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Rotary powder bed chemical vapour deposition of titanium nitride on spherical iron powder

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Titanium nitride (TiN) was coated on to spherical iron powder by the rotary powder bed chemical vapour deposition technique using a reactant gas of the $TiCl_4$–N_2–H_2 system. The dispersibility of the coated powder was significantly improved by the adsorption of the reactant gas on to the rotating particles during raising the temperature. Polycrystalline TiN film, having a columnar structure of a few micrometres was coated on to the iron powder, typically at a deposition temperature of 1000° C and at a treatment time of 80 min. The TiN-coated iron powder showed an oxidation resistance up to about 650° C.

1. Introduction

In the previous paper [1], we reported that titanium nitride-coated titanium or graphite powders can be prepared by the rotary powder bed chemical vapour deposition (RPB–CVD) technique, in which a rotary powder bed specimen cell is heated in a CVD reactant gas stream. The rotary powder bed CVD was recommended as a more versatile coating technique for powders, compared with the fluidized-bed CVD [2–4]. A detailed investigation of the dispersibility of the coated powder and the uniformity of the coated film is required using a starting powder which has a homogeneous particle shape and size distribution. In the present work, spherical iron powder with a uniform particle size distribution was chosen as a starting powder. Coating conditions of titanium nitride (TiN) on to the iron powder were invesitgated in relation to the structure and some properties of the coated powder.

2. Experimental procedure

The rotary powder bed CVD apparatus used is the same as that in the previous paper [1]. Commercial spherical iron powder (150 to 200 mesh) obtained by the gas atomizing method, was used as starting powder, which was packed into the rotary quartz specimen cell. The powder specimen (about 2 g) was degassed at 300° C for 20 min under 1×10^{-5} torr. Subsequently, the specimen was treated in an argon atmosphere and heated at the rate of 15 to 80° C min^{-1} with the specimen cell rotated at 90 r.p.m. The reactant gas mixture ($TiCl_4$–N_2–H_2) was introduced at a given temperature (300 to 600° C) during the process of raising the temperature. The CVD treatment was carried out at a constant temperature (800 to 1050° C) for 40 to 180 min under 760 torr with a rotary speed of the cell of 90 r.p.m. The reactant gas flow rates were kept constant as follows by reference to the previous paper [1]; $TiCl_4$ 3 ml min^{-1}, N_2 200 ml min^{-1}, H_2 300 ml min^{-1}, Ar 20 ml min^{-1}.

The coated powder was identified by X-ray diffraction. The surface and cross-section of the coated film were observed by scanning electron microscope (SEM). As-deposited powder or the powder embedded into epoxy resin was acid-treated in HCl aqueous solution. An oxidation resistance test in air was also carried

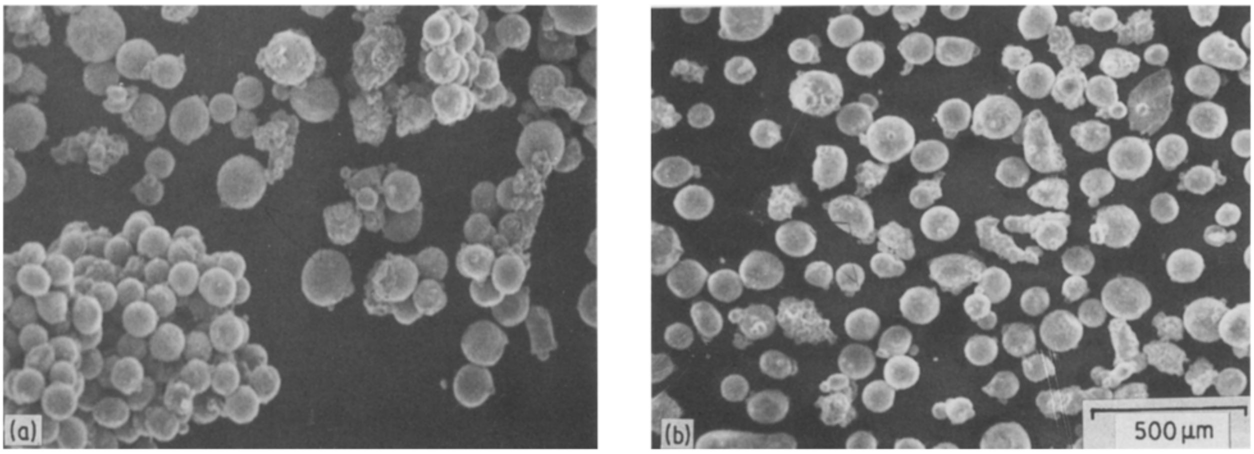

Figure 1 Scanning electron micrographs of the pretreated iron powder after treatment at 1050° C for 1 min. Onset temperature of the reactant gas introduction: (a) 600° C, (b) 300° C; heating rate (a) 80° C min^{-1}, (b) 15° C min^{-1}.

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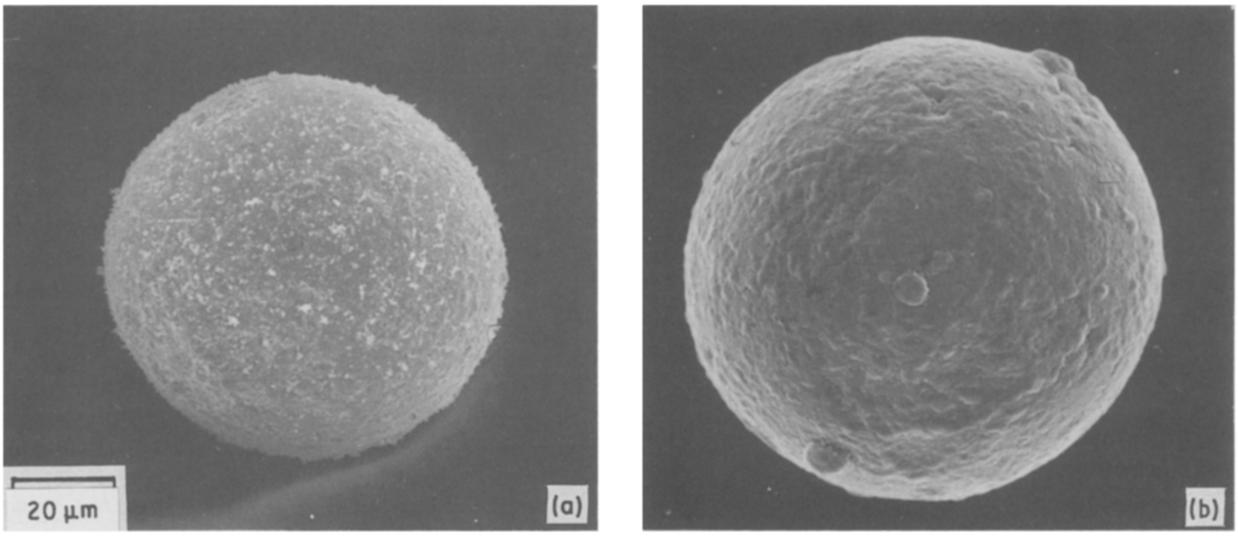

Figure 2 Surface appearance of the coated powder, treatment time 80 min. Treatment temperature: (a) 800° C (b) 1000° C.

out using the thermogravimetric analysis (TGA) apparatus.

3. Results and discussion

3.1. Coating conditions of titanium nitride on dispersed iron particles

Coagulation or partial sintering of iron powder begins at 600° C in an inert atmosphere. As the temperature is raised further, iron particles are consolidated to form a sintered lump. It was necessary to introduce the reactant gas to temperatures lower than the CVD treatment temperature (> 800° C) in order to prevent particle consolidation. Fig. 1 shows the scanning electron micrographs of the pretreated iron powder. When the onset temperature of introducing the reactant gas was 600° C and the heating rate was 80° C min^{-1}, a partial coagulation of pretreated particles was observed (see Fig. 1a). The dispersibility of iron particles was improved by decreasing the onset temperature to 300° C. Little coagulation was seen at the decreased heating rate of 15° C min^{-1} and the onset temperature of 300° C (see Fig. 1b). Adsorption of the reactant gas on to the rotating particles in the heating process was effective in improving the dispersibility of the pretreated iron particles.

The effects of treatment temperature on TiN deposition behaviour on iron particles were investigated. Figs 2, 3 and 4 show the temperature dependence of the surface appearance of the coated particle, X-ray diffraction patterns of the coated powder, and the film thickness of TiN, respectively. The colour of every coated powder treated at 800 to 1050° C for more than 40 min, was yellow or golden-yellow, which was easy to recognize as the presence of deposited TiN on the iron powder. Fig. 2a shows a coated particle treated at 800° C for 80 min. From the X-ray diffraction pattern in Fig. 3a, a small amount of TiN as well as a trace Ti_2N can be detected, although strong peaks of iron may still be identified. Island-like deposits of titanium nitride can be observed on the surface of the spherical iron particles, a continuous film of titanium nitride being found nowhere. Above the treatment temperature of 850° C, a uniform film of TiN was observed

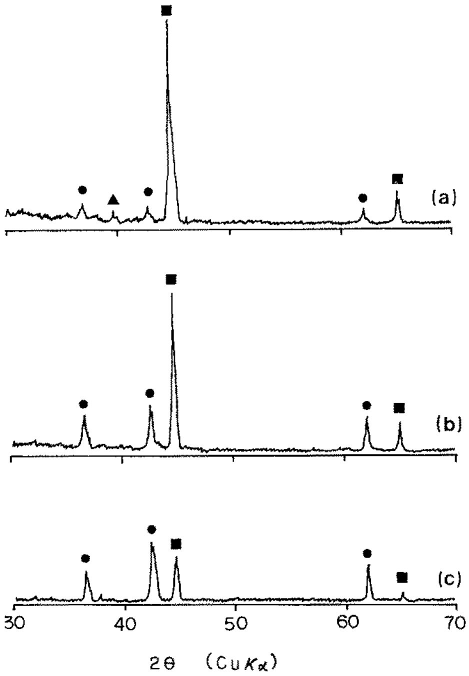

Figure 3 X-ray diffraction patterns of the treated iron powder: treatment temperature (a) 800° C, (b) 900° C, (c) 1050° C; (●) TiN, (▲) Ti_2N, (■) Fe.

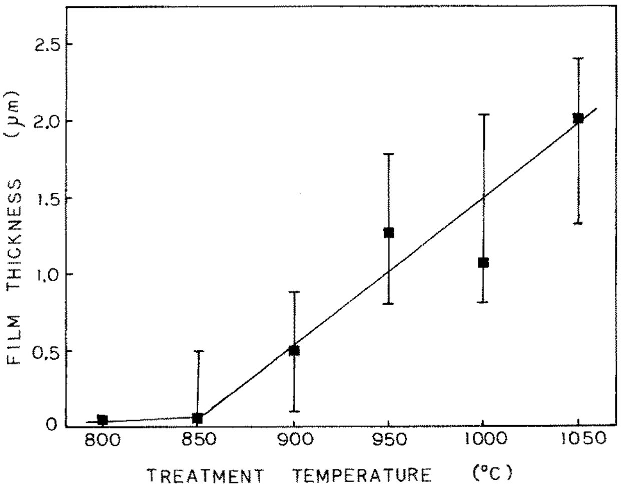

Figure 4 Variation of film thickness of TiN with treatment temperature; treatment time 80 min.

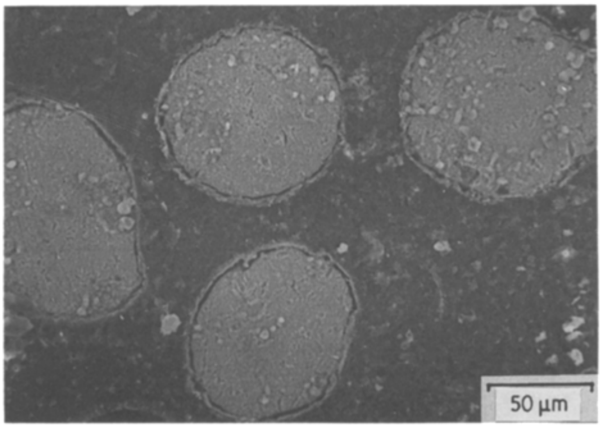

Figure 5 Cross-section of TiN-coated iron particles: CVD treatment 1000° C, 80 min; post-treatment in 1N-HCl, 90° C, 10 min.

with the crystallinity and the film thickness increasing as the temperature increased (see Figs 3b, c and 4). Porous and non-adherent TiN film was deposited at 900° C. A crack free and adherent coating was obtained by the treatment at 1000° C for 80 min, as shown in Fig. 2b. On the particle surface treated at 1050° C, cracks were occasionally observed presumably due to the increased film thickness and thermal stress in the cooling process of the specimen after the CVD treatment.

Fig. 4 shows a linear relationship between the film thickness and treatment temperature. It is noted that no depression of growth rate at temperature above 1000° C is confirmed. The kinetics of the TiN deposition process [5] would be surface reaction controlled even in the higher temperature range because the diffusion boundary layer between the TiN film and the vapour phase would be very thin in the rotating powder cell.

3.2. Structure and some properties of TiN-coated iron particles

Fig. 5 shows a scanning electron micrograph of the cross-section of TiN-coated iron particles, which were prepared by treatment at 1000° C for 80 min. The particles were embedded into the epoxy resin, then abraded and polished, after which the polished specimen was treated at 90° C for 10 min in 1N-HCl aqueous solution in order to distinguish the iron particles and the deposited TiN film. A uniform coating of TiN film with a thickness of a few micrometres can be seen.

Fig. 6a shows the appearance of a TiN shell, which was obtained by the CVD treatment at 1000° C for 80 min and the post-treatment at 90° C for 80 min in 2N-HCl aqueous solution. Iron was entirely corroded out of the sphere through the crack of TiN film, which might have been introduced during the cooling process of the coated powder after the CVD treatment. Fig. 6b shows a magnified view of the cross-section of the residual TiN shell in Fig. 6a. The columnar structure of TiN with a thickness of about 2 μm can be seen.

Fig. 7 shows the relationship between the TiN film thickness and treatment time, when the treatment temperature was 1000° C. Film thickness is found to increase linearly with treatment time, from which the growth rate of TiN film is about 1 μm h^{-1}.

TGA curves of the uncoated iron powder (a) and the coated powder (b) in air are shown in Fig. 8, where the sample of 100 mg was heated at 10° C min^{-1}. The uncoated powder began to be oxidized at about 400° C, while the coated powder (the same powder as in Fig. 5) was gradually oxidized at 500 to 700° C and a rapid weight increase was observed above 700° C (see Fig. 8b). The oxidation temperature of the coated powder (about 650° C) was higher by about 150° C than that of the uncoated powder (about 500° C). The oxidation resistance of the iron powder was apparently improved by RPB-CVD of TiN.

4. Conclusions

The following conclusions on the coating of spherical iron powder with TiN were obtained using the rotary powder bed CVD of the $TiCl_4$–N_2–H_2 system.

1. The dispersibility of the coated iron particles was increased considerably by the adsorption treatment of

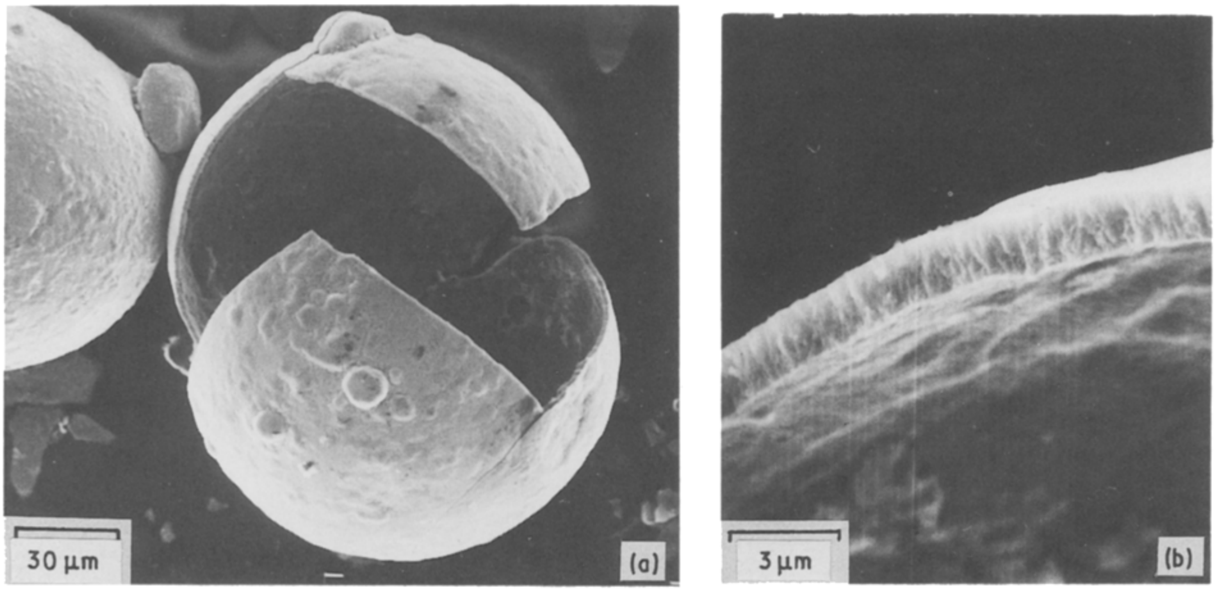

Figure 6 Scanning electron micrographs of TiN shell: CVD treatment 1000° C, 80 min; post-treatment in 2N-HCl, 90° C, 80 min; (a) outer shell after acid treatment, (b) a magnified fractured surface of the TiN film.

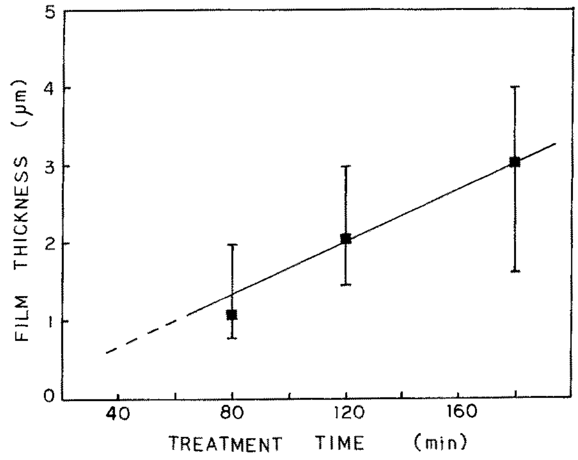

Figure 7 Variation of film thickness of TiN with treatment time: treatment temperature 1000° C.

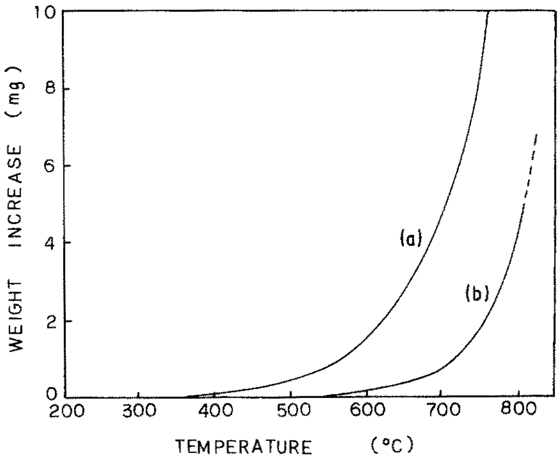

Figure 8 TGA curves of the uncoated powder (a) and the TiN coated powder (b): specimen 100 mg, heating rate 10° C min^{-1}.

the reactant gas on to the iron powder during heating prior to the CVD treatment.

2. Polycrystalline TiN film having a columnar structure was deposited on to the spherical iron powder at deposition temperatures of 900 to 1050° C and a treatment time of 60 to 180 min. The TiN-coated powder treated at 1000° C for 80 min has fewer pores and cracks, which improved the oxidation resistance of the coated powder.

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