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Investigations in the Scandium–Nitrogen System

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Single-phase samples of δ-ScN_{1-x} and two-phase Sc/ScN alloys were prepared by direct nitridation of Sc metal and by arc-melting of ScN + Sc, respectively. The lattice parameters of δ-ScN_{1-x} prepared at 1370–1770 K were measured. The lattice parameter $a = 0.45018(5)$ on the nitrogen-rich phase boundary and $a = 0.45055(9)$ nm for δ-ScN_{1-x} are in equilibrium with Sc metal. Chemical analysis of nitrogen and oxygen in single-phase δ-ScN_{1-x} prepared at 25 kPa nitrogen pressure and 1770 K yielded a stoichiometry of $ScN_{0.98\pm0.005}O_{0.02\pm0.01}$. Microprobe Sc profiles across diffusion layers of δ-ScN_{1-x} on Sc metal prepared at 1380 and 1770 K indicate that in this temperature range ScN_{1-x} has a homogeneity range of $ScN_{0.87}$–$ScN_{1.00}$. In the diffusion layers the dark blue color of ScN on the nitrogen-rich surface takes on a clearly visible violet tinge near the Sc/ScN boundary. Nitridation of solid Sc metal results in a porous or hollow nitride sample. This is probably due to the preferential diffusion of Sc^{3+} ions through the originally formed ScN layer.

Introduction

Chemical bonding in scandium nitride seems to be of an intermediate character between the ionic bonding prevailing in the nonconductor calcium nitride and that of the metallic bonding in the (super)conducting group IV transition nitrides. δ-$ScN_{1.00}$ was reported to be a semiconductor with an optical energy gap of 2.2 eV (*1*). A study of the literature on scandium nitride shows discrepancies with respect to the stoichiometry. Values of $ScN_{1.00}$ (*1*), $ScN_{0.87}$ (*2*), $ScN_{0.92}$ (*3*) have been reported, and one study (*4*) reports a homogeneity region of $ScN_{0.74}$–$ScN_{0.87}$. Experimental details are not conclusive as to whether or not the samples were really homogeneous since relatively low temperatures (down to 1073 K (*4*)) were applied for the preparation.

The work described in the present paper was carried out in order to obtain more conclusive information about the stoichiometry of δ-ScN_{1-x} and to contribute to the knowledge of the scandium–nitrogen system.

Experimental

Sc plates and Sc sponges were heated in a cold-wall autoclave in pure nitrogen at pressures between 25 kPa and 3.6 MPa and temperatures between 1380 and 1770 K. In order to avoid contamination with oxygen the samples were wrapped in zirconium foil with a protective sheet of Mo foil to avoid direct contact. For the preparation of diffu-

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sion couples the heating current of the autoclave was switched off before nitridation was complete.

Two-phase alloys were prepared by arc-melting Sc/ScN mixtures in an Ar atmosphere. These samples were heat treated in sealed Ar-filled silica tubes. In order to avoid contact with the SiO_2 wall the samples were wrapped in Mo foil. The heat-treated samples were investigated by metallography, X-ray diffraction (114.6-mm Debye–Scherrer camera and powder diffractometry with Ni-filtered Cu$K\alpha$ radiation), scanning electron microscopy, and electron probe microanalysis. In order to avoid potential buildup the samples were sputtered with a carbon layer for SEM and EPMA.

The lattice parameters were calculated from Debye–Scherrer films with a computer program (*5*) which applies extrapolation to $2\theta = 180°$. For this procedure all observed interferences (including $K\alpha 2$ at high diffraction angles) were used. For the reassessment of powder intensity data a computer program for the calculation of powder diffractograms (*6*) was used.

The nitrogen analysis was carried out by the Dumas method. The oxygen content was analyzed by vacuum hot extraction.

Results and Discussion

ScN samples resulting from the autoclave process had a nearly lusterless dark blue color. Within the pressure range investigated (see Table I) no significant change in the lattice parameter of δ-ScN_{1-x} was observed. Obviously even the lowest nitrogen pressure used was sufficient to ensure the maximum nitrogen content. The average value of the lattice parameter for the nitrided samples is $a = 0.45018(5)$ nm.

Sample 7A was chemically analyzed and found to have a stoichiometry of [N]/[Sc] = 0.98 ± 0.005. The oxygen content was found to be about 1 at.%, resulting in a gross composition of $ScN_{0.98\pm0.005}O_{0.02\pm0.01}$. This is consistent with those values reported in the literature where it is stated that ScN has a 1 : 1 stoichiometry (*1*).

TABLE I

CONDITIONS OF PREPARATION AND RESULTS

Sample	p (N_2)	T/K	Lattice parameter	Comments
ScN 1	3 MPa	1700	0.45019(1)	
ScN 2	0.1 MPa	1670	0.45020(3)	
ScN 4A	—	1370	0.45059(3)	Arc-melted samples
ScN 4B	—	1370	0.45047(9)	annealed in silica tubes
ScN 4C	—	1170	0.45060(4)	average: a = 0.45055(9) nm
ScN 5	3.6 MPa	1430	0.45020(4)	
ScN 6	31 kPa	1380	—	Diffusion couple
ScN 7A	25 kPa	1770	0.45013(6)	[N]/[Sc] = 0.98 ± 0.005
ScN 7B	25 kPa	1770	—	Rim-type sample (Fig. 1)
ScN 7C	25 kPa	1770	—	Diffusion couple

At the low-nitrogen phase boundary δ-ScN_{1-x} has a lattice parameter of a = 0.45055(9) nm. This is the average value of samples ScN 4A–ScN 4C which had been annealed in silica tubes at 1370 and 1170 K for 2 and 3 weeks, respectively. α-Sc in equilibrium with δ-ScN_{1-x} was found to have lattice parameters of $a = 0.3310(1)$ nm and $c = 0.5280(6)$ nm, not significantly different from pure Sc metal (*7*). Obviously scandium metal does not take up any appreciable amounts of nitrogen in solid solution in the temperature range investigated.

The differences in the lattice parameters of δ-ScN_{1-x} are indicative for a homogeneity region. Profiles of Sc across the diffusion couples yielded a homogeneity region of ≈2 wt% Sc. With respect to the [N]/[Sc] ratio this yields a value of $ScN_{0.87}$–$ScN_{0.98}$. It should be noted, however, that the presence of pores in the nitride layer led to considerable discontinuities in the scan and made it difficult to obtain reliable quantitative results. Table I gives a summary of preparation and lattice parameters.

Since the available data on the powder diffractogram of δ-ScN_{1-x} (*8*) need some revision, the observed (diffractometer) and

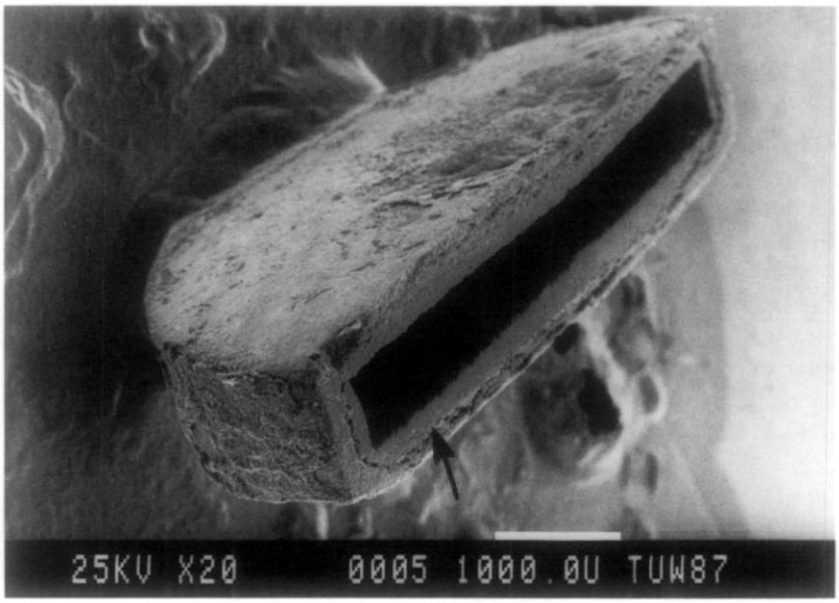

FIG. 1. Rim-type hollow ScN plate (sample ScN 7B) obtained by nitridation of a compact Sc plate. The white bar represents 1 mm. The arrow points to the slit corresponding roughly to the original Sc surface. The material outside the slit was most probably formed by diffusion of Sc^{3+} ions through the originally formed ScN layer and subsequent nitridation.

TABLE II

OBSERVED AND CALCULATED X-RAY POWDER DIFFRACTOGRAM OF $ScN_{0.98}$

System: cubic, space group *Fm3m* (No. 225)
Unit cell: a = 0.45013(6) nm
Point positions: 4 Sc at 4(a), 4 N at 4(b) occupancy: 98%
Wavelength: Ni-filtered Cu$K\alpha$ radiation, $K\alpha$1: 0.154056 nm

h k l	d_{obs}	I_{obs}	d_{cal}	I_{cal}
1 1 1	2.594	66	2.599	63
2 0 0	2.247	100	2.251	100
2 2 0	1.590	57	1.591	58
3 1 1	1.357	22	1.357	25
2 2 2	1.299	15	1.299	18
4 0 0	1.125	7	1.125	8
3 3 1	1.032	10	1.033	11
4 2 0	1.007	19	1.007	26
4 2 2	0.919	14	0.919	25
5 1 1	—	—	0.866	12
3 3 3	—	—	0.866	4
4 4 0	—	—	0.796	26

calculated diffraction pattern of δ-$ScN_{0.98}$ (sample 7A) is given in Table II.

Further evidence for the existence of a homogeneity region in ScN_{1-x} can be derived from the fact that the ScN layer in the diffusion couple showed a color change. The dark blue color of ScN on the outer surface takes on a clearly visible monotonically increasing violet tinge when the ScN/Sc boundary is approached.

Metallographic investigations of Sc plates that had been fully nitrided revealed that the obtained scandium nitride was highly porous. By choosing thicker Sc plates hollow ScN samples as shown in Fig. 1 can be obtained. This is quite contrary to the experience with TiN, VN, and NbN, which can be obtained as fully dense samples upon nitridation of the bulk metals.

The fact that ScN has a larger lattice parameter at substoichiometric compositions than at $ScN_{1.00}$ is most probably due to un-

occupied Sc sites at a stoichiometric composition. It is thus similar to FeO, where part of the Fe^{2+} sites are vacant (*9*). Just as with the diffusion of Fe^{2+} in FeO, the diffusion of Sc^{3+} in ScN takes place predominantly via migration of Sc^{3+} ions which diffuse from the Sc core to the surface of the originally formed ScN-rim where they react with nitrogen. In Fig. 1 the original surface of the sample can be seen as the highly porous zone (slit) situated parallel to the outer and inner surfaces (arrow). The size of the original Sc plate corresponds to the size of the slit.

The diffusion process of Sc^{3+} is probably supported by the considerable decrease in molar volume during nitridation in the sense that ScN contracts relative to the Sc metal and thus makes room for the diffusion of Sc. Sc metal has a molar volume of 15.03 cm^3/mole whereas ScN_{1-x} has a molar volume of 13.74–13.77 cm^3/mole, which is 8.4–8.6% less.

In the reverse direction, the diffusion of relatively large nitrogen ions appears to be rather slow. In order to satisfy the electroneutrality requirements, electrons must diffuse from the outer surface to the Sc/ScN boundary. If these assumptions are correct, the hollow space in Fig. 1 could be considered to be a very large Kirkendall pore.

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References

1. J. P. Dismukes, W. M. Yim, J. J. Tietjen, and R. E. Novak, RCA Review, p. 680, RCA Laboratories, Dec. (1970).
2. M. I. Aivazov and T. V. Rezchikova, *Russ. J. Inorg. Chem.* **22,** 250 (1977).
3. V. S. Bogdanov, V. S. Neshpor, Y. D. Kondrashev, A. B. Goncharuk, and A. N. Pityulin, *Poroshk. Metall. (Kiev)* **5,** 79 (1981).
4. M. I. Aivazov, T. V. Rezchikova, and S. V. Gurov, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **13,** 1235 (1977).
5. I. Smid, Program GITIVI, Institute for Physical Chemistry, University of Vienna (1986).
6. K. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.* **10,** 73 (1977).
7. P. Villars and L. D. Calvert, Eds., "Pearson's Handbook of Crystallographic Data of Intermetallic Compounds," Metals Park, OH (1985).
8. JCPDS Powder Data File, Card. No. 3-951.
9. R. M. Hazen and R. Jeanloz, *Rev. Geophys. Space Phys.* **22,** 37 (1984).