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Nano-Composite Coatings by Supersonic Free-Jet PVD

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Ti-Al and TiN nano-composite coatings are prepared by depositing nanoparticles with supersonic free-jet PVD (SFJ-PVD). 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. The high velocity of nanoparticles is produced by the supersonic gas flow of inert gas. The gas flow is generated by pressure difference between evaporation and deposition chambers and accelerated to supersonic velocity (Mach 3.6) by specially designed supersonic nozzles. A smooth, compact and defect-free microstructure is formed both at the interface between substrates and coating films and inside the coating films. The microstructures of Ti-Al and TiN coatings have very fine grain size. It is confirmed with nano-indentation hardness tester that graded coatings of Ti/Ti-Al and Ti/TiN have graded hardness corresponding to the graduation of composition.

Key words: nanoparticle, microstructure, functionally graded material, nano-indentation hardness

1. INTRODUCTION

High efficient heat resistant or wear resistant material is usually expensive. These properties are often required only at the surface of the materials. If a hard coating is applied on a tool and it stands long use, it is very useful for saving energy and saving resources. Thus, the coating is studied enthusiastically. And, nano-composite materials in which nano-meter size material is dispersed in base material and micro/nano structure materials are attractive candidates to improve mechanical properties.

The aim of our research is to produce nano-composite coating with supersonic free-jet PVD (SFJ-PVD). For the fabrication of nano-composite materials, various techniques are included hot pressing, HIP, ion implantation, sputtering, and so on have been employed. However, in case of powder metallurgy, hot pressing or HIP is usually adopted[1] to fabricate nano-composite materials, in which difficulty is a high temperature of sintering. On the other hand, in conventional coating processes such as CVD, PVD or spaying, it is difficult to form a coating film without void, pin-hole and crack with high deposition rate process. [2-7]

The authors have developed SFJ-PVD[8-13] as a new coating method in which a coating film is formed by depositing nanoparticles with very high velocity onto a substrate. The SFJ-PVD apparatus has two evaporation chambers that make possible to mix different nanoparticles from different source materials and to produce nano-composite on a substrate in a deposition chamber.

In this paper, Ti-Al and TiN nano-composite coatings are prepared by depositing nanoparticles with SFJ-PVD, and their microstructures and hardness of gradient composition were investigated.

2. EXPERIMENTAL PROCEDURE

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 designed supersonic nozzle joined to the tip of the transfer pipe. In the vacuum deposition stage, the nanoparticles are deposited onto the substrate. In the evaporation chamber 1, the evaporation source material was placed in a graphite crucible then heated and evaporated by the surrounding Ta ribbon heater. In the evaporation chamber 2, the evaporation source material was placed in a water-cooled copper crucible then heated and evaporated by arc plasma. The substrate was fixed on a stage that was driven in X-Y directions, and the coated area was 5mm square on the substrate. The stage and the nozzle are heated by electric resistance heating systems. The temperature of substrate is measured nearly the coated area on the substrate by thermocouple and controlled during and after depositing. The evacuation tube suppresses gas stagnancy caused by the excess gas, which in turn reduces coarse particles by suppressing the stagnancy and secondary agglomeration of particles. In this method, the deposition rates of various evaporation sources can be controlled independently using heating systems, and them we have successfully prepared compositional graded coatings. [12] Further experimental details of the deposition technique were reported in the previous paper. [12,13]

The cross-sections of coated specimens were observed by scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer. Specimens of the observation were polished with SiC paper up to #2000, and then mechanical polished with up to 0.3μm Al_2O_3. Microstructures of coated specimens were observed by transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM). The hardness of the coated specimens was examined using a nano-indentation tester (ENT-1040a) at Elionix Inc with applied load of 9.8mN.

3. RESULTS

3.1 Ti-Al composite coating

Figure 2 shows a typical SEM image and the characteristic X-ray mappings of Al and Ti elements taken from the cross-sections of Ti-Al coating on Ti substrate. The specimen was produced by mixing Ti and Al nanoparticles from the two evaporation chambers with the same deposition rate. The figure 2 (a) shows smooth, compact and defect-free interface and coating film have been formed. Large Al or Ti particle is invisible in Fig. 2(b) and (c). Figure 2 indicates the same atomic fraction of Al and Ti nanoparticles is mixed without crack and defect. Similar results were found in all the coated specimens of Ti, Al, Ti-Al and TiN, respectively. Figure 3 shows TEM and HRTEM images of Ti-Al coating film. As seen from the Fig. 3(a), the grain sizes were very fine, varying from 30 to 700 nm and them crack or defect in the coating film is invisible. The Fig. 3(b) shows the part of Al_3Ti in Fig. 3(a). It is notable that the depositing of the Ti and Al nanoparticles on the substrate synthesizes

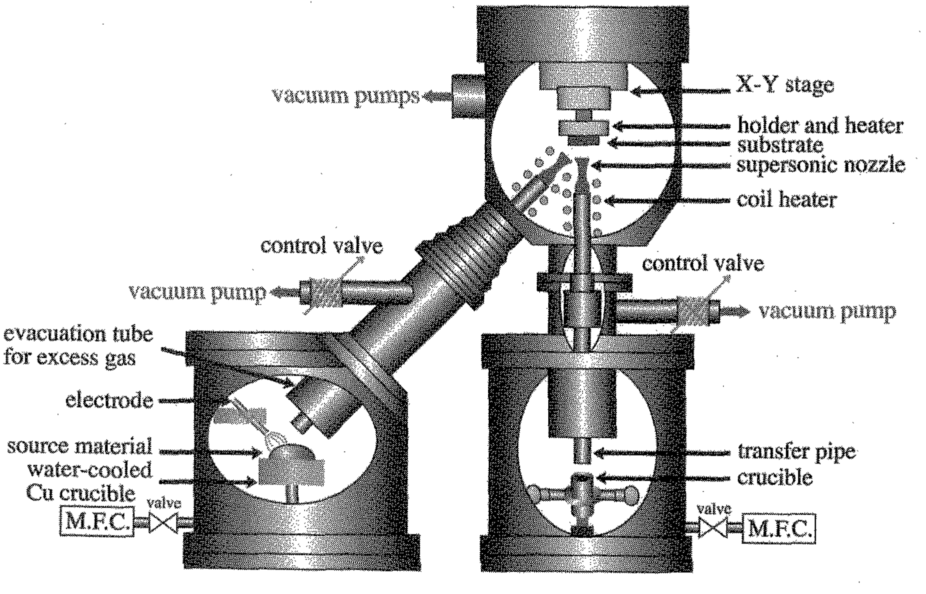

Fig. 1 Schematic diagram of Supersonic Free-Jet PVD apparatus.

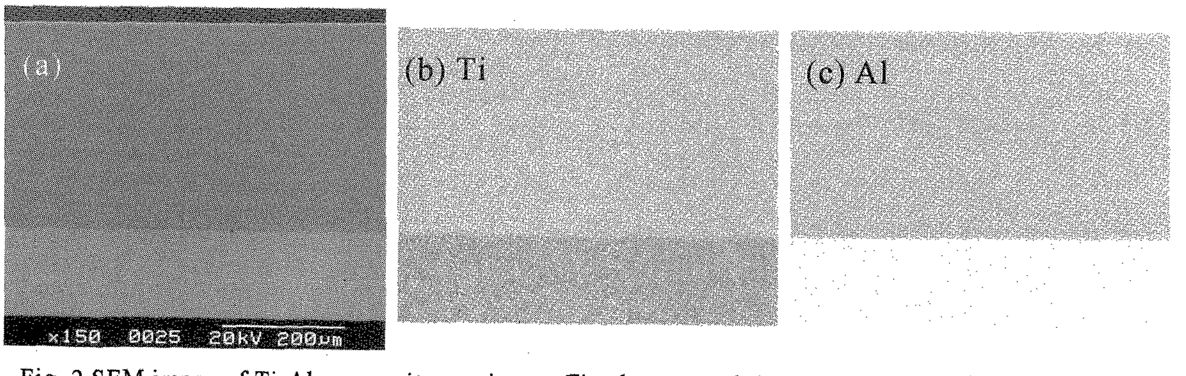

Fig. 2 SEM image of Ti-Al composite coating on Ti substrate and the corresponding X-ray mappings o Al and Ti elements.

titanium-aluminide, i.e., *in-situ* synthesis of titanium-aluminide intermetallic compound with the SFJ-PVD.

One of the advantages of the SFJ-PVD is an ability to control the desired composition of coatings by mixing and depositing different source nanoparticles onto a substrate with varying the deposition rate respectively. This advantage is very attractive for the fabrication of graded composition coatings. Graded coatings starting from the composition of base materials or compatible composition with base materials to that of compounds or ceramics should make up for the lack of properties of base materials and compounds each other and reduce the discontinuity of interface, thus, the SFJ-PVD is a promising method to prepare graded coatings.

Figure 4 shows the relation between nano-indentation hardness and composition of pure Ti to Ti-50at%Al graded coating film. In the Fig.4, the hardness gradually increases from 3.5GPa to 9.8GPa as increase of graded composition of Al. And, the nano-indentation hardness of Ti substrate was 3.1GPa with the same measuring condition. Hardness increase should be due to the strengthening effect of intermetallic compounds in the composites coating film by graded composition coatings.

3.2 TiN composite coating

Figure 5 shows TEM and HRTEM images of TiN graded coating film. As seen from the Fig. 5(a), the grain sizes were very fine, varying from 80 to 600 nm and them crack or defect in the

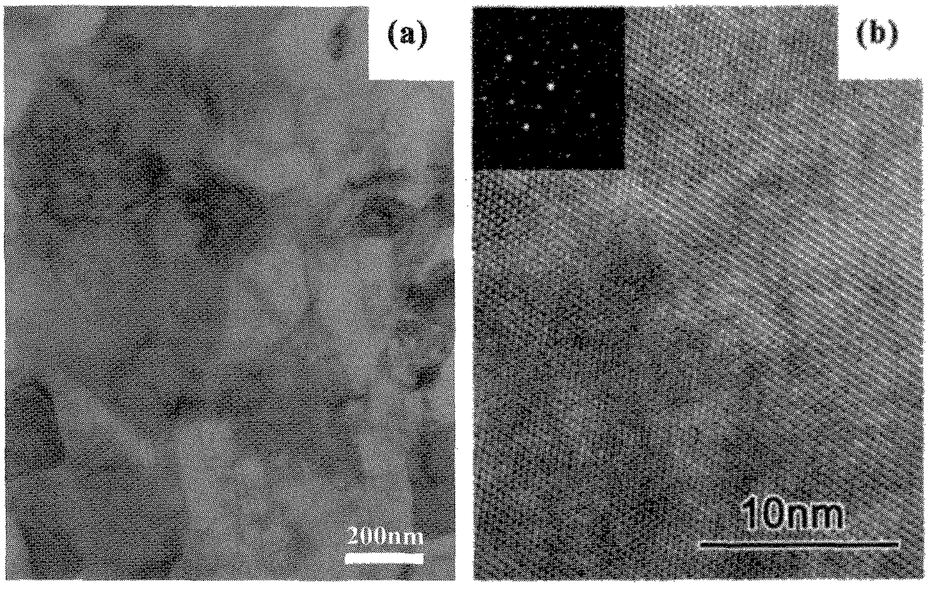

Fig. 3 TEM micrographs of Ti-Al composite coating film. (a) TEM image. (b) HRTEM image and diffraction pattern of $D0_{22}$ structure.

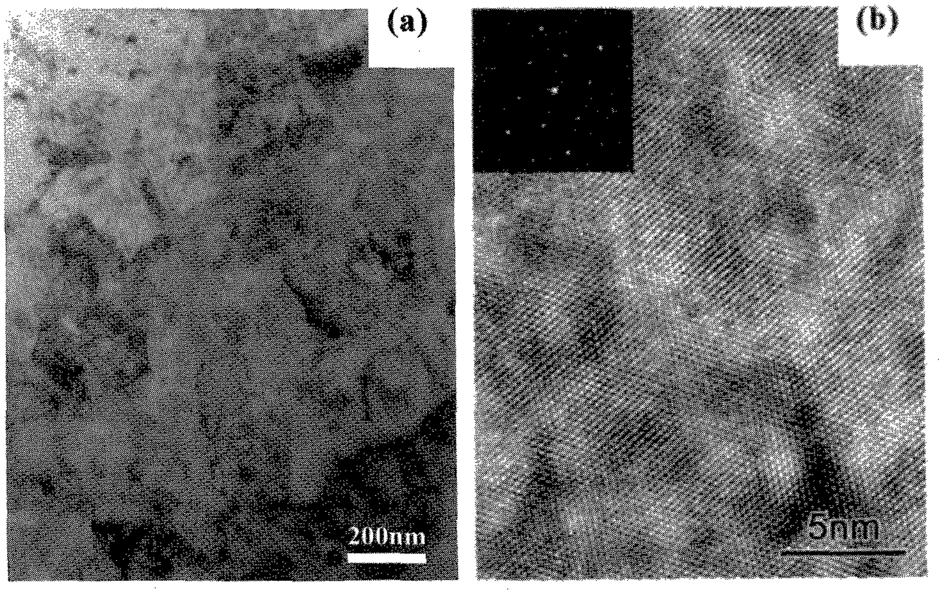

Fig. 5 TEM micrographs of TiN composite coating film. (a) TEM image. (b) HRTEM image and diffraction pattern of cubic TiN structure.

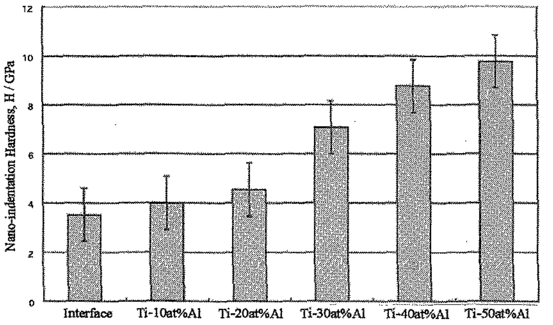

Fig. 4 the relation between nano-indentation hardness and composition of pure Ti to Ti-50at%Al graded coating film.

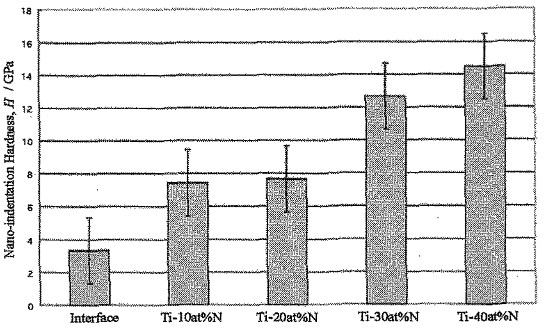

Fig. 6 the relation between nano-indentation hardness and composition of pure Ti to Ti-40at%N graded coating film.

coating film is invisible. The Fig. 5(b) shows a cubic TiN crystal. The graded TiN coating film was produced with reactive plasma-metal reaction process by controlling the atmosphere of helium and nitrogen gas in the evaporation chamber.

Figure 6 shows the relation between nano-indentation hardness and composition of pure Ti to Ti-40at%N graded coating film. In the Fig.6, the hardness gradually increases from 3.3GPa to 14.5GPa as increase of graded composition of N. And, the nano-indentation hardness of Ti substrate was 3.1GPa with the same measuring condition. Hardness increase with the increase of N in the composite coating film should be due to the strengthening effect of nitride ceramics. In Fig. 6, TiN layer in the graded coating film has the hardness value of about 13-15.5GPa that is a little lower than the conventional PVD/CVD coating hardness value of about 14.5-20GPa[14-15] by Vickers hardness. However, Y. Sawahira et. al. [16] has reported that TiN coatings had hardness value of about 10GPa by nano-indentation hardness tester at Elionix Inc.

4. CONCLUSIONS

The results obtained in this experiment using SFJ-PVD are as follows:

1) Deposition of mixture different kind of source nanoparticles produces high-density compact coatings without voids and cracks.
2) Ti-Al composite coating has very fine grain size varying approximately from 30 to 700 nm.
3) TiN composite coating also has very fine grain size varying approximately from 80 to 600 nm.
4) Titanium-aluminide is synthesized by mixing Ti and Al nanoparticles on the substrate.
5) Both Ti/Ti-Al and Ti/TiN graded coatings are possible by controlling the composition of Ti, Al and N, respectively.
6) The graded coating films have the increase of hardness as increase of Titanium-Aluminide and Titanium-Nitride ceramics, respectively.

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