Effect of Starting Compositions on the Growth of Calcium Tungstate Crystals from Sodium Tungstate Flux

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(Received July 10, 1989)

Experimental evidence for the effect of starting compositions on the growth of $CaWO_4$ crystals from Na_2WO_4 flux was given on the basis of the obtained solubility data. Crystal growth was conducted by heating mixtures at 1100 °C for 5 h, followed by cooling to 500 °C at a rate of 5 °C h^{-1}. Octahedral crystals up to 4.5 mm in size were grown. Mixture with $\Delta T_{SL}(=T_{\text{Soak temperature}}-T_{\text{Liquidus temperature}})=340$ °C produced 226 crystals measuring about 2.2 mm on the average. The crystal sizes decreased gradually and crystal numbers increased remarkably with a decrease in ΔT_{SL}. The crystal sizes were mainly determined by the number of crystals grown. The value of ΔT_{SL} played an important role in controlling the size and number of the crystals grown. It was experimentally confirmed that a greater ΔT_{SL} or lower solute content resulted in larger crystals.

The flux growth of many inorganic substances has been carried out by a slow cooling method with spontaneous nucleation. In attempting to grow large crystals of an oxide from a flux, it is generally necessary to perform many "trial and error" experiments. First, choosing the flux is very difficult due to a lack of fundamental data as well as the crystal-chemical principles of bonding in solution. Even if a suitable flux is chosen, large numbers of small crystals are usually obtained. The flux-solute ratios are varied at a given soak temperature until a small number of crystals of the desired size grow. In this way, it is empirically well known that the sizes of crystals grown from fluxes are significantly influenced by the starting composition. However, unambiguous evidence for the effect of the starting compositions on the sizes of crystals grown has scarcely been reported. As an example of the attention given to starting compositions, Wanklyn[1] has proposed empirical rules for the starting compositions for producing large crystals of some complex oxides.

We have proposed the guiding principle to choose a suitable flux for the growth of oxide crystals.[2] On the basis of this principle, Na_2WO_4 was chosen as flux for the growth of $CaWO_4$ crystals.[2] Octahedral crystals of $CaWO_4$, up to 3 mm in size, were grown from the flux.[2] According to the growth runs, it was also found that Na_2WO_4 flux was non-volatile at high temperatures. Therefore, $CaWO_4$-Na_2WO_4 is a suitable system to investigate the effect of starting compositions on the flux growth of oxide crystals. Another advantage of Na_2WO_4 flux is that it dissolves rapidly in water. Some papers have been reported[3—6] regarding the growth of $CaWO_4$ crystals from Na_2WO_4 flux; Roy et al.[4,5] and Roy[6] have investigated the effect of the cooling rate on crystallization.

The present paper describes the effect of the starting compositions on the growth of $CaWO_4$ crystals from Na_2WO_4 flux. The sizes and numbers of crystals grown were examined. The solubility of $CaWO_4$ in Na_2WO_4 was also determined. On the basis of solubility data, the effect of the difference between the soak and liquidus temperatures, $\Delta T_{SL}(=T_{\text{Soak temperature}}-T_{\text{Liquidus temperature}})$, on the sizes and numbers of crystals grown is discussed.

Experimental

Reagent grade $CaCO_3$, WO_3, and Na_2CO_3 were used for the flux growth of $CaWO_4$. Mixtures having $CaWO_4$ contents of 5, 10, 15, 20, 25, 30, 35, 40, and 45 mol% were prepared. The weights of the mixtures were about 41 g (about 36 g as $CaWO_4$-Na_2WO_4) during all growth runs. The mixtures were put into platinum crucibles of 30 cm^3 capacity. After the lids were closely fitted, the crucibles were placed in an electric furnace with silicon carbide heating elements. The furnace was heated at a rate of about 50 °C h^{-1} to 1100 °C, held at this temperature for 5 h and then cooled at a rate of 5 °C h^{-1} to 500 °C. When the cooling program was completed, the furnace was allowed to cool down to room temperature. Crystal products were separated by dissolving the flux in warm water. The obtained crystals were investigated by X-ray diffraction. Photographs of the crystals grown were taken. The numbers of the crystals of over 0.5 mm in size were counted during respective growth runs. The sizes of grown crystals were measured. In addition, the morphology of the crystals grown was also observed.

The solubility of $CaWO_4$ in Na_2WO_4 was determined by subtracting the amount of $CaWO_4$ crystals left after heating at temperatures 550—1200 °C from the amount of the original $CaWO_4$. Prepared mixtures of excess crystals (1—3mm in size) of $CaWO_4$ and Na_2WO_4 powder prepared were put into platinum vessels. The total charge was 3—10 g. After dissolution of $CaWO_4$ in Na_2WO_4 flux had proceeded for 5 h at a controlled temperature, the undissolved $CaWO_4$ crystals were separated from the quenched $CaWO_4$-Na_2WO_4 system by dissolving the Na_2WO_4 flux in warm water, where small crystals of $CaWO_4$ dissolved in the flux were left.

Results and Discussion

Solubility of $CaWO_4$ in Na_2WO_4. The solubility of $CaWO_4$ in Na_2WO_4 was determined within the range 550 to 1200 °C. It was confirmed in prelimi-

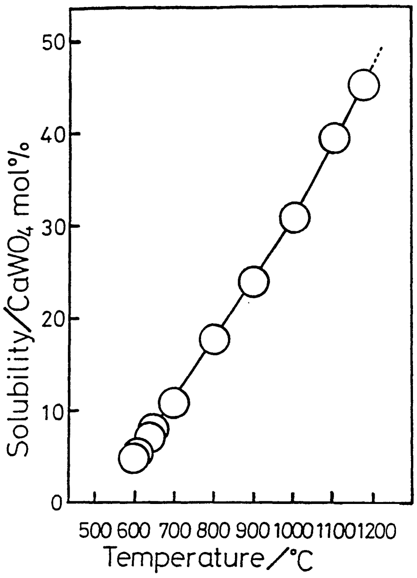

Fig. 1. Solubility of $CaWO_4$ in Na_2WO_4 as a function of temperature.

nary experiments that maintaining a given temperature for 5 h was sufficient for equilibration. Evaporation of Na_2WO_4 was scarcely observed during solubility experiments.

The dependence of the solubility on the temperature is shown in Fig. 1. At temperatures below 595 °C, the $CaWO_4$-Na_2WO_4 system did not melt. At 600 °C, $CaWO_4$ was dissolved in Na_2WO_4 at a concentration of about 4.7 mol% (about 4.8 g in 100 g Na_2WO_4). The solubility increased with temperature. At 1200 °C, $CaWO_4$ had a solubility of about 47.5 mol% (about 88.6 g in 100 g Na_2WO_4). The solubility at a soak temperature of 1100 °C corresponds to a starting composition of $CaWO_4$ (39.4 mol%)-Na_2WO_4(60.6 mol%). On the basis of the solubility curve, the saturation temperatures of the mixtures containing 5, 10, 15, 20, 25, 30, 35, 40, and 45 mol% solute are about 600, 680, 760, 830, 910, 980, 1050, 1110, and 1170 °C, respectively. It was found that mixtures containing between 5 and 35 mol% solute are unsaturated at the soak temperature of flux growth runs. In the case of a mixture containing 40 or 45 mol% solute, the solution is incomplete at the soak temperature. Figure 1 indicates that mixtures containing 10 to 45 mol% solute can produce $CaWO_4$ crystals by slow cooling. On the other hand, a mixture containing 5 mol% solute can not produce $CaWO_4$ crystals.

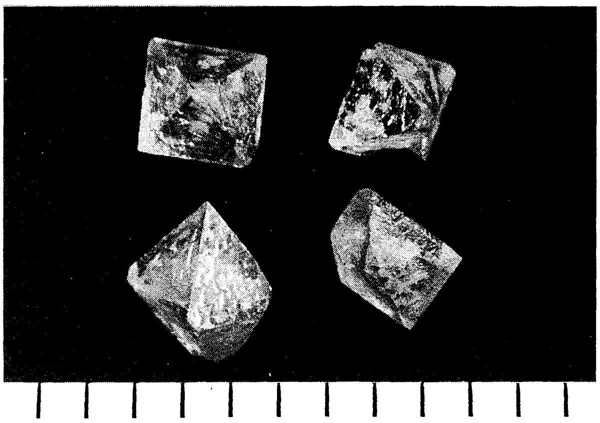

Fig. 2. $CaWO_4$ crystals grown in Na_2WO_4 flux (1 division=1 mm).

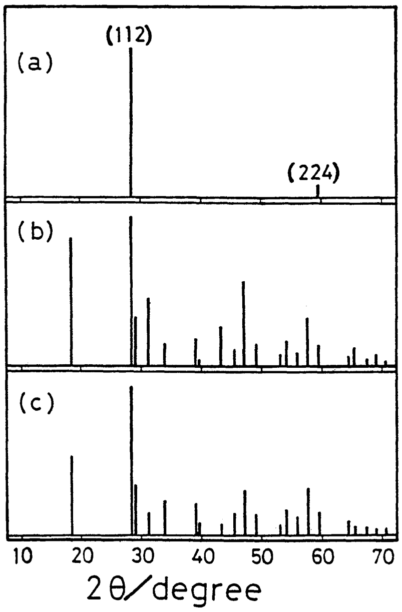

Fig. 3. X-ray diffraction patterns (Cu $K\alpha$) of $CaWO_4$ crystals.
(a): Octahedral crystal, (b): Pulverized crystallite, (c): $CaWO_4$ JCPDS data.[9]

Regarding the solubility of $CaWO_4$ in Na_2WO_4 or a pseudobinary system, $CaWO_4$-Na_2WO_4, some data have been reported.[3,4,7,8] However, they are in disagreement with one another. The solubility measured in this study is close to that reported by Roy and Packter[4] at temperatures between 650 and 900 °C. At 1000 or 1100 °C, our solubility is somewhat lower than that obtained by them.[4] In this study, solubility investigations were performed under equilibrium conditions. It is therefore considered that the obtained solubility is well suited for studying flux growth by slow cooling.

Flux Growth of $CaWO_4$ Crystals. Mixtures containing 15 to 45 mol% solute produced crystals of varying sizes. On the other hand, mixtures containing 5 and 10 mol% solute did not produce crystals of over 0.5 mm in size. It can be seen from Fig.1 that a mixture containing 5 mol% solute did not produce crystals. Ten mol% solute was considered to be insufficient for growing crystals of over 0.5 mm in size.

Some typical crystals grown are shown in Fig. 2. The obtained crystals were identified as $CaWO_4$ by an X-ray powder diffraction method. Calcium tungstate crystals were octahedral, colorless, and transparent. Solute contents in mixtures did not change this habit. The proportion of well-formed crystals was larger at lower solute contents. In order to determine the Miller indices of grown crystal faces, the crystals were laid on a holder plate and investigated by X-ray diffraction. Figure 3 shows X-ray diffraction profiles of octahedral crystals, pulverized crystallites, and $CaWO_4$ JCPDS data.[9] As shown in Fig. 3(a), only the diffraction patterns of the (112) and (224) planes were predominent. It is therefore considered that octahedral crystals are bounded by well-developed {112} faces.[10] The basic form of $CaWO_4$ crystals is a regular octahedron. Bulky $CaWO_4$ crystals grown from KCl flux were also bounded by the {112} faces.[11] According to observations under a microscope, visible flux inclusions were rarely found in colorless crystals.

During these growth runs, evaporation of the flux was less than 1 wt%. The influence of evaporation on crystal growth was negligible. The platinum crucibles were found to be undamaged after use. Sodium tungstate flux did not attack the platinum crucibles.

Sizes of $CaWO_4$ Crystals. In the same way as the usual exploratory flux growth, successive cooling runs from the soak temperature were carried out. The starting compositions of varied solute-flux ratios in the range from 5 to 45 mol% solute were used. On the basis of the obtained information from solubility data, the $\Delta T_{SL}(=T_{\text{Soak temperature}}-T_{\text{Liquidus temperature}})$ values of the mixtures containing 5, 10, 15, 20, 25, 30, 35, 40, and 45 mol% solute were estimated to be about 500, 420, 340, 270, 190, 120, 50, −10, and −70 °C, respectively. Figure 4 shows the relation between the number of grown crystals over 0.5 mm in size and ΔT_{SL} (solute content in mixture). The number of crystals grown from a mixture with ΔT_{SL}=340 °C was 226. The crystal numbers tended to increase as ΔT_{SL} decreased. When ΔT_{SL} was −70 °C, crystals amounting to 1788 were grown. In the case of ΔT_{SL}=340 to 50 °C, crystals were grown from unsaturated solutions at a soak temperature of 1100 °C on subsequent slow cooling. The numbers of crystals grown from the mixtures with ΔT_{SL}=−10 and −70 °C appeared to be related to the presence of an undissolved solute. Any undissolved solute particles in the solution were likely to act as nucleation centers when crystallization occurred. Wanklyn et al.[12] have reported that the number of α-Fe_2O_3 crystals grown from a PbO-V_2O_5

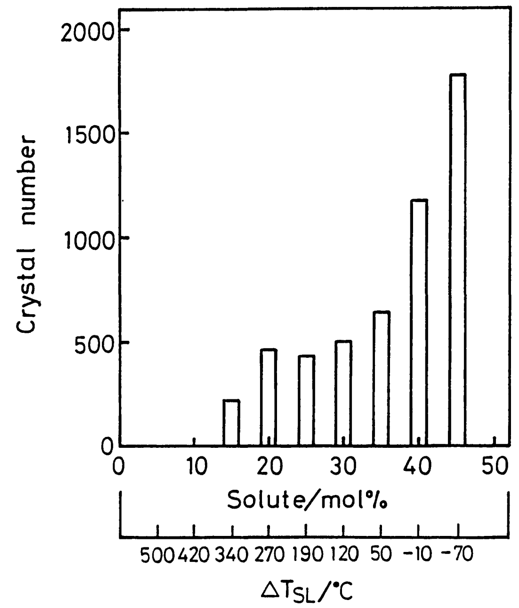

Fig. 4. Relation between number of crystals and ΔT_{SL} (solute content in mixture).

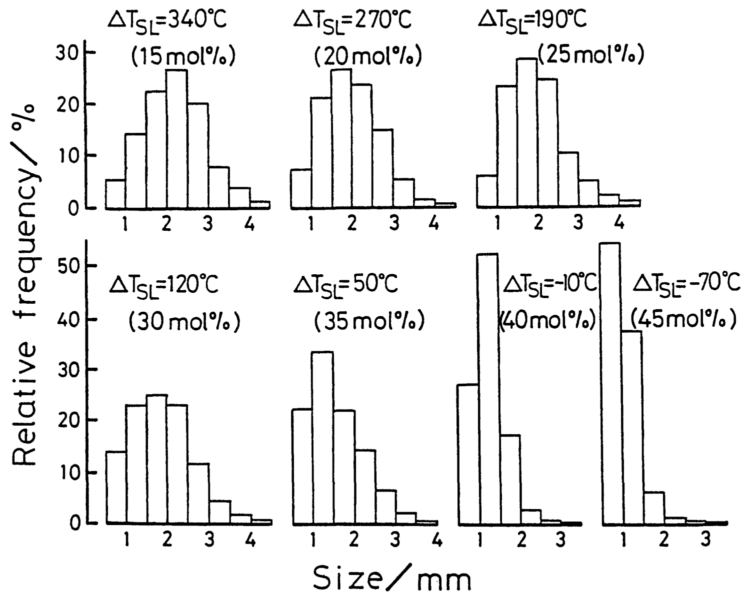

Fig. 5. Frequency histograms of size of crystals grown at respective growth runs.

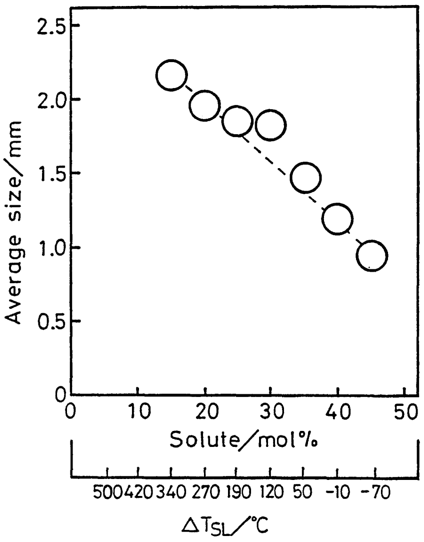

Fig. 6. Variation of average crystal size with ΔT_{SL} (solute content in mixture).

flux increased as ΔT_{SL} decreased. In order to grow a small number of α-Fe_2O_3 crystals, the soak temperature was at least 65 °C above the liquidus temperature.[12]

The size distributions of grown crystals of over 0.5 mm in size are shown in Fig. 5. In Fig. 5, the relative frequency is plotted against the size of the crystals. Crystals up to 4.5 mm in size were grown. The sizes of grown crystals were dependent on the value of ΔT_{SL}. It was found that mixtures with a higher value of ΔT_{SL} tended to produce larger crystals. The variation of the average sizes of grown crystals of over 0.5 mm in size with ΔT_{SL} (solute content in mixture) is shown in Fig. 6. The average size of crystals grown from the mixture with ΔT_{SL}=340 °C was about 2.2 mm. The average sizes of the crystals gradually decreased as ΔT_{SL} decreased. When ΔT_{SL} was −70 °C, the average size was about 0.9 mm.

It is obvious from Figs.4—6 that the crystal sizes were mainly determined by the numbers of crystals grown. The crystal sizes decreased and the crystal numbers increased with decreasing ΔT_{SL}. The smaller the number of crystals grown, the more favorable the growth was likely to be. This tendency is similar to that for growth from aqueous solution.[13] When ΔT_{SL} was great, the rate of formation of nuclei was small and the growth of the nuclei previously formed proceeded faster than those formed later. When ΔT_{SL} was small, the rate of formation of nuclei was large and the new particles were formed even after the nucleation. When ΔT_{SL} was −10 or −70 °C, an excessive degree of nucleation was likely to result due to undissolved solute particles. These effects are mainly related to the increase in nucleus number with the decrease in ΔT_{SL}. It is considered that, at greater value of ΔT_{SL}, smaller numbers of nuclei were formed and larger crystals grew onto these nuclei.

In this way, the value of ΔT_{SL} played an important role in controlling the number or size of the crystals grown. It is confirmed from Figs. 1 and 4—6 that a greater ΔT_{SL} results in a smaller number of large crystals. Soaking at temperatures well above the liquidus reduced the number of crystals obtained on subsequent slow-cooling. Taking the results of flux growth and solubility into account, it is usually rewarding to use mixtures with greater value of ΔT_{SL}, or dilute solution, to grow larger crystals.

Conclusion

The growth of $CaWO_4$ crystals from Na_2WO_4 flux was found to be influenced by the starting compositions of mixtures. The experimental evidence was given on the basis of the obtained solubility data.

(1) The crystal sizes gradually decreased with decreasing ΔT_{SL}.

(2) The crystal numbers increased as ΔT_{SL} decreased.

(3) It is confirmed that a greater ΔT_{SL}, or lower solute content, resulted in larger crystals.

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