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Growth of $NiWO_4$ crystals from a $Na_2W_2O_7$ flux

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Well-formed rod crystals of $NiWO_4$ were grown from a $Na_2W_2O_7$ flux by a slow cooling method. The solubility of $NiWO_4$ in $Na_2W_2O_7$ increased with increasing temperature. At 1100 °C, $NiWO_4$ was dissolved in $Na_2W_2O_7$ at a concentration of about 45 mol %. The eutectic temperature was 615 ± 5 °C. Flux growth was conducted by heating mixtures at 1100 °C for 10 h, followed by cooling to 500 °C at a rate of $5\,°C\,h^{-1}$. The brownish and transparent crystals up to 15 mm in length were grown from the mixtures of about 40 g. The most suitable solute content was 30 mol %. The grown crystals were bounded by the {100}, {010}, {110}, {102}, and {111} faces. In certain instances, the {111} faces disappeared. The EPMA data showed that sodium from the flux used was not contained within the grown crystals. The crystals of $NiWO_4$ had a d.c. electrical resistivity of about $1 \times 10^{11}\,\Omega$cm.

1. Introduction

Nickel tungstate has the wolframite ((Fe, Mn) WO_4) structure and is a member of the isomorphous series of tungstates containing small cations. Magnesium tungstate and $ZnWO_4$ also have the wolframite structure. The melting point of $NiWO_4$ has been reported as 1390 ± 10 °C [1]. Crystals of $NiWO_4$ have been grown by the Czochralski [2] and flux [1, 3, 4] methods. In the case of flux growth, the following fluxes can be used; Li_2WO_4 [3], Na_2WO_4 [3, 4], $Na_2W_2O_7$ [3], Na_2WO_4–$NiCl_2$–NaCl [1] and Na_2SO_4 [3]. The $NiWO_4$ crystals up to $6 \times 6 \times 6$ mm in size were grown from the high-temperature solution (3 g NiO, 53.4 g Na_2WO_4, 10 g WO_3) soaked at a temperature of 1250 °C and subsequent slow cooling [4]. No detailed study has been reported on the growth of $NiWO_4$ crystals from a $Na_2W_2O_7$ flux. The morphology of $NiWO_4$ crystals has not yet been reported.

The present paper describes the growth of $NiWO_4$ crystals from a $Na_2W_2O_7$ flux by a slow cooling method. The effect of the starting composition on the flux growth of the $NiWO_4$ crystals was studied. The morphology, density and electrical resistivity of the $NiWO_4$ crystals grown were investigated. Impurities contained within the grown crystals were examined. The solubility of $NiWO_4$ in $Na_2W_2O_7$ was determined. The eutectic temperature was also measured.

2. Experimental procedure

2.1. Solubility

The solubility of $NiWO_4$ in $Na_2W_2O_7$ was determined by measuring the weight loss of $NiWO_4$ crystals in the $Na_2W_2O_7$ melts at temperatures between 600 and 1100 °C. Mixtures of excess crystals (2–4 mm in size; 5–15 g) of $NiWO_4$ and $Na_2W_2O_7$ powder (about 10 g) were put into platinum vessels. After dissolution had proceeded for 3 h at a controlled temperature, undissolved crystals were present on quenching. The undissolved crystals were separated from the solidified saturated solution in warm water and reweighed. The loss in weight due to dissolution represents the solubility at that temperature. The eutectic temperature of the $NiWO_4$–$Na_2W_2O_7$ system was determined on the basis of measured differential thermal analysis (DTA) curves.

2.2. Flux growth

Reagent grade NiO, WO_3 and Na_2CO_3 were used for the flux growth of $NiWO_4$ crystals. An equimolar mixture of NiO and WO_3 was used as a solute. Stoichiometric amounts of Na_2CO_3 and WO_3 were mixed and used as a flux. The mixtures containing solute of 10–60 mol% were prepared. The weights of the mixtures were about 40 g. The mixtures were put into 30 cm^3 capacity platinum crucibles. The lids were fitted and the crucibles were placed in an electric furnace with silicon carbide heating elements. The furnace was heated at a rate of about $45\,°C\,h^{-1}$ to 1100 °C, held at this temperature for 10 h and then cooled at a rate of $5\,°C\,h^{-1}$ to 500 °C. When the cooling programme was completed the furnace was allowed to cool down to room temperature. Crystalline products were separated by dissolving the flux in warm water.

2.3. Characteristics

The crystals obtained were investigated by X-ray diffraction (XRD) and observed using optical microscopy. The sizes and interfacial angles of the grown crystals were measured. The cross sectional interfaces (parallel and perpendicular to the ⟨001⟩ direction) of the grown crystals were analysed by an electron probe microanalyser (EPMA). The direct current (d.c.) electrical resistivity (parallel to the ⟨001⟩ direction) of the as-grown rod crystals was measured by a digital multimeter at room temperature. The two electrodes were formed using a platinum conducting paste.

3. Results and discussion

3.1. Solubility of $NiWO_4$ in $Na_2W_2O_7$

The solubility of $NiWO_4$ in $Na_2W_2O_7$ was determined within the range 600–1100 °C. It was confirmed in preliminary experiments that maintaining a given temperature for 3 h was sufficient time for equilibration. The evaporation of $Na_2W_2O_7$ was less than 0.5 wt% during the solubility experiments. The influence of evaporation on the solubility was negligible.

The dependence of the solubility on temperature is shown in Fig. 1. The mixtures of $NiWO_4$–$Na_2W_2O_7$ did not melt at 600 °C. At 650 °C, $NiWO_4$ was dissolved in $Na_2W_2O_7$ at a concentration of about 3 mol% (about 1.8 g in 100 g $Na_2W_2O_7$). The solubility increased gradually with increasing temperature. At 1100 °C, $NiWO_4$ had a solubility of about 45 mol% (about 48 g in 100 g $Na_2W_2O_7$). The solubility curve obtained had an appreciable temperature coefficient of solubility so that $NiWO_4$ could be crystallized by slowly cooling the solutions. Thus $Na_2W_2O_7$ is expected to be an excellent flux for the growth of $NiWO_4$ crystals.

The obtained DTA data showed that the $NiWO_4$–$Na_2W_2O_7$ system had a eutectic temperature of 615 ± 5 °C. Judging from the solubility data and DTA, the eutectic composition was considered to be about 2 mol% $NiWO_4$–98 mol% $Na_2W_2O_7$.

Fig. 1 shows that mixtures containing between 10–40 mol% solute are unsaturated at the soak temperature of 1100 °C of the flux growth runs. In the case of mixtures containing 50 and 60 mol % solute, the solution is incomplete at the soak temperature.

3.2. Flux growth of $NiWO_4$ crystals

Well-formed rod shaped crystals of $NiWO_4$, up to 15 mm in length, were grown from the mixtures of about 40 g weight. The crystals were brownish and transparent. Typical crystals grown are shown in Fig. 2. The crystals obtained were identified from their XRD patterns, using data given on the JCPDS card [5].

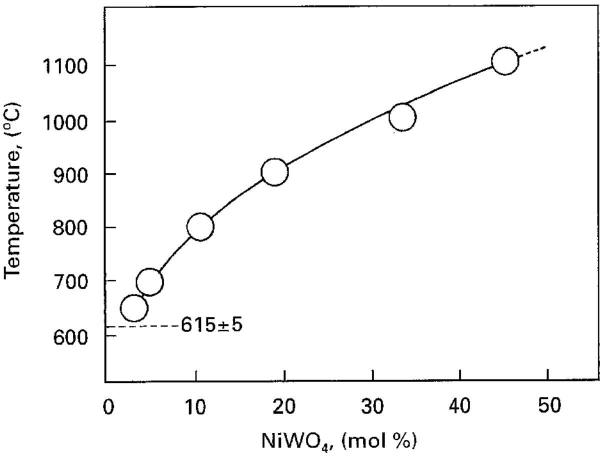

Figure 1 Solubility of $NiWO_4$ in $Na_2W_2O_7$ as a function of temperature.

Mixtures containing 10–60 mol% solute produced crystals of varying sizes. Fig. 3 shows the maximum length (L_{max}) of grown crystals plotted against solute content. The sizes of the crystals grown were dependent on the solute content. Crystals of up to 8 mm in length were grown from a mixture containing 10 mol% solute. The crystal sizes increased as the solute content increased. The mixture containing 30 mol% solute produced the largest crystal of 15 mm in length. Any further increase in the solute content resulted in a decrease in the crystal size. The most suitable solute content in the mixture was 30 mol%. In this case, the difference between the soak and liquidus temperatures was about 100 °C on the basis of the solubility curve shown in Fig. 1. It was found that large crystals were obtained when the soak temperature was well above the liquidus temperature. This tendency is similar to that for the flux growth of α-Fe_2O_3 [6] and $CaWO_4$ [7] crystals. When the solute contents were 10–40 mol%, crystals were grown from unsaturated solutions at a soak temperature of

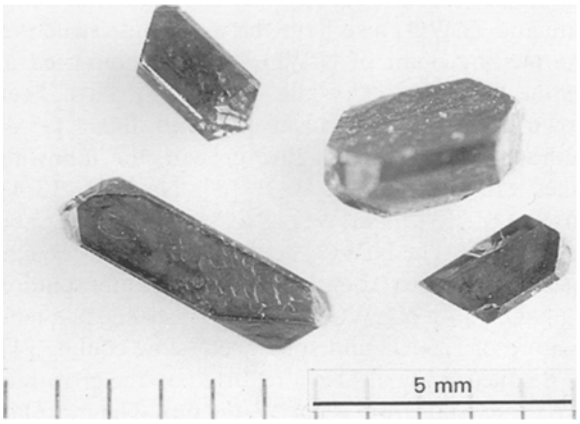

Figure 2 $NiWO_4$ crystals grown from $Na_2W_2O_7$ flux.

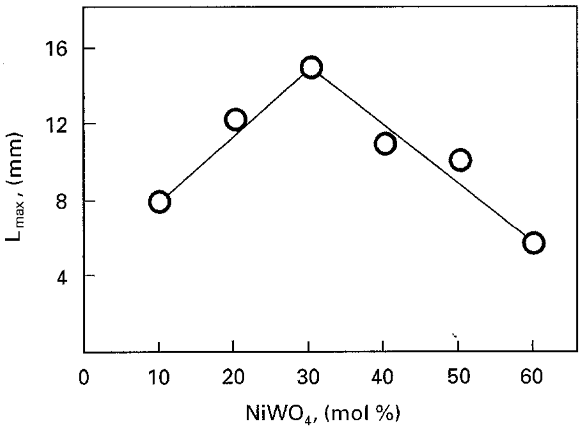

Figure 3 Variation of the maximum length (L_{max}) of $NiWO_4$ crystals with solute content.

1100 °C on subsequent slow cooling. The sizes of the crystals grown from the mixtures containing 50 and 60 mol % solute appeared to be related to the presence of an undissolved solute.

When the solute content was 30 mol%, $NiWO_4$ crystals weighing about 7.1 g were grown. About 95 percent of the solute employed was recovered in the form of crystals. On the basis of the yield of crystals in the growth run, the eutectic composition was estimated to be approximately 1.6 mol% $NiWO_4$–98.4 mol% $Na_2W_2O_7$. This eutectic composition agrees very closely with that obtained by the solubility and DTA data.

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

3.3. Characteristics of the grown $NiWO_4$ crystals

The brownish $NiWO_4$ crystals grown were rod shaped, and the surfaces of these crystals were very flat. In order to determine the Miller indices of the grown crystal faces, the orientated crystals were investigated by the XRD method. Fig. 4 shows the XRD profiles of (a) orientated rod crystals, (b) pulverized crystallites and (c) the $NiWO_4$ JCPDS data [5]. As shown in Fig. 4(a), only the diffraction intensities of the (0 k 0) planes were predominant. The XRD data of the $NiWO_4$ crystals shows that the indices of some prism faces are {0 1 0}. On the basis of the results of the interfacial angle measurements, it was found that the crystals were bounded by {1 0 0}, {0 1 0} and {1 1 0} faces arranged as prisms, and {1 0 2} and {1 1 1} faces arranged as pyramids. The rod crystals were elongated in the ⟨001⟩ direction, which corresponds to the direction for the L_{max} mentioned before. The schematic drawings of the typical habit of the $NiWO_4$ crystals are shown in Fig. 5. The {1 0 0}, {0 1 0}, and {1 0 2} faces were well-developed. The larger the {1 0 2} faces, the smaller the {1 1 1} faces. In certain instances, the {1 1 1} faces disappeared. The form of the $NiWO_4$ grown crystals is similar to that of natural wolframite crystals [8], $MgWO_4$ crystals [9] grown from a KCl flux or $ZnWO_4$ crystals [10] grown from a Na_2O–WO_3 flux.

The EPMA data showed that the nickel, tungsten and oxygen were uniformly distributed in the $NiWO_4$ crystals. Sodium was not detected in the crystals. The chief disadvantage of the flux growth technique is the incorporation of ions from the flux into the crystal lattice. However, no Na^+ ions were incorporated into the $NiWO_4$ crystals obtained in this work. Therefore, it is possible that the grown $NiWO_4$ crystals have no point defects such as Na'_{Ni} and $Na_i^{\bullet}$. This can be ascribed to the large difference in ionic radii between Na^+ (0.102 nm) and Ni^{2+} (0.069 nm) [11]. Flux inclusions were rarely found in the crystals. Impurity incorporation of platinum from the crucible material was also not detected in the crystals. The crystals of $NiWO_4$ had a d.c. electrical resistivity (parallel to ⟨0 0 1⟩ direction) of about 1×10^{11} Ω cm at room temperature. This high resistivity demonstrates that the grown $NiWO_4$ crystals are electrically insulating and

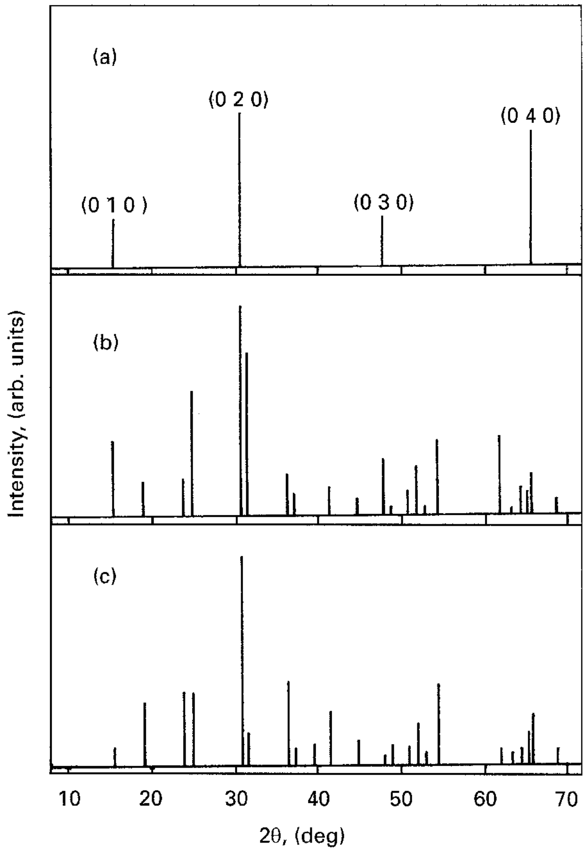

Figure 4 XRD patterns (CuKα) of $NiWO_4$ crystals. (a) Orientated crystals; (b) pulverized crystallites; (c) JCPDS data [5].

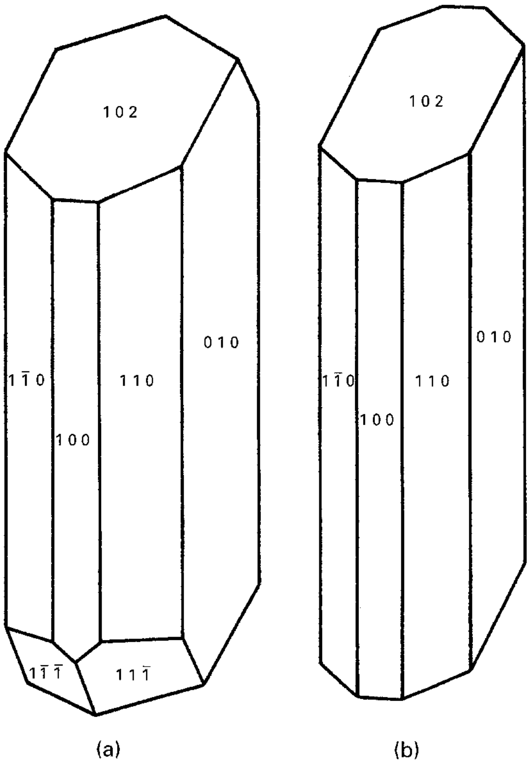

Figure 5 Schematic drawings of the habit of $NiWO_4$ crystals.

suggests that the grown crystals contain no substantial Ni^{3+} ions since the Ni^{3+} substitution should result in a low resistivity value. Thus, the results of the EPMA and resistivity measurements support the fact that only the Ni^{2+} ion is present as a cation in the grown $NiWO_4$ crystals. Bharati *et al.* [12] have reported that $NiWO_4$ crystals grown from a Na_2WO_4 flux had a d.c. resistivity of about 10^8 Ωcm at room temperature. The value obtained in this study was much higher than the literature one [12]. The direction of the crystals measured by Bharati *et al.* [12] was not determined owing to the lack of morphological studies.

The density of the $NiWO_4$ crystals was pycnometrically determined to be 7.97 ± 0.02 g cm^{-3}. This was in good agreement with the literature value (7.95 g cm^{-3}) [5].

In this way, it was found that the quality of the grown $NiWO_4$ crystals from $Na_2W_2O_7$ flux was very high.

4. Conclusions

Highly perfect $NiWO_4$ crystals were grown from a $Na_2W_2O_7$ flux by the slow cooling method.

1. Rod shaped crystals up to 15 mm in length were grown from 40 g mixtures. The most suitable solute content was 30 mol%. Grown crystals were brownish and transparent.
2. The grown crystals were well-formed and bounded by the {100}, {010}, {110}, {102}, and {111} faces. On the basis of the EPMA, density and electrical resistivity data, the quality of the crystals was very high.
3. The solubility of $NiWO_4$ in $Na_2W_2O_7$ increased with increasing temperature. The eutectic temperature was 615 ± 5 °C.

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References

1. R. O. KEELING Jr., *Acta Cryst.* **10** (1957) 209.
2. L. G. VAN UITERT, J. J. RUBIN and W. A. BONNER, *J. Am. Ceram. Soc.* **46** (1963) 512.
3. D. SCHULTZE, K. T. WILKE and C. WALIGORA, *Z. Anorg. Allg. Chem.* **352** (1967) 184.
4. B. M. WANKLYN, *J. Mater. Sci.* **7** (1972) 813.
5. JCPDS card 15–755.
6. B. M. WANKLYN and H. A. LIPKO, *J. Cryst. Growth* **49** (1980) 182.
7. S. OISHI and M. HIRAO, *Bull. Chem. Soc. Jpn.* **63** (1990) 984.
8. E. S. DANA and W. E. FORD, "A Textbook of Mineralogy" (John Wiley & Sons, New York, Charles E Tuttle Company, Tokyo, 1972) p. 771.
9. Y. ENDO, S. OISHI, Y. KANAZAWA and I. TATE, *Chishitsu Chosasho Geppo* **37** (1986) 53.
10. S. OISHI and Y. FURUICHI, *Nippon Kagaku Kaishi* **1993** (1993) 891.
11. R. D. SHANNON, *Acta Cryst.* **A32** (1976) 751.
12. R. BHARATI, R. A. SINGH and B. M. WANKLYN, *J. Mater. Sci.* **18** (1983) 1540.

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