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Evaporation from molten TiC_x

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A new floating zone technique for keeping a molten zone composition constant has been developed. Using this new technique, the evaporation composition and the evaporation rate could be easily obtained as a function of molten TiC_x composition in the range of 2800 to 3100° C. In addition, the dependence of the evaporation rate on the ambient helium gas pressure was examined in the range of 3.6 to 32 atm.

1. Introduction

We have developed a new floating zone technique for keeping a molten zone composition constant, and measured the composition of the evaporation product and the evaporation rate as a function of molten TiC_x composition. Because TiC_x has a high melting point (maximum 3067° C [1]) as shown in Fig. 1, a floating zone technique must be utilized to maintain the molten TiC_x. However, in a usual floating zone method, the zone composition changes due to evaporation and due to carbon redistribution at the crystal–zone interface. Therefore, a new technique for keeping the zone composition constant has been developed (a modified zone levelling method [2]). The principle is shown in Fig. 1. The composition of the initial molten zone is controlled so as to produce a zone levelling condition on initial melting. The composition of feed sintered rod is controlled so as to compensate for the composition change due to evaporation. Fig. 1 shows the case of keeping a zone composition to be $C/Ti = 1.3$ at a rate of $0.5\,\mathrm{cm\,h^{-1}}$. In this way, the zone composition can be kept constant in spite of evaporation. The evaporation composition and rate can be easily measured as a function of zone composition.

2. Experimental details

The experiment was carried out in an induction heating furnace (Athur D. Little Inc., HP type, 200 kHz, 40 kW) usually under 10 atm of ambient helium gas because of suppressing the arc discharge. The relationship in composition between the feed rod and the molten zone under zone levelling conditions was determined from the analyses of the feed rod and the zone of 4 cm zone-passed crystal rod [3]. On the basis of this result, the sintered rods with a fixed composition were set on the upper and lower shafts, and an estimated amount of carbon disk was put between the sintered rods, as shown in Fig. 1. The initial zone with a desired composition was formed by melting the part around the disk. The zone was passed usually at a rate of $1\,\mathrm{cm\,h^{-1}}$. The work coil with large inside diameter (20 mm) was used in order to decrease the amount of evaporation product which adhered to the coil. The detail was described by Otani *et al.* [2, 3]. After the zone pass, the zone and evaporation product were analysed, and the weight loss and the surface area of the zone were measured. The relationship in composition between the molten zone and the evaporation product was determined from the analytical result. The evaporation rate per unit time and unit area was obtained by dividing the weight loss by the zone pass time and the zone surface area. In addition, it was confirmed from the analysis of initial and final parts of the prepared crystal rod that the zone composition was kept constant during a zone pass.

3. Results and discussion

Fig. 2 shows the relationship in composition between the molten zone and the evaporation product. The measurements were carried out in the composition range of lower than $C/Ti = 1.41$, which is the TiC–C eutectic point. In the range of higher than $C/Ti = 1.25$, the evaporation composition was near the zone composition. Only TiC_x ($x < 0.97$) could be detected in the evaporation product by X-ray powder diffraction method. Amorphous carbon should be contained in the evaporation product because the composition of TiC_x with maximum carbon content is $C/Ti = 0.97$ [2]. In the range of lower than $C/Ti = 1.25$, the carbon content in the evaporation product decreased rapidly with decreasing the molten zone composition. In this composition range, the evaporation product consisted mainly of titanium metal and TiC. Therefore, it was found that the composition of the molten TiC_x approaches to $C/Ti = 1.3$ when the molten zone is maintained for a long time. Fig. 2 also shows that the evaporation product with a stoichiometric composition can be prepared from a molten zone with $C/Ti = 1.2$, that is, when $TiC_{0.93}$ crystal is prepared [4]. In this way, the composition of the evaporation product is very different from that of molten TiC_x. Therefore, we can deduce that titanium and carbon evaporate separately from the molten zone and react with each other to form the carbide.

Fig 3 shows the evaporation rate from molten TiC_x. In the composition range $C/Ti > 1.3$, the evaporation rate is not dependent on the zone composition. In the range lower than $C/Ti = 1.2$, the evaporation rate increases rapidly with decreasing the carbon content in the zone because of violent evaporation

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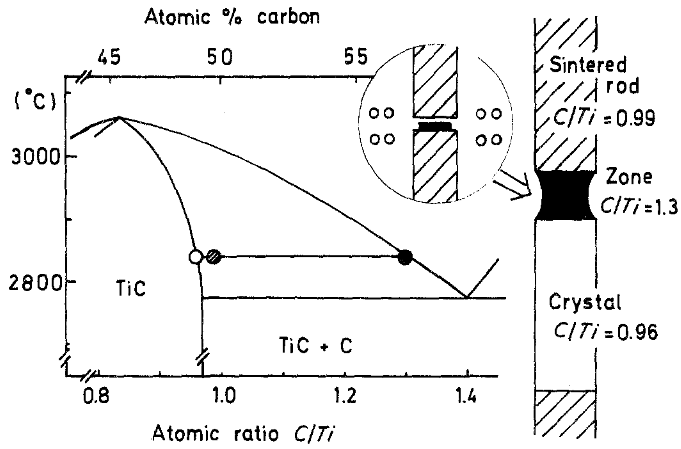

Figure 1 Phase diagram of TiC_x and principle of a modified zone levelling method.

of titanium metal. Fig. 3 also shows the contribution of titanium metal and carbon to the rate, which was obtained from Fig. 2. The evaporation rates of titanium and carbon depend on the zone temperature and composition. The zone temperature depends on the zone composition, and changes according to the liquidus line shown in Fig. 1. In the case of titanium metal, with increasing the carbon content in the zone, the temperature and the molar fraction of titanium in the zone decrease. Therefore, the evaporation of titanium decreases rapidly. On the other hand, in the case of carbon, with increasing carbon content in the zone, the temperature decreases but the molar fraction in the zone increases. Therefore, the evaporation rate of carbon does not change as much as that of titanium.

In order to confirm the above data on evaporation, an attempt was made to explain the composition change along the crystal rod prepared by a usual floating zone technique. Fig. 4 shows the composition change along the crystal rod prepared using a feed rod with $C/Ti = 0.988$ by a usual floating zone technique [2]. The grown crystal has a composition gradient from $C/Ti = 0.90$ to 0.96. The zone composition changed from $C/Ti = 0.99$ to 1.3 during a zone pass. The dashed line shows the composition change calculated on the basis of the data on evaporation shown in Figs. 2 and 3 and the carbon redistribution at the interface [2]. The calculation was carried out with the following assumptions: (1) the rod radius is 0.5 cm; (2) the molten zone has a cylindrical shape with 0.6 cm in length; (3) the rate of feed rod is controlled so as to compensate for the evaporation loss; (4) the crystal growth rate is $0.5\,cm\,h^{-1}$. The experimental and calculated results agreed well with each other. Therefore, both the evaporation composition and the evaporation rate were found to be measured accurately. The dash-dotted line in Fig. 4 shows the result which was calculated by considering only the carbon redistribution [2]. Comparing the dashed and dash-dotted lines, it was found that the crystal prepared at the initial stage of zone pass has a higher carbon content, and the final part of the crystal rod has lower carbon content because of evaporation. This composition deviation can be easily understood from Figs. 2 and 3. Therefore, it is found from Fig. 4 that the data on evaporation can not be measured using the usual floating zone technique, but that a new floating zone technique (a modified zone leveling method) must be used.

The dependence of the evaporation rate on the ambient gas pressure (P) was examined in the composition range of higher than $C/Ti = 1.3$, because the rate hardly depend on the zone composition as shown in Fig. 3. The result is shown in Fig. 5. The evaporation rate was proportional to $P^{-3/4}$ in the range of 3.6 to 32 atm. Haggerty *et al.* [5] have previously reported on its dependence on the ambient pressure, using a model in which the rate controlling step for evaporation

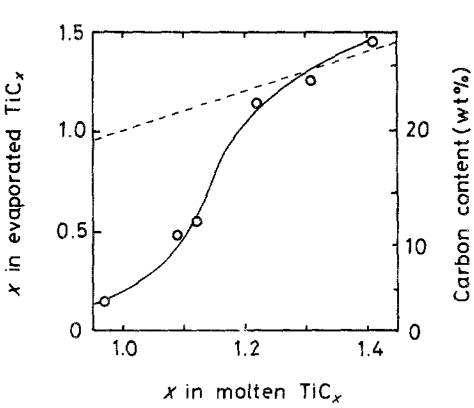

Figure 2 Composition of evaporation product as a function of molten TiC_x composition. The dashed line shows the case of congruent evaporation.

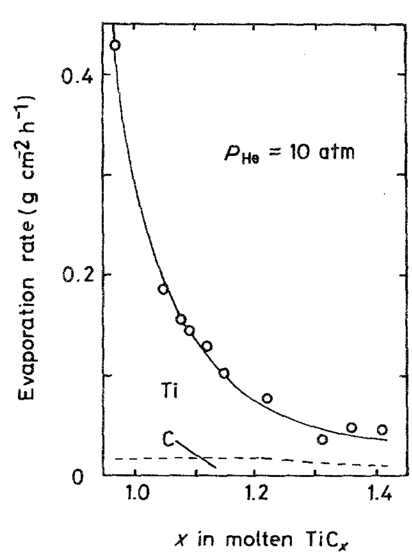

Figure 3 Evaporation rate as a functiuon of molten TiC_x composition. The dashed line shows the contribution of titanium and carbon on the evaporation rate.

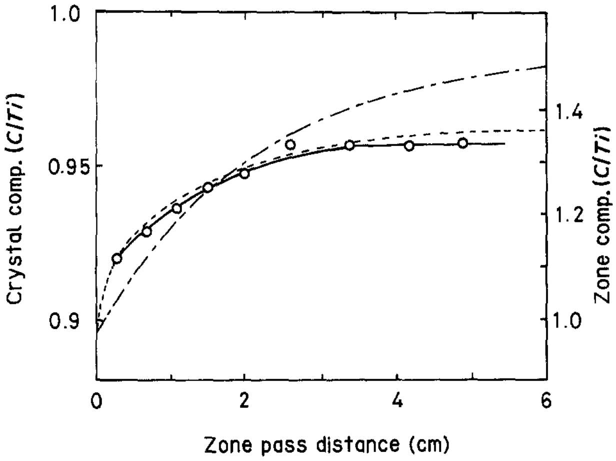

Figure 4 Composition change along the crystal rod prepared by a usual floating zone technique. The feed rod composition is C/Ti = 0.988. The radius is 0.5 cm. The growth rate is 0.5 cm h^{-1}. The dashed line shows the result calculated by considering the evaporation and the carbon redistribution at the interface. The dash-dotted line shows the results calculated by considering only the redistribution [2].

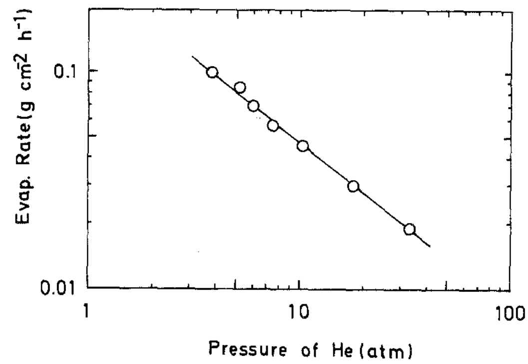

Figure 5 Dependence of evaporation rate on the ambient helium gas pressure. The composition of molten TiC_x is C/Ti = 1.3 to 1.35.

loss from a surface is the diffusion of the gas species through a concentration boundary layer. In their model, the evaporation rate is proportional to the diffusion coefficient, which is proportional to P^{-1}, and inversely proportional to the layer thickness, which is proportional to $P^{-1/2}$. Therefore, their conclusion was that the rate is proportional to $P^{-1/2}$ ($= P^{-1}/P^{-1/2}$). However, the dependence of the layer thickness on the pressure had been obtained using a forced convection model, and consequently the effect of the pressure on the layer thickness is deduced to be overestimated because a free convection model should be used in this floating zone condition. Therefore, the evaporation rate should be proportional to $P^{-(0.5\sim 1)}$, which the measured result ($P^{-3/4}$) supports.

4. Conclusion

Using a new floating zone technique for keeping a molten zone composition constant, the evaporation composition and the evaporation rate were measured as a function of molten TiC_x composition. In the range greater than $C/Ti = 1.3$, the evaporation composition was nearly equal to the composition of molten TiC_x, and the evaporation rate was almost constant. However, in the range of lower than $C/Ti = 1.2$, with decreasing the carbon content in the molten TiC_x, the evaporation of titanium metal rapidly increased. Therefore, the titanium content in the evaporation product and the evaporation rate rapidly increased. In addition, in the range of higher than $C/Ti = 1.3$, where the evaporation rate hardly depends on the zone composition, the dependence of the evaporation rate on the ambient helium gas pressure (P) was examined, and it was found that the evaporation rate is proportional to $P^{-3/4}$.

In this report, utilizing the zone levelling conditions, the evaporation composition and rate from the molten TiC_x were examined. Further, this technique can be applied to other measurements, for example, the structural analysis of molten refractory materials and the preparation of solid-solution crystals with controlled uniform composition.

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