JOURNAL OF MATERIALS SCIENCE 9 (1974) 258–260

Preparation and crystal growth of NiS(h)

S. E. R. HISCOCKS, H. C. WEBBER
Physics Department, Royal Radar Establishment, Great Malvern, Worcs, UK

A procedure is described for the preparation of 90 g batches of NiS. Molten NiS has been shown to exert a pressure of about 9 atm of sulphur and to be compatible with liquid B_2O_3. Near single crystals of NiS(h) have been grown by the high pressure liquid encapsulated Czochralski technique. Evidence suggests that the as-grown crystals exhibit variable stoichiometry and an annealing procedure which gives apparently homogeneous samples is described.

1. Introduction

Nickel monosulphide, NiS, has been the subject of considerable interest in recent years because it has been shown to exhibit a metal-insulator, paramagnetic-antiferromagnetic phase change in its high temperature, hexagonal form [1]. The transition is first-order and the electrical conductivity has been shown to increase abruptly by a factor of at least forty when the temperature is raised through 264K [1, 2].

While much useful work has been done on NiS powders [1] and thick films [3], some experimental techniques require sizeable single crystals. The work reported here was undertaken with the aim of providing the Neutron Scattering Group at AERE, Harwell, UK, with bulk single crystals of NiS with volumes of at least 1 to 2 cm^3 for the investigation of phonon and magnon spectra by neutron inelastic scattering at various temperatures. The latter has been reported elsewhere [4]. NiS exists in two forms: the high temperature form – NiS(h) – having the hexagonal NiAs structure and exhibiting the metal-semiconductor transition, and the low temperature form NiS(1) which is of no present interest. NiS(h) melts congruently at 992 ± 3°C and at a composition of 52.3 at. % S, and decomposes eutectoidally to form NiS(1) + Ni_3S_4 at 280 ± 5°C. It shows a variable composition of between 50.0 and about 51.5 at. % over most of its stability range [5]. NiS(h) appears to remain metastable for considerable periods at room temperature and below.

In the absence of any useful data on the equilibrium pressure of sulphur over NiS at its melting point, a preliminary experiment was carried out in an RRE medium pressure (0 to 50 atm) crystal puller chamber to determine the sulphur pressure [6] and to check that molten NiS and B_2O_3 are mutually immiscible and compatible. This experiment indicated an equilibrium sulphur pressure of about 9 atm – well within the working range of the puller – and also that B_2O_3 should prove a satisfactory encapsulant. It was concluded that liquid encapsulated Czochralski growth at about 10 atm should provide an effective technique for the production of bulk crystals of NiS(h).

2. Preparation of NiS

Nickel and sulphur powders were supplied by Johnson Matthey Ltd with quoted purities of 99.999 and 99.9999% respectively, and were reacted directly together in sealed ampoules. Known data [7] on the variation of sulphur vapour pressure with temperature indicated that at 1000°C ampoules should, for safety, be able to contain about 160 atm. The ampoules used had an i.d. of 20 mm, a wall thickness of not less than 3.5 mm, and a length of 120 mm. They were cleaned in 3:1 HNO_3:HCl for 24 h and then rinsed in distilled water, and isopropyl alcohol. They were finally evacuated to 10^{-5} Torr and baked at 900°C.

Some 30 g of sulphur plus the calculated stoichiometric quantity of nickel were weighed into the ampoule which was then evacuated, flushed with N_2 three times, finally evacuated, and sealed off. The ampoule was heated in the isothermal section of a furnace to 400°C over a period of 4h and held at 400°C for 24 h. It was then raised to 600°C, held there for 7 days and finally raised to 1000°C for 1 h before furnace cooling [8]. The furnace was enclosed in a ventilated metal box as a precaution against possible explosions due to flawed ampoules.

3. The growth of NiS(h) crystals

The RRE high pressure crystal puller has been described elsewhere [9] as has the liquid encapsulation process [9-11]. The B_2O_3 encapsulant was supplied, pre-dried and sealed in glass ampoules, by BDH Ltd. Charges of 80 to 85 g of NiS were melted under 12 to 13 g of B_2O_3 in SiO_2 crucibles in a graphite susceptor. It was found, in practice, that there tended to be an initial loss of sulphur vapour which ceased after 5 to 10 min leaving the B_2O_3 encapsulant murky and the inside of the pressure chamber thinly coated with sulphur. If the melt was now cooled and removed, the system cleaned, and the resulting ingot remelted under fresh B_2O_3, no further losses were observed, the melt was clean and bright, and visibility remained excellent. A pre-melt was, therefore, carried out before attempting to pull a crystal in all cases.

The procedure leading to the final melt differed from that for the preliminary melt only in the addition of 1 wt.% of $NaHF_2$ to the B_2O_3 to reduce the viscosity and, incidently, to increase the gettering action of the encapsulant. Before both melt-ups the system was evacuated and flushed three times with N_2 and then pressurized to 9.5 atm of N_2 and in both cases the temperature was raised slowly through 500 to 600°C so that the viscous encapsulant had time fully to cover the NiS before a sufficient temperature to allow significant losses from the charge surface was attained. NiS(h) crystals were pulled from the melt onto a tantalum capillary seed [12]. In order to promote single crystallinity, a "neck" of 1 to 3 mm diameter and 10 to 15 mm length was pulled before growing-out to form the bulk of the crystal. The pull rate was 10 mm hr^{-1} on first seeding on, 5 mm h^{-1} throughout the growth of the neck, and 2.5 mm hr^{-1} for the bulk of the crystal. The rotation rate was 30 rpm for the seed-on and neck and 20 rpm for the bulk of the crystal.

Grown crystals had a rough surface which apparently prevented the draining off of the encapsulant as the crystal emerged above its surface. As a result there were no losses from the surface of the hot crystal as can sometimes happen [11]. The rough texture of the crystal surface was linked with the crystallographic orientation and polycrystallinity was thus easily visible, without etching, usually in the form of thin stripes of minor grain which had nucleated at or near the shoulder and extended down the length of the crystal.

NiS(h) is hard and brittle and it was found that attempts to cut it with a diamond wheel led to highly pitted surfaces or even cleavage. It was found that the material could, however, be satisfactorily cut with a wire saw and fine (600 grade) carborundum in oil. Crystals were cut perpendicular to the growth direction at the shoulder and base and the entire central section was etched for 1 min in a solution of 10% Br_2 in methanol to show the grain structure on the cut surfaces. Crystals were generally found to have one large grain, comprising 75 to 90% of the bulk, and several small grains forming the stripes along the crystal as mentioned above. These penetrated only a short distance (say 1 to 3 mm) into the main grain. It proved, because of their regular shapes, a simple, if tedious, task to cut out the minor grains to leave single crystal lumps of up to 2 cm^3 in volume.

4. Annealing

The larger crystals produced as described above were used in the neutron inelastic scattering experiments reported elsewhere [4]. The cutting out of the secondary grains produced, incidentally, long strips of crystal from which were cut samples of approximately $1 \times 1 \times 10\ mm^3$ both from the main grain and from the secondary grains. These also were supplied to the Harwell group for resistivity measurements. Investigation of these samples as-supplied showed that their change from low resistivity to high resistivity on cooling was not abrupt but took place over a temperature range of as much as 70°C. It seemed probable that this effect was due to variable stoichiometry and samples were, therefore, annealed in an attempt to remove excess sulphur and attain homogeneity.

Samples were annealed in an evacuated silica ampoule, 12 cm long, placed in a two zone furnace such that the hotter end, containing the samples, was at 825°C, the highest temperature at which the Ni-rich boundary of the homogeneity range appears [5] to correspond closely to 50.0 at. % Ni. The cooler end was at 495°C, that being the temperature at which sulphur exerts a vapour pressure of 2 atm. The anneal was continued for three weeks and the samples were air quenched. A small amount of sulphur was observed at the cooler end of the ampoule. The annealed samples were tested at Harwell and it was now found [13] that the resistivity transition was very abrupt, approximately 2°.

5. Conclusions

It has been shown that NiS exerts a vapour pressure of about 9 atm of sulphur at its melting point and that its melt is compatible with liquid B_2O_3 at that temperature. Near single crystals of NiS(h) have been grown by the liquid encapsulation technique on tantalum capillary seeds and cutting and etching procedures established. Tests have suggested that the crystals as grown exhibit a variable sulphur content and an annealing procedure has been shown to reduce this apparent variability to negligible proportions.

Acknowledgements

The authors wish to thank Dr R. D. Lowde and his colleagues at the AERE, Harwell, UK for permission to mention aspects of their work. This paper is contributed by permission of the director of the Royal Radar Establishment.

References

1. J. T. SPARKS and T. KOMOTO, *J. Appl. Phys.* **34** (1963) 1191.
2. *Idem, Rev. Mod. Phys.* **40** (1968) 752.
3. T. OHTANI, K. KOSUGE, and S. KACHI, *J. Phys. Soc. Japan.* **28** (1970) 1588.
4. G. A. BRIGGS *et al*, Proceedings of the Conference on Neutron Inelastic Scattering, Grenoble, 1972. To be published, Proceedings Publishing, IAEA, Vienna, 1973.
5. R. P. ELLIOTT, "Constitution of Binary Alloys" (ed. M. Hansen) (McGraw-Hill, New York, 1965) 668.
6. S. E. R. HISCOCKS, *J. Sci. Instrum. Series 2,* **2** (1969) 417.
7. E. H. BAKER, *Trans. Inst. Mining and Metallurgy, Section C,* **80** (1971) C93.
8. Information on the preparation of NiS was kindly provided by R. M. White of Stanford University. While the actual procedure used was different in temperature regime from that suggested by Dr White, the authors are grateful for the timely warning of the extreme explosiveness of this reaction.
9. J. B. MULLIN, R. J. HERITAGE, C. H. HOLLIDAY and B. W. STRAUGHAN, *J. Crystal Growth* **3** (1968) 281.
10. J. B. MULLIN, B. W. STRAUGHAN, and W. S. BRICKELL, *J. Phys. Chem. Solids* **26** (1965) 782.
11. C. T. ELLIOTT and S. E. R. HISCOCKS, *J. Mat. Sci.* 3 (1968) 174.
12. S. E. R. HISCOCKS, *ibid* 4 (1969) 310.
13. G. A. BRIGGS, Materials Physics Division, AERE, Harwell, UK, private communication.

Received 12 June and accepted 21 August 1973.