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Effects of microstructures of the sintered rod on the single crystal grown by the floating zone method

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Floating zone법에 의한 결정성장시 소결봉의 미세구조에 의한 영향

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Abstract In general, a sintered rod is used as a feed in the growth of crystals by the floating zone (FZ) method. The sintering condition of the feed rod affected the stability of molten zone because it influenced the interface shape between the feed and the melt during the crystal growth. In this study, rutile and ruby crystals were chosen as samples to analyze the effect of the microstructures of the feed rods. In sintering of the feed rod for the growth of rutile and ruby single crystals, the difference of grain size between the inner and the outer region of the feed rod increased with the sintering temperature and dwelling time. As a result, it altered melting behavior of the feed. The uniform grain size of the sintered rod was necessary for the optimum growing condition of crystals. The effect of pores in the feed rod was not a dominant factor to grow crystals by the FZ method, which was confirmed by growing crystals with non-sinterd rods as feeds.

요 약 일반적으로 floating zone법에 의한 결정성장시에는 소결봉이 원료로서 사용되며 이러한 원료봉의 소결조건에 의해 결정성장시 용융대의 안정성이 영향을 받게 된다. 그 원인은 FZ법에 의한 결정성장시 소결조건에 따른 원료봉의 미세구조의 변화가 소결봉과 융액사이의 계면형태를 변화시키기 때문이다. 본 연구에서는 FZ법에 의해 TiO_2(rutile)과 ruby 단결정을 성장하였으며 이를 통해 소결봉의 미세구조가 FZ법에 의한 결정성장시에 용융대의 안정성에

미치는 영향을 분석하였다. TiO_2(rutile)과 ruby의 결정성장에 사용되는 원료봉의 소결시 소결온도가 높아지고 소결시간이 길어질수록 원료봉 중앙부와 바깥부분의 입자크기의 차이가 커져서 결국에는 그로 인하여 원료봉의 용융양상이 바뀌어졌다. FZ법에 의한 결정성장시 원료봉의 최적소결 조건은 입자의 크기가 소결봉 전영역에 걸쳐 균일하게 분포되는 것이었다. 반면 일반적으로 중요하다고 여기는 소결봉의 porosity는 FZ법에 의한 결정성장시 영향력 있는 인자가 아니라는 점을 소결하지 않은 원료봉을 사용해 결정성장 실험을 행하여 봄으로써 확인할 수 있었다.

1. Introduction

In the FZ method, the feed for the molten zone is supplied as the form of the sintered rod [1,2]. The sintering conditions of the feed rod are dependent on the composition of the feed rod. However, the most important factors for sintered rods are temperature and dwelling time.

In this study, the stability of the molten zone in the FZ technique was examined in the view of difference in the average grain sizes between the inner region and the outer surface, and the porosity of a sintered rod. The average grain size across the cross-section of the sintered rod was dependent on the sintering conditions, i.e., temperature and dwelling time.

The shape of interface between the sintered rod (feed rod) and the melt was kept stable by temeprature gradient given by the FZ apparatus when the feed exhibiting the same average grain size between the inner and the outer region was used. Whereas the molten zone became unstable when the sintered rods had different grain sizes, resulting in the fluctuation of the molten zone, the overflow of the melt and the separation of the melt from the sintered rod.

When the sintered rod was porous, molten zone was easily bloat by the reaction between the feed and atmosphere gas and then, became unstable. However, such concept was applied to only several materials which are very sensitive to atmosphere, such as YIG ($Y_3Fe_5O_{12}$) [3]. In the other cases, the porosity of the feed did not have any effect on the stability of melt, especially when the crystals were grown in air.

In this work, the growths of ruby and rutile crystals were attempted using the sintered feed rods of α- and γ-Al_2O_3 for the ruby, and rutile and anatase phase powder for rutile crystals, respectively. The relationships between the difference of the average grain size in the cross-section of the feed rod and the shape of the interface, and the effect of porosity were studied in details.

The most optimum microstructure of the sintered rod for crystal growth was the uniform grain size across the cross-section of the feed rod and the porosity was not a critical factor for the growth of crystals by the FZ technique. This was confirmed by using the non-sintered feed rods of rutile and anatase phase for the crystal growth.

2. Experimental

TiO_2 (rutile and anatase) powder (99.9 %), α- and γ-alumina (99.9 %) and Cr_2O_3 powder (99.9 %) were used for the starting materials. The powder was sealed in a rubber tube and moulded into a rod, typically 12 mm in diameter and 70 mm in length, under cold isostatic pressure of 2000 Kgf/cm^2. The mouled rods were sintered in the box furnace. The sintering conditions were listed in Table 1.

The dimension of the feed rod became 10 mm in diameter and 60 mm in length after sintering. The sintered feed rod, the non-sintered feed rod and the seed crystal were loaded to the upper and the lower shaft, respectively. The two types of growing machines were used : Asgal-FZSS10W was the infrared convergence type with double ellipsoidal mirrors and home-made FZHY1 was the arc convergence type with single ellipsoidal mirror. Two halogen lamps of 3.5 kW and one xenon arc lamp of 8 kW were used as heat sources. The growth conditions were as follows : growth rate 8 mm/hr (downward direction) and rotation rate of the feed rod and the seed crystal 25 and 15 rpm in rutile crystal, 5 mm/hr, 20 and 10 rpm in ruby crystal, respectively. The schematic principle of FZ method is shown in Fig. 1.

For characterization, the sintered feed rods were cut to 2 mm in thickness and were polished to a mirror finish. Then these specimens were thermally etched in the box furnace. The etching conditions were dependent on the sintering conditions of the feed rod. Table 2 shows the thermal etching conditions of the specimens. Grain morphologies of specimens were characterized using the optical microscope and SEM, and growth be-

Table 1
Sintering conditions of the feed rods in air

Powder (phase)	Temperature	Sintering time
TiO_2 (rutile)	none	none
TiO_2 (rutile)	1200℃	2 hr
TiO_2 (rutile)	1400℃	15 hr
TiO_2 (rutile)	1600℃	10 hr
TiO_2 (anatase)	none	none
TiO_2 (anatase)	1200℃	2 hr
TiO_2 (anatase)	1400℃	15 hr
Al_2O_3 (γ-type)	1700℃	8 hr
Al_2O_3 (α-type)	1700℃	8 hr

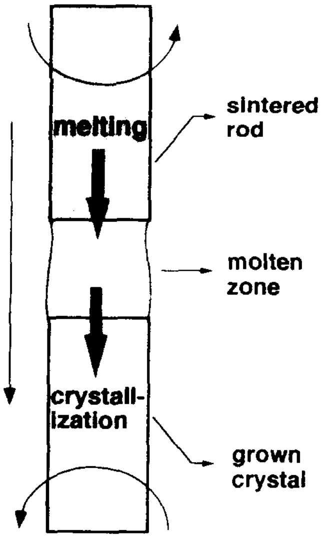


Fig. 1. Schematic principle of FZ method.

Table 2
Thermal etching conditions of the sintered feed rods in air

Powder (phase)	Temperature	Etching time
TiO_2 (rutile)	none	none
TiO_2 (rutile)	1000℃	4 min
TiO_2 (rutile)	1200℃	4 min
TiO_2 (rutile)	1400℃	4 min
TiO_2 (anatase)	none	none
TiO_2 (anatase)	1000℃	4 min
TiO_2 (anatase)	1200℃	4 min
Al_2O_3 (γ-type)	1500℃	5 min
Al_2O_3 (α-type)	1500℃	5 min

haviors of each sintered rods were observed through the screen which was attached to the FZ apparatus. The interfaces between the feed rod and the melt were observed after the sintered rods were quenched. Finally, the interface shape and the microstrucure were corelated with growth phenomena and the apparent quality of grown crystals.

3. Results and discussion

The conditions of the crystal growth and the interface between the crystal and the melt are considered as important factors in every technique of the single crystal growth. However, there are another factors in FZ technique. Those are sintering conditions of the feed rod and the interface between the feed and the melt because the sintered rod was used as a feed in FZ technique. The molten zone is suspended by the surface tension between the feed and the crystal, so two interfaces exist in the crystal grown by the FZ technique. Therefore, the microstructure of the sintered feed rod will affect the interface shape between the melt and the feed, and then the stability of the molten zone finally.

The grain size of the sintered rod is dependent on the sintering temperature and time. In the cross-section of the sintered rod, generally, the grain size of inner (core) region was smaller than the outer (periphery) region because the temperature of periphery part was higher than that of core part [4]. This temperature difference depended on the thermal conductivity of the feed rod itself. Therefore for high toughness, the sintering time should be reduced to keep the grain size uniform in typical ceramics. However in growing single crystals, the effect of the grain size distribution can be ignored because sintered rods should be changed to the melt. Temperature gradient can be observed in the sintered rod, the molten zone and the crystal during the growth. In fact, many researchers reported that the temperature gradient in the crystal changed the interface shape between the crystal and the molten zone, and it affected the quality of the as-grown crystals [5-7]. If the interface of crystals was convex or flat toward melt, the quality is good. However, inclusions and pores would be involved in as-grown crystals if it was concave [5,6,8].

The same principle mentioned above was also applied to the interface between the sin-

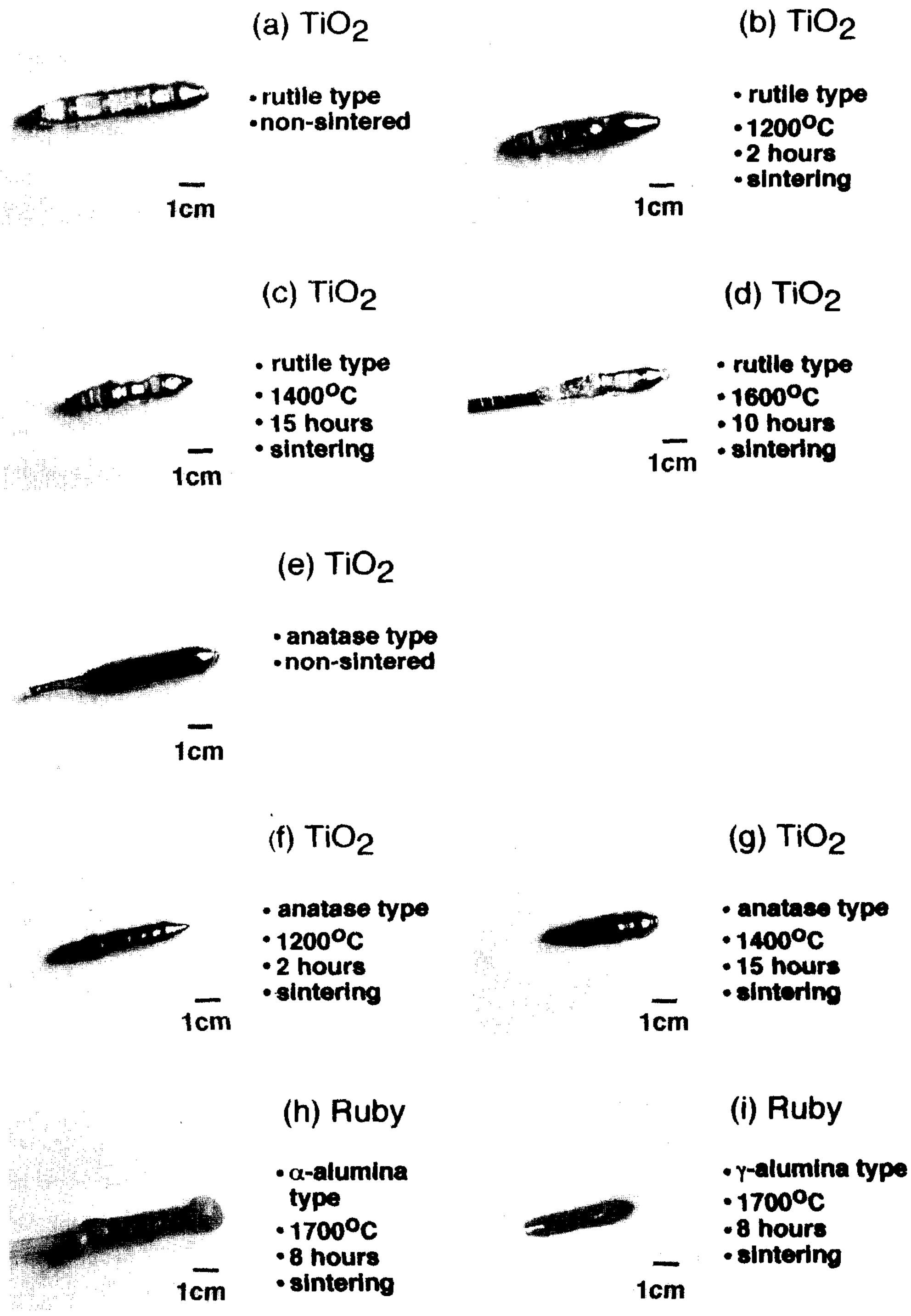
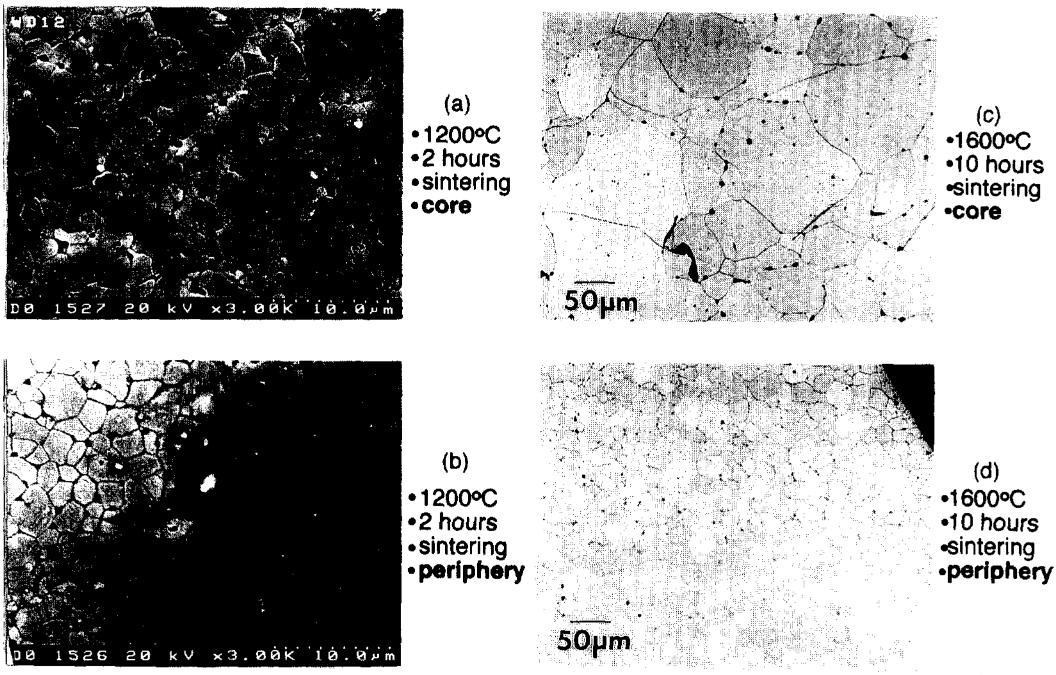


Fig. 2. Photographs of the as-grown crystals.

tered feed rod and the melt. As-grown crystals with sintering conditions is shown in Fig. 2. According to Fig. 2, the shapes of as-grown crystals were varied with sintering conditions. When growing state was stable, the diameter of the as-grown crystal was almost constant along the growth direction. If the growing state was not stable, however, as-grown crystals had large variation of the diameter, some cracks, other forms of undesirable defects and the melt dropped on the surface of crystals.

The optical microscopic images of grains in sintered TiO_2 (rutile phase) feed rod is shown in Fig. 3. When the feed rod was sintered at 1200℃ for 2 hrs, there was no difference between the grain size of the core and the periphery. However, the non-uniformity of the grain size of the sintered rod became significant at sintering of 1600℃ for 10 hrs. The feed rod which sintered at 1200℃ had the stable molten zone during the growth and the diameter of the as-grown crystal was constant. However, the state of molten zone of the feed rod sintered at 1600℃ for 10 hrs was very unstable and the melt flew down over the as-grown crystal, resulting in cracks on the as-grown crystal.

The surface of crystals were observed by stereomicroscope to confirm the apparent qualities of grown crystals. As shown in Fig. 4, the crystal quality of Fig. 4 (a) was bet-



(a)
•1200°C
•2 hours
•sintering
•core

(c)
•1600°C
•10 hours
•sintering
•core

(b)
•1200°C
•2 hours
•sintering
•periphery

(d)
•1600°C
•10 hours
•sintering
•periphery

Fig. 3. Comparision of the microstructures of the sintered rods, prepared by rutile phase powder.

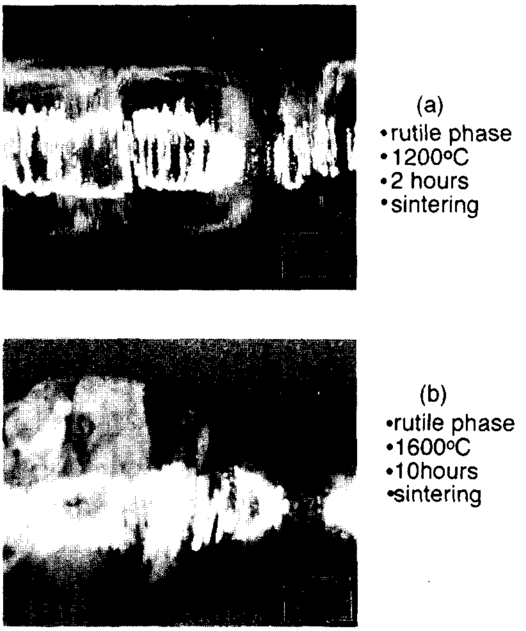


Fig. 4. Micrographs of the as-grown TiO_2 single crystal ; (a) sintered at 1200℃ for 2 hours and (b) sintered at 1600℃ hours.

ter than that of Fig. 4 (b). In case of Fig. 4 (a), the as-grown crystal had almost constant diameter and the interval between striations was almost same. The interval in the crystal of Fig. 4 (b), however, was irregular and some cracks were observed.

The similar phenomena were observed in the growth of ruby crystals. Though the sintering condition was same, the resultant microstructure of the feed rod was different, depending on the phase of Al_2O_3 powder. The SEM micrographs of two types of the sintered ruby rod were shown in Fig. 5. The grain size of the periphery of the α-Al_2O_3 sintered rod was much larger than that of the core region, in contrast with the feed rod of rutile phase powder sintered at 1600℃ for 10 hrs.

Figure 6 shows the grain size distribution

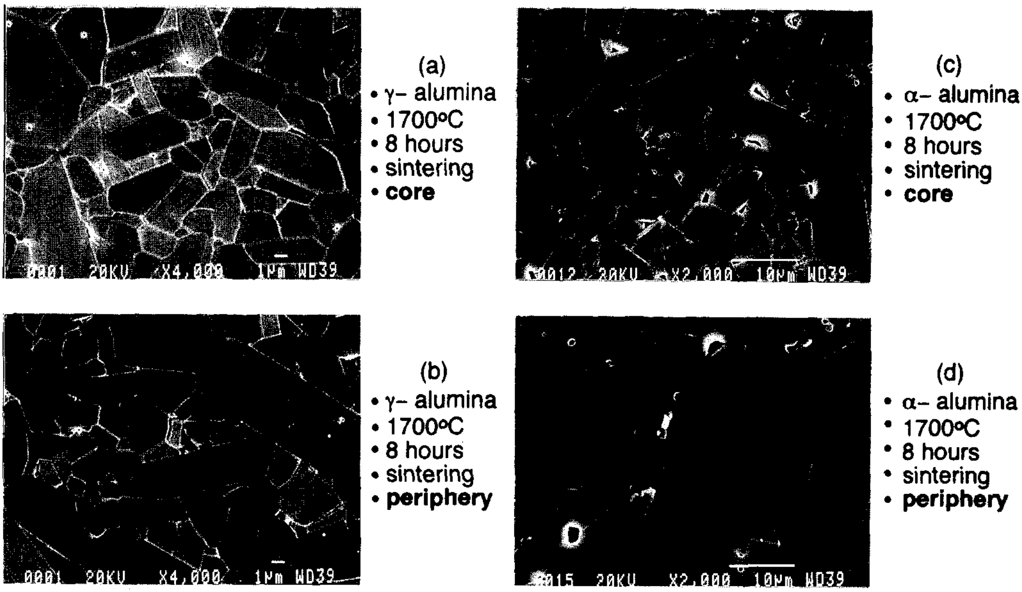


Fig. 5. Comparision of the microstructures of the sintered rods, prepared by α- and γ-Al_2O_3 powder.

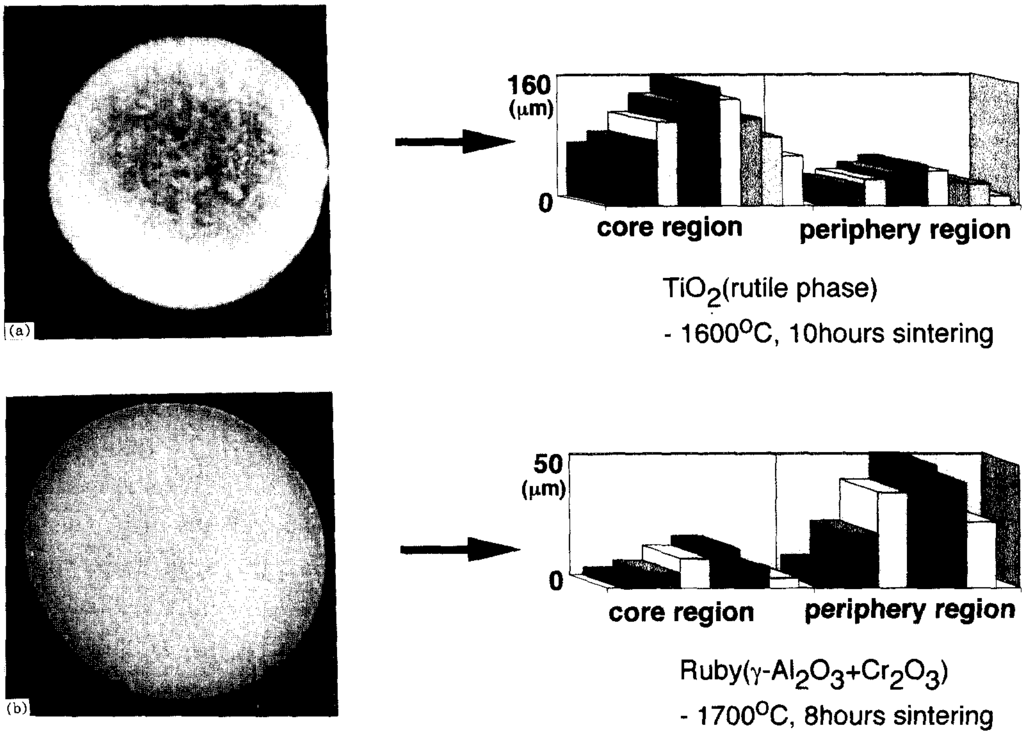
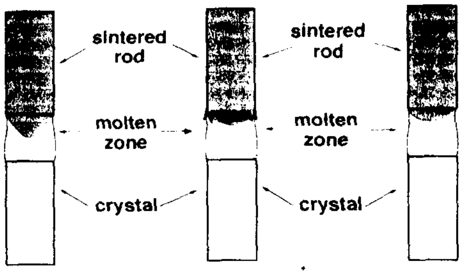


Fig. 6. Cross-sections and grain size distributions ; (a) rutile sintered rod and (b) ruby sintered rod.

of the rutile and the ruby sintered rod. The melting behavior of the feed rods became different, due to the grain size difference between two cases. The interface shape between the melt and the feed rod of rutile was constant in the beginning stage apparently, but the molten zone and the feed began to fluctuate together about 1 hr later. This phenomenon continued to the end of growth periodically and similar situation was observed during the growing process of ruby. To understand this problem, the molten zone was quenched during the growth and cut the molten zone parallel to the growth direction. The prepared samples was etched in the solution of $(NH_4)_2SO_4$-H_2SO_4 and H_3PO_4. Figure 7 shows the schematic results of the etched section of rutile and ruby feed rod, including ideal case.

As shown in Fig. 7, the interface between the feed and the melt was heavily convex toward the melt during the growth of rutle crystal. Therefore when the feed and the grown crystal were counter-rotated, the tip of the feed rod collided with the tip of the grown crystal, resulting in the unstability of the molten zone. In case of the ruby crystal growth, the interface shape of the feed and



sample (d) of Fig. 2 - unstable

sample (h) of Fig. 2 - unstable

ideal case - stable

Fig. 7. Interface shapes between the sintered feed rod and the melt.

the crystal was similar with ideal case. However, the periphery region of the feed rod contacting with the melt was not melted continuously, so convecting melt and unmelted part of the feed stuck together. After some degree of rotation, the melt was separated from the feed. The molten zone of ruby became unstable by repeating this phenomenon. Due to this irregular fluctuation, melt eventually flew down over the grown crystal and crystallized to the polycrystalline solid like Fig. 2 (i).

The rutile single crystal had a characteristic of convex interface toward the melt [9]. The interfaces between the solid (feed rod and grown crystal) and the liquid (melt) were an isothermal lines and could be changed by the melt convection and the thermal conductivity. However, the interface shape between the feed rod and the melt can be changed by the microstructure of the sintered feed rod. As shown in Fig. 3, the grain size of the core was larger than that of the periphery. Therefore the surface area of the core grain was smaller than that of the periphery, creating the difference of surface energies between core and periphery. The difference of surface energies affected the melting behavior of sintered rod. As the surface energy of the grains increased, the feed rod could melt easily. It could be explained by the concept of the heat of fusion.

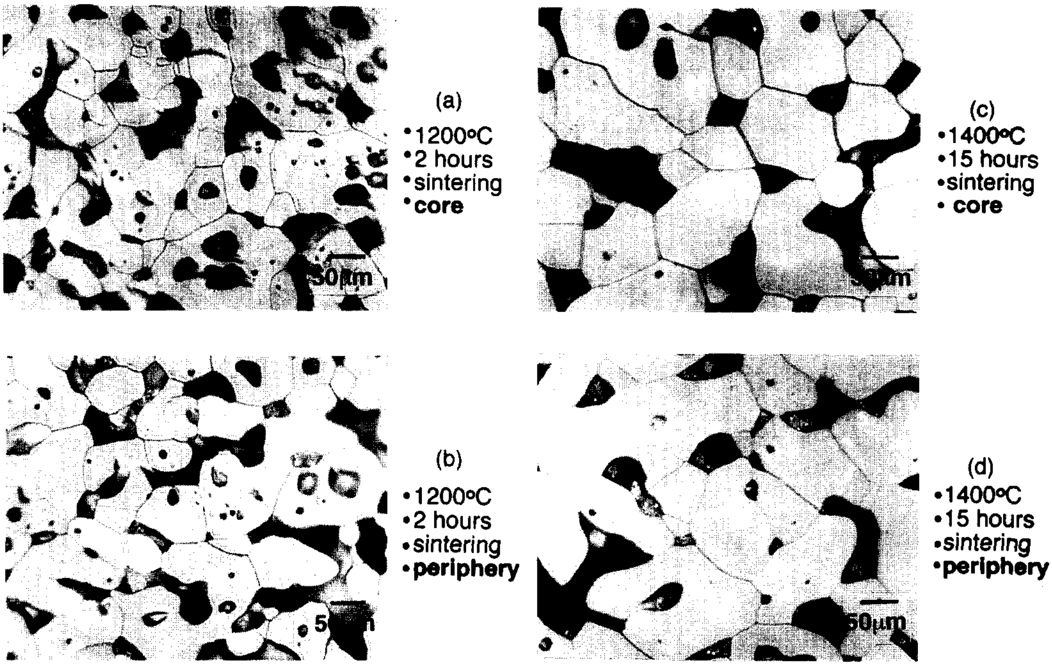
The sintered TiO_2 (rutile) rod should overcome the energy barrier to be a molten state. If the one part of the feed to be melted had higher energy than the other part, it could reach the heat of fusion more easily than the other part. Therefore the core region was more difficult to be melted and the interface shape of the feed became more convex toward the melt. Thus, the collision between the tips of the feed and the crystal resulted in the change of interface shapes. The difference of the grain size also brought about continuous effect in the part of sintered rod which was tangent to the melt. In order to lower the free energy of the sintered feed rod, the grains in the core region continuously grew larger while the grains in the periphery region became samller or vanished away. This phenomenon aggravated the situation mentioned above.

In case of ruby, non-uniform melting of the feed could be explained by the same way. However, in contrast with rutile, grains in the core region were smaller than those of the periphery region, i.e, the situation was opposite. Therefore while the core region was melted easily, the surface of the feed is more difficult to be melted with same power. For preventing from this non-uniform melting of the sintered feed rod during the crystal growth by FZ technique, the same grain size of the inner and the outer region of the feed was desirable.

The porosity of the feed had not a significant effect on the crystal growth by FZ method. It can be proved by the crystal growth with a non-sintered feed rod. The crystal growth with the non-sintered rod was easier than with the sintered rod. To study the effect of porosity of the sintered rod, anatase powder was used for preparing the feed rod. The sintered feed rod of the anatase phase powder was more porous than that of the rutile phase (Fig. 8) but crystals could be grown more easily with the anatase rod than the rutile phase. The degree of easiness for crystal growth could be simply determined by power and the diameter change of the as-grown crystal during the growth. As shown in Fig. 8, there was no difference in grain size between the core and the periphery region of the anatase phase feed. Thus the grain size difference of the feed rod was the most important factor to obtain the single crystal of a good quality.

4. Conclusion

Rutile and ruby crystals were grown by FZ technique using the sintered feed rods which were sintered in various conditions. As the sintering temperature and time in-


(a) •1200°C •2 hours •sintering •core

(c) •1400°C •15 hours •sintering •core

(b) •1200°C •2 hours •sintering •periphery

(d) •1400°C •15 hours •sintering •periphery

Fig. 8. Comparision of the microstructures of the sintered rods, prepared by anatase phase powder.

creased, the non-uniform melting behavior of the feed rod became significant and the interface shape between the feed and the melt was changed by this non-uniform melting of the feed rod. Thus, the stability of the molten zone decreased, resulting in degrading of the crystal quality. The stability of the molten zone was the most significant factor in FZ method. The crystal quality was degraded as the stability of the molten zone was decreased. As a result, it was found that the uniformity of the grain size in the core and the periphery region was the most important, while the porosity of the feed rod almost did not affect the quality of crystals grown by FZ method.

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