AlN within the cubic lattice of CrN. The hardness of an AlCrN coating increases approximately in proportion to the Al content. However, theoretical band parameters indicate the maximum solid solubility of AlN in the cubic structure of AlCrN to be 77 at%.[4)] Additionally, coating properties depend on the characteristics of the plasma generated by the AIP evaporation source. A challenge with conventional AIP evaporation sources is that when the Al content in AlCrN exceeds 70 at%, hexagonal AlN precipitates, reducing the hardness of the coating.[5)] As explained previously, the arc discharge in AIP causes the formation of an electron emission point called an arc spot, which is several micrometers in diameter, on the surface of the target. A current on the order of dozens of amperes (at a discharge voltage of about 30 V) flows through the arc spot, instantaneously delivering a high energy input of 10^9 W/cm^2. This instantaneously ionizes the metal and causes some of the target to be ejected as molten droplets, which adhere to the substrate as metal particles (hereafter, macroparticles). Herein lies one of the challenges associated with AIP, as these droplets increase the surface roughness of the coating. To solve this issue, Kobe Steel developed a new AIP evaporation source, μ-ARC, in 2022. We confirmed that it can form AlCrN coatings that exhibit high hardness even with an Al content above 70 at% and that have fewer macroparticles than coatings produced by conventional AIP evaporation sources.[6)] This paper reports on our findings from investigating the effects of Al content and coating conditions on the properties of AlCrN coatings applied using μ-ARC. We produced AlCrN-coated cold forging dies based on our findings and compared performance with coatings applied using a conventional AIP evaporation source. We also evaluated the dies in terms of reciprocating sliding friction tests conducted under conditions simulating the actual environment in which the dies are used.

1. Experimental method

1.1 Coating method

AlCrN coatings were applied using an AlCr target produced by powder metallurgy. **Table 1** shows the test conditions. **Figs. 1** and **2**, respectively, show diagrams of the coating process using the conventional AIP evaporation source Super Fine Cathode 2 (hereafter, SFC2) and the new AIP evaporation source μ-ARC. With the conventional AIP evaporation source SFC2, when the target metal evaporates and ionized particles are deposited onto the substrate, macroparticles emitted from the target also adhere to the substrate. The μ-ARC source, however, has a cylindrical neck between the target and substrate and an electromagnetic coil encircling this neck. With this design, the neutral macroparticles are captured before entering the neck, so only ionized particles are directed to the substrate by the magnetic field.

1.2 Analysis of coating composition

We measured the average composition of the metal elements in the AlCrN coating using an energy-dispersive X-ray spectrometer (EDS) (detector: C3400 x-act, Oxford Instruments; analysis software: INCA) on a scanning electron microscope (SEM) (S-3400N, Hitachi High-Tech Corporation), with an electron beam accelerating voltage of 15 kV.

Table 1 Coating conditions

Evaporation source	New model (μ-ARC) Conventional model (SFC2)
Target composition	Al70at%-Cr30at% Al75at%-Cr25at% Al80at%-Cr20at%
Arc discharge current (A)	150
Process gas	Nitrogen
Gas pressure (Pa)	4
Substrate bias voltage (−V)	75, 100, 125, 150
Substrate temperature (℃)	500
Substrate	Solid carbide coupon
Coating thickness (μm)	4

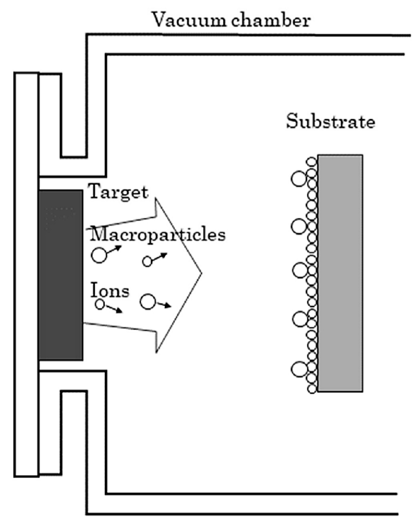


Fig. 1 Schematic diagram of coating process by SFC2

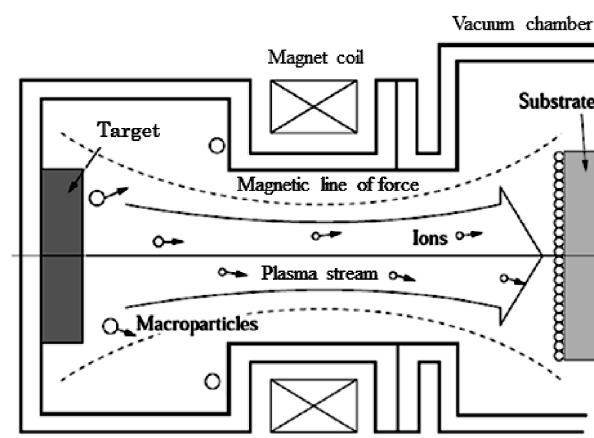


Fig. 2 Schematic diagram of coating process by μ-ARC

1.3 Surface roughness of the coating

We measured surface roughness using a combination surface roughness and contour measuring machine (Surfcom NEX, Tokyo Seimitsu Co., Ltd.) in accordance with JIS B 0601 (2001).

1.4 Hardness and Young's modulus of the coating

We measured hardness and Young's modulus using a nanoindentation tester (ENT-1100b, Elionix

Inc.). Measurements were performed using a Berkovich indenter at a loading rate of 1 mN/s and a maximum load of 10 mN. Fused quartz was used as the standard sample, and analysis was performed with indenter tip correction using the Oliver-Pharr method.[7)]

1.5 Analysis of the crystalline structure via X-ray diffraction (XRD)

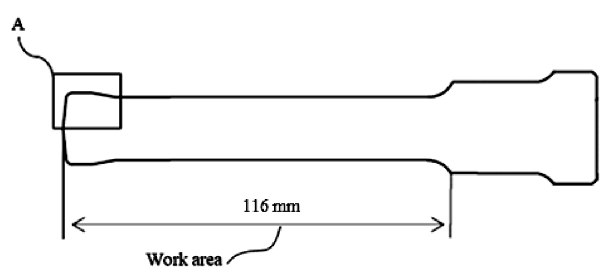
We analyzed the crystalline structure of the coating using an X-ray diffractometer (SmartLab, Rigaku Holdings Corporation). Measurements were conducted using a Cu Kα source at an output of 40 kV, 40 mA, with a $2\theta/\theta$ scanning axis and a sampling width of 0.01°.

1.6 Testing the cold forging dies

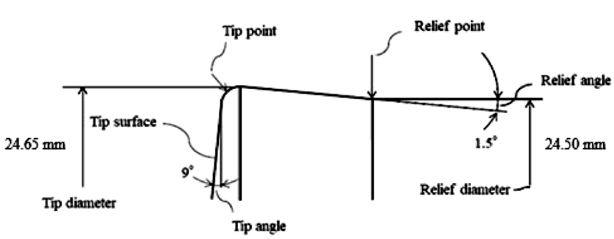
The punches for the dies were made of cemented carbide equivalent to VC30 per the CIS standard (CIS019D classification). The cemented carbide was ground and cut to yield the test punch shape shown in **Fig. 3**. After machining, the surface of the functional section ("Work area" in Fig. 3(a)) was mirror-polished to achieve surface roughness values of Ra of 0.03 μm or less and Rz of 0.3 μm or less. We then coated the samples using the SFC2 and Kobe Steel μ-ARC evaporation sources. The metal particles (droplets) adhering to the surface of the coating were removed by blasting to prepare the punches for testing. **Table 2** shows the cold forging test conditions. **Figs. 4**(a) and (b), respectively, show a schematic and an image of the 6-stage cold forging former used for the test.

1.7 Reciprocating sliding friction tests

We performed reciprocating sliding friction tests using a reciprocating tribometer (RTF-070, TPR Trading Co., Ltd.) under the conditions in **Table 3** and **Fig. 5**. According to forging simulations, the highest surface pressure load on the cemented carbide punch, which is at the tip radius, is 1,380 MPa. Therefore, the pin shape was designed such that the load on the tip of the pin during the sliding friction test corresponded to this value. The pins used for the sliding friction test were made from the same material as the cemented carbide punches used in the forging test. The pins for the sliding friction test were coated with AlCrN using a target with 70 at% Al via SFC2 and μ-ARC. The pins were blasted before testing to remove metal particles adhering to the coating surface. These test pins were then subjected to sliding friction testing.



(a) Schematic shape of cold forging punch

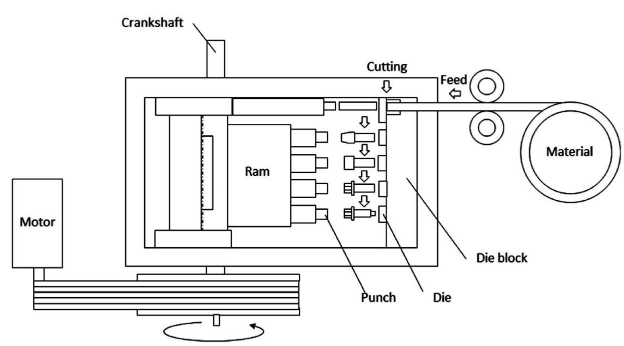


(b) Details of "A" in (a)

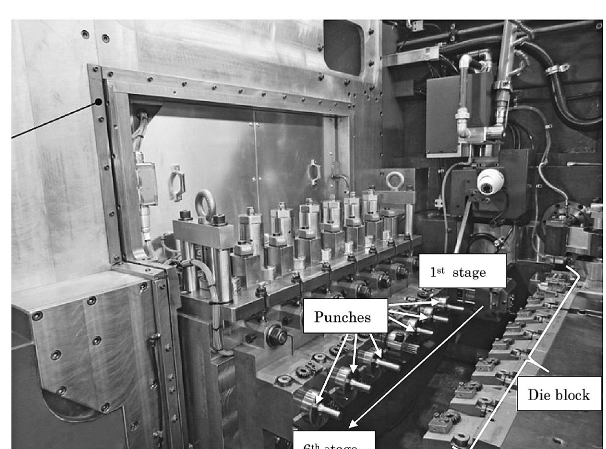
Fig. 3 Cold forging punch

Table 2 Cold forging test conditions

Cold forging former	BPF-680SSL (Six-stage former)
Stage	Second stage
Forging method	Forward extrusion process
Drawing depth (mm)	110
Reduction of area (%)	50 to 65
Work material	SCM440
Lubricant	Forging oil
Shot number	7,000



(a) Schematic diagram of cold forging former



(b) Cold forging six stage former (BPF-680SSL)

Fig. 4 Cold forging former

Table 3 Reciprocating sliding test conditions

Load (N)	1,000 (Pmax 1,380 MPa)
Sliding speed (m/second)	0.5
Sliding length (mm/sliding)	50
Lubricant	Oil
Reciprocating sliding number	50,000
Replacement frequency of counter material	2,000 reciprocating
Pin material	Solid carbide
Counter material	SUJ2

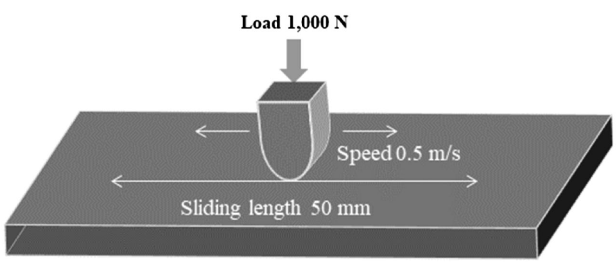


Fig. 5 Schematic diagram of reciprocating sliding test

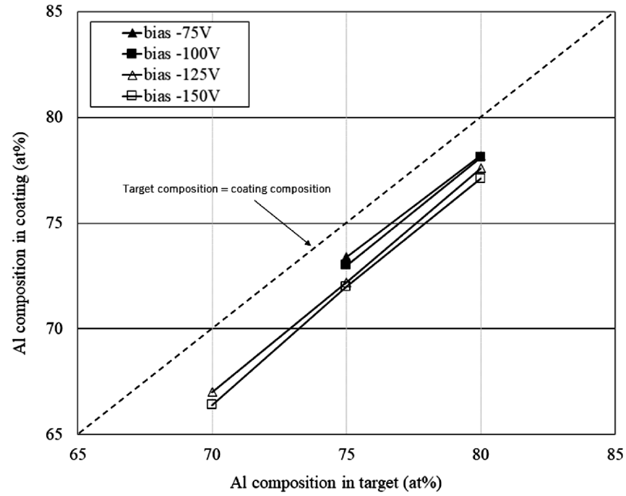


Fig. 6 Relationship between Al composition in target and Al composition in coating

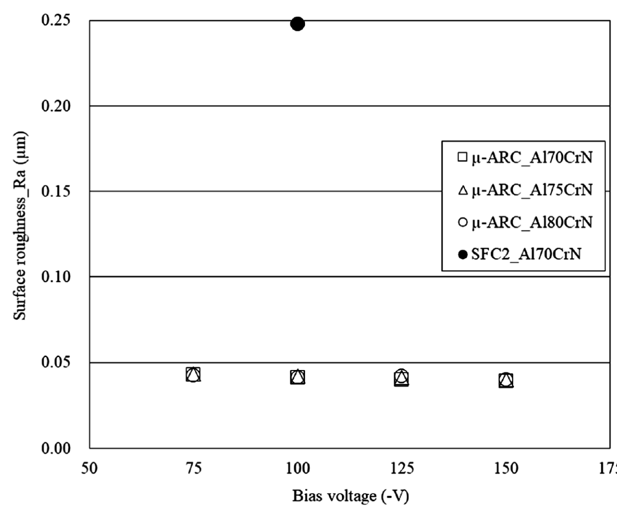


Fig. 7 Relationship between bias voltage and surface roughness

2. Results and discussion

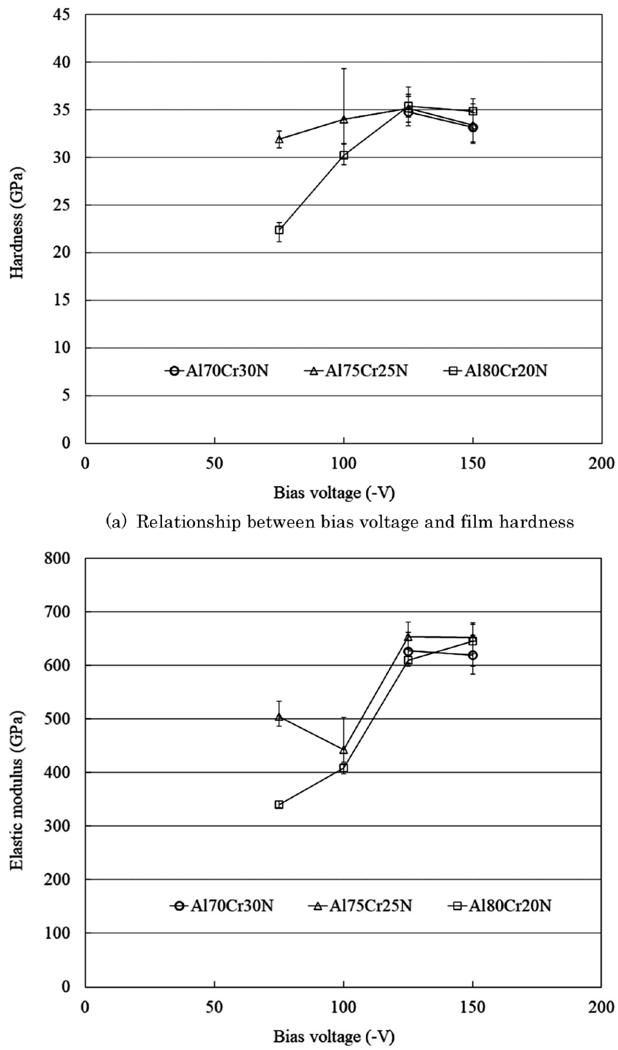
2.1 Coating composition and surface roughness

Fig. 6 shows the results of the SEM/EDS (scanning electron microscopy/energy dispersive spectroscopy) analysis to determine coating composition. In all samples, the Al composition in the coating was 2 to 3 at% below the Al composition in the target. Furthermore, comparing samples coated using targets of the same composition shows that samples coated at higher bias voltages have a lower Al content. As explained above, AIP is characterized by a high ionization rate of the deposited atoms. This is presumed to be due to the acceleration of ions by the negative bias applied to the substrate, causing partial sputtering of the coating. It is further hypothesized that the Al atoms, which are lighter than Cr atoms, are preferentially sputtered from the coating, reducing the Al composition of the coating.

Fig. 7 shows the results of the surface roughness measurements. There are no significant differences among the samples coated via μ-ARC. Al has a melting point of 660℃, which is relatively low among the metals. Therefore, some of the metal is readily released as molten droplets during arc discharge. These droplets adhere to the substrate, which tends to increase surface roughness. However, as described above, the physical structure of the μ-ARC system and its characteristic magnetic field enable this technology to form coatings with minimal droplets.[8] As such, our research demonstrates that μ-ARC can maintain low surface roughness even when using a target with a high Al content, which otherwise tends to result in high surface roughness, such as with the Al70CrN coating applied via SFC2.

2.2 Mechanical properties and crystalline structure of the coating

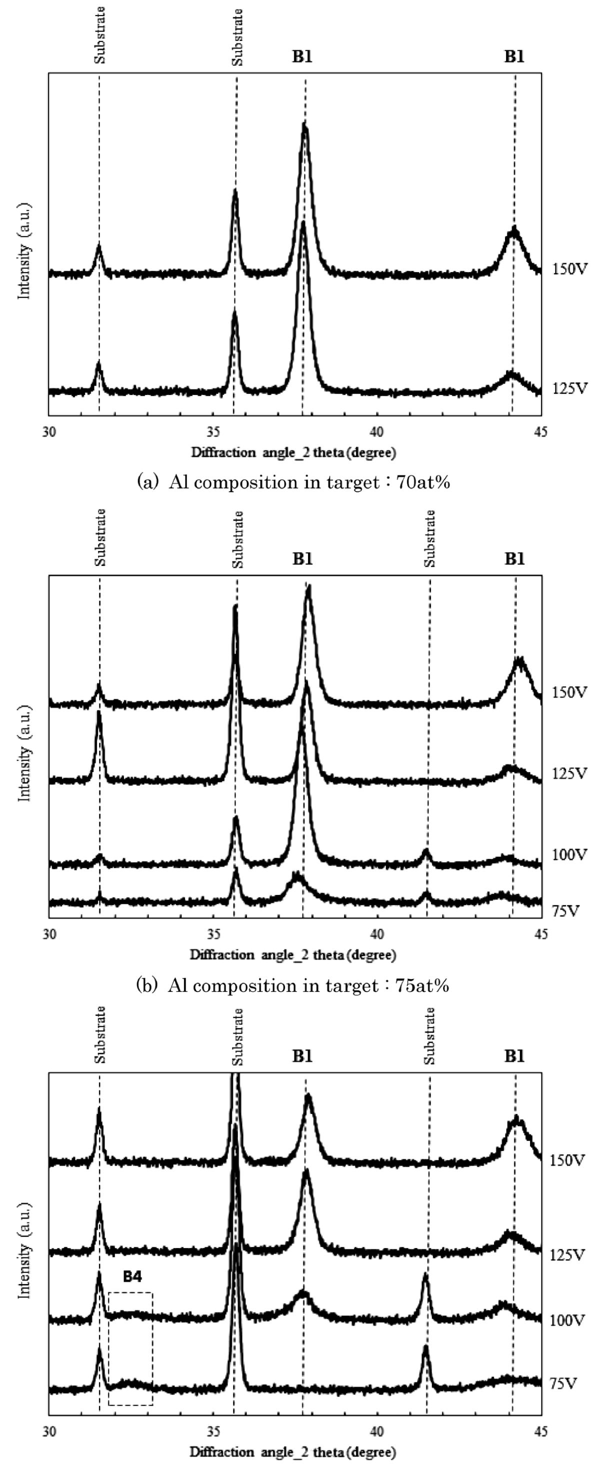
Fig. 8 shows the coating hardness and Young's modulus as measured by nanoindentation testing. Samples with higher bias voltages tended to exhibit higher values for both hardness and Young's modulus. However, there were no significant differences in these properties for bias voltages of 125 V and 150 V. Samples produced from a target with an Al content of 80 at% exhibited a lower hardness and Young's modulus at the lower bias voltages of 75 V and 100 V. This suggests that due to insufficient ion irradiation energy during coating,



(a) Relationship between bias voltage and film hardness

(b) Relationship between bias voltage and elastic modulus

Fig. 8 Relationship between bias voltage and mechanical properties for each AlCrN coating



(a) Al composition in target : 70at%

(b) Al composition in target : 75at%

(c) Al composition in target : 80at%

Fig. 9 Relationship between bias voltage and AlCrN crystal structure

AlN with a metastable cubic structure (B1) did not form a solid solution within the crystalline CrN, and instead, soft AlN with a stable hexagonal structure (B4) precipitated.

Fig. 9 shows the results of the crystalline structure analysis via XRD. Among the samples produced using a target with an Al content of 80 at% at bias voltages of 75 V and 100 V, there were peaks originating from the cubic structure (B1) of CrN around 38° and 44° and from the hexagonal structure (B4) around 33°. This indicates that hexagonal AlN precipitated in the cubic CrN in these samples, supporting the aforementioned theory regarding a reduction in coating hardness. All other samples were single-phase cubic crystals. These results show that by using μ-ARC and applying a bias voltage above a certain value, it is possible to form a solid solution of cubic AlN in AlCrN up to the theoretical upper limit of 77 at%.

2.3 Cold forging tests of AlCrN-coated cemented carbide punches

Previous testing confirms that when applying AlCrN using μ-ARC, a bias voltage of at least 125 V enables the formation of cubic AlCrN if the Al content of the target is 70 at% to 80 at%. Conversely, when using SFC2, coating hardness decreases due to the precipitation of hexagonal AlN when the Al content exceeds 70 at%.[9] Therefore, for this test, we used an AlCr target with 70at% Al, which can form cubic AlCrN with both μ-ARC and SFC2. The bias voltage and coating duration were adjusted to yield AlCrN-coated samples with a hardness of approximately 35 GPa and a coating thickness of 5 μm for each evaporation source. The coated cemented carbide punches were blasted before testing by means of up to 7,000 cold forging shots. Imaging of the edge of the punch tip after testing was performed at angles of 0°, 90°, 180°, and 270°, as shown in **Fig.10**. **Fig.11** shows the width of exposed substrate and imaging of the punch after the 7,000-shot forging test. As shown in Fig.11(a), the coating on the punch coated with SFC2 was gone after 7,000 shots, exposing the substrate. By contrast, the surface of the coating on the punch coated with μ-ARC (Fig.11(b)) was only slightly scratched, with no substrate exposure. These results indicate that using μ-ARC to apply an AlCrN coating to cemented carbide punches for cold forging extends punch life.

Next, we conducted reciprocating sliding friction tests simulating the test environment to analyze the results of the cold forging tests. **Fig.12** shows SEM images of the pin surfaces after coating, after blasting, and after the sliding friction test. As shown in Fig.12(a), the coating applied via SFC2 has a rough surface with numerous adhered metal particles, whereas the coating applied via μ-ARC has a smooth surface and fewer adhered metal particles. Fig.12(b) compares the samples after blasting to remove metal particles from the surface. Although the metal particles were removed from the surface of both samples, the sample coated via SFC2 exhibits the formation of numerous small dimples where the metal particles were removed. Fig.12(c) compares the surfaces of the samples after the sliding friction test. The coating applied using μ-ARC shows absolutely no change in surface characteristics. Conversely, the coating applied using SFC2 has filler material in the dimples from before the test. **Fig.13** shows the results of SEM/EDS analysis of this area, which shows that the filler material contains oxygen, chromium, and iron, corresponding to the worn and oxidized counter material. This indicates that the worn counter material was rubbed into and filled the dimples during sliding. Based on the results of this sliding friction test, we surmise that the process of the wear mechanism of the coating on the cold forging die is as shown in **Fig.14**. Step 1 represents the state immediately after coating via SFC2. There are many metal particles on and in the surface of the coating. Since the surface roughness of a die has an effect on its performance, coated dies are polished before use to remove these particles, causing the formation of numerous dimples in the surface of the

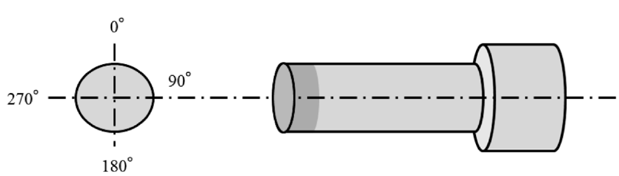
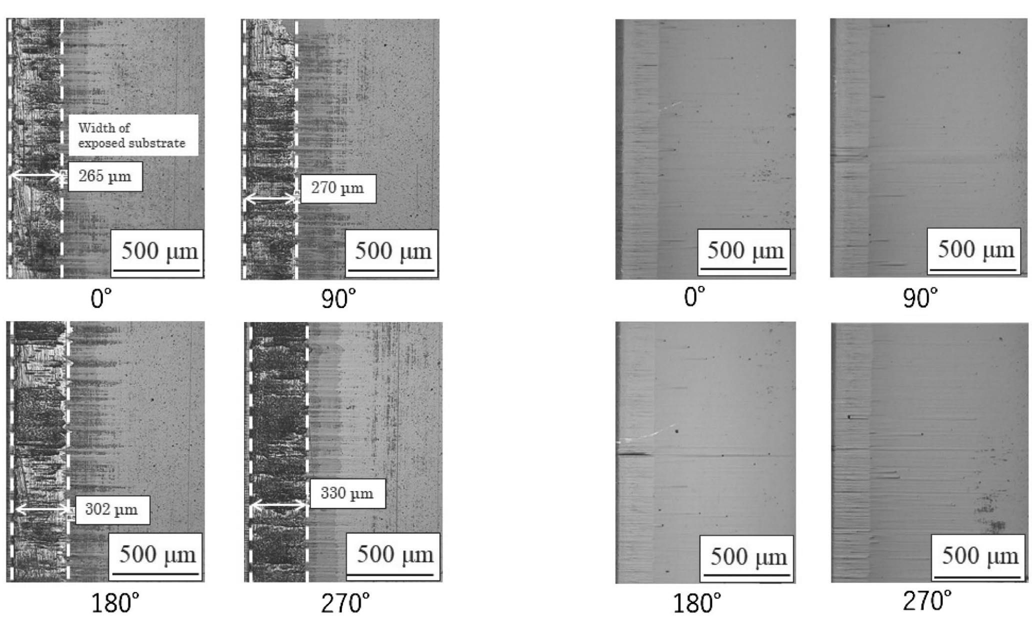


Fig.10 Observation angle of punch after forging test



(a) Edge of tip of punch (with Al composition in target : 70 at%) coated by SFC2 after forging test

(b) Edge of tip of punch (with Al composition in target : 70 at%) coated by μ-ARC after forging test

Fig.11 Images of edge of tip of punch with Al70Cr30 coated by μ-ARC and SFC2 after forging test coating (Step 2). When this die is used, oxidized iron from the workpiece fills the dimples (Step 3). The workpiece comes into contact with the workpiece material embedded in the coating surface, and adhesion occurs due to the high load of processing (Step 4). As the workpiece slides horizontally across the surface of the coating, it pulls the mating surface layer of the coating in the same direction.

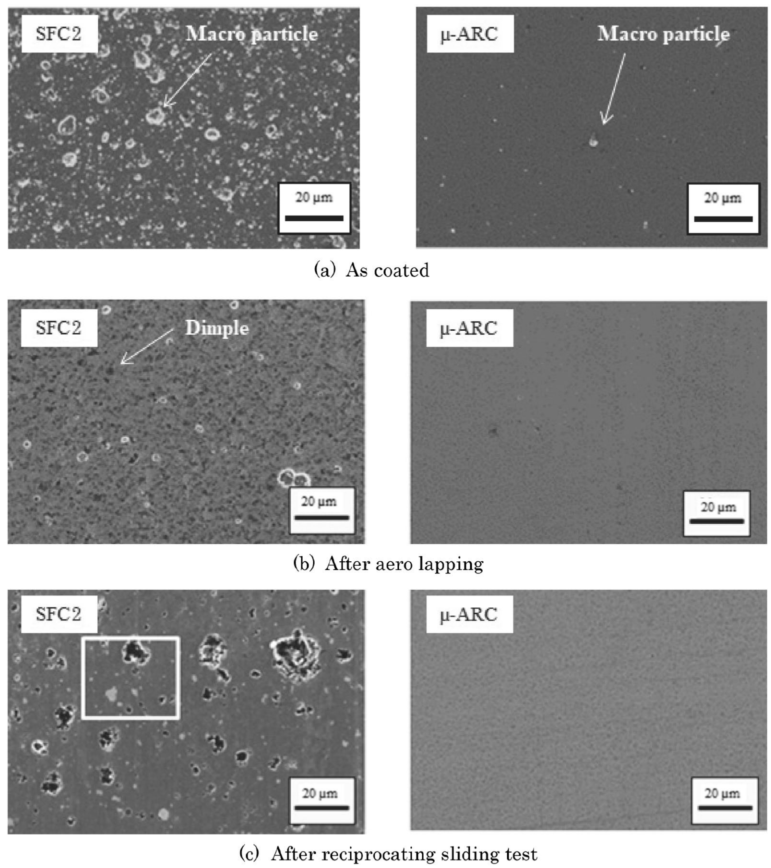


Fig.12 Surface properties for before/after polishing and after sliding test

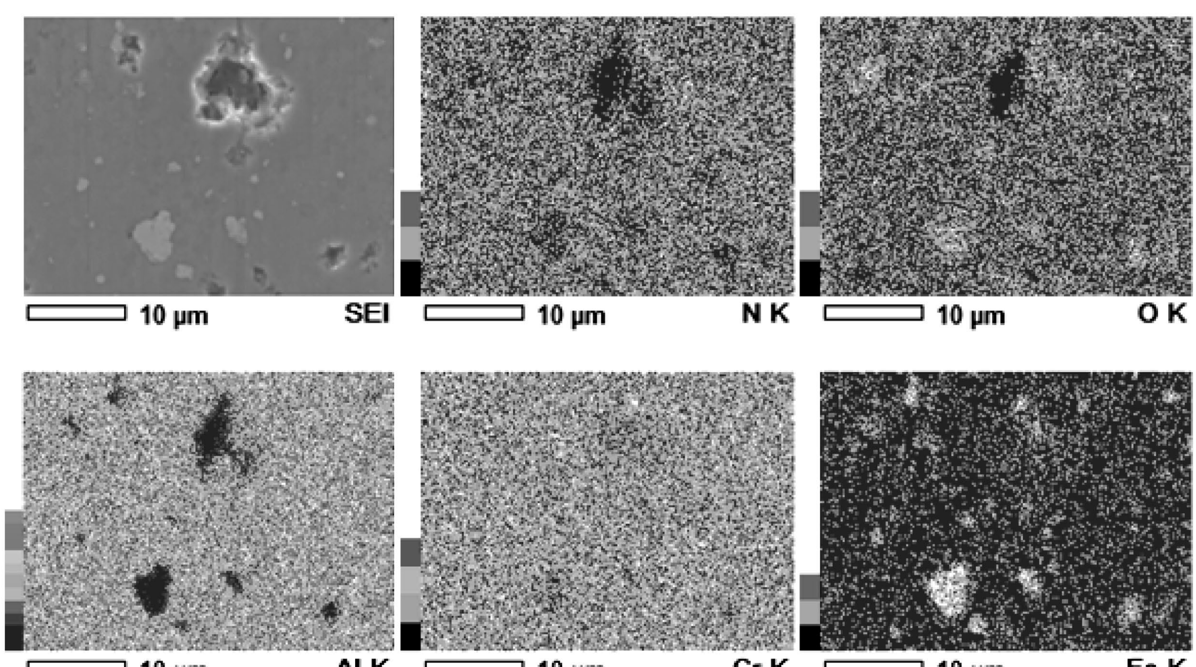


Fig.13 Elemental mapping of SFC2 coating after sliding test using SEM-EDS

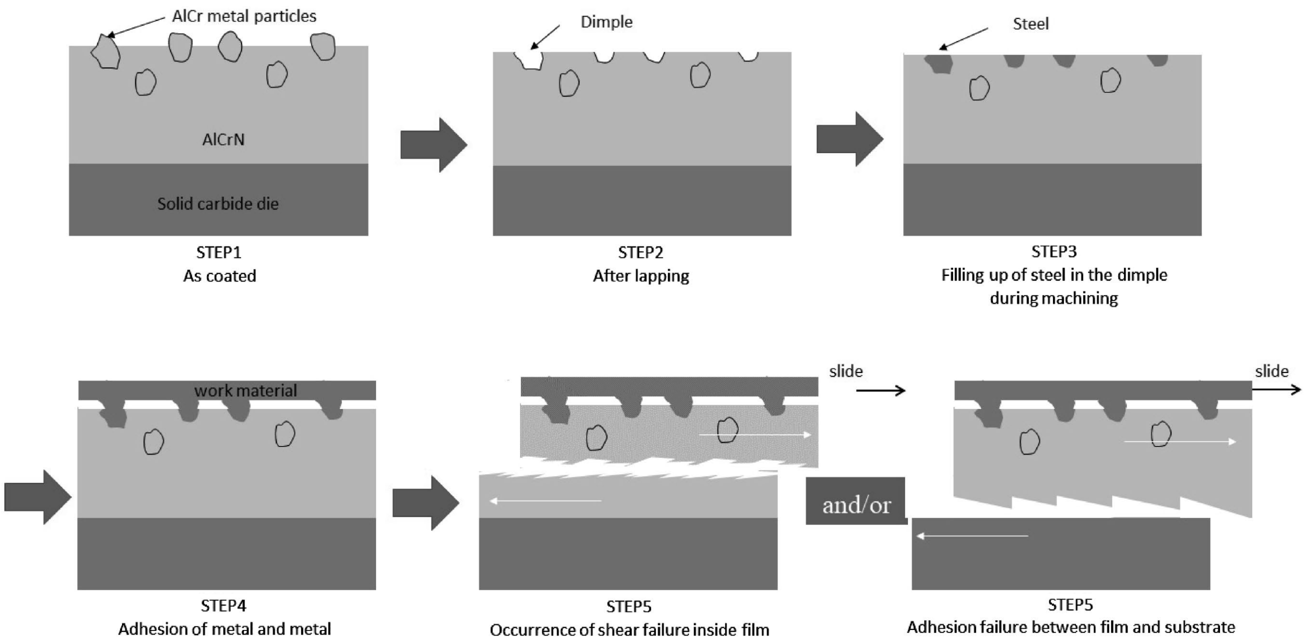


Fig.14 Coating wear mechanism for cold forging process

This creates a shear force within the coating in the opposite direction, resulting in fracture either within the coating or at the interface, wherever mechanical strength is lower (Step 5).

Based on the results of the sliding friction tests, we surmise that the forging test caused shear fracture within the coating, originating from the droplets in the coating as described previously, and delamination at the substrate/coating interface. Therefore, since the AlCrN has fewer droplets when formed by μ-ARC as opposed to SFC2, this technology is hypothesized to extend the service life of dies.

Conclusions

We used Kobe Steel's new AIP evaporation source, μ-ARC, to produce AlCrN coatings with varying concentrations of Al. Our findings from investigating the effects of target composition and bias voltage on coating properties and crystalline structure are as follows:

The Al content in the target has no effect on the surface roughness of the AlCrN coating. We hypothesize that this is because the structure characteristic to the μ-ARC evaporation source eliminates droplets.

Applying a bias voltage of at least 125 V during coating enables the solid solution of cubic AlN in AlCrN up to the theoretical upper limit of 77 at%.

Furthermore, we used SFC2 and μ-ARC to coat cold forging dies with a target containing 70 at% Al and then compared die performance. Our findings from the reciprocating sliding friction tests simulating die testing conditions are as follows:

Using μ-ARC technology, cold forging dies coated with AlCrN using a target with an Al content of 70 at% could be used for continuous processing without exposing the substrate, yielding a longer lifespan compared with coatings applied by SFC2.

AlCrN coatings applied by μ-ARC are characterized by fewer droplets on the surface and within the coating, which is believed to have a positive effect on the service life of the die.

References

1) A. Anders, Cathodic Arcs, Springer. 2008.
2) P. Van Camp et al. Physical Review B. 1991, Vol.44, p.9056.
3) M. Ueno et al. Physical Review B. 1992, Vol.45, p.10123.
4) Y. Makino. Materia Japan. 1997, Vol.36, No.10, p.996.
5) J. Vetter et al. Coatings. 2021, Vol.11, No.3, p.344.
6) M. Nakamura. Journal of The Surface Finishing Society of Japan. 2024, Vol.75, No.7, p.314.
7) W. Oliver et al. Journal of Materials Research. 1992, Vol.7, No.6, pp.1564-1583.
8) K. Takahara et al. R&D Kobe Steel Engineering Reports. 2000, Vol.50, No.2, p.53.
9) R. Takei et al. ICMCTF 2024, G3-WeM-2.