

# Graded TiN Coating by Supersonic Free-Jet PVD Combined with Reactive Plasma

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Ceramic coating is a very popular technology for improving the properties of structural materials. A titanium nitride (TiN) coating is a typical example and has been widely applied to cutting tools, electronic devices and many other fields utilizing its superior physical properties. This paper sought to produce a graded TiN coating on a Ti substrate by combining Supersonic Free-Jet PVD (SFJ-PVD) with a reactive plasma-metal reaction technique. The authors have developed SFJ-PVD as a new coating method in which a coating film is formed by depositing nanoparticles with very high velocity onto a substrate. SFJ-PVD can provide a high deposition rate and thick film coating. Gradually changing the nitrogen flow rate during deposition produces a graded TiN coating, in which composition changes gradually from pure Ti to TiN. A monolithic TiN coating is also produced with SFJ-PVD. XRD analysis of the graded TiN detected peaks for Ti, Ti<sub>2</sub>N and TiN, while only a TiN peak is observed in the monolithic TiN coating. EPMA analysis of a graded coating reveals a gradual compositional change from pure Ti to TiN. Few pores or cracks are observed in a graded TiN or in a monolithic TiN formed under the optimized conditions of SFJ-PVD.

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## 1. Introduction

Ceramic coating is a very popular technology for improving the properties of structural materials. A titanium nitride (TiN) coating is a typical example and has been widely applied to cutting tools, electronic devices and other industrial applications utilizing its high hardness at elevated temperature, high melting point, high thermal conduction, and other superior properties.

Various methods such as ion plating,<sup>1-4)</sup> sputtering<sup>5-7)</sup> and CVD<sup>8,9)</sup> have been used to form TiN coatings. These methods have shortcomings, such as low deposition rate and difficulty in obtaining a thick, high-density film. Cracks and many pores are often observed in the coated film. Moreover, it is difficult to obtain sufficient bonding strength at an interface by direct coating of nitrides on a substrate metal because of residual stress caused mainly by the difference of thermal expansion coefficients between ceramics and substrate metals.<sup>10)</sup> Recently, compositional grading from the interface in a metal/ceramic composite coating has received attention because it reduces the residual stress. This concept was successfully applied to prepare metal/ceramic composite coatings.<sup>10-15)</sup>

The authors developed a new coating method called “supersonic free-jet PVD (SFJ-PVD)”.<sup>16-20)</sup> In SFJ-PVD, a coating film is formed by depositing nanoparticles at very high velocity onto a substrate. The schematic diagram of SFJ-PVD is illustrated in Fig. 1, showing the two stages in SFJ-PVD, “gas evaporation” and “vacuum deposition”. In the gas evaporation stage, a source material is evaporated to form nanoparticles in an inert gas atmosphere. The nanoparticles are then carried to a substrate with the inert gas through a transfer pipe where a gas flow is generated by the pressure difference between the evaporation and deposition chambers. The gas flow is accelerated to supersonic velocity (Mach 3.6) by a specially

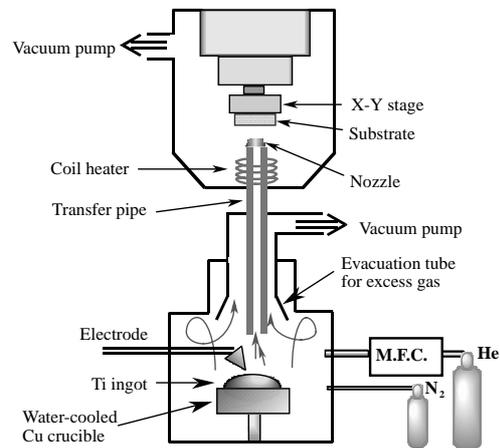


Fig. 1 Schematic diagram of supersonic free-jet PVD apparatus.

designed supersonic nozzle joined to the tip of the transfer pipe. In the deposition stage, the nanoparticles are deposited onto the substrate in the deposition chamber.

The authors succeeded in obtaining a uniform, high-density, thick metallic coating of Al or Ti on metal substrates with SFJ-PVD.<sup>16,19)</sup> M. Uda, S. Ohno *et al.*<sup>21-23)</sup> and other researchers<sup>24)</sup> produced nitride particles with a reactive plasma-metal reaction technique. They produced the nitride particles with a gas evaporation process in an N<sub>2</sub> atmosphere.

This paper sought to produce a graded TiN coating on a Ti substrate by combining SFJ-PVD with the reactive plasma-metal reaction technique.

## 2. Experimental Procedure

The purity of the Ti source for evaporation exceeded 99.999 mass%. The source material was placed in a water-cooled copper crucible then heated and evaporated by arc plasma. The 20 mm × 20 mm substrate was fixed on an X-Y stage that was driven in X-Y directions, and the coated area

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was 5 mm square. The stage and the nozzle are heated by electric resistance heating systems.

The evaporation chamber is equipped with an evacuation tube with a needle valve to evacuate excess gas that is not suctioned through the transfer pipe. The evacuation tube also suppresses gas stagnancy caused by the excess gas, which in turn reduces coarse particles by suppressing the stagnancy and secondary agglomeration of particles.

To form a graded TiN coating, we began evaporating Ti in a purified He gas atmosphere and gradually increased the flow rate of N<sub>2</sub> gas. The preparation conditions are shown in Table 1.

We performed SEM and TEM observations and EPMA analysis on the cross section of coating films. We also conducted X-ray diffraction (XRD) analysis of the coated area and compared it with the XRD profile of the substrate because in our samples, the XRD profile of coated samples might contain the profile of a 5 mm square coated area as well as the profile of the substrate area surrounding it.

We produced a monolithic TiN coating on an SUS304 substrate to confirm the possibility of producing a TiN single-phase film with SFJ-PVD by controlling the flow rate of N<sub>2</sub> gas because a graded TiN coating film might contain TiN as well as other phases. The SUS304 substrate was chosen to eliminate the XRD profile of Ti.

### 3. Results and Discussion

Figure 2 shows the surface of a graded coating from Ti to TiN on a Ti substrate. The photograph shows that there were no cracks in the coating. The XRD profiles of a graded

Table 1 Preparation conditions of TiN or graded TiN coatings.

	TiN coatings	graded TiN coatings
Source material	Pure Ti (>99.999)	
Arc current (A)	20	
Nozzle heater (W)	750	
Substrate temperature (K)	773	
Substrate materials	SUS304	Ti (JIS 1)
He gas flow rate (L/min)	2.0	3.0–2.0
N <sub>2</sub> gas flow rate (L/min)	1.0	0–1.0

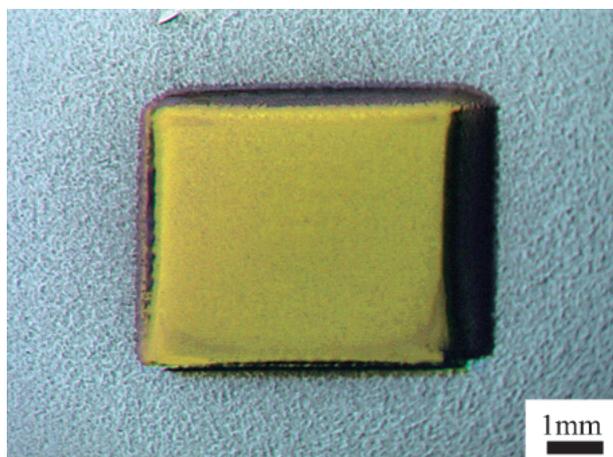


Fig. 2 Photograph of a graded TiN film surface.

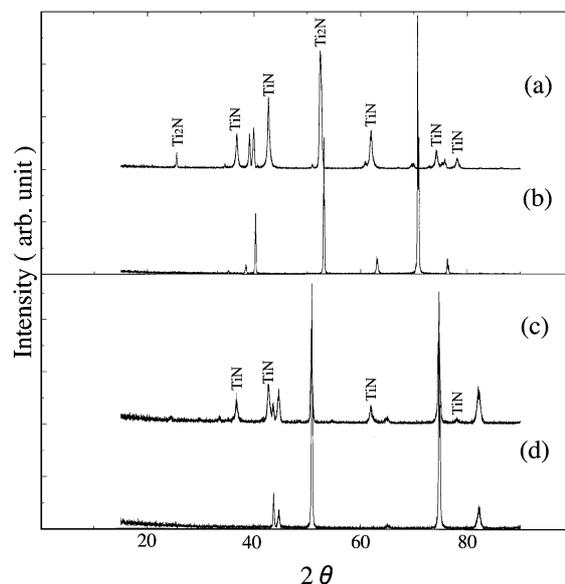


Fig. 3 X-ray diffraction profiles of (a) Graded TiN, (b) uncoated Ti substrate, (c) TiN coating on SUS304 and (d) uncoated SUS304 substrate.

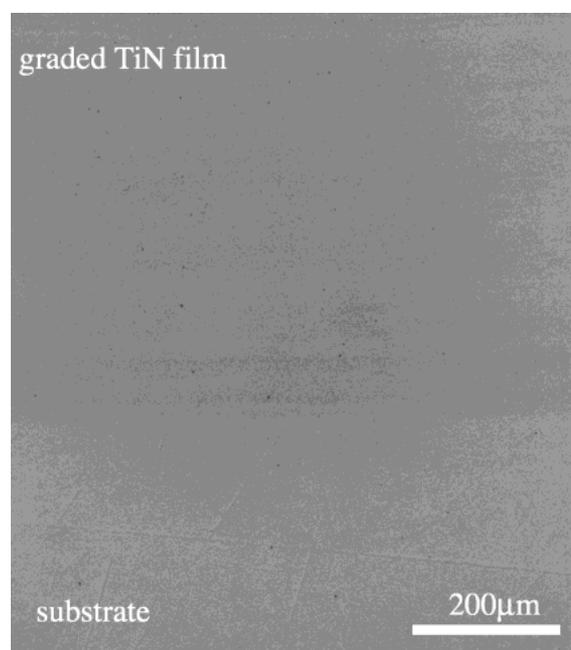


Fig. 4 Photograph of the cross-section of a graded TiN film.

TiN film on a Ti substrate, an uncoated Ti substrate, a monolithic TiN coating on an SUS304 substrate, and an uncoated SUS304 substrate are shown in Figs. 3(a), (b), (c) and (d). We measured the XRD profiles of the substrates to subtract the diffraction from the substrates around the coated areas.

The XRD profile shown in Fig. 3(a) reveals that three phases (Ti metal, tetragonal sub-nitride Ti<sub>2</sub>N and cubic TiN) coexist in a graded TiN coating on a Ti substrate. The diffraction profile shown in Fig. 3(c) indicates that only TiN exists in a monolithic TiN coating on an SUS304 substrate.

Figure 4 presents a SEM photograph of the cross-section of a graded TiN coating on a Ti substrate where no pores and cracks are found.

Figure 5 shows the result of an EPMA line analysis of the cross-section of a graded TiN coating. EPMA revealed that

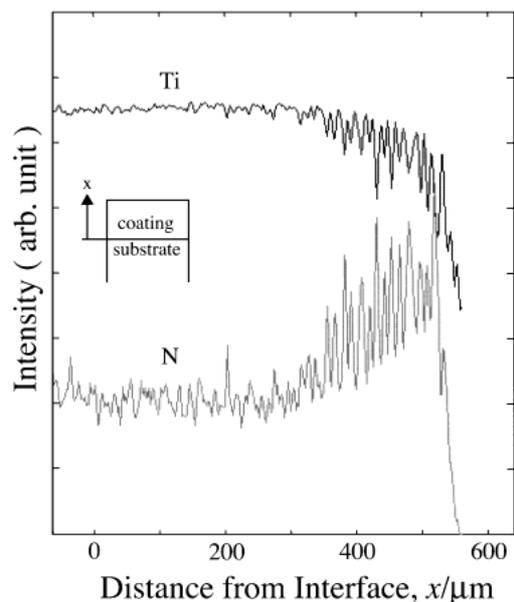


Fig. 5 EPMA line analysis of the cross-section of a graded TiN film.

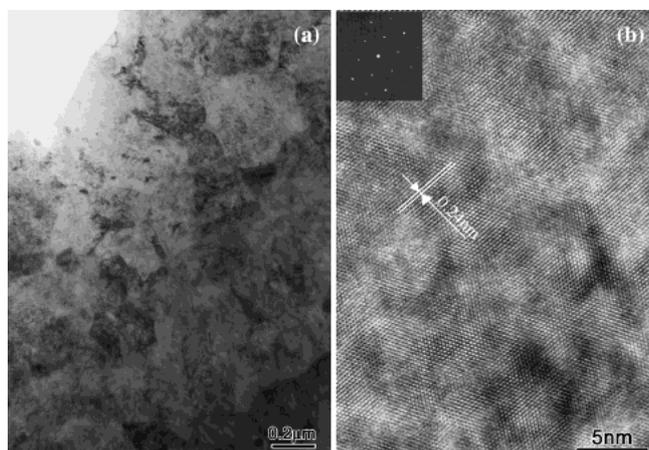


Fig. 6 TEM micrographs of the area near the surface of a graded TiN film. (a) TEM image. (b) HRTEM image and diffraction pattern of cubic TiN structure.

the coating started with pure Ti, then gradually increased in nitrogen content as shown in Fig. 5.

Figure 6 shows TEM photographs of an area near the surface of a graded TiN coating. The TEM photographs revealed cubic TiN as detected in XRD analysis, and the grain sizes of TiN were very fine, varying from 80 to 600 nm.

#### 4. Conclusions

We successfully achieved a TiN coating and a graded TiN coating using the new SFJ-PVD technique.

The results obtained in this paper are as follows,

- (1) A TiN film and a graded TiN film were produced by depositing nanoparticles formed in the evaporation chamber with a controlled atmosphere of He and N<sub>2</sub>.
- (2) XRD analysis and TEM observation revealed the crystal structure of the TiN film to be cubic.
- (3) Neither the graded TiN film nor the TiN film contains

pores and cracks on the surfaces or inside the films.

- (4) The grain size of TiN in the films is from 80 to 600 nm.

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