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Flux growth and characterization of TiC crystals

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Single crystals of TiC were grown using nickel and cobalt metal as a flux at soaking temperatures of 1500 to 1800° C and at compositions of 12.5 to 30 mol % TiC. The use of cobalt flux produced crystal sizes less than 0.5 mm under all conditions. With a nickel flux, a maximum crystal size of 1.5 mm was obtained at 1700 and 1800° C and at 20 and 25 mol % TiC composition, using a cooling rate of 3° C min^{-1}. A slower cooling rate of 0.2° C min^{-1} also gave crystals of 1.5 mm at 1600° C. The crystals were cubic and metallic-lustre silver grey in colour. The lattice parameter of the crystal was measured to be $a_0 = 0.43275 \pm 0.00005$ nm, with nearly stoichiometric composition. The grown faces were of the $\{100\}$ family with a dislocation density around $10^7\,\mathrm{cm}^{-2}$. The Vickers' microhardness on these faces was in the range 2600 to 2800 kg mm^{-2}. The nickel impurity and free carbon contents in the crystals were 700 to 1000 p.p.m. and 0.8 to 4 wt %, respectively.

1. Introduction

Titanium carbide, TiC, is a potentially important material for high-temperature engineering and electronic applications. The preparation of single crystals of TiC is fairly difficult because of its high melting point (~ 3067° C). Although the single crystals have been grown recently by means of the floating zone [1, 2], Berneuil method [3] and flux method [4, 5], the former two methods tend to produce the crystals of TiC_x ($x < 1$) due to vaporization of carbon under the high-temperature operation. In this respect, the flux method would be advantageous for producing single crystals with stoichiometric composition, because of the relatively low growth temperature, if a suitable solvent could be found. The flux method has been carried out by several authors; Higashi *et al.* [4] have produced crystals of a complicated form less than 2 mm in size using aluminium solution at 1500° C, and Kieffer and colleagues [5] have grown very tiny crystals in nickel solution. However, growth conditions have not been discussed in detail, nor have the crystals been characterized. We have investigated the formation of NbC and TaC by solid state reaction [6], and also prepared single crystals of NbC and TaC by the flux method and characterized the crystals [7–9]. This work, undertaken as part of an experimental programme of the preparation of transition metal carbides, reports the successful growth of TiC crystals using nickel and cobalt metal flux, and their characterization.

2. Experimental procedure

The starting material was titanium carbide (Rare Metallic Co. Ltd, purity 99.5%). Granular nickel and cobalt metals (purity of both 99.9%) were used as flux. The mixing ratio of TiC powder to the flux varied in the range 12.5 to 30 mol %. A charge of about 70 g flux and TiC powder was placed in a graphite crucible with a bored lid through which the gases formed in it could escape, soaked in an r.f. furnace at temperatures of 1500 to 1800° C for 4 to 8 h in argon (0.5 l min^{-1}), and then cooled to 1300° C at a rate of 0.2 to 3° C min^{-1}. As-grown crystals of TiC and concurrently deposited graphite were removed from the crucible by leaching the remaining metals in HCl solution. The crystals of TiC and graphite were separated by decantation, using a bromform solution (specific gravity $d_{15} = 2.89$).

The lattice parameter of TiC crystals was determined, using silicon as an internal standard material, by X-ray powder diffraction (XRD). The total carbon content in the crystals was determined from the weight gain obtained when the powdered crystals were heated at 1050° C in air by a thermobalance. The grown face of the crystal was confirmed by the back-reflection Läue method. The impurity content of nickel in the crystals was determined by atomic absorption spectrometry, for which a solution was made up by dissolving TiC crystals in a hot solution of $\mathrm{HNO_3/H_2O} = 1:3$. The Vickers microhardness on the (1 0 0) crystal surface in the $\langle 100 \rangle$ direction was determined at a load of 1000 g and 30 sec. The crystal surfaces were etched in hot H_2SO_4 solution for 5 min, after which the etched surfaces were observed by scanning electron microscopy (SEM).

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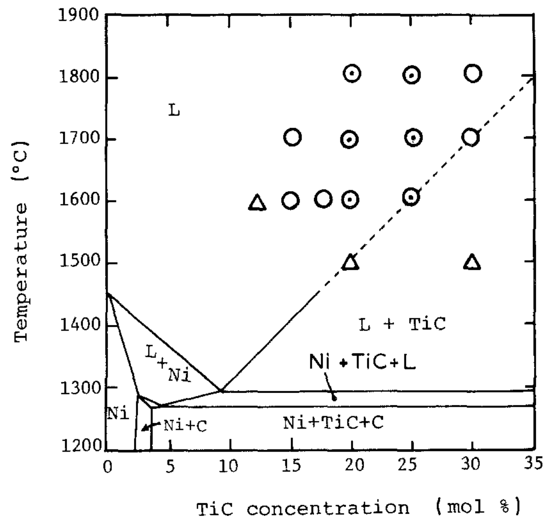

Figure 1 The maximum sizes of TiC crystal represented on the phase diagram of TiC–Ni system. Soaking time = 4 h, cooling rate = 3° C min^{-1}. Maximum size: (⊙) > 1.2 mm, (○) 0.8 to 1.2 mm, (△) < 0.8 mm.

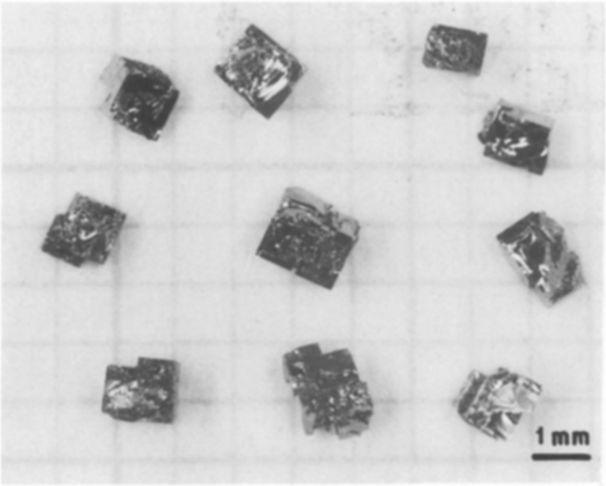

Figure 2 Single crystals of TiC grown from 1800° C at a cooling rate of 3° C min^{-1} and at 20 mol % composition, using a nickel flux.

3. Results and discussion

Prior to the growth experiments, it was necessary to preheat a sample of TiC + Ni or Co to 1400° C in vacuum (~ 10 Pa) and to expel gases formed in the crucible, because unless this was done, the melt contained large voids or bubbled out of the crucible, as was found by sectioning and examining the quenched crucible. After treatment, the growth system was switched to an argon atmosphere.

The experimental conditions of soaking temperature and composition were determined by reference to the phase diagram of the TiC–Ni system [10], as shown in Fig. 1, where the broken straight line shows the liquid-phase line postulated by the authors. The growth experiments were carried out in the liquid phase or on the liquid-phase line at soaking temperatures of 1500 to 1800° C and 12.5 to 30 mol % TiC using a soaking time of 4 h and a cooling rate of 3° C min^{-1}. The correlation of the maximum crystal size with the above experimental conditions is also summarized in Fig. 1. Compositions less than 12.5 mol % TiC or temperatures lower than 1500° C produced small crystals. Increasing the temperature to 1600 to 1800° C and the composition to 20 to 25 mol % TiC increases the crystal size to 1.2 to 1.5 mm, but further increase of the composition reduced the crystal sizes at any temperature. No great change in size with soaking times of 4 and 8 h was observed. The cooling rate was found to have a large effect on the size: slowing the rate from 3 to 0.2° C min^{-1} increased the size from 1.0 to 1.5 mm at 1600° C and 15 mol %. Similarly to the growth experiments of NbC and TaC, many graphite crystals concurrently formed, resulting from the carbon component dissolving from the graphite crucible into the nickel melt. The concurrent growth of graphite became significant with increasing soaking temperatures or slower cooling rate and these graphites were occasionally deposited on the TiC crystal surface, apparently disturbing its crystal growth.

The growth experiments with cobalt flux were also carried out at soaking temperatures of 1600 to 1800° C and 10 to 20 mol %, using a soaking time of 4 h and a cooling rate of 3° C min^{-1}: these conditions were determined by reference to the phase diagram of TiC–Co [11]. The size of the crystals grown under all conditions was less than 0.5 mm, and the crystals had an irregular form.

Fig. 2 shows the single crystals of TiC grown at 1800° C at a cooling rate of 3° C min^{-1} and at a 20 mol % composition using a nickel flux. The crystals are cubic in shape and metallic-lustre silver grey in colour. Twin crystals with imperfect shapes as well as regular ones were grown, as shown in Fig. 3. The formation of the twin crystals could be due to the

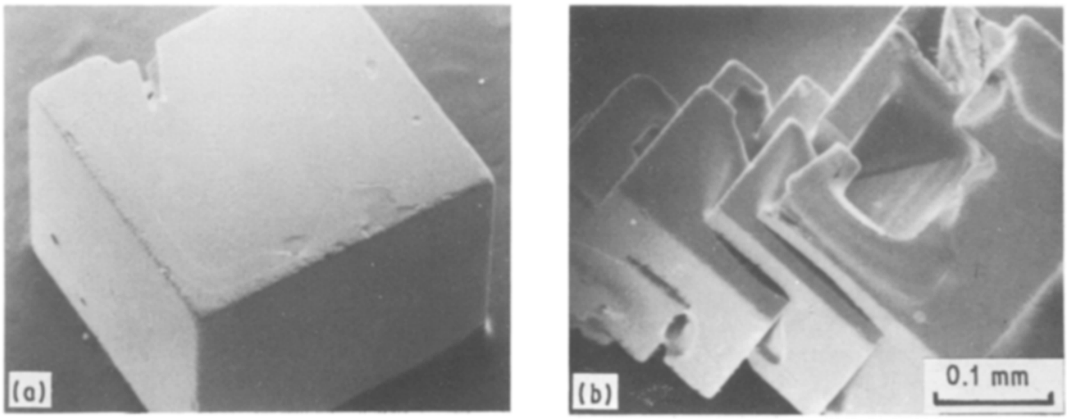

Figure 3 Scanning electron micrographs of TiC crystals. The growth conditions are the same as in Fig. 2. (a) Cubic crystal, (b) Twin crystal.

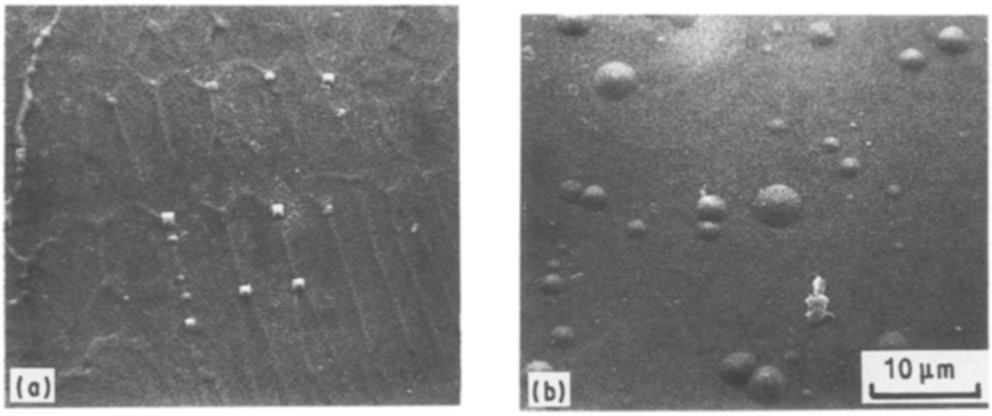

Figure 4 Scanning electron micrographs of the etched (1 0 0) face of a TiC crystal grown at different soaking temperatures. (a) 1600° C, (b) 1700° C.

growth from the melt with very high viscosity. The growth faces of these crystals were found to be of the {1 0 0} family. The lattice parameter of the crystal was measured to be $a_0 = 0.43275 \pm 0.00005$ nm, from which the atomic ratio of C/Ti in the crystal was estimated to be 0.97, according to the relationship between the ratio C/Ti and the lattice parameter [12]. No variation in the lattice parameter with composition, soaking temperature or cooling rate was observed.

The density of the crystal was found to be $4.93 \pm 0.02\,\mathrm{g\,cm^{-3}}$, comparable to the theoretical density (4.91) for the stoichiometric composition. Measurement of the Vickers microhardness showed that the crystals grown under all conditions had a microhardness in the range 2640 to $2880 \pm 300\,\mathrm{kg\,mm^{-2}}$ which corresponds to that (2600 to $2800\,\mathrm{kg\,mm^{-2}}$) [13] of a crystal with the composition of $TiC_{0.97}$. It can be concluded from the above measurements of the lattice parameter, density and microhardness that crystals with the nearly stoichiometric composition of $TiC_{0.97}$ were grown under all conditions. The ratio of total carbon to titanium in the crystal was determined to be 1.02 ± 0.03 by TG measurement at 1050° C in air during which the TiC crystals were completely oxidized to TiO_2 (rutile) as confirmed by XRD. Thus, the crystals are shown to contain 0.8 to 4 wt % free carbon.

The nickel impurity content in the crystal was about 700 to 1000 p.p.m. for the crystal grown at 1600 to 1800° C and 20 mol %, using a soaking time of 4 h and a cooling rate of $3^\circ\mathrm{C\,min^{-1}}$, but increases to 2600 to 4000 p.p.m. on increasing the composition to 25 mol %, or the soaking time to 8 h, or decreasing the cooling rate to $0.2^\circ\mathrm{C\,min^{-1}}$ at 1600° C. SEM observations of etching patterns of the (1 0 0) face of the crystal obtained at 1700 and 1600° C are shown in Fig. 4, the shape of the pits being of concave circles and flat-bottomed squares, respectively. The difference in the shape of the pits at different growth temperatures cannot be explained at present. The dislocation density was found to be around $10^7\,\mathrm{cm^{-2}}$.

4. Conclusion

Single crystals of TiC were successfully grown in the melt of nickel and cobalt metals at soaking temperatures of 1500 to 1800° C and at compositions of 12.5 to 30 mol % TiC using a cooling rate of $3^\circ\mathrm{C\,min^{-1}}$. The use of cobalt flux produced crystal sizes less than 0.5 mm under all conditions. With nickel metal, a maximum crystal size of 1.5 mm was obtained at 1700 and 1800° C and at 20 and 25 mol %. A slower cooling rate of $0.2^\circ\mathrm{C\,min^{-1}}$ also gave crystals of 1.5 mm in size at 1600° C. The crystals were cubic and metallic-lustre silver grey in colour. The lattice parameter of the crystal was measured to be $a_0 = 0.43275 \pm 0.00005$ nm, with nearly stoichiometric composition. The growth faces were of the {1 0 0} family and their dislocation density was around $10^7\,\mathrm{cm^{-2}}$, with Vickers microhardness in the range 2600 to $2800\,\mathrm{kg\,mm^{-2}}$. The nickel impurity and free carbon contents in the crystals were 700 to 1000 p.p.m. and 0.8 to 4 wt %, respectively.

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