Effect of Axisymmetric Magnetic Field on Properties of TiN-Cu Nanocomposite Films Deposited by Arc Ion Plating: Postprint

Authors: Song Guihong, Xiao Jinquan, Du Hao, Chen Lijia

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Abstract

An axisymmetric coil magnetic field was applied behind the arc ion plating target to prepare TiN-Cu nanocomposite films. The effects of coil magnetic field strength on the movement velocity of arc spots on the target surface and arc column shape, as well as its influence on the surface morphology, deposition rate, nanoindentation hardness, and elastic modulus of the deposited films were investigated. The results show that increasing the coil magnetic field strength can enhance the movement velocity of arc spots, thereby reducing the ejection probability of metal droplets from the target surface and decreasing the size and quantity of macroparticles in the deposited films. X-ray diffraction (XRD) patterns reveal that the deposited films contain only the TiN phase, with no diffraction peaks of metallic Cu or its compounds detected; the films exhibit a pronounced (111) crystallographic plane preferred orientation. With increasing coil magnetic field strength, the film deposition rate, indentation hardness, and elastic modulus initially increase, reaching maximum values before decreasing slightly; the maximum hardness and elastic modulus reach 35.46 GPa and 487.61 GPa, respectively.

Full Text

Influence of Axisymmetric Magnetic Field on Properties of TiN-Cu Nanocomposite Films Prepared by Arc Ion Plating

SONG Guihong[1], **XIAO Jinquan**[2], **DU Hao**[2], **CHEN Lijia**[1]

[1] School of Material Science and Technology, Shenyang University of Technology, Shenyang 110870, China
[2] Division of Surface Engineering of Materials, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

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To whom correspondence should be addressed:
Tel: 13898829530, E-mail: ghsongsut@126.com

Abstract

TiN-Cu nanocomposite films were deposited on high-speed steel substrates by arc ion plating with an axisymmetric coil magnetic field positioned at the back of the target. The influence of coil magnetic field intensity on the moving rate of cathode spots and arc column shape on the target surface, as well as on the surface morphology, deposition rate, nanoindentation hardness, and elastic modulus of the deposited films was investigated. The results show that increasing the coil magnetic field intensity enhances the moving rate of arc spots, which reduces the emission probability of molten metal droplets from the target surface and decreases both the size and quantity of macroparticles in the deposited films. X-ray diffraction (XRD) analysis reveals that the deposited films contain only the TiN phase, with no diffraction peaks corresponding to metallic Cu or its compounds, and exhibit a pronounced preferred orientation along the (111) crystal plane. As the coil magnetic field intensity increases, the deposition rate, indentation hardness, and elastic modulus of the films initially increase, reach maximum values, and then decrease slightly. The maximum hardness and elastic modulus achieved are 35.46 GPa and 487.61 GPa, respectively.

KEY WORDS composites, TiN-Cu nanocomposite film, hardness, arc ion plating, magnetic field intensity, macroparticle, deposition rate

Introduction

Nanocomposite films have attracted considerable attention from materials researchers due to their ultra-hard characteristics and other excellent properties. These films can be divided into two categories: one composed of crystalline MeN and hard phases such as amorphous Si_3N_4 and TiB_2 [1,2], and the other composed of crystalline MeN and soft phases such as Cu, Ni, and Ag, where Me represents transition metal elements including Ti, W, Zr, Cr, Mo, and Nb [3-5]. The second type of nanocomposite film, consisting of hard transition metal nitrides and soft metallic phases, exhibits not only high hardness but also enhanced toughness, which reduces the brittle fracture tendency and significantly improves wear resistance, making these films commercially promising.

Arc ion plating offers high ionization rates, strong film-substrate adhesion, and rapid deposition, making it widely used for surface strengthening of cutting tools and dies to enhance their performance and service life. The fundamental principle of arc ion plating relies on low-pressure cathodic arc discharge, which produces moving arc spots on the target surface. Although cathode spots are very small, their power density is extremely high, resulting in intense emission of electrons, atoms, and ions (evaporation) along the spot path, accompanied by continuous ejection of molten metal droplets or solid particles. These droplets and particles, which become incorporated into the deposited film, appear as macroparticles under electron microscopy and represent an unavoidable feature of arc ion plating that adversely affects film properties.

To maintain stable arc discharge on the target surface, in addition to applying a high-current, low-voltage electric field between the target and chamber, permanent magnets are typically placed behind the target to confine the arc spots within a moving region through magnetic field effects. Meanwhile, atoms evaporated from the target surface undergo electron collisions and ionization under electromagnetic field action, achieving ionization rates of 80-90%. Studies [6-8] have shown that the axial magnetic field intensity (perpendicular to the target surface) can control the moving area of arc spots, with increased field intensity enlarging this area. In conventional equipment, small adjustments to the distance between permanent magnets and the target enable arc discharge across the entire target surface. The transverse magnetic field intensity (parallel to the target surface) controls the moving rate of arc spots. Higher spot moving rates reduce the probability of molten metal droplet and solid particle ejection from the target surface. Therefore, adjusting the transverse magnetic field intensity can control the spot moving rate and consequently the ejection probability of droplets or particles. Higher transverse field intensity yields greater spot moving rates and reduces both the size and ejection probability of molten droplets or solid particles, resulting in fewer and smaller macroparticles in the deposited films.

For convenience, current arc ion plating equipment typically uses permanent magnets installed behind the target to control the arc spot moving area. However, this approach has several drawbacks: magnetic field intensity is not easily adjustable, the transverse magnetic component is too small, permanent magnets are prone to demagnetization under prolonged exposure to magnetic fields generated by arc spots, and magnets immersed in ordinary cooling water for extended periods adsorb large amounts of corrosion products that clog the magnetic circuit. Additionally, magnetic fields influence charged particle motion beyond just controlling arc spot movement. When a charged particle moves with velocity $\mathbf{V}$ in a uniform magnetic field $\mathbf{B}$, it experiences a Lorentz force $\mathbf{F} = q\mathbf{V} \times \mathbf{B}$, where q is the particle charge. Charged particles undergo circular motion in the direction perpendicular to the magnetic field, with stronger fields producing smaller radii, effectively confining the particles and preventing divergence. When a constant electric field $\mathbf{E}$ is additionally introduced, the particle trajectory becomes a composite of circular motion and drift motion.

Therefore, introducing both magnetic and electric fields between the target and substrate can confine ions in the gas-phase plasma formed by arc discharge, significantly reducing ion divergence probability. This is highly beneficial for achieving uniform film thickness and deposition on complex three-dimensional surfaces. Compared with Ti targets, Ti-Cu targets are more prone to generating macroparticles during film preparation. In this study, a variable-intensity coil magnetic field was installed at the back of the target while maintaining a constant pulse negative bias of 100 V, introducing the magnetic field between the target and substrate. By varying the coil magnetic field intensity to control arc spot movement on the target surface and focus the ion flux between target and substrate, we investigated the effects of magnetic field intensity on the microstructure and properties of deposited films.

Experimental

High-speed steel was used as the substrate material, cut into rectangular specimens measuring 20 mm × 15 mm × 3 mm. The specimens underwent mechanical grinding, polishing, and shot peening, followed by ultrasonic cleaning in anhydrous ethanol, blow-drying, and placement in the deposition chamber.

A MIP-8-800 arc ion plating system was employed for film deposition. The working gases were 99.99% pure argon and 99.99% pure nitrogen. TiN-Cu films were deposited using a powder-sintered Ti-Cu alloy target containing 5.0 at% Cu. Prior to deposition, the chamber was evacuated to 6.7×10^{-3} Pa. Argon gas was then introduced at a flow rate of 54 mL/min, maintaining a chamber pressure of 0.6 Pa. Substrate cleaning was performed for 3-4 minutes under the following conditions: arc current 60 A, arc voltage 20 V, pulse bias -800 V, duty cycle 40%, and frequency 52 kHz.

During deposition, only nitrogen gas was introduced at a flow rate of 65 mL/min, maintaining the chamber pressure at 0.6 Pa. The arc current and voltage remained unchanged from the cleaning step, while the pulse bias was set to -100 V with a duty cycle of 20% and the same frequency. The deposition time was 60 minutes. The target-to-substrate distance was 240 mm. A magnetic field coil was positioned behind the target with a coil-to-target distance of 150 mm, as shown in [Figure 1: see original paper]. The applied coil currents were 0, 1.0, 1.5, and 2.0 A, corresponding to magnetic field intensities of 0, 472, 681, and 885 Gs measured at the coil top core, and 14, 48, 54, 59, and 65 Gs at the center of the target surface. When the coil current was zero, the magnetic field at the target center originated from the permanent magnet behind the target. With applied coil current, the magnetic field at the target center was slightly higher than at the periphery of the 30 mm radius circular target, with a difference of approximately 5 Gs.

The surface morphology and cross-sections of deposited films were examined using an S-3400 scanning electron microscope. X-ray diffraction patterns were obtained with an XRD7000 diffractometer. The arc spot and arc column states were photographed with a conventional Canon camera. Film hardness and elastic modulus were measured using an MTS XP nanoindenter.

2.1 Arc Spot and Arc Column Under Magnetic Field

[Figure 2: see original paper] compares the movement of arc spots on the metal target surface with and without the coil magnetic field. Without the coil magnetic field, the target surface exhibits an irregular, randomly moving rope-like bright arc spot. With the applied coil magnetic field, the target surface shows bright spots covering the entire target area. The arc spot moving rate is relatively low without the coil magnetic field, and within the camera exposure time, the spot trajectory appears as an irregular rope-like curve. When the coil magnetic field is applied, the arc spot moving rate increases significantly, and the spot trajectory covers the entire target surface within the camera exposure time, resembling an electron cloud formed by electrons moving around an atomic nucleus. Rapid movement of arc spots reduces the residence time at any particular location on the target surface, thereby decreasing the probability of molten metal droplet or solid particle ejection.

[Figure 3: see original paper] shows the arc column shape observed from the side of the target with and without the coil magnetic field. Without the coil magnetic field, the arc column appears relatively divergent, whereas with the applied coil magnetic field, the arc column becomes more convergent with an elongated central column. The accelerated arc spot movement and convergent, elongated arc column influence the surface morphology, microstructure, and properties of the deposited films.

2.2 Surface Morphology and Cross-Section of Deposited Films

[Figure 4: see original paper] presents the surface morphology of TiN-Cu films deposited under different magnetic field intensities at a bias voltage of 100 V. The film surfaces contain white particles of various sizes, which result from condensation of molten metal droplets ejected from the target surface during arc ion plating. A coil magnetic field installed behind the target was used to modify the magnetic field distribution and reduce the size and quantity of these droplets. Within the magnetic field intensity range of 0-885 Gs, increasing the field intensity reduces both the size and number of white particles, although some large particles remain even at the maximum field intensity of 885 Gs. This result is consistent with literature [6].

Energy-dispersive spectroscopy analysis of the films reveals Cu contents of 2.74%, 2.55%, 1.88%, and 1.86% at magnetic field intensities of 0, 472, 681, and 885 Gs, respectively, indicating a decreasing trend in Cu content with increasing coil magnetic field intensity. Higher coil magnetic field intensity enhances ion confinement in the deposition environment, increasing the number of ions reaching the substrate surface per unit time. Since Cu is more easily sputtered than Ti, increased coil magnetic field intensity leads to greater sputtering of Cu atoms from the film surface, similar to the effect of increasing substrate bias [9]. However, overall, the Cu content variation in the deposited films is relatively small within the studied magnetic field intensity range, though it may still influence film properties.

[Figure 5: see original paper] shows the thickness of films deposited under different coil magnetic field intensities. Without a magnetic field, the film thickness after 60 minutes of deposition is 3.3 µm, while at field intensities of 472, 681, and 885 Gs, the film thicknesses are 3.7, 8.5, and 5.2 µm, respectively. These results demonstrate that the applied coil magnetic field increases film thickness, but the degree of enhancement depends strongly on the field intensity. The thickness increase is minimal when the field intensity rises from 0 to 472 Gs, but increases dramatically to 8.5 µm at 681 Gs. Further increasing the field intensity leads to a slight thickness reduction.

The coil magnetic field installed behind the target creates an axial magnetic field between the target and substrate. When a portion of this magnetic field is not parallel to the ion motion direction, it constrains ion movement, focusing the ion flux and reducing the number of divergent ions. Combined with the pulsed substrate negative bias, the electric and magnetic fields work together to decrease ion divergence probability, increasing the number of ions reaching the substrate surface per unit time. Consequently, film thickness increases, and more uniform thickness can be achieved on three-dimensional surfaces. However, excessively high magnetic field intensity produces overly strong focusing effects, and the back-sputtering effect from ion bombardment during film growth becomes significant, causing a slight reduction in film thickness. Additionally, [Figure 5c: see original paper] reveals a distinct transition layer between the film and substrate.

2.3 XRD Patterns of Deposited Films

[Figure 6: see original paper] shows the XRD patterns of films deposited under different magnetic field intensities. The films contain only the TiN phase, with no diffraction peaks corresponding to metallic Cu or Cu compounds. In TiN-Cu films, Cu may exist in an amorphous state or as very fine crystalline particles segregated at TiN grain boundaries or dispersed within the TiN crystal structure, making them undetectable by X-ray diffraction [10,11]. In standard TiN powder diffraction data, the (111) peak intensity is 72% of the (200) peak intensity. In all films deposited in this study, the (111) diffraction peak intensity exceeds that of the (200) peak, indicating a clear preferred orientation (texture) along the (111) crystal plane, with the degree of preferred orientation depending on the applied magnetic field intensity.

According to literature [12], the degree of preferred orientation (texture coefficient) is given by:

$$T(hkl) = \frac{I(hkl)/I_0(hkl)}{\frac{1}{n}\sum[I(hkl)/I_0(hkl)]}$$

where $I(hkl)$ is the integrated intensity of the (hkl) diffraction peak for the deposited film, $I_0(hkl)$ is the integrated intensity of the (hkl) peak for standard powder, and n is the number of diffraction peaks. A $T(hkl)$ value of 1 indicates no preferred orientation, $T(hkl) > 1$ indicates preferred orientation of the (hkl) plane (with larger values indicating stronger preferred orientation), and $T(hkl) < 1$ indicates fewer columnar grains with (hkl) planes perpendicular to the surface, suggesting preferred orientation in other directions.

presents the texture coefficients for various diffraction planes of the deposited films. The texture coefficients for (111) and (222) planes significantly exceed 1, confirming a strong preferred orientation along the (111) plane. The $T(111)$ value increases gradually with coil magnetic field intensity, reaching a maximum of 2.9 at 681 Gs, then decreasing slightly with further field intensity increase. During film growth, nucleation occurs first on the substrate surface, followed by longitudinal and lateral growth. The mechanism for preferred orientation formation may involve selective growth of particle flux under strong magnetic fields, where bombardment by particles or ions allows only grains with specific orientations to grow while suppressing others through selective etching or sputtering. Without the coil magnetic field, particle flux divergence and ion collisions result in relatively fewer high-energy ions, leading to growth primarily along (111) and partial (200) planes. With the applied coil magnetic field, ion motion is strongly constrained by the electromagnetic field despite ion collisions, increasing the number of high-energy ions reaching the substrate surface per unit time. This promotes growth predominantly along the (111) plane, significantly increasing the $T(111)$ value while (200) plane growth is etched or sputtered away by high-energy ions. Excessively high magnetic field intensity produces overly strong confinement, increasing ion collision probability and energy loss, which slightly reduces the $T(111)$ value. However, changes in the $T(111)$ value may affect film hardness and elastic modulus.

2.4 Indentation Hardness and Elastic Modulus of Deposited Films

[Figure 7: see original paper] shows the relationship between applied magnetic field intensity and film indentation hardness. Without a magnetic field, the film hardness is 15.83 GPa. As the magnetic field intensity increases from 0, the film hardness gradually increases, reaching 35.46 GPa at 681 Gs, then decreasing slightly with further field intensity increase. The elastic modulus follows a similar trend, as shown in [Figure 8: see original paper].

The influence of coil magnetic field intensity on film hardness can be attributed to changes in Cu content and preferred orientation induced by the magnetic field, which in turn affect hardness values. Literature [10,11] indicates that an optimal Cu content exists in TiN-Cu nanocomposite films that maximizes hardness and modulus, though reported optimal values differ: approximately 1.5% in reference [11] and about 3% in reference [10]. In this study, a Cu content of 1.88% yields maximum hardness and elastic modulus for the prepared TiN-Cu films. Additionally, the (111) crystal plane in the TiN structure is a close-packed plane with slightly higher hardness and elastic modulus than other orientations. Furthermore, the significant reduction in macroparticle size and quantity also contributes to increased hardness and elastic modulus, though these properties are not solely determined by surface macroparticle characteristics.

The ratio of hardness (H) to elastic modulus (E) can describe a material’ s resistance to plastic deformation (toughness). [Figure 9: see original paper] shows the relationship between the H/E ratio of deposited films and applied coil magnetic field intensity. The H/E ratio increases significantly with the coil magnetic field, which is beneficial for film deformation resistance and improves wear resistance.

2.5 Discussion

The experimental results demonstrate that the coil magnetic field added behind the metal target superimposes with the existing permanent magnet field, creating an adjustable magnetic field that couples synergistically with the negative bias electric field to establish a controllable electromagnetic field between the target and substrate. To avoid affecting chamber vacuum, the coil is positioned outside the chamber behind the target, with a certain distance between the coil core and target. This arrangement significantly increases the transverse magnetic field component at the target surface, which helps accelerate arc spot movement. Between the target and substrate, the deposited ion flux undergoes helical precession under the electromagnetic field, limiting outward divergence and increasing the number of ions reaching the substrate surface. This enhances deposition efficiency and increases film thickness on three-dimensional surfaces, while also influencing film hardness and elastic modulus.

Conclusions

1. The application of a variable-intensity coil magnetic field behind the arc ion plating target increases the arc spot moving rate, reduces the number

and size of macroparticles in deposited films, and improves mechanical properties.

2. As coil magnetic field intensity increases from zero, film thickness initially increases slowly, then rises rapidly after reaching a certain value, but decreases slightly when the field intensity continues to increase beyond the point of maximum thickness.
3. With increasing coil magnetic field intensity, the hardness and elastic modulus of deposited films gradually increase, but decrease slightly after reaching an optimal value.

References

1. G. Ramírez, D. Oezer, M. Rivera, S.E. Rodil, R. Sanjinés, TaSiN nanocomposite thin films: Correlation between structure, chemical composition, and physical properties, Thin Solid Films, 558, 104 (2014).
2. J. Shi, C. M. Muders, A. Kumar, X. Jiang, Z.L. Pei, J. Gong, C. Sun, Study on nanocomposite Ti-Al-Si-Cu-N films with various Si contents deposited by cathodic vacuum arc ion plating, Applied Surface Science, 258, 9642 (2012).
3. J. H. Hsieh, M. K. Cheng, C. Li, S. H. Chen, Y. G. Chang, Study of Cu emergence on the surface of TaN-Cu nanocomposite thin films and its effects on tribological property, Thin Solid Films, 516, 5430 (2008).
4. Mukesh Kumar, R. Mitra, Effect of substrate bias on microstructure and properties of Ni-TiN nanocomposite thin films deposited by reactive magnetron co-sputtering, Surface and Coatings Technology, 251, 239 (2014).
5. Z. G. Li, SD. Miyake, M. Kumagai, H. Saito, Y. Muramatsu, Hard nanocomposite Ti-Cu-N films prepared by d.c. reactive magnetron co-sputtering, Surface and Coatings Technology, 183, 62 (2004).
6. Hyun S. Myung, Jeon G. Han, Jin H. Boo, A study on the synthesis and mechanical characterization of TaN -Ag nanocomposite thin films, Thin Solid Films, 516, 5424 (2008).
7. SONG Guihong, ZHANG Jingjing, YANG Xiaoping, LI Feng, CHEN Lijia, HE Chunlin, Influence of negative pulse bias on structure and properties of TiN-Cu composite films, Journal of Shenyang University of Technology, 36(3), 275 (2014).
8. SUN Chao, WEN Lishi, Influence of axisymmetric magnetic field on the microstructure and friction performance of TiN film deposited by arc ion plating, Acta Metallurgica Sinica, 47(5), 566 (2011).

9. J. Q. Xiao, W. C. Lang, J. Gong, C. Sun, R. F. Huang, L. S. Wen. Effects of axisymmetric magnetic field on the distribution of Macroparticles on TiN and (Ti, Al) N films by arc ion plating, Physics Procedia, 18, 193 (2011).
10. LANG Wenchang, XIAO Jinquan, GONG Jun, SUN Chao, HUANG Rongfang, WEN Lishi, Influence of axisymmetric magnetic field on cathode spots movement in arc ion plating, Acta Metallurgica Sinica, 46(3), 372 (2010).
11. SONG Guihong, ZHENG Jingdi, LIU Yue, SUN Chao, Influence of TiAl interlayer on TiAlN coating deposited by arc ion plating, Journal of Synthetic Crystals, 33(3), 422 (2004).

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