Influence of Al Content on Micro-Properties of TiAlSiN Coatings Deposited by Plasma Enhanced Magnetron Sputtering

Yulong Wang, Hao Zhang*, Chengang Luo, Xiaoyu Ran, Zhangpeng Ren and Shuwang Duo*

Jiangxi Key Laboratory of Surface Engineering, Jiangxi Science and Technology Normal University, Nanchang, Jiangxi 330013, China

*Corresponding author: mail: zhangyinghao1985@126.com (HZhang), swduo@126.com (S Duo)

Abstract: TiN coating has attracted substantial attention due to its high hardness and good wear resistance. To meet the current more demanding service environment, Al and Si were added to TiN coating to further improve its comprehensive performance in this work. TiAlSiN coatings with different Al content governed by Al target power were prepared on GH169 superalloy by plasma enhanced magnetron sputtering, and the Al content effects on microstructure and mechanical properties of the coatings were explored in detail. The crystal structure, chemical composition, micromorphology and surface roughness of the coatings were analyzed by XRD, SEM, EDS and AFM, respectively. The mechanical properties of the coatings at room temperature including micro-hardness, elastic modulus and bonding strength were evaluated by nano-indentation and nano-scratch, respectively. With the increase of Al target power, Al content in coatings increased, and the preferred orientation of TiN(111) plane was also more and more obvious. At the same time, the surface morphology of the coatings changed from the round cell shape to the hexagonal star shape. The hardness, elastic modulus and adhesion of the coatings increased first and then decreased with the Al content. The TiAlSiN coating with Al content of 19.25% possesses the best comprehensive properties.

1. Introduction
The development of the manufacturing industry is inseparable from metal cutting, in which cutting tools play a pivotal role. Cutting tools in the harsh service environment will be prematurely defeated due to oxidation, wear and tear, etc., resulting in a large amount of material waste and huge economic losses. Studies found that the preparation of hard coatings with high strength, high toughness, wear and corrosion resistance is a practical and effective way to improve work efficiency and reduce economic loss. The advancement of technology and the development of modern industry have made the application conditions of materials more and more demanding. It is necessary to use expensive materials to meet the high demands for industrially used tools. Thus, modern surface technologies become an integral part of industrial production processes, increasing hard protective coatings are applied on tools [1]. At present, commonly used coating preparation techniques include multi-arc ion plating, magnetron sputtering, etc. Among them, the magnetron sputtering technology has the unique advantages of “low temperature and high speed”, and the prepared coating is uniform and smooth. Therefore, magnetron sputtering technology has been widely used in the industrial field [2]. However,
the conventional magnetron sputtering technology has a low metal ionization rate, and the sputtered particles are mostly in an atomic state, and the overall performance of the coating is poor. Plasma enhanced magnetron sputtering (PEMS) [3] can simultaneously ensure high metal ionization rate and coating deposition rate. This preparation technology is expected to further improve the comprehensive performance of existing coating types.

TiN coatings possess high hardness, good abrasion resistance and beautiful golden yellow and have been widely used in the industry. With the development of industry, binary TiN coatings are difficult to meet the current more demanding working environment. In order to improve the overall performance of TiN coating, various elements (Cr, Al, Si, B, Y) [4-8] were added into the single TiN coatings. For example, TiAlN coatings are used to prevent premature tool wear due to their excellent tribological properties, high temperature oxidation resistance up to 800°C and high chemical stability [9]. Increasing requirements for high-speed dry cutting applications are becoming higher and higher, especially for high hardness and high oxidation resistance, which also put forward new demands on the quality of wear-protective coatings materials. Improvement of their properties can be obtained by incorporation of Si into TiAlN coatings [10]. The effect of Si content and deposition conditions on TiAlSiN coatings, which play an important role in deciding the final microstructure and mechanical properties of Ti–Al–Si–N system, are widely researched by different groups [11–14]. Si is only present as nitride incorporated, either as a substitutional solid solution into TiAlN or via the formation of a separate amorphous nitride phase, which might affect the structural evolution of the remaining TiAlN crystallites [15,16]. The addition of Al to the coatings can increase the density [17], hardness and wear resistance of the coating, and Al can form a protective $\alpha$-Al$_2$O$_3$ film during oxidation [18]. Due to the lattice distortion effect, grain refinement, the hardness of the coatings increases. However, the Al content is not as high as possible. It is found that the critical solid solution of AlN in TiN is 65.3% [19], and the crystal structure of TiAlN coatings consists of cubic-TiN and hcp-AlN. The resulting new phase has a low hardness and reduces the hardness of the coatings, indicating that Al also has the same effect on TiAlSiN coatings. In this study, the Ti-Al-Si-N nanocomposite coatings with different Al doping were deposited by PEMS, and the effect of Al content on microstructure and mechanical properties of the coatings was investigated.

2. Materials and methods
Use GH169 superalloy as the substrate material (15 mm × 10 mm × 2 mm). Pre-treatment of the sample before coating, firstly grind the substrate surface with water-abrasive paper to 2000 mesh and then polish the surface with metallurgical paste to 2.5 μm. The samples were separately ultrasonically washed in acetone and ethanol solutions for 20 minutes and then dried for use. After the sample is placed in the vacuum chamber, the vacuum is pumped to $3 \times 10^{-3}$Pa and then the sample is heated to 300°C. The vacuum is again drawn to the set value and argon gas (60 SCCM) is introduced to control the working pressure at 1.8 Pa. -800 V bias was applied and the glow was cleaned for 30 min to remove surface impurities. TiAlSiN coatings were prepared by a MS650B rotary magnetron sputtering system (Shenyang Keyou Vacuum Technology Co, Ltd). Unlike conventional magnetron sputtering systems, this coating system adds a separate set of electron-emitting devices that use tungsten filaments to heat up the electrons. These electrons ionize the gas in the vacuum chamber under the action of Plus negative pressure, so that the plasma density and metal ionization rate in the vacuum chamber are greatly improved. Therefore, the coating with high deposition efficiency and excellent comprehensive performance can be obtained by using PEMS system. In order to further improve the coating quality, a certain thickness of the metal Ti bonding layer and the TiN transition layer are pre-deposited before depositing TiAlSiN coating on the substrate surface. Ti, Si and Al target (purity: 99.9%) are selected as coating raw materials. The Ti target, Si target power and other experimental parameters were unchanged, and three TiAlSiN coatings with different Al content were obtained by controlling the Al target power. The detailed process parameters are shown in Table 1.
Table 1. Deposition conditions of TiAlSiN coatings.

| Parameter                  | Value                      |
|----------------------------|----------------------------|
| Base pressure              | $3 \times 10^{-3}$ Pa      |
| Working pressure           | 0.5 Pa                     |
| Gas purities and flows     | $N_2$ (99.999%): 30 SCCM   |
|                            | $Ar$ (99.999%): 60 SCCM    |
| Substrate temperature      | 300°C                      |
| Powers of cathodes         | $P_{Ti}$: 1200W, $P_{Si}$: 100W |
|                            | $P_{Al}$: 550W, 700W, 850W |
| Substrate bias voltage     | -100 V                     |

The coating crystal structure was measured by an X-ray diffractometer (XRD, Cu-K$_\alpha$, Shimadzu XRD-6100, Japan) (scanning speed 5°/min, scanning range 20°-80°). Field morphology scanning electron microscopy (FE-SEM, Zeiss Sigma, Germany) and X-ray energy spectrometer (EDS, Oxford Inca, UK) were used to analyze the microscopic morphology and chemical composition of the coating. The coating thickness was obtained by observing the cross-sectional morphology of the coating. The three-dimensional morphology and surface roughness of the coating were characterized by atomic force microscopy (AFM, Being CSPM5500, Guangzhou, China). The mechanical properties including hardness, elastic modulus and bonding strength were measured by nano-indentation and nano-scratch (PB1000, Nanovea, USA), respectively. To obtain a reliable mean hardness value, at least 9 points at a thickness of 1/10 of the coating thickness were tested for each sample.

3. Results and discussion

Table 2 lists the main chemical compositions of the three TiAlSiN coatings. Herein, the atomic percentage of the Al element is used to indicate the content of Al in the coating. As can be seen from the table, as the power of the Al target increases, the Al content in the coating becomes higher and higher. The Al element content increased from 16.85% to 22.07%.

Table 2. Elemental Composition (at%) of TiAlSiN Coatings Prepared at Different Al Powers.

| $P_{Al}$ (W) | Ti  | Al  | Si  | N   |
|--------------|-----|-----|-----|-----|
| 550          | 30.68 | 16.85 | 4.49 | 47.98 |
| 700          | 28.79 | 19.52 | 3.99 | 47.70 |
| 850          | 27.68 | 22.07 | 3.92 | 46.33 |

The SEM measurement showed that the sum of the number of N atoms and the atomic number of Ti, Al and Si was about 1:1. It can be seen from Table 2 that as the Al target power increases, the Al content increases linearly, the Si content does not change much, and the Ti content decreases. This indicates that the coating element composition is mainly affected by the target power. The increase in Al content does not affect the change in Si content.

Figure 1 shows the XRD patterns of three TiAlSiN coatings. It can be seen from the figure that the Al content has a great influence on the crystal structure of the coating. It can be seen from the figure that the phase in the coating is mainly composed of TiN phase, and the diffraction peak of the (111) crystal plane is strong and sharp, indicating that the coating has good crystallinity and the inner grain size of the coating is large. When the Al content is changed between 16.85% and 22.07%, the phase structure of the coating does not change much, but the preferred orientation is obvious. The existence of Si may be only as a nitride, as a substituted solid solution of TiAlN or by forming a separate amorphous nitride phase, so Si is not detected [15, 16], and so is Al. When the Al content is 16.85%,
the coating is preferred in the TiN phase (111) plane orientation. As the bias voltage increases, the preferred orientation of the TiN phase (222) crystal plane in the coating becomes more and more obvious, and the crystallization performance becomes better and better. A weak matrix diffraction peak was detected in all of the coatings because the deposited coating was very thin, as can be seen from the thickness of the coating in the cross-sectional morphology of the coating (not shown here).

![Image](image_url)

**Figure 1.** XRD pattern of TiAlSiN coatings with different Al contents.

![Image](image_url)

**Figure 2.** Surface morphology of TiAlSiN coatings with different Al contents: (a) 16.85%; (b) 19.52%; (c) 22.07%.

Figure 2 shows the surface topography of TiAlSiN coatings with different Al contents. It can be seen from the figure that as the Al content increases, the grain size increases, and the morphology of the coating changes, changing from the original circular unit shape to the hexagonal star shape, and the coating compactness is deteriorated. The Al element replaces part of the Ti atom in the TiAlN coating to form a TiAlN coating. Al atom radius is smaller than Ti atom, and Al element replaces part of Ti atom in TiAlN coating to form AlN coating, which inevitably leads to lattice distortion. As the Al content increases, the degree of lattice distortion becomes larger and larger, and a crystal phase transition occurs when the critical value is exceeded. When the Al content is 22.07%, the critical content of AlN in TiN is exceeded, so the crystal structure changes from the face-centered cubic structure to the hexagonal structure, resulting in the surface morphology of the coating changing from a round cell shape to a triangular pyramid shape. The density of the coating is deteriorated and the mechanical properties are lowered.

The hardness of nanocomposite TiAlSiN coatings is shown in Figure 3 as a function of the Al content in the coatings. An increase in hardness is obtained from 37 GPa to 42GPa. The hardness increases continuously with increasing Al content in coatings, acquires the maximum value of 42GPa. The hardness of coatings increases insignificantly with the incorporation of Si, compared with the
value of 30 GPa as reported TiAlN coatings in our previous works. The combined hardening effects of grain size refinement and the strong interphase boundary between TiAlN crystallite and amorphous Si₃N₄ tissue phase with high cohesive energy should be responsible for the hardness enhancement. The ratio of Si₃N₄ tissue phase volume to the specific interface area of the TiAlN nanocrystalline phase as well as Si₃N₄ phase content, which depends on the TiAlN crystallite size and shape, also plays a decisive part in hardness value of nanocomposite TiAlSiN coatings, as reported by Veprek and co-workers. The crystallites of regular shape with a size of about 3–4 nm for the nc-MenN/a-Si₃N₄ systems, which the thickness of the a-Si₃N₄ layer is about 0.3–0.5 nm, i.e., about one monolayer of a-Si₃N₄, give rise to the maximum hardness [20]. Our coatings agree well with this result. Figure 3 shows the hardness and elastic modulus of TiAlSiN coatings with different Al contents. It can be seen from the figure that the hardness and elastic modulus increase first and then decrease with the increase of Al content. When the Al content is 19.52%, the hardness and elastic modulus reach a maximum of 42 GPa and 286 GPa. The hardness of the nitride is directly related to the bond energy and the atomic gap. The overall coatings hardness is lower than that of the TiSiN coatings without Al, mainly because the Al target poisoning leads to a decrease in coatings compactness.

![Figure 3](image-url)  
**Figure 3.** Hardness and elastic modulus of TiAlSiN coatings with different Al powers.

![Figure 4](image-url)  
**Figure 4.** Scratch morphology of TiAlSiN coatings with different Al contents: (a) 16.85%; (b) 19.52%; (c) 22.07%.

Figure 4 shows the scratch morphology of TiAlSiN coatings with different Al contents. It can be seen from the figure that the coating adhesion is similar to the hardness and elastic modulus of the
coating. As the Al content increases, the coating adhesion increases first and then decreases, and the coating is applied when the Al content is 19.52%. The layer has the greatest bonding force. It can be seen from the figure that when the Al content is 16.85%, the bonding strength is 8.7N. When the Al content increases to 19.52%, the binding force rises to 23.5N, and when the Al content increases to 22.07%, the binding force is 23.8N. As the Al content increases, the bonding force gradually increases because of the addition of Al, which improves the toughness of the coatings and reduces the brittle crack at the scratch. When the Al content is low, the coating structure is loose, the coating hardness is low, and the bonding strength between the coating and the substrate is also low; as the Si content in the coating increases, the AlN crystal phase in the coating increases. Causes lattice distortion, which improves the cohesion of the coating to a certain extent, so the bonding force between the coating and the substrate increases; When the Al content is further increased to 19.52%, the coating is still a nanocrystalline face-centered cubic structure, and the surface roughness of the coating is low. Observing the surface morphology (Figure 2), the coating is dense and the bonding strength is improved. When the Al content is too high, it reaches 22.07%, and the hexagonal structure changes in the direction of the face center, resulting in poor density of the coating, which is not conducive to the improvement of the coating adhesion. Conversely, it is not conducive to the improvement of coating adhesion. In summary, too low or too high Al content is not conducive to the comprehensive performance of TiAlSiN coating, the appropriate amount of Al can make the coating surface even and dense. In this paper, the TiAlSiN coating has the best comprehensive mechanical properties when the Al content is 19.52%.

4. Conclusions
The microstructure and mechanical properties of Ti–Al–Si–N coatings with various Al content were evaluated in detail. Al content plays an essential role in the surface morphology of the coatings. The main conclusions are as follows:

As the Al content increases, the preferred orientation of the (111) crystal plane in the TiN phase becomes more and more pronounced. When the Al content exceeds 22.07%, the phase structure changes from a face-centered cubic structure to a hexagonal structure, and the surface morphology of the coating changed from the round cell shape to the hexagonal star shape.

With the increase of Al content, the crystallization property of the coatings is improved. The denseness decreases. The hardness and elastic modulus of the coatings increased first and then decreased. When the Al content is 19.52%, the hardness, elastic modulus and bonding force are considered to be the best, and the values are 42 GPa, 286 GPa, and 23.5 N respectively.

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