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Morphology of TiN coating produced by laser ablation

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The morphology of TiN thin films on a steel surface produced by the process of laser ablation has been investigated. The process involves material removal from a titanium target by means of an ultraviolet excimer pulse laser. Both the target and the steel substrate are in an ammonia atmosphere and therefore the titanium atoms react with the nitrogen under the influence of a laser-induced plasma, and the product, which is TiN, is deposited on the surface of the steel. The investigation revealed that at the beginning of the process the TiN film is uniform; however, with increasing number of pulses, small micrometre-sized particles begin to appear on the surface and after a large number of pulses all the surface is covered with these particles.

1. Introduction

TiN coatings are used extensively on metal surfaces, especially steels, due to their high hardness and very low wear coefficient. The commercially used coating processes involve chemical reactions (chemical vapour deposition, CVD) in a mixture of titanium chloride and ammonia gases at high temperatures, typically above 800 °C. Another commercially used process is physical vapour deposition (PVD), sputtering of a titanium target by means of argon ions in a nitrogen or ammonia environment. The temperature of this process is approximately 500 °C [2].

The disadvantage of these processes is the high temperature. There are applications where the temperature of the substrate cannot be raised much above the ambient. For example, low melting point materials, or alloys which have been heat treated to a certain hardness and strength. One of the methods which can produce coatings at relatively low temperature is laser ablation.

It has been reported that chemical reactions between various gases induced by ultraviolet laser radiation produced coatings in a low-temperature range [3–12]. These consisted of ceramic-type coatings such as Al_2O_3 [3], SiO_2 [4] and Si_3N_4 [5], semiconductor coatings [6–8], metallic coatings [9–11] and silicide coatings [12].

There is no evidence in the literature that TiN coatings have been produced by one of the above processes. A preliminary study revealed that there are two different ways to apply TiN coatings on various substrates by means of pulse laser beam radiation: (i) laser chemical vapour deposition (LCVD) and (ii) laser physical vapour deposition (LPVD). The first method utilizes the laser beam for the decomposition of a certain mixture of gases by a photolithic mechanism; a reaction among its components and the deposition of the appropriate composition on the substrate. The second method uses the laser beam as a sputtering source of a proper target. The substrate is located in the vicinity of the target and therefore it becomes coated.

In this investigation, the LPVD was used. This is an intermediate report and deals with one topic only, the morphology of the TiN coating and its variation with the process parameters.

2. Experimental procedure

The laser used in this investigation is an excimer-pulse laser, produced by Lambda Physik, Model 201. The properties of this system are wavelength 193 nm, pulse duration 24 ns, maximum pulse energy 250 mJ and maximum repetition rate 80 Hz.

Fig. 1 is a schematic representation of the experimental apparatus. The cell is made from a glass bell-jar connected to a vacuum system. The cell contains the following details: target holder (stationary or rotating) and stage for the substrate, furnace for heating the substrate, thermocouples and other measuring equipment. The cell is connected through an elaborate gas system to a l.b. of high-purity ammonia gas.

A typical experiment was conducted as follows. After inserting the titanium target and the steel substrate, a vacuum of approximately 5×10^{-6} mm Hg was pumped. The target material was high-purity titanium; the steel was SAE 52100 bearing steel. The steel was coated either in the quenched and tempered condition or in the normalized condition. The appropriate heat treatments were performed according to specifications [13]. Both target and substrate materials were polished metallographically, but few

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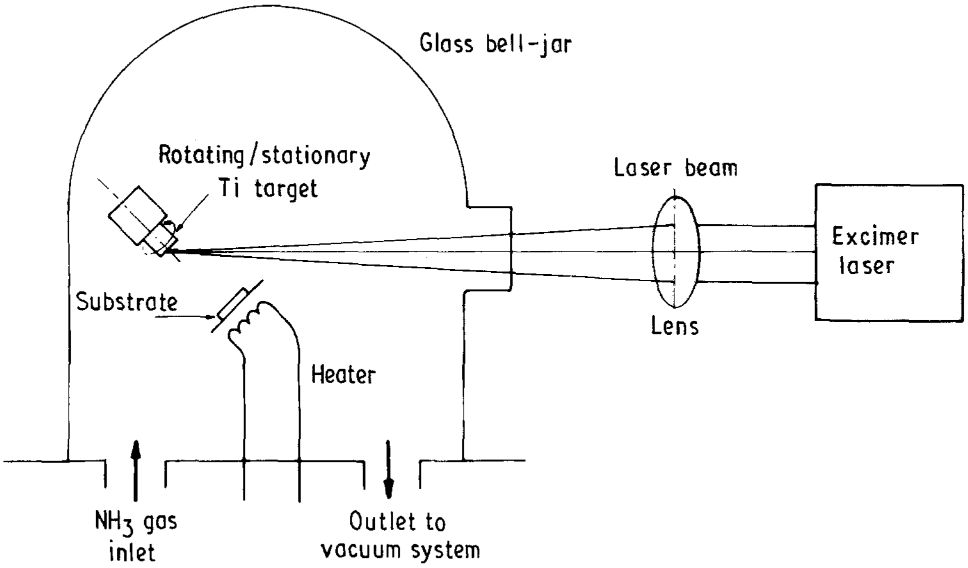

Figure 1 Schematic representation of the experimental apparatus.

scratches were deliberately left on the steel surface. After vacuum is reached, the cell was filled with partial pressure of ammonia gas (0.5 torr; 1 torr = 1.333 $\times 10^2$ Pa), and the heater was activated. After many trial runs it was decided that the optimal substrate temperature for coating was 270 °C. A lower temperature coating resulted in a film which was poorly bonded to the steel, while higher temperature changed the condition of the quenched and tempered steel. At this stage the apparatus was ready for the experiment.

The laser was then activated. It penetrated through the window and caused the decomposition of the ammonia molecules to various radicals such as NH_2^+, NH^+, etc. Finally it hit the titanium target, removed titanium atoms from the surface into the surroundings and produced a plasma plume. The sputtered titanium atoms reacted with the ammonia molecules and the product of the process, TiN, was deposited on the substrate. The impact of the laser beam also created a crater on the polished surface of the target and the efficiency of the sputtering process decreased. If the crater became too deep (~ 100 μm) no plasma plume was created and the coating process came to an end. There were two ways in which partially to overcome this problem. If the target was stationary, the laser beam was displaced after a few thousand pulses and therefore it hit a polished surface again. If the target was rotating, typically 1 r.p.m., after two complete rotations the beam was displaced and it hit the target along another circle.

At the beginning of the investigation all the parameters of the experiment were studied in order to obtain satisfactory coatings. The main experimental parameters were power density and repetition rate of the laser beam, the geometry (distance and angle) between target and substrate, the partial pressure of ammonia, and the temperature of the substrate. Once the optimal value of any parameter had been established it became a constant value for all the experiments.

All the experiments were subsequently carried out in order to study the effect of the number of laser pulses on the thickness, chemistry, crystallography, adhesivity and morphology of the TiN coatings. The investigation is still in progress, and this paper presents only the influence of the laser ablation process on the morphology of the TiN film on the steel surface.

3. Results

The very first indication that the steel became coated during the process described above was the appearance of various colours on the surface. After a few hundred pulses the colour was a cobalt blue, which turned to gold on further coating. After about 8000 pulses, the colour changed to golden green and to red (~ 12 000 pulses). The colour of a "thick" coating after 40 000 pulses was brown. The approximate thickness of this layer was 1 μm.

The morphology of both target and substrate have been studied by scanning electron microscopy and the results are shown in the following figures.

3.1. Stationary target

Fig. 2 shows the surface of the steel after 1000 pulses. The few scratches are on the steel's surface, indicating

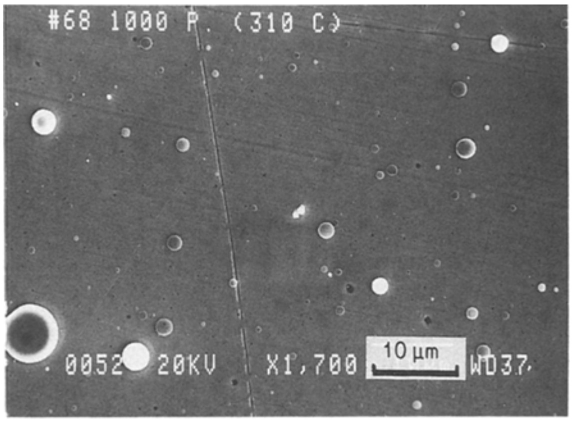

Figure 2 Scanning electron micrograph of the steel surface after 1000 pulses.

that the film is very thin. In fact, from this picture alone, it is not possible to deduce the existence of a coating; the change in colour and Auger spectroscopy proves this. A few large, 5 μm size particles, in the shape of "bagles" can be observed. These were identified as pure titanium.

Fig. 3 of the surface of the titanium target after 1000 pulses shows a deep crater. Similar craters are formed even after fewer pulses, only they were shallower. In larger magnification (top corner) It can be seen that the material of the crater wall was removed by melting and evaporation, rather than by a mechanical means. After approximately 1000 pulses the laser beam was displaced and a new crater was created by further pulses.

Figs 4 and 5 depict the steel surface after 20 000 and 40 000 pulses, respectively. Even after 20 000 pulses, a few scratches can still be observed, but they disappear completely with increasing number of pulses. The maximum size and the number of bagles increased with the number of pulses; they were of various sizes and shapes, sometimes overlapping each other. After 40 000 pulses there were very few areas on the surface which were not covered by them. The larger ones were all analysed as pure titanium; we assume that the smaller ones were also titanium; however, they are too small to be analysed. Most of the bagles were coated with a very thin film of TiN.

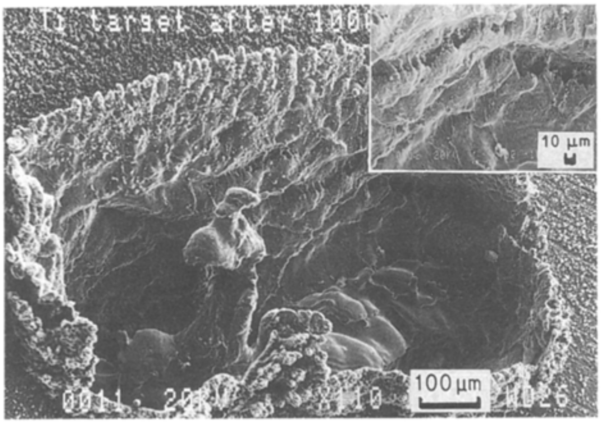

Figure 3 Scanning electron micrograph of the titanium target after 1000 pulses.

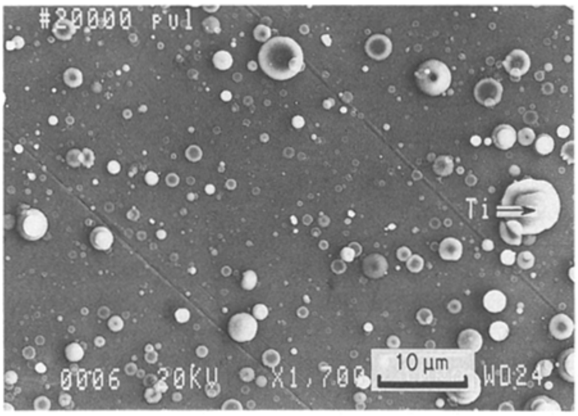

Figure 4 Scanning electron micrograph of the steel surface after 20 000 pulses, showing splashed particles.

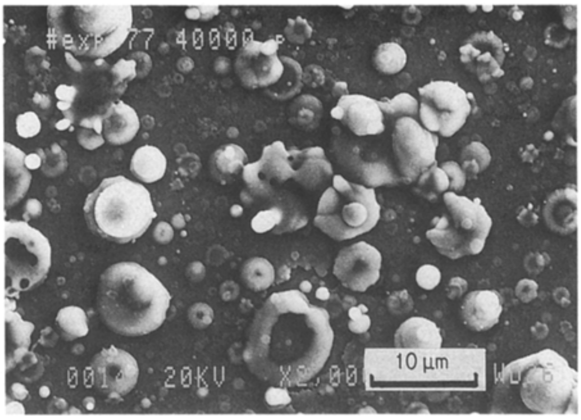

Figure 5 Scanning electron micrograph of the steel surface after 40 000 pulses. The coating is almost completely covered with splashed particles.

3.2. Rotating target

The laser pulses on a rotating titanium target created a shallow ring, such as is shown in Fig. 6. In larger magnification (top corner) It can be seen that the material inside the ring is melted. However, in a rotating target the number of pulses which hits a certain location is much smaller than in a stationary target; the depth of the molten zone is also much smaller.

With the rotating target, 1000 pulses result in a surface such as that shown in Fig. 7. This micrograph

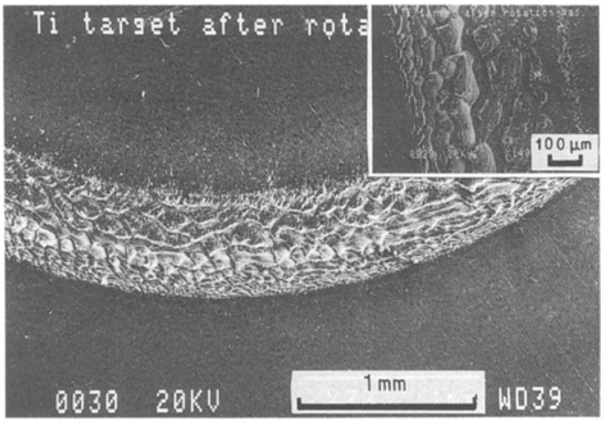

Figure 6 Scanning electron micrograph of rotating target (0.2 r.p.m.).

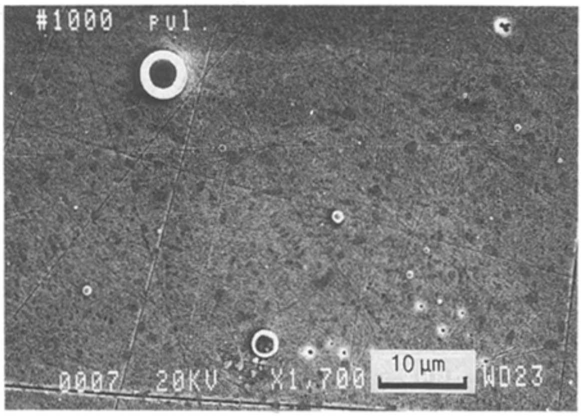

Figure 7 Scanning electron micrograph of the steel surface after 1000 pulses with a rotating target.

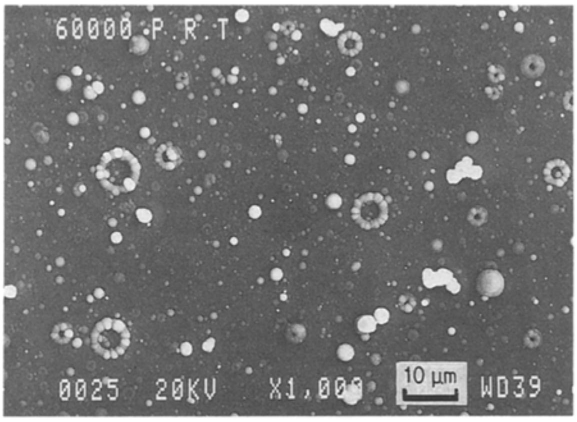

Figure 8 Scanning electron micrograph of the steel surface after 60 000 pulses with a rotating target.

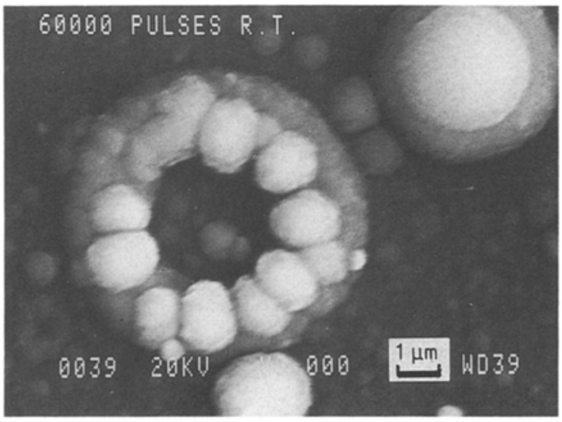

Figure 9 Scanning electron micrograph showing a typical "bagle"-shaped splash particle.

is for the same number of pulses as that shown in Fig. 2, i.e only a few bagles appear on the surface. With increasing number of pulses, the number of particles also increases but the rate of increase is lower. For example, Fig. 8 shows the surface of the specimen after 60 000 pulses. Not only is the rate of formation of the bagles different with the rotating target, but also their shape differs. They seem to be built from impinging little balls. Fig. 9 shows a typical bagle at a large magnification.

4. Discussion

The results presented in Figs 2–9 demonstrate that the morphology of the coating depends on the parameters investigated, i.e. number of pulses and the conditions of the target.

The process of laser ablation of titanium causes a buildup of a homogeneous film on the steel surface, together with very small particles of various shapes and sizes. The thickness of the film as well as the number of particles increase with the number of pulses. When the target is rotating, the number of particles is much smaller for a given number of pulses compared to the stationary target. In order to explain these results it is necessary to understand the mechanism of the deposition of the film and the formation of the particles.

4.1. Deposition of the film

The laser beam, upon hitting the target, causes evaporation of titanium on the surface. The titanium atoms react with the ammonium gas in the plasma cloud and the product, which is TiN, is deposited on the surface of the film. The homogeneous build-up of the film would continue with increasing number of pulses, unless another process causing the formation of particles, interferes.

4.2. Formation of particles

Splashing of particles for many materials has been reported in the literature [14–17]. In general, the effect is more prominent if a pulsed laser is used for evaporation. Of the many reasons for the generation of particles, let us mention only two.

1. Splashing occurs if the transfer of laser energy into heat is faster than that needed to evaporate a thickness of layer equal to half of the diffusion depth. For the titanium surface this energy is 5×10^8 $\mathrm{W\,cm^{-2}}$ [18].
2. Splashing is also related to the surface morphology [16]. A smooth target surface produces less splashing than a rough one. After removal of the top layer from a fresh target, the surface becomes rough with the formation of pits and craters. These features are weak and disintegrate under the subsequent laser pulses.

The results of this investigation indicate that the reason for the formation of the particles is more or less in accordance with the latter. However, this theory fails to explain our observation of liquid traces on the target as well as the liquid-like shape of the particles. It is proposed that during the interaction of the laser beam with the rough surface of the pits and craters, liquid pockets are formed and splashed under the force of the plasma plume. When the target is fresh and smooth its reflection is much higher and the probability for the formation of liquid pockets is much smaller. This reasoning is in accordance with the fact that in the case of the rotating target the number of particles for a given number of pulses is much less.

5. Conclusions

In this investigation the morphology of TiN coatings produced by ultraviolet laser ablation has been studied. The results of the study can be summarized as follows.

1. A few hundreds of pulses are sufficient to induce a continuous and homogeneous coating on the polished steel surface.
2. The thickness of the coating increases with the number of pulses.
3. On the continuous layer, there are small micrometre-sized particles of various shapes and sizes.
4. The average size and density of these particles increase with the number of pulses.
5. When a rotating target is used, the rate of increase of the particles is much slower than that with a stationary target.

6. It is suggested that the mechanism of film formation is different from that of the multiplication of the particles.

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