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Formation of TiN whiskers through carbothermal reduction of TiO_2

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Formation of TiN whiskers through carbothermal reduction of TiO_2 in nitrogen was studied. Effect of (i) addition of potassium (K_2CO_3) and nickel ($NiCl_2$), (ii) reaction temperature on the formation of whiskers was studied. Addition of K_2CO_3 has strong influence on the formation whiskers. The yield of whisker was maximum at 920–1000°C. At higher temperatures, formation of particulates of TiN was the dominant process. Increase in K_2CO_3 concentration increased the formation of (i) whiskers at low temperatures 815°–920°C, (ii) particulates at high temperatures 1000°–1100°C. A vapor-liquid-solid growth mechanism of whisker formation was identified. K_2CO_3 has been identified as an essential constituent for the formation of a low melting liquid by reaction with TiO_2 and $NiCl_2$. Continuous supply of TiO, nitrogen and CO to this complex K-Ni-Ti liquid droplet lead to the precipitation of TiN whisker. © *2002 Kluwer Academic Publishers*

1. Introduction

Due to high strength, and oxidation resistance, SiC whiskers are widely considered for reinforcing various materials. However, SiC whiskers have some limitations because of their high chemical stability. Except SiC whiskers, there are very few types of whiskers commercially available on a large scale. There is a need to produce new whisker materials on a large scale.

Titanium nitride (TiN) is a technologically very important material because of its extreme hardness (8 to 9 on the Mohs scale), abrasion resistance comparable to diamond, its high melting point (2950°C), gold colour and high electrical conductivity. It is stable at high temperatures in inert atmospheres. But air, oxygen, and oxidising acids like HNO_3 convert TiN into TiO_2 above ambient temperature. According to thermodynamic calculations TiN should be compatible with SiC, Al_2O_3, ZrO_2, Si_3N_4 and TiB_2 [1]. TiN whiskers are said to have better chemical stability toward iron aluminides and nickel aluminides than has SiC [2]. They may be useful in these aluminides and other metal matrix composites.

There are several reports on the formation of TiN whiskers [3–9]. They are essentially based on chemical vapour deposition using a set of reagents: $TiCl_4$, N_2, and H_2. Aivazov *et al.* [3] used these reagents at 1400°C to grow large millimetre sized crystals of TiN. With same set of reagents at 1200°–1300°C Kat *et al.* [4] could form TiN needle type crystals on graphite plates. Sugiyama *et al.* [5] studied the effect of gold metal droplets on the growth of TiN whiskers on quartz glass. The whisker growth was detected at 1050°–1065°C. Bojarski *et al.* [6] studied the growth and morphology of TiN whiskers formed on tungsten substrate at temperatures >1300°C. Kamiya *et al.* [8] prepared TiN fibers by nitridation of TiO_2 fibers prepared by a solgel method. By exposing to NH_3 for 5 h at 1100°C the TiO_2 fibers were completely converted into TiN fibers. The production of TiN whiskers by reaction of sodium titanium bronze (Na_x TiO_2), with excess sodium cyanide (NaCN) at 1000°C is reported by Bamberger *et al.* [1]. Similarly the formation of TiN whiskers from oxide containing cyanide melts was studied by Bamberger *et al.* [9].

Literature of recent patents [10–12] revealed the process of carbothermal preparation of TiC and TiN whiskers via a VLS mechanism. Kida [10] and Nygren *et al.* [11] used TiO_2, carbon, and MCl (M = Li, Na, or K) as raw materials, and Ni as a catalyst. TiN whiskers formed in nitrogen, whereas argon is used for TiC whiskers. Influence of various parameters on the yield and morphology of TiC whiskers has been reported by Ahlen *et al.* [13]. In the process revealed by Nixdorf *et al.* [12] the TiO_2 fine powder was mixed with carbonized organic fibers and small quantity of Co and Mg metal catalyzing or nucleating agent powder. By heat treating in a mixture of nitrogen and chlorine gas, TiN whiskers were produced. In our previous work [14], the effect of potassium, nickel, and heating rate on the formation of TiC whiskers was studied. In this work the formation of TiN whiskers was studied using reactants: TiO_2, C, K_2CO_3, and $NiCl_2$.

2. Experimental procedure

2.1. Materials

Laboratory reagent grade TiO_2 powder was obtained from Glaxo laboratories (India) Ltd, Bombay-400025. Laboratory reagent grade $NiCl_2$ was supplied by Qualigens Fine chemicals, Bombay-400075, India. Specpure K_2CO_3 was procured from Johnson Mathey chemicals

TABLE I Purity of reactants used for synthesis of TiN

Chemical	Manufacture	Impurity level	
K_2CO_3	Johnson Matthey U.K., England	Sr	3 ppm
		Mg, Na	1 ppm
		Ca, Fe, Li	<1 ppm
$NiCl_2$	Qualigens Fine Chemicals, Ltd. Mumbai, India	SO_4	0.005%
		Co	0.002%
		Fe	0.002%
TiO_2	Glaxo Laboratories India Ltd, Mumbai	Fe	0.005%
		LOI	0.5%
C. Black	Philips Carbon Black Ltd. Durgapur, India.	Grade N220, ISAF-HM	

limited, Hertfordshire, England. Carbon black of grade N220, was obtained from Philips carbon black Ltd., Durgapur, India. The level of impurities in above chemicals is given in Table I. Amorphous carbon was prepared by carbonizing cotton fibers in nitrogen atmosphere for 1 h at 815°C.

2.2. Experimental

Three types of powder mixtures were prepared by dry ball milling for 5 h. TiO_2, carbon black, $NiCl_2$, and K_2CO_3 were taken in weight ratio; ($TiO_2 : C : NiCl_2 : K_2CO_3 = 20 : 6 : 5 : x$), where $x = 2.5/5.0/7.5$. Its equivalent molecular ratio is (TiO_2 : C: $NiCl_2$: $K_2CO_3 = 1 : 2 : 0.15 : x$), where $x = 0.072/0.144/0.216$. $NiCl_2$ solution was prepared by dissolving 5 g of $NiCl_2$ in 30 ml of de-ionised water. Similarly 2.5 g of K_2CO_3 was dissolved in 30 ml of de-ionised water to make a solution of K_2CO_3. Twenty grams of TiO_2 powder was added to $NiCl_2$ solution taken in a 500 ml capacity glass beaker. After thorough mixing, K_2CO_3 solution was added. The mixture was dried in an oven at 110°C. The dried mix and 6 g of carbon black were taken in an agate pot and dry ball milled for 5 h; this powder mixture was designated as TNKC2.5. To study the effect of concentration of K_2CO_3 on the formation of whiskers two more TNKC powder mixes were prepared. The mixes containing 5 g and 7.5 g of K_2CO_3 are designated as TNKC5 and TNKC7.5, respectively. Finally one more mixture of TiO_2 and K_2CO_3 in 1 : 3 molar ratio was prepared and designated as TK.

Cylindrical graphite holders of 2.5-mm wall thickness and 10-mm inner diameter were filled with powder mixtures. The holders were closed with graphite stoppers and placed in the hot zone of high-temperature graphite resistance furnace (ASTRO, U.S.A., Model 1000-3060-FP20). The furnace was evacuated to a moderate vacuum (5×10^{-2} Torr) and back filled with 1-atm nitrogen. Experiments were conducted at 815°, 883°, 920°, 1000°, and 1100°C for 45 min. The heating rate employed was $\approx$40°C min^{-1}. The temperature was maintained with a Model 939A3 Honeywell radiation pyrometer. After reviewing the results, to study the effect of another form of carbon, cotton fibers were carbonized for 1 h at 815°C in nitrogen atmosphere. Using this carbonized cotton fibers two powder mixes of composition similar to that of TNKC2.5 and TNKC7.5 were prepared. These two mixes were also pyrolysed at 920°C for 45min in 1-atm nitrogen. A sample of TK was pyrolysed in nitrogen at 1150°C for 45 min.

The reacted samples were ground in an agate mortar and analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A Philips X-ray diffractometer, Model PW3710, with Cu radiation through Ni filter was used. The morphology of the reacted powders was examined with a Model ISI-100A International Scientific Instruments SEM. Energy Dispersive X-ray Analysis (EDX) was done by ISIS Linc, Oxford system connected to an SEM, Leo440i, England. Scanning Electron Probe Microanalysis (SEPMA) was carried out with CAMECA (model CAMEBAX-MICRO, France) equipment.

3. Results and discussion

Depending on the temperature of reaction the samples existed in the form of loose or an agglomerated powder. Upto a reaction temperature of 883°C, the samples appeared like unreacted powders. At 1100°C all the three sample were in gold colour. XRD patterns revealed the fact that TiN has formed in all samples at all reaction temperatures (Fig. 1). At 815°C the intensities

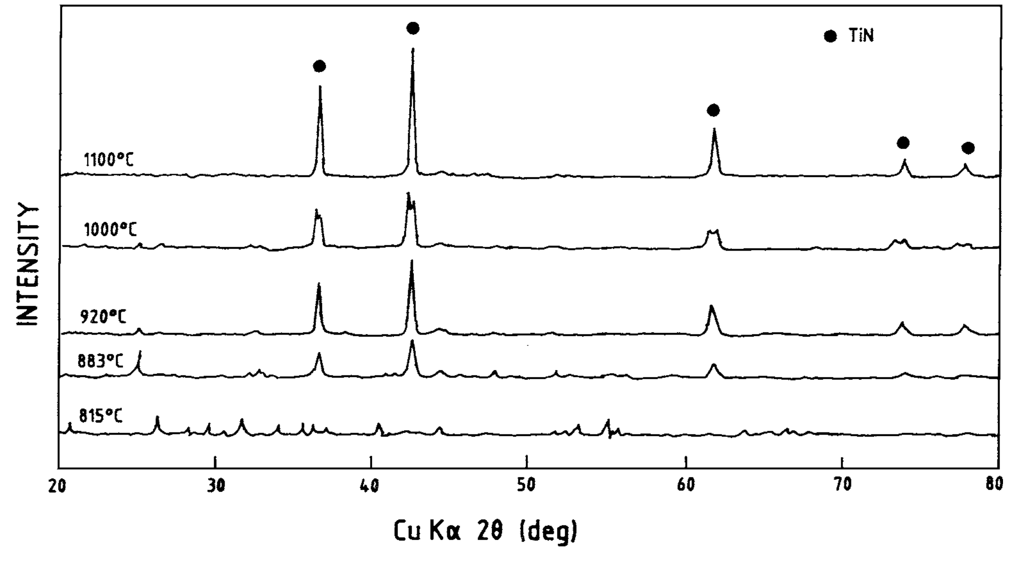

Figure 1 XRD patterns of TNKC2.5 reacted at different temperatures.

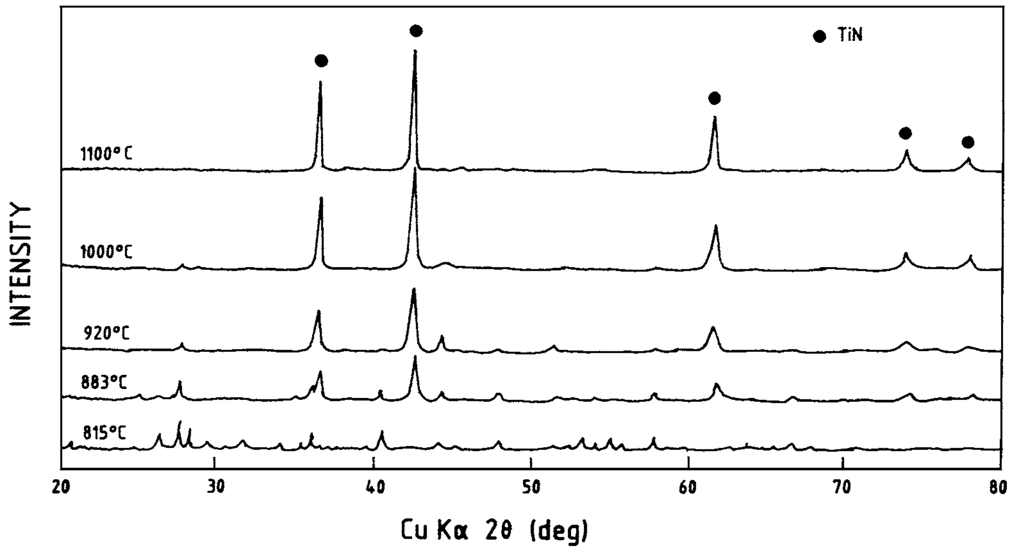

Figure 2 XRD patterns of TNKC5 reacted at different temperatures.

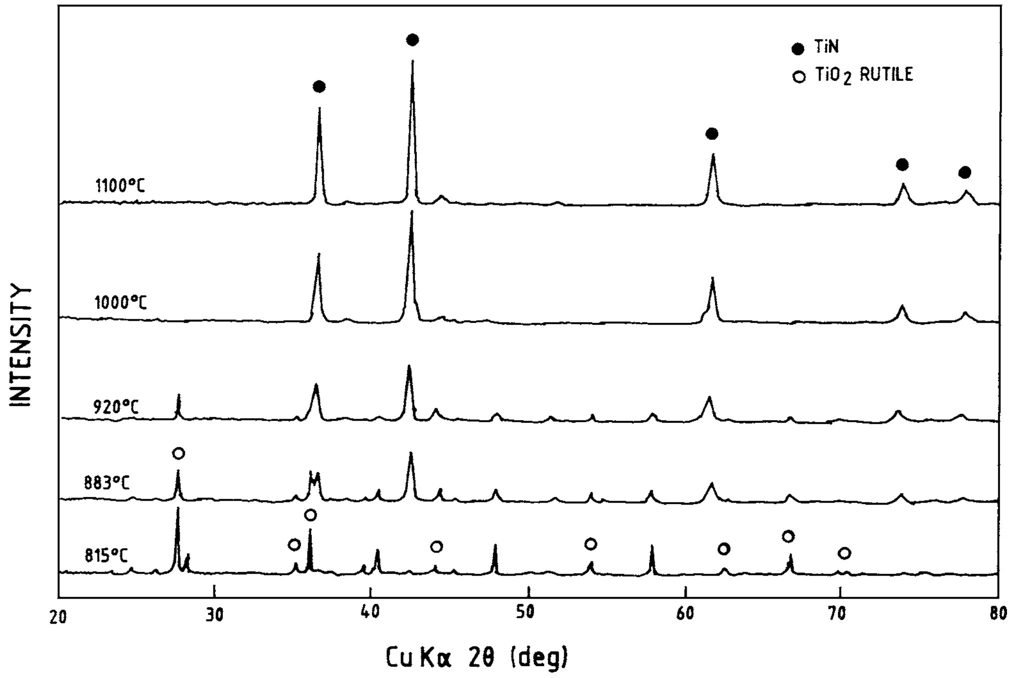

Figure 3 XRD patterns of TNKC7.5 reacted at different temperatures.

of TiN peaks were small (Fig. 2). At this temperature peaks corresponding to unreacted TiO_2 (rutile) were also observed In TNKC7.5 (Fig. 3). Above 920°C peaks corresponding to TiN only were seen. The intensities of TiN peaks increased with an increase in reaction temperature.

The morphology of TNKC2.5 samples reacted at different temperatures is shown in SEM micrographs (Fig. 4). At 815°C very few whiskers were observed. The whisker content increased with reaction temperature and attained a maximum at 1000°C (Fig. 4b). After reaction at 1100°C the formation of particulates by agglomeration of whiskers was observed (Fig. 4c). It appears that the whiskers formed at lower temperatures converted into thick and short particles. Spherical tips of whiskers suggest that they are formed by vapour-liquid-solid growth mechanism.

Similar results were observed in TNKC5 also. But the formation of whiskers at 815°C is slightly more than that formed in TNKC2.5. At 920°C maximum quantity of whiskers were formed (Fig. 5a). In this system at 1000°C itself formation of totally particulates was observed. In TNKC7.5 at temperature as low as 815°C, large number of whiskers were formed (Fig. 5b). But at 920°C the formation of particulates by agglomeration of whiskers was observed. In this system only particulates were formed at 1000°C and 1100°C. In the samples containing carbonized cotton fibers, no whisker morphology was observed.

Potassium titanate whiskers were formed by the reaction between K_2CO_3 and TiO_2 in TK (Fig. 6). Energy dispersive X-ray (EDX) analysis confirmed the presence of Ti, and N in stems and spherical tips of TiN whiskers. In the EDX of spherical tips, peaks of potassium and nickel were also observed (Fig. 7). The peak of aluminium in Fig. 7 is from the sample holder. Though the compositions varied, all whisker tips contained Ti, N, K, and Ni. The EPMA analysis also confirmed the

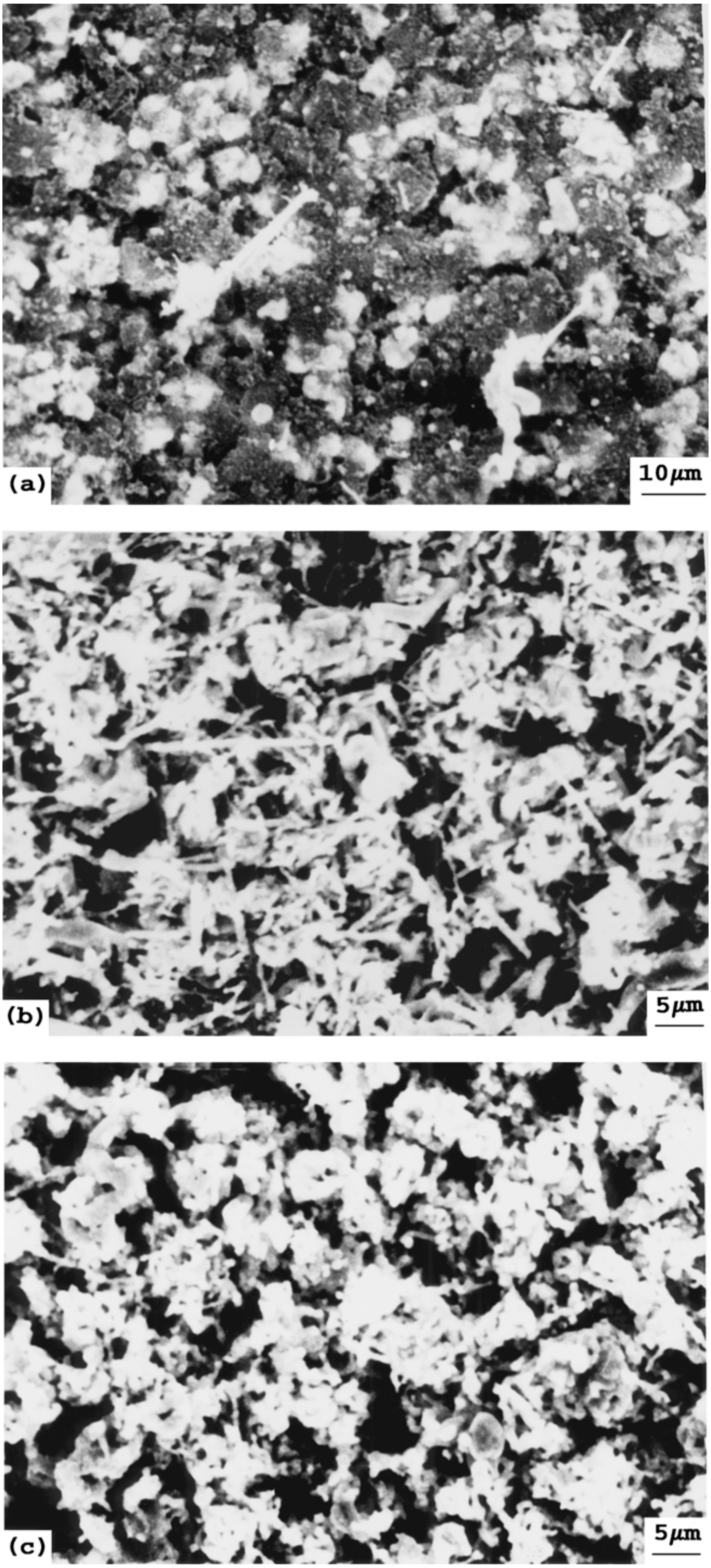

Figure 4 Morphology of TNKC2.5 reacted at (a) 815°C, (b) 1000°C and (c) 1100°C.

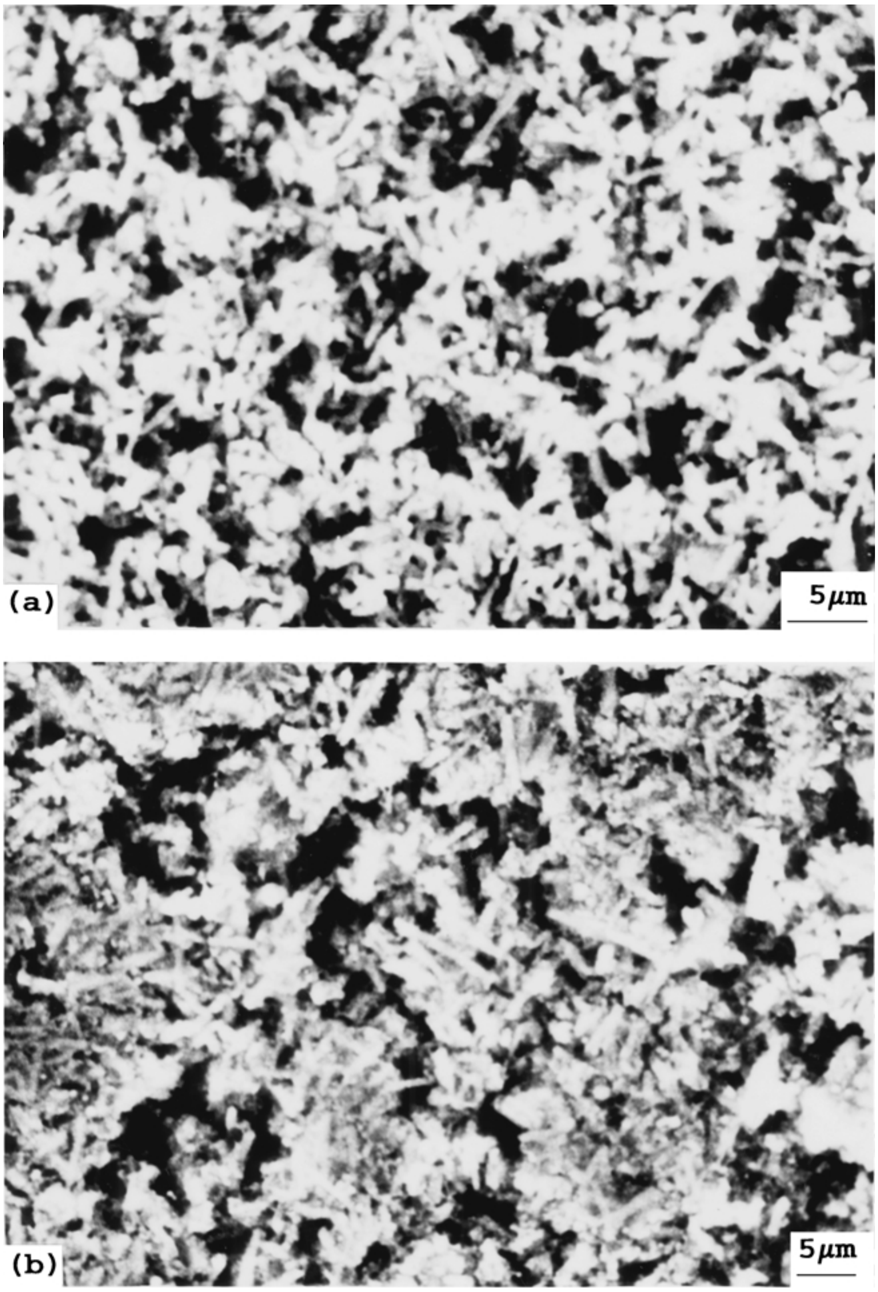

Figure 5 Morphology of (a) TNKC5 reacted at 920°C and (b) TNKC7.5 reacted at (a) 815°C.

Figure 6 SEM of potassium titanate whiskers formed by the reaction between K_2CO_3 and TiO_2 in TK at 1150°C.

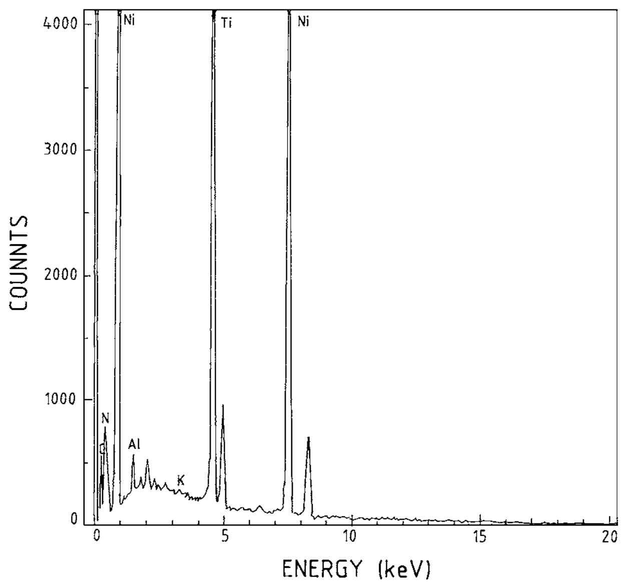

Figure 7 EDX of spherical tip of whisker formed in TNKC2.5.

presence of Ni, Ti, and N in whisker tip (Fig. 8). The overall reaction of carbothermal reduction of titanium oxide by heating with carbon powder in a nitrogen atmosphere, which simultaneously nitrides the reaction product can be written as

$$TiO_2 + 2C + 1/2N_2 \rightarrow TiN + 2CO \quad (1)$$

Several parameters influence the process. The reaction temperature effects the kinetics [15] and the thermodynamically favoured products [16]. The morphology and character of raw materials [17] influence the reaction and morphology of the product. Initially TiO_2 is reduced to lower metal oxides.

$$TiO_2(s) + C(s) \rightarrow TiO + CO \quad (2)$$

$$TiO_2 + CO \rightarrow TiO + CO_2 \quad (3)$$

$$TiO + CO + 1/2N_2 \rightarrow TiN + CO_2 \quad (4)$$

The CO_2 formed in reactions (3) and (4) further react with C to form CO.

$$CO_2 + C \rightarrow 2CO \quad (5)$$

The progress of these reactions depends on the intimate contact between the reactants, which is essential for complete conversion of TiO_2 into TiN. There is a lot of literature on catalysis of carbon gasification [18]. Iron, cobalt and nickel acts as a strong catalyst for gasification of carbon in carbon-carbon dioxide reaction [19], and in water vapor and hydrogen [20]. By introduction of metal atoms into the structure, a more reactive carbon (CO) is produced. Due to the catalytic effect of Ni, reactions (2) to (5) are more favourable.

Krishnarao *et al.* [14] studied the formation of TiC whiskers in TNKC, TKC, TNC, and TC systems; where $T = TiO_2$, $N = NiCl_2$, $K = K_2CO_3$, and $C =$ carbon. Whiskers of TiC were formed in TKC and TNKC only. Though K_2CO_3 is an essential constituent, $NiCl_2$ acts as a catalyst for maximization of formation of TiC whiskers. The morphology of whiskers (spherical tips) suggests that they were grown by VLS mechanism. In TNKC2.5 system, K_2CO_3 dissociates into K_2O and CO_2 at 891°C. K_2O can form a thin liquid layer around TiO_2 particle and react with it. The reaction between K_2O and TiO_2 can lead to the formation of rod shaped titanates [21]. The formation of potassium titanate whiskers has been studied in detail by

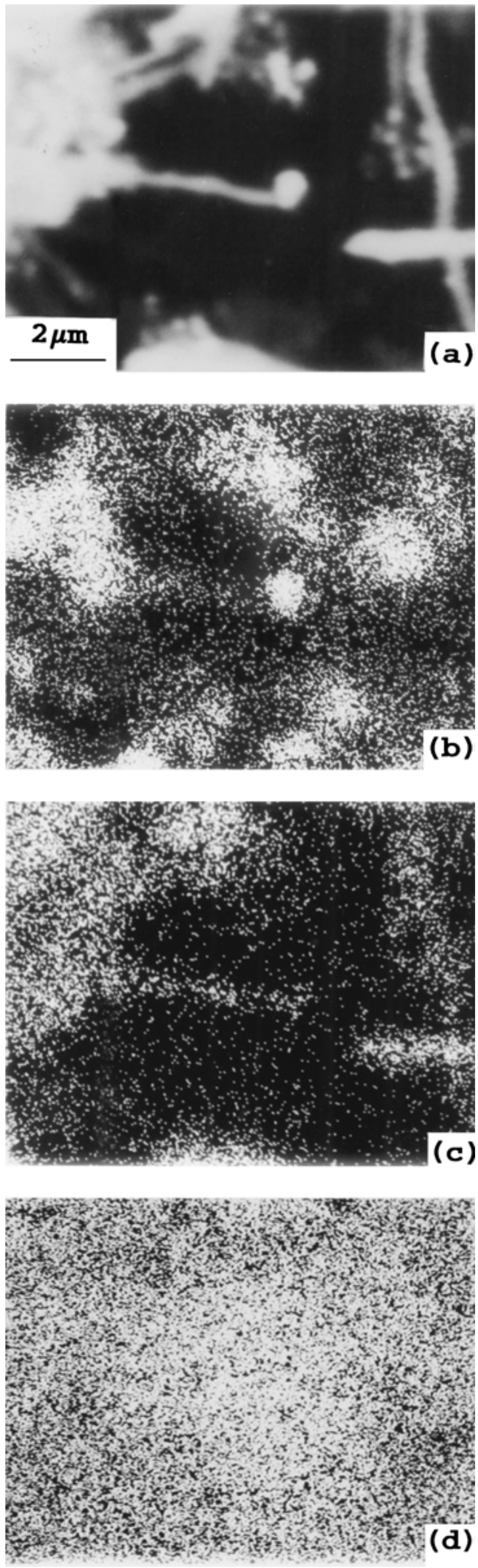

Figure 8 EPMA analysis of whisker formed in TNKC2.5 (a) SEM, (b) Ni X-ray map, (c) N X-ray map, and (d) Ti X-ray map.

Lee *et al.* [22] and Watanabe *et al.* [23]. In TK system the formation of potassium titanate whiskers (Fig. 6) confirm the existence of a low melting liquid. In TNKC system, TiN whiskers must have grown from such K_2O rich liquid. This requires continuous supply of TiO or TiO_2, CO and nitrogen to the liquid droplet. The important role of potassium is formation of a low melting liquid. When Ni is added, a complex K-Ni-Ti liquid droplet containing Ni-Ti alloy is forming. This is confirmed from EDX, and EPMA (Figs 7 and 8). For the precipitation of TiN crystal, continuous supply of TiO, CO, and nitrogen is required to this liquid droplet. The presence of Ni, in TNKC increases the availability of carbon as CO (reactions (5) and (4)) and facilitates the growth of TiN whiskers from a complex K-Ni-Ti liquid droplet.

When K_2CO_3 content increased from TNKC2.5 to TNKC5, the formation of whiskers increased drastically (Fig. 5). Due to the increase in K_2O more and more nucleation sites of K_2O rich liquid could be available. So in TNKC7.5 still more whiskers were formed at 815°C itself (Fig. 5b). But the temperature of on set of formation of particulates was decreased with increase in K_2CO_3 content. The formation of particulates is dominant process at and above 1000°C in TNKC5 and TNKC7.5. In these systems, before the sample reaches the reaction temperature large quantities of K_2O melt engulf the entire powder mix and causes agglomeration and formation of lumps or spherical particles. Therefore no whiskers were formed at higher temperatures. The use of carbonized cotton and transition-metal chlorides are reported [12] to enhance the formation of TiN. But whisker formation was not observed in the TNKC2.5 and TNKC7.5 samples containing carbonized cotton.

4. Conclusions

(i) K_2CO_3 has strong positive effect on the formation of TiN whiskers during the carbothermal reduction of TiO_2 in nitrogen.

(ii) Maximum yield of TiN whisker was observed in the temperature range of 920°–1000°C.

(iii) At temperatures higher than 1000°C the formation of particulates of TiN is the dominant process.

(iv) Increase in K_2CO_3 concentration increased the whisker growth at low temperatures 815°–920°C and formation of particulates at high temperatures 1000°–1100°C.

(v) A vapor-liquid-solid growth mechanism has been identified for the formation of TiN whiskers.

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