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Production of Ti–TiN short fibres with a structurally gradient cross-section by a reaction between nitrogen plasma and rotating molten titanium metal

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Ti–TiN short fibres in which the outer surface was composed of a TiN phase were formed through a reaction between nitrogen plasma and rotating molten titanium metal in a rotating electrode process. The cross-section of the fibres was an ellipsoidal shape. The mean diameter and average length were about 0.15 mm and 2.9 mm, respectively, and the thickness of the TiN surface layer was in the range 2–6 μm. The cross-sectional structure of the fibre changed gradually from the TiN surface layer to titanium phase in the central region through the coexistent Ti + TiN phases. Vickers hardness also changed gradually from 1860 in the surface region to 300 in the central region. The nitrogen content was evaluated to be 4.6 at% for the titanium phase and 30 at% for the TiN phase from the lattice parameters. In addition, the weight ratio of the fibres to the consumed titanium electrode reached as high as 80% under conditions where the mixing ratio of N_2 to $(Ar + N_2)$ was 0.2 and the rotation speed of the titanium rod was 10 000 r.p.m. It is therefore concluded that the present technique is useful for the production of the structurally gradient short-fibres consisting of titanium and TiN phases.

1. Introduction

In recent years, there has been increasing attention to fine ceramics with high packing density in which the composition, crystal structure and microstructure are intentionally controlled. The fine ceramics have usually been produced by chemical vapour deposition, physical condensation and chemical reaction in forms of thin film or consolidated bulk made from ultrafine powders. The powder particles which have usually been used for the consolidation of the finely structure-controlled ceramics have a spherical morphology. In addition to a strong need for spherical ceramic powders, fibrous ceramics with a circular or an ellipsoidal cross-section have also attracted great attention because of a significant engineering need. However, little has been reported about the production of fibrous ceramics with a circular or an ellipsoidal cross-section by a direct method from liquidus phase. Recently, we carried out a series of investigations on the production and properties of ultrafine metallic, oxide, nitride and carbide powders by a reaction method between gas plasma and molten metal [1–3]. In the investigations, Ti–TiN fibres coated with a TiN phase with a diameter of about 0.2 mm and a length of 2–3 mm, were found to be produced through the reaction between nitrogen plasma and rotating molten titanium in a rotating electrode process. Furthermore, it was notable that the cross-section in the fibres had a compositionally gradient structure consisting of Ti → Ti + TiN → TiN along the radial direction from the central region. The present work studied the preparation conditions, gradient structure and hardness of Ti–TiN short fibres with an ellipsoidal cross-section and investigated the mechanism for the formation of the short fibres with a structurally gradient cross-section.

2. Experimental procedure

Fig. 1 shows a schematic illustration of newly designed equipment in which fibres in various component systems are produced through the reaction between gas plasma and rotating molten metal. A cylindrical titanium ingot with a diameter of 20 mm and a length of 60 mm was produced by melting in an arc furnace, followed by casting into a ceramic crucible and then mechanical polishing. The titanium cylinder was placed at the rotating axis so as to act as a rotating consumable anode in an atmosphere-controlled chamber. The distance between the tungsten cathode and the anode titanium rod was maintained in the range 1–2 mm. Furthermore, the cone-shaped copper rotator shown in Fig. 1 has inner and outer diameters of 160 and 50 mm, respectively, and a thickness of 6 mm. The consumable titanium rod is rotated at speeds, r_s, ranging from

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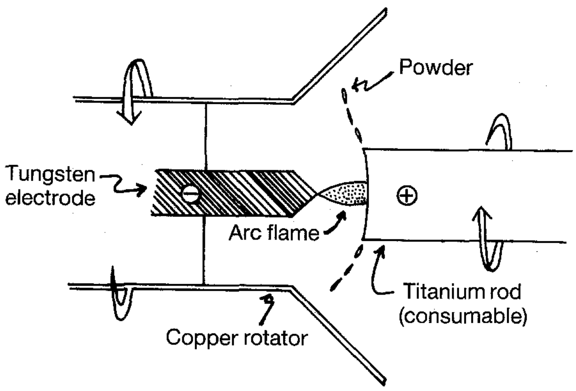

Figure 1 Schematic illustration of a rotating electrode process leading to a reaction between nitrogen plasma and rotating molten titanium metal.

5000–10 000 r.p.m. and then remelted by an arc at a constant current of 200 A for various periods, in different gas mixtures of argon and nitrogen. The mixing gas ratio of nitrogen to argon plus nitrogen, N_m, was changed in the range 0–1.0. The total gas pressure in the reaction chamber was fixed at 100 kPa. In addition, the rotation speed of the copper rotator was fixed at 2000 r.p.m. and the rotation direction was inverse to that of the titanium rod. The resulting fibres were collected in a vessel through the cyclone mechanism. The structure of the fibres was examined by X-ray diffractometry and scanning electron microscopy (SEM) and their morphology and size were evaluated by optical microscopy (OM) and SEM. The hardness on the cross-section of the fibres was measured by a Vickers microhardness tester with a load of 10 g.

3. Results

Fig. 2 shows the outer surface appearance of the titanium-based powders produced at a mixing gas ratio, $N_m(= N_2/(N_2 + Ar))$, of 0.3. The powder morphology is in a short-fibre form with a mean diameter of 0.2 mm and an average length of 2.5 mm. Fig. 3 shows the X-ray diffraction patterns of the short fibres produced in the N_m range of 0.3 and 0.8. All the diffraction peaks can be identified to be hcp Ti and fcc TiN as indexed in Fig. 3, indicating that the short fibres are composed of titanium and TiN phases. The lattice parameters of both the phases determined from the peak positions in Fig. 3 are $a = 0.2953$ nm and $c = 0.4704$ nm for the titanium phase and 0.4226 nm for the TiN phase. On comparing these lattice parameters with those for pure titanium metal [4], Ti(N) solid solution [5, 6] and stoichiometric TiN compound ([4] p. 998) the a and c values of the titanium phase are found to be slightly larger by 0.09 % and 0.44 %, respectively, while the a_0 value of the TiN phase is smaller by 0.40 %. The measured lattice parameters indicate that the nitrogen content is estimated to be 4.6 at % for the titanium phase and 28–30 at % for the TiN phase. Thus, the TiN phase has a composition largely deviated from the stoichiometric composition.

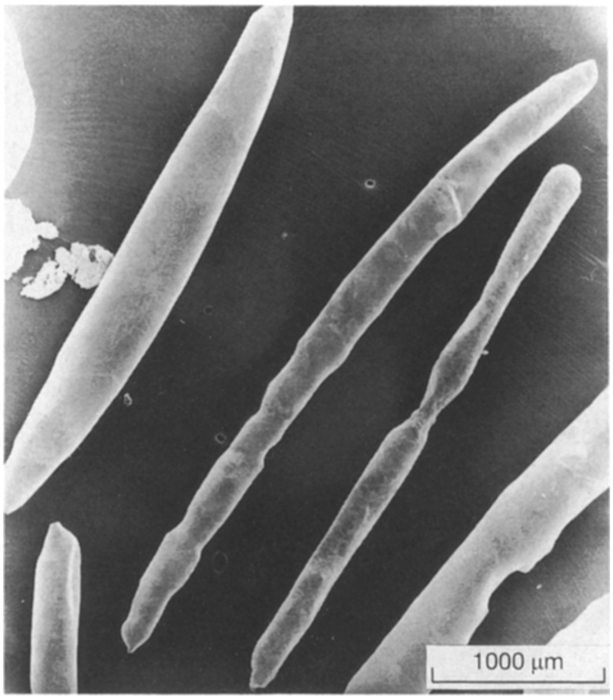

Figure 2 Scanning electron micrograph revealing the morphology of titanium-based fibres produced under the conditions of $N_m = 0.7$ and $r_s = 5000$ r.p.m. by a reaction method between nitrogen plasma and rotating molten titanium metal.

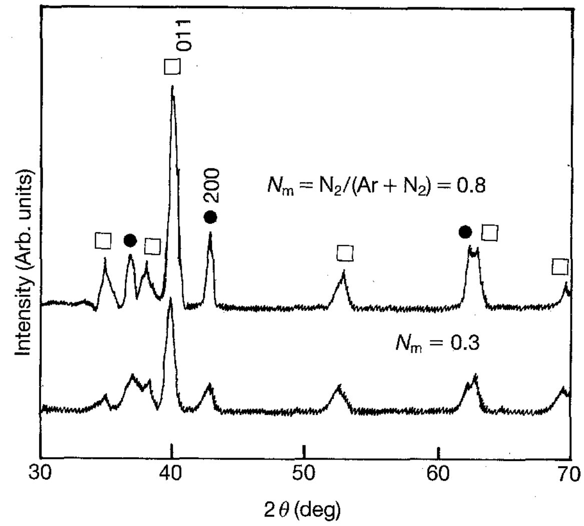

Figure 3 X-ray diffraction patterns of titanium-based fibres produced under the conditions of $r_s = 5000$ r.p.m. and $N_m = 0.3$ or 0.8. (●) TiN, (□) Ti.

It is also seen in Fig. 3 that the intensity of the TiN peaks for the fibres produced at $N_m = 0.8$ is much larger and the half-width is much smaller. The intensity ratio of the $(200)_{TiN}$ peak to the $(011)_{Ti}$ peak is plotted as a function of mixing gas ratio, N_m, in Fig. 4. The intensity ratio increases gradually in the N_m range below 0.6 and then significantly in the N_m range above 0.7. Furthermore, the intensity ratio of $(200)_{TiN}$ to $(011)_{Ti}$ is always higher for the 5000 r.p.m. condition than for the 10 000 r.p.m. condition. The difference is induced because the reaction time between molten titanium and nitrogen plasma is longer for the 5000 r.p.m. condition. It should be noticed that the intensity of the TiN peak exceeds that of the titanium

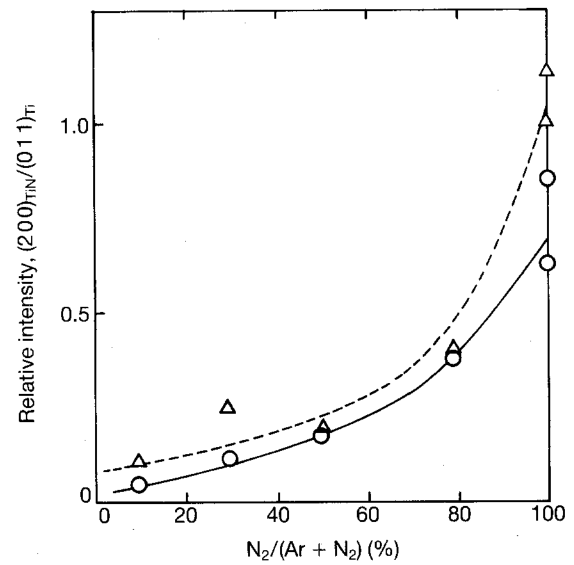

Figure 4 Change in the relative intensity of the TiN and titanium diffraction peaks $(200)_{\mathrm{TiN}}/(011)_{\mathrm{Ti}}$, for Ti–TiN fibres as a function of N_m. (△) 5000 r.p.m., (○) 10 000 r.p.m.

peak under the conditions of $N_m = 1.0$ and $r_s = 5000$ r.p.m.

In order to clarify the microstructure of the coexistent titanium and TiN phases, the cross-sectional structure of the short fibres was examined by OM and SEM. Fig. 5 shows the cross-sectional structure of the short fibre produced at $N_m = 0.3$ and $r_s = 5000$ r.p.m. The structure was observed after etching for 10 s at 293 K in a solution of HNO_3 and HF with a mixing volumetric ratio of 4:1. The contrast in the cross-section can be divided into three regions; (1) h c p Ti phase with dark contrast in the central region, (2) coexistent Ti + TiN phases with a dendritic morphology, and (3) TiN phase with bright contrast in the outer surface region. Here, it is important to point out that the degree of the bright contrast increases gradually on approaching the sample surface. That is, the volume fraction of the TiN phase increases gradually with increasing distance from the central point, indicating clearly the formation of structurally (compositionally) gradient fibres. Furthermore, the volume fraction of TiN phase in the whole cross-section, as well as the thickness of the TiN surface layer, increases significantly with increasing N_m. Fig. 6 shows the change with N_m in the thickness of the TiN surface layer in the Ti–TiN fibres. Although no TiN layer is formed in an argon atmosphere, the thickness is about 2 μm at $N_m = 0.1$, remaining almost unchanged in the N_m range 0.1–0.5, and then increasing to 6 μm at $N_m = 1.0$. It is also seen in Figs 2 and 5 that the fibres usually have an ellipsoidal cross-section. With the aim of confirming the formation of the Ti–TiN fibres with the structurally gradient cross-section, Vickers hardness was measured on the cross-section of the fibres. Fig. 7 shows the sites at which the measurement of Vickers hardness, H_v, was made and the change in H_v of the Ti–TiN fibre produced at $N_m = 0.2$ and $r_s = 5000$ r.p.m. as a function of distance from the outer surface. H_v is as high as 1860 in the surface region below 2 μm from the outer surface edge, decreases gradually to 400 with increasing distance from the surface edge to 16 μm, and then becomes constant ($\simeq 300$) in the central region. The significant change in H_v indicates distinctly that the fibre has a structurally gradient cross-section in which the outer surface layer is composed of TiN and the volume ratio of TiN/(Ti + TiN) decreases with increasing distance from the outer surface layer. It has previously been reported that $H_v = 2500$ for a stoichiometric TiN

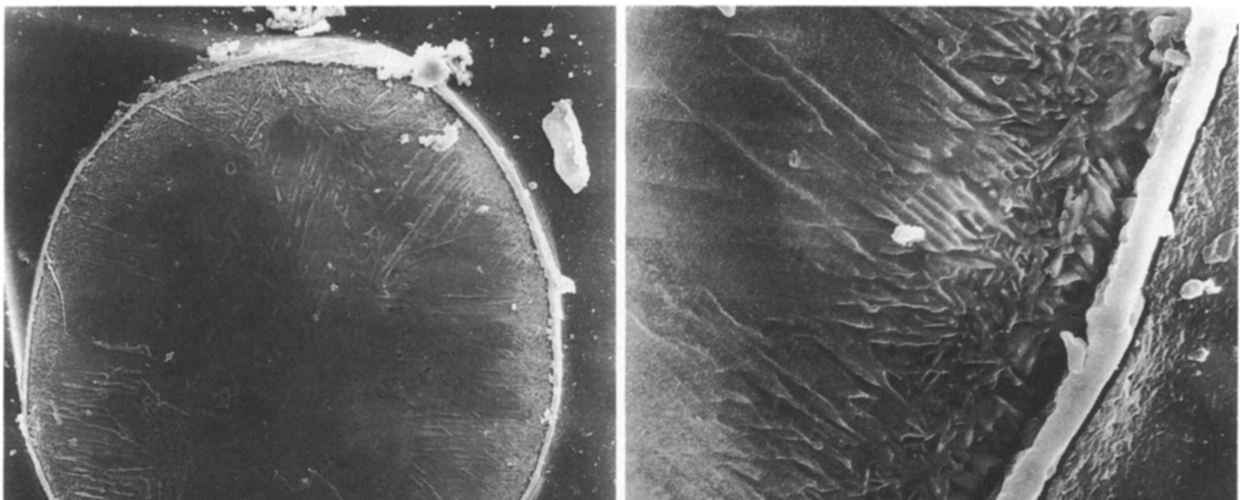

Figure 5 Scanning electron micrographs revealing the cross-sectional structure of a Ti–TiN fibre produced at $N_m = 0.3$ and $r_s = 5000$ r.p.m.

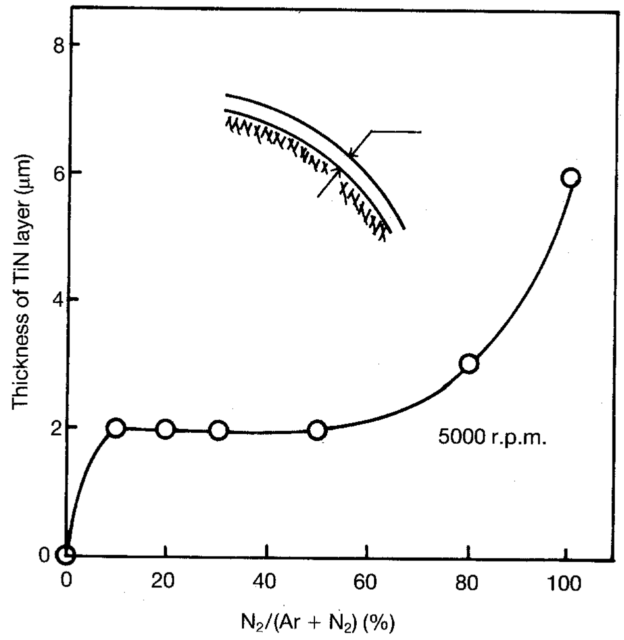

Figure 6 Change in the thickness of the TiN surface film in Ti–TiN fibres as a function of N_m.

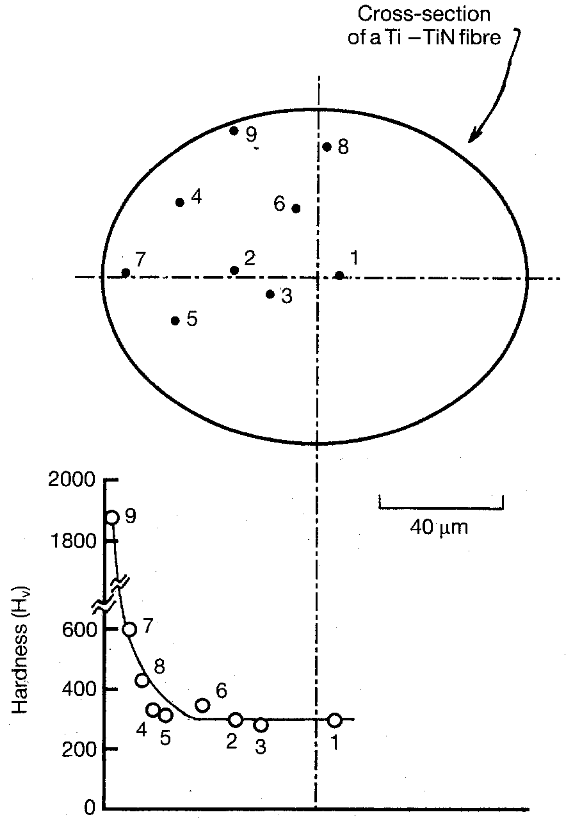

Figure 7 Change in the Vickers hardness on the cross-section in Ti–TiN fibres as a function of distance from the outer surface. The numbers represent the sites where the measurement of hardness was made.

phase ([7] p. 154) and 120 for a pure titanium metal ([7] p. 181). The H_v value of the present titanium phase is considerably higher than that of pure titanium, indicative of the dissolution of nitrogen. On the other hand, that of the present TiN phase is considerably lower because of the nitrogen content smaller than that of the stoichiometric TiN phase. The results of H_v values for the titanium and TiN phases are consistent with that derived from the X-ray diffractometry shown in Fig. 3.

Fig. 8 shows the changes in the length and mean diameter of the Ti–TiN fibres as a function of N_m. The length and diameter are in the range 1.5–4 mm and 0.1–0.3 μm, respectively, being almost independent of N_m. In addition, the length of the fibres is slightly longer for the 5000 r.p.m. condition, although no distinct difference in diameter is seen. The difference in length is presumably due to a larger size of the liquid droplets in the case of 5000 r.p.m. because of the decrease in the centrifugal force with decreasing r_s.

Fig. 9 plots the ratio of the weight of the fibres to the weight loss of the consumed titanium electrode as a function of N_m. The weight ratio corresponding to the yield ratio of the fibres shows a sharp maximum around $N_m = 0.2$ and decreases significantly with deviation from the N_m value. The maximum yield ratio of the fibres reaches as high as about 80% under the condition of 10 000 r.p.m. The reason why the fibres are produced at the high yield ratio around $N_m = 0.2$ is presumably because the liquid droplets have an optimum viscosity which is favourable for the change in morphology from sphere to fibre. With further increase in N_m from 0.2, the viscosity of the liquid droplets increases rapidly because of an increase in the dissolution amount of nitrogen and the thickness of the surface TiN layer, resulting in an increasing difficulty of morphology change from sphere to fibre. Furthermore, no short fibres are formed at $N_m = 0$ and the resulting powders have a flaky shape produced by impact flattening of liquidus spherical droplets against the copper rotator. Consequently, the formation of liquid droplets covered with a TiN surface film with an appropriate thickness seems to be

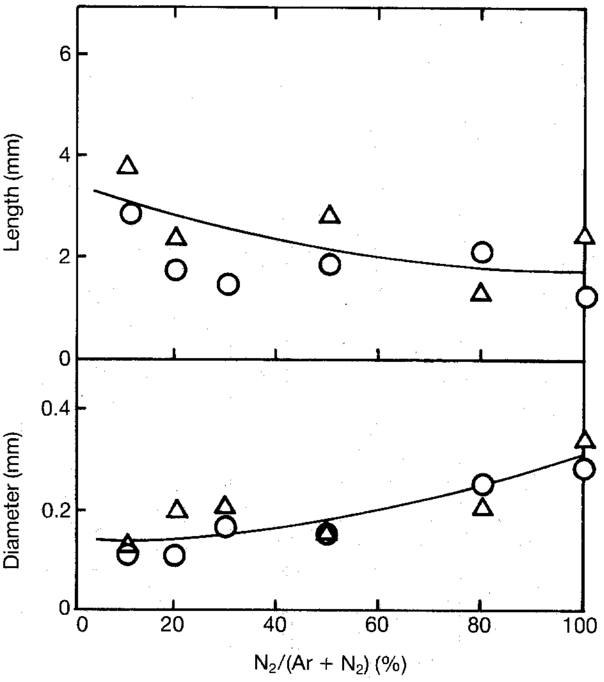

Figure 8 Changes in the length and diameter of Ti–TiN fibres as a function of N_m. (○) 10 000 r.p.m., (△) 5000 r.p.m.

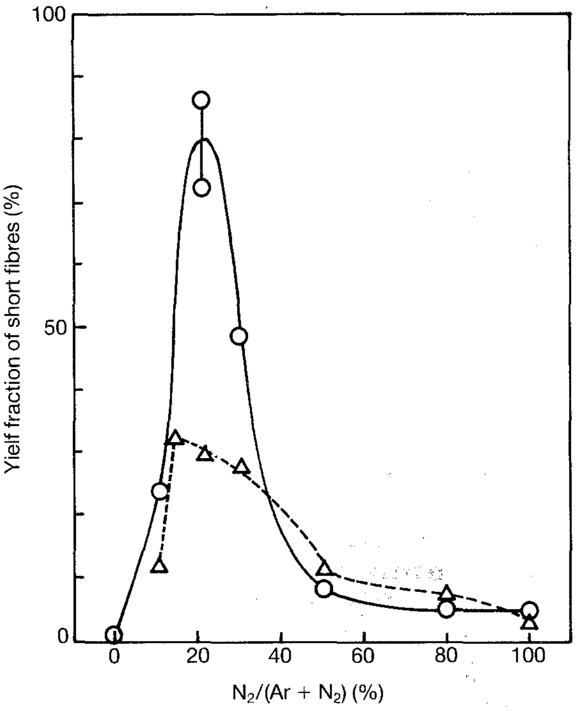

Figure 9 Change in the yield fraction of Ti–TiN short fibres as a function of N_m. (○) 10 000 r.p.m., (△) 5000 r.p.m.

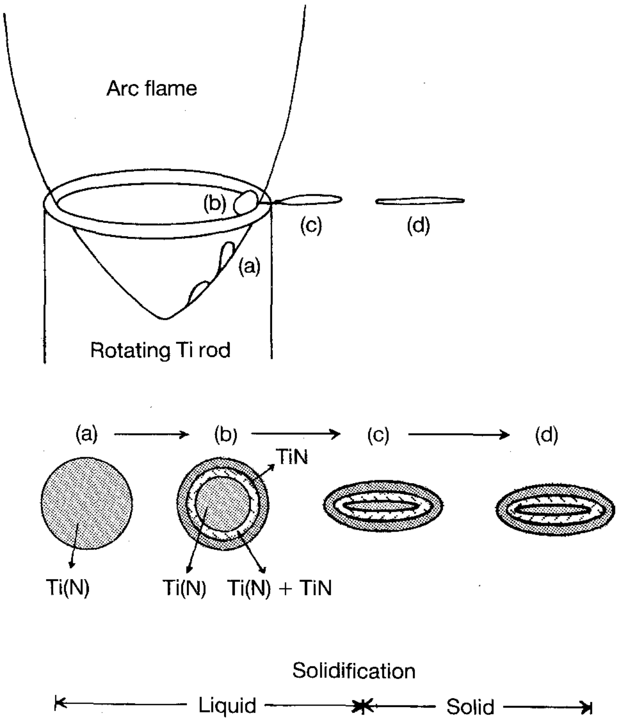

Figure 10 Schematic illustration of the formation process of the Ti–TiN fibres with a structurally gradient cross-section.

essential for the formation of the short fibres at a high yield ratio. In addition, the yield ratio of the fibres at $r_s = 10\,000$ r.p.m. and $N_m = 0.2$ is about three times as high as that at $r_s = 5000$ r.p.m. and $N_m = 0.2$. The significant difference in the yield ratio indicates that a large centrifugal force is also required for the morphology change from sphere to fibre. Accordingly, it is presumed that the unique fibres are produced through the simultaneous achievement of an appropriately high viscosity of the liquid droplets resulting from the dissolution of nitrogen and the formation of TiN surface film and the large centrifugal force leading to the morphology change from sphere to fibre even for the liquid droplets with approximately high viscosity. Based on these two criteria for the production of short fibres, the production of similar short fibres with a structurally gradient cross-section has been attempted in a number of metallic–ceramic systems.

4. Discussion

Fig. 10 illustrates the formation process of the Ti–TiN fibres with a structurally gradient cross-section. It is known that the temperature in the nitrogen plasma reaches as high as about 10^4 K [8] which is much higher than the melting temperature (3223 K) of the stoichiometric TiN phase. Accordingly, immediately after the liquid droplet of titanium metal is formed, nitrogen enters the liquid droplet and simultaneously TiN phase is formed near the outer surface of the liquid droplet. After the TiN surface film was once formed, further dissolution of nitrogen into the TiN phase is thought to be considerably sluggish compared with that into titanium phase, because the nitrogen content in the TiN phase is about 30 at %, corresponding to the lowest composition in the TiN phase field in an equilibrium Ti–N phase diagram [9]. In the nitrogen plasma atmosphere, the titanium and TiN phases are in a liquid state and the liquid droplets consisting of the two phases are estimated to have a rather low viscosity, although the outer surface is covered with the TiN phase. Subsequently, the liquid droplets are flung off by the centrifugal force from the nitrogen plasma atmosphere to the conventional nitrogen gas atmosphere. The centrifugal force is presumed to cause the change in the shape from sphere to fibre, accompanying rapid cooling which leads to the solidification of the liquid droplet in the fibre form.

Here, it is of value to estimate the size, flight velocity and centrifugal force for the liquid droplets. As shown in Fig. 8, the mean diameter and average length of the fibre are 0.17 mm diameter × 3.6 mm long at $r_s = 5000$ r.p.m. and 0.14 mm diameter × 2.1 mm long at $r_s = 10\,000$ r.p.m. Assuming that the volume of the fibre is equal to that of the liquid droplet, the diameter of the liquid droplets immediately before the flow by the centrifugal force is calculated to be 0.538 mm at $r_s = 5000$ r.p.m. and 0.396 mm at $r_s = 10\,000$ r.p.m. Under the assumption that the density of the liquid droplets is equal to that (4.11 Mg m^{-3}) for pure titanium, the weight of the liquid droplets is 0.336 mg at $r_s = 5000$ r.p.m. and 0.133 mg at $r_s = 10\,000$ r.p.m. The flight velocity of the liquid droplets by the centrifugal force is calculated to be 5.24 m s^{-1} at $r_s = 5000$ r.p.m. and 10.47 m s^{-1} at $r_s = 10\,000$ r.p.m. and hence the centrifugal force becomes 9.23×10^{-4} and 1.47×10^{-3} kg m s^{-2} at $r_s = 5000$ and 10 000 r.p.m., respectively. In the present equipment shown in Fig. 1, a copper rotator is rotating at a distance of 50 mm from the outer edge of the rotating electrode. The flight time of the fibre up to the copper plate is as short as 9.5 and 4.8 ms at $r_s = 5000$ and

10 000 r.p.m., respectively. The formation of the fibre with an ellipsoidal cross-section indicates that the shape of the fibre remains almost unchanged even by the collision against the rotating copper rotator. The maintenance of the original shape is presumed to be achieved from the high hardness of the TiN surface film and the rather low flight velocity of the fibre. Furthermore, achievement of the high hardness which can retain the original shape also suggests that the cooling rate within the short flight time is rather high.

5. Conclusion

The application of the rotating electrode process combined with a nitrogen plasma arc melting to pure titanium alloy was found to cause the formation of Ti–TiN fibres with an ellipsoidal cross-section. The mean diameter and average length are 0.17 and 3.6 mm at $r_s = 5000$ r.p.m. and 0.14 and 2.1 mm at $r_s = 10\,000$ r.p.m. The fibre can be produced at a high yield fraction of about 80% under the conditions of $N_m = 0.2$ and $r_s = 10\,000$ r.p.m. The cross-sectional structure changes gradually from h c p Ti(N) phase in the central region to f c c TiN phase in the outer surface region, through coexistent Ti(N) plus TiN phases along the radial direction. From the lattice parameters, the nitrogen content is evaluated to be about 4.6 at % in the central titanium phase region and about 30 at % in the outer surface TiN layer. Vickers hardness also changes gradually from 1860 in the outer surface region to 400 within the distance of 16 μm from the outer surface edge and remains almost constant ($\simeq 300$) in the central region. The Ti–TiN fibres with the structurally gradient cross-section are presumed to be formed through a sequential process of the formation of liquid droplets, followed by the dissolution of nitrogen, the formation of TiN surface film, the change in the morphology from sphere to fibre, and then solidification.

References

1. A. INOUE, B. G. KIM, K. NOSAKI, T. YAMAGUCHI and T. MASUMOTO, *J. Mater. Sci. Lett.* **11** (1992) 865.
2. A. INOUE, T. YAMAGUCHI, B. G. KIM, K. NOSAKI and T. MASUMOTO, *J. Appl. Phys.* **71** (1992) 3278.
3. A. INOUE, B. G. KIM, K. NOSAKI, T. YAMAGUCHI and T. MASUMOTO, *ibid.* **71** (1992) 4025.
4. W. B. PEARSON, "A Handbook of Lattice Spacing and Structures of Metals and Alloys" (Pergamon Press, London, 1958) p. 129.
5. H. T. CLARK, *J. Metals* **1** (1949) 588.
6. A. E. PALTY, H. MARGOLIN and J. P. NIELSEN, *Trans. ASM* **46** (1954) 312.
7. "Metals Databook", edited by The Japan Institute of Metals (Japan Institute of Metals, Maruzen, Tokyo, 1983) p. 154.
8. C. E. JACKSON, *J. Am. Weld. Soc.* **39** (1960) 225s.
9. T. B. MASSALSKI (ed.), "Binary Alloy Phase Diagrams", 2nd Edn (ASM, Metals Park, OH, 1990) p. 2705.

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