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Nitrogen Ceramics Meeting in France
Louis Cartz
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19 ABSTRACT (Continue on reverse if necessary and identify by block number) Presentations given at this meeting--JENI7--held in Rennes, France, in September 1987, are briefly reported. A very wide range of nitrogen ceramics properties was discussed at the meeting; in particular, their chemistry, crystallography, and sintering behavior. <i>Contents of this paper include: cont'd</i>			
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1 INTRODUCTION

The meeting "Journées d'Etudes sur le Nitrures" (JENI 7) (studies on Nitride Ceramics) was held at the University of Rennes, France, on 14 and 15 September 1987. This was the seventh of the series of meetings JENI has held at 2- or 3-year intervals in Limoges, Corbeil, St. Etienne, or Rennes, and most of the people attending these meetings have been from these universities. There has also always been a participation at the JENI meetings of research workers from the University of Newcastle-upon-Tyne (UK). About 40 scientists were present, three-quarters from France and the remainder from several western European countries. Most of the lectures were in French, with a few in English. The papers are to be published in *Revue Chimie Minérale*, though not as a special issue.

Several studies reported at the meeting are of special interest, and these are summarized in this report.

2 NITROGEN PYROXENES

The presentation on nitrogen pyroxenes was the first announcement that a pyroxene structure containing nitrogen has been identified. D.P. Thompson, of the University of Newcastle-upon-Tyne, reported on a new phase observed on crystallization of Si_3N_4 ceramics sintered with Y_2O_3 and MgO additives when extra lines were observed in the x-ray diffraction pattern. The new phase was prepared of purity approximately 95 percent by careful devitrification of the glass corresponding to the composition of the grain boundary glassy phase used in the sintering of Si_3N_4 .

The new phase is triclinic of lattice parameters

$$a=0.6515 \text{ nm}, b=0.6813 \text{ nm}, c=0.5180 \text{ nm} \\ \alpha=99.298^\circ, \beta=100.891^\circ, \gamma=87.055^\circ$$

and is isostructural with minerals of the pyroxene group. The composition of the new phase is very nearly $\text{MgYSi}_2\text{O}_5\text{N}$, of

melting point 1450°C , and so is analogous to diopside $\text{CaMgSi}_2\text{O}_6$, of melting point 1390°C , where an oxygen has been replaced by a nitrogen. D.P. Thompson discussed other mineral silicate types that might be prepared as N-phases.

3 PRECURSORS OF SiC AND Si_3N_4

P. Goursat (Université de Limoges) reported on the synthesis and pyrolysis of octamethylcyclotetrasilazane polymers, relating the polymer structure and the pyrolysis conditions to the microstructure of the resulting silicon nitride and SiC . Low-angle x-ray scattering, gel permeation chromatography, and infrared and Raman spectra were used to follow the polymer structure changes. The polycyclic macromolecules are organized in domains of high density separated by regions of lower density. There are a very large number of polysilazanes and these can pyrolyze by several different reactions: the $\text{Si}(\text{N})_2$ group converts to a $\text{Si}(\text{N}_3)$ group, and the $\text{Si}(\text{N}_2)(\text{CH}_3)_2$ group converts to an amorphous Si-N-C material. On heating, the amorphous phase recrystallizes with the precipitation of Si_3N_4 . It may be possible to form $\text{Si}(\text{C},\text{N})$ by this method. The thermal decomposition under N_2 of the polysilazane occurs in three steps: (1) from 220°C - 450°C , the evolution of gases leaves a highly porous body; (2) from 450°C - 750°C , the organic groups, such as CH_3 , break off, and the structure of the microdomains becomes less organized with an overall compaction of the material; (3) up to 1400°C , the amorphous Si carbonitride is stable, but above 1400°C , $\alpha\text{Si}_3\text{N}_4$ crystallizes.

4 A PURE FORM OF AlN

A reaction between Al_2O_3 and NH_3 was described by J. Jarrige (Université de Limoges) which results in the formation a pure form of AlN . At 1200°C , powdered Al_2O_3 undergoes nitration in NH_3 atmosphere to form a white powder of AlN . Other methods of preparation of AlN result usually in a dark-coloured AlN due to traces of C.

Jarrige described sintering studies on these fine powders of AlN using two different additives, YF₃ and Y₂O₃. The use of the fluoride is found to be very interesting since the AlN grains are cleaned of absorbed oxygen. This is an important advantage since the thermal conductivity of the AlN is very sensitive to the presence of oxygen; consequently, there is distinct interest in the use of YF₃ as the sintering aid. The sintering condition used are 1800°C for 15 minutes, using 1-weight-percent fluoride additive.

5 THE Ti-N SYSTEM

W. Langauer et al. (Technical University of Vienna, Austria) have carried out extensive studies of the Ti-N system with N content approximately 33 atomic percent. They used TiN prepared by melting TiN with Ti, by the sintering of TiN with Ti, and by diffusion across TiN-Ti boundaries.

The new phases they reported are:

- o η -Ti₃N_{2-x}, isostructural with ϵ -Hf₃N_{2-x}, which crystallizes in space group R $\bar{3}m$ with rhombohedral lattice parameters $a=0.74236(26)$ nm and $\alpha=23.16(1)^\circ$. The nitrogen content of this phase is 29 atomic percent. It was observed in the temperature range of 1320 K to about 1400 K.
- o ζ -Ti₄N_{3-x}, isostructural with ζ -Hf₄N_{3-x}, which crystallizes in space group R $\bar{3}m$ with lattice parameters of $a=0.98072(15)$ nm and $\alpha=17.47(1)^\circ$. This phase is stable at 31.5 atomic percent N and in the temperature range of 1320 K to about 1550 K.

The phase ϵ Ti₂N was found by x-ray diffraction studies at high temperature to decompose at 1359 \pm 27 K. Langauer reported on the stability range of δ -TiN_{0.50}, δ' -TiN_{0.50} and presented a tentative Ti-N phase diagram for N \sim 33 atomic percent.

The oxidation of TiN and other transition metal nitrides and carbides was discussed by J.N. Clark (Plymouth Polytechnic, UK). Though these are relatively hard materials, of high m.p. above

2000°C, their use is limited by their oxidation in air at low temperatures of 400 to 1000°C. Clark reported on the reactivity of nitrides and carbides of Ti, Zr, and Cr in air and CO₂; he carried out the measurements by x-ray diffraction and thermogravimetry, and used nitrogen absorption to determine surface area. The oxide Cr₂O₃ does form a protective coating on Cr, but this is not the case for Ti and Zr. TiN is oxidized in air at 900°C, ZrN at 700°C, and ZrC at 800°C. Discussions covered the brittle nature of the oxide coatings, the different kinetics of oxidation which vary with temperature, and sintering processes of the oxide protective layers.

6 NITROGEN GLASSES

M. Billy (Université de Limoges) discussed the nitrogen glasses of the system M₁-Al-O-N where M₁ is Ca or Y. These glasses are formed during sintering studies of AlN which require additives of CaO or Y₂O₃ when liquid phase sintering occurs. Billy is carrying out studies of the CaO-Al₂O₃-AlN diagram in order to determine the glass-forming region, crystallization temperatures, and softening temperature of the glasses.

F. Desmaison-Brut (Université de Limoges) described the oxidation kinetics of nitrogen glasses of the system Ca-Si-Al-O-N in air from 900-1250°C. The weight loss observed between 900 to 1100°C can be explained by the decomposition of the outer parts of the specimen, with the formation of wollastonite. Above 1100°C, the linear kinetics are due to the growth of a nonprotective oxide layer of pseudowollastonite, anorthite, and cristobalite.

R. Marchand et al. (Université de Rennes) reviewed the effect of replacing oxygen by nitrogen in glasses of the system M₂-Si-Al-O-N where M₂ can be Li, Na, Mg, Ca, Sr, Ba, Mn, or Nd. The glassy region becomes smaller in extent as the amount of nitrogen present increases, though the physical and chemical properties of the glasses improve in general, with a higher refractive index, higher density and hardness, and decrease in

leachability. Marchand also reviewed the phosphate glasses of general formula $M_3P_3O_{3-3x}N_{2x}$, where M_3 is Li, Na, or K. The strong P-N bond tends to increase the glass softening temperature and to modify the physical and chemical properties.

7 Zn AND Ge OXYNITRIDES

The detection of NH_3 can be carried out using the change of resistance of pellets of the semiconductors of Zn and Ge oxynitride. G. Rosse et al. (Université de Rennes) have shown that 100 ppm of NH_3 can be detected in a dry air flow of 6 litres per minute at between 100 and 300°C. Other semiconductors are sensitive to a very large number of gases, but only NH_3 affects the electrical resistivity of Zn and Ge oxynitrides.

8 Zr_3AlN AND Hf_3AlN

J. Bauer et al. (Université de Rennes) have determined the crystal structure of Zr_3AlN and Hf_3AlN . The compound Zr_3AlN , a new ternary phase, was found during a study of the system Zr-Al-N. The crystal structures have now been determined using single-crystal data.

Zr_3AlN is orthorhombic, belongs in space group $Cmcm$, and is isostructural with Re_3B . The lattice parameters are

$$\begin{aligned} a &= 0.33690(5) \text{ nm}, & b &= 1.1498(2) \text{ nm} \\ c &= 0.89825 \text{ nm} \end{aligned}$$

with four formula units Z per unit cell.

Hf_3AlN is isostructural with Zr_3AlN and Re_3B , with orthorhombic lattice parameters $a=0.33185$ nm, $b=1.1326$ nm, $c=0.88646$ nm, and with $Z=4$.

9 OTHER STUDIES

A wide range of studies presented at this meeting concerned the ceramic Si_3N_4 : hot isostatic pressure sintering; pressure sintering after a preliminary heat

treatment; use of rare earth oxides as sintering aids; the creep properties of Si_3N_4 ceramics; thin films of amorphous Si_3N_4 prepared by plasma methods; the low-temperature oxidation problem of Si_3N_4 with Y_2O_3 additives.

Several papers were given on the system Al-O-N; preparation of fine powders suitable for sintering; the thermal expansion coefficient of Al oxynitride by neutron (time of flight) diffraction; and the use of Y_2O_3 as a sintering aid for Al_2O_3 -Al oxynitride.

The reaction of AlN with ZrO_2 to form ZrN and Al_2O_3 was described by A. Mocellin (Ecole Polytechnique de Lausanne, Switzerland); this reaction is observed when sintering powder mixtures at 1400-1600°C (Mocellin, 1986). Mocellin described how the reaction is affected by the presence of CaO or Y_2O_3 , which is added to stabilize the tetragonal ZrO_2 form.

10 GENERAL

The JENI meetings are relatively small and intimate gatherings where graduate students and young research workers have the opportunity to present papers and to have their studies discussed. At this meeting a very wide range of nitrogen ceramic properties was discussed, in particular their chemistry, crystallography, and sintering behavior.

The future of these meetings was considered as to whether they should be continued. The consensus of opinion was in favor of continuing the meetings, and JENI 8 is expected to be held in 1990. Further information can be obtained from M. Billy, Université de Limoges, France.

11 REFERENCE

Mocellin, A., *Revue de Chimie Minérale*, 23 (1986), 80.