Int. J. High Technology Ceramics **1** (1985) 119–127

Phase Equilibrium Studies in Si_2N_2O-containing Systems: I. Phase Relations in the Si_2N_2O–Al_2O_3–Y_2O_3 System

G. Z. Cao, Z. K. Huang, X. R. Fu and D. S. Yan (T. S. Yen)

Shanghai Institute of Ceramics, Academia Sinica, Shanghai, People's Republic of China

SUMMARY

Sub-solidus phase relations have been studied in the Si_2N_2O–Al_2O_3–Y_2O_3 system. The results show that Si_2N_2O forms a small range of compositions with Al_2O^3 (O'ss) containing up to 15 m/o Al_2O_3, and that $2Y_2O_3 \cdot Si_2N_2O$ forms a continuous solid solution series with $2Y_2O_3 \cdot Al_2O_3$ (Jss). In the Si_2N_2O-rich corner of the system, Si_2N_2O reacts with Y_2O_3 at 1550°C to form Si_3N_4 and $Y_{10}(SiO_4)_6N_2$(H-phase). Four quaternary phase regions occur in this system:

H–Si_3N_4–$Y_2O_3 \cdot Si_2N_2O$–$3Y_2O_3 \cdot 5Al_2O_3$

H–Si_3N_4–$3Y_2O_3 \cdot 5Al_2O_3$–$O'ss$

H–Si_3N_4–O' ss–Si_2N_2O

H–$Y_2O_3 \cdot Si_2N_2O$–$3Y_2O_3 \cdot 5Al_2O_3$–$4Y_2O_3 \cdot Si_2N_2O \cdot Al_2O_3$

From the results of this work, the sub-solidus phase diagram and the isothermal section at 1550°C in the Si_2N_2O–Al_2O_3–Y_2O_3 system are presented. A large liquid-phase area near the Si_2N_2O–Al_2O_3 side that may effect the sintering of O'-sialon ceramics is reported. The difference between our results and those previously reported in the Si_3N_4–SiO_2–Y_2O_3 phase diagram is also discussed.

1. INTRODUCTION

In recent years silicon oxynitride ceramics as high temperature structural material have received more and more attention from the point of view of their excellent oxidation resistance at elevated temperature. Although

Int. J. High Technology Ceramics 0267-3762/85/$03·30

silicon nitride ceramics possess very high mechanical strength, their oxidation resistance at high temperatures can be significantly degraded by oxide additives used to promote the densification process. Therefore, a combination of silicon nitride matrix with silicon oxynitride grain boundary might give a material with both high strength and good oxidation resistance. Thus the investigation of the system containing Si_2N_2O is of interest. The present paper is based on the understanding that the reaction between Si_3N_4 and SiO_2 to form Si_2N_2O solid solution occurs essentially in the presence of Al_2O_3.[1] The current commercial 'sialon' ceramics are of the β'-form and have an overall composition quite close to the Si_3N_4–Al_2O_3–Y_2O_3 plane. They contain an oxygen-rich yttrium sialon glass and therefore the Si_2N_2O–Al_2O_3–Y_2O_3 plane should cut across the tie line joining β'-sialon to glass for this composition range. Hence, a study of the phase relationships in this system is of importance to the understanding of the grain boundary characteristics of the related silicon nitride ceramics and the preparation of two-phase β'- and O′-sialon ceramics.

Phase relationships previously reported in the Y_2O_3–Al_2O_3 system[2] show two stable compounds, $2Y_2O_3 \cdot Al_2O_3$ and $3Y_2O_3 \cdot 5Al_2O_3$, and one metastable compound, $Y_2O_3 \cdot Al_2O_3$, which has two phases. The low temperature form has the same structure as $Y_2O_3 \cdot Si_2N_2O$ but is only stable up to ~1100°C;[3] the high temperature form is stable above 1825°C. In the Si_2N_2O–Y_2O_3 system there exist two compounds, $2Y_2O_3 \cdot Si_2N_2O$ and $Y_2O_3 \cdot Si_2N_2O$, corresponding to $2Y_2O_3 \cdot Al_2O_3$ and $Y_2O_3 \cdot Al_2O_3$, respectively, in the Y_2O_3–Al_2O_3 system. However, no compound similar to $3Y_2O_3 \cdot 5Al_2O_3$ has been found. A continuous solid solution can be formed between $2Y_2O_3 \cdot Si_2N_2O$ and $2Y_2O_3 \cdot Al_2O_3$.[4] As to the Si_2N_2O–Al_2O_3 system, no new compound has been found, but a certain amount of Al_2O_3 can enter into the crystal structure of Si_2N_2O, forming a partial solid solution, the so-called O′-sialon. The limiting solubility of Al_2O_3 in Si_2N_2O ss was reported by different authors to be 6 e/o Al^{3+} (equivalent to 8 m/o Al_2O_3),[5] or 20 m/o Al_2O_3.[6]

2. EXPERIMENTAL

The starting materials used were silicon oxynitride, aluminium oxide and yttrium oxide. Silicon oxynitride powder was synthesized in our laboratory and after analysis shown to have the composition, Si 57·17, N 24·83, and O 16·40 %, corresponding to $Si_{2.04}N_{1.77}O_{1.02}$ which is deficient in nitrogen, but powder X-ray diffraction showed a single phase of Si_2N_2O only. Aluminium oxide was prepared by the decomposition of ammonium aluminium sulphate and its purity reached 99·9 %. The yttrium oxide was a high purity (99·99%) reagent produced by Shanghai Yuolong Chemical works. About 50 compositions were prepared with these starting materials. The powder mixes were milled, using an agate mortar, in 100% ethanol for 2 h, dried and cold isostatically pressed at 300 MPa into pellets.

The melting method was used to determine the liquid-phase area at 1550 °C. The pellets were placed in small boron nitride-coated and screw-topped graphite crucibles filled with boron nitride powder and fired for 1 h in a graphite heating furnace at 1550 °C in a nitrogen atmosphere. The molten area on the specimens was observed by its visual appearance and by microscopy. Similar firings were carried out at lower temperatures, thus decreasing the liquid-phase formation area until the eutectic was identified. The eutectic point was determined by means of differential thermal analysis (DTA) and high temperature microscopy observation.

For the determination of sub-solidus phase compositions, hot-pressing was used in order to promote reactions to reach equilibrium and to minimize weight loss. Powder mixtures were placed in graphite dies coated with boron nitride on the inner surface, and hot-pressed under a pressure of 20 MPa in a nitrogen atmosphere. The hot-pressing temperature used was 1400 °C for the compositions which could form a liquid phase at 1550 °C and was 1400–1550 °C for all other compositions. The phase compositions of the specimens after hot-pressing were detected by X-ray diffraction analyses. Energy dispersion analysis of X-ray (EDAX) was used to determine the solid solubility of Al_2O_3 in Si_2N_2O ss.

3. RESULTS AND DISCUSSION

3.1. Phase relations in two Si_2N_2O-containing binary systems

Results obtained for the Si_2N_2O–Al_2O_3 system show that no binary compound is formed and there is only a limited solid solution of Al_2O_3 in Si_2N_2O to form O′-sialon. The extent of solid solubility of Al_2O_3 in Si_2N_2O was determined to be 15 m/o by X-ray diffraction and by EDAX. For the former method the composition at which X-ray peaks of Al_2O_3 virtually disappeared on the join O′ ss–Al_2O_3 was considered as the limit of solid solubility.

In the Si_2N_2O–Y_2O_3 system experiments confirm the existence of two compounds, $2Y_2O_3 \cdot Si_2N_2O$ and $Y_2O_3 \cdot Si_2N_2O$. The latter is formed at a temperature as low as 1400 °C and is stable; its structure is the same as the low temperature form of $Y_2O_3 \cdot Al_2O_3$ (stable only up to ~1100 °C) in the Y_2O_3–Al_2O_3 system.[3] At the Si_2N_2O-rich corner, Si_2N_2O reacts at 1550 °C with Y_2O_3 to form $Y_{10}(SiO_4)_6N_2$(H-phase) and Si_3N_4 (mainly α-form, with a little β) by the following reactions:

$$10Si_2N_2O + 6Y_2O_3 \rightarrow Y_{10}(SiO_4)_6N_2 + 4Si_3N_4 + Y_2O_3 \cdot Si_2N_2O$$

$$9Si_2N_2O + 5Y_2O_3 \rightarrow Y_{10}(SiO_4)_6N_2 + 4Si_3N_4$$

3.2. Sub-solidus phase relations in the Si_2N_2O–Al_2O_3–Y_2O_3 system

The main compositions studied and the results of X-ray diffraction phase analyses are shown in Table 1, and the sub-solidus phase diagrams of the Si_2N_2O–Al_2O_3–Y_2O_3 system constructed on the basis of these data are shown in Figs 1 and 2. In this quasi-ternary system, a continuous solid solution (J ss) is formed between $2Y_2O_3 \cdot Si_2N_2O$ and $2Y_2O_3 \cdot Al_2O_3$. The solid solution phase of $2Y_2O_3 \cdot Si_2N_2O$ and $4Y_2O_3 \cdot Si_2N_2O \cdot Al_2O_3$ forms a triangular phase area with $Y_2O_3 \cdot Si_2N_2O$. Another triangular phase area is formed by $3Y_2O_3 \cdot 5Al_2O_3$ and the solid solution phase between $2Y_2O_3 \cdot Al_2O_3$ and $4Y_2O_3 \cdot Si_2N_2O \cdot Al_2O_3$. The experimental results in the Y_2O_3-rich area are very similar to the phase diagram of the Si_3N_4–Y_2O_3–$AlN \cdot Al_2O_3$ system reported by Sun *et al.*[7] As some decomposition and reactions occur in the Si_2N_2O-rich corner

TABLE 1
Compositions Studied and X-ray Analysis Results for the Si_2N_2O–Al_2O_3–Y_2O_3 System

No.	*Y_2O_3*	*Si_2N_2O*	*Al_2O_3*	*Phases present*[a]	*Phase regions*[a]
1	8	1	1	Y_2O_3; J ss	Y_2O_3–J ss
2	6	2	1	J ss	
3	6	1	3	J ss; YAG	J ss–YAG
4	6	3	1	J ss; K	J ss–K
5	3	1	2	J ss; K; YAG	J ss–K–YAG
6	3	2	1	J ss; K; YAG	
7	1	1	0	K	
8	3	4	0	K; H; SN	K–H–YAG–SN
9	3	2	2	K; H; SN; YAG	
10	5	9	0	SN; H	
11	3	5	2	SN; H; YAG; O′	H–SN–YAG–O′
12	1	7	2	SN; H; YAG; O′	
13	1	9	0	SN; H; Si_2N_2O	SN–H–Si_2N_2O
14	1	8·5	0·5	SN; H; O′	
15	0	9	1	O′ ss	
16	0	1	1	O′; Al_2O_3	
17	2	9	9	YAG; O′; Al_2O_3	YAG–Al_2O_3–O′
18	2	2	6	YAG; O′; Al_2O_3	

[a] For key see Fig. 1 and text.

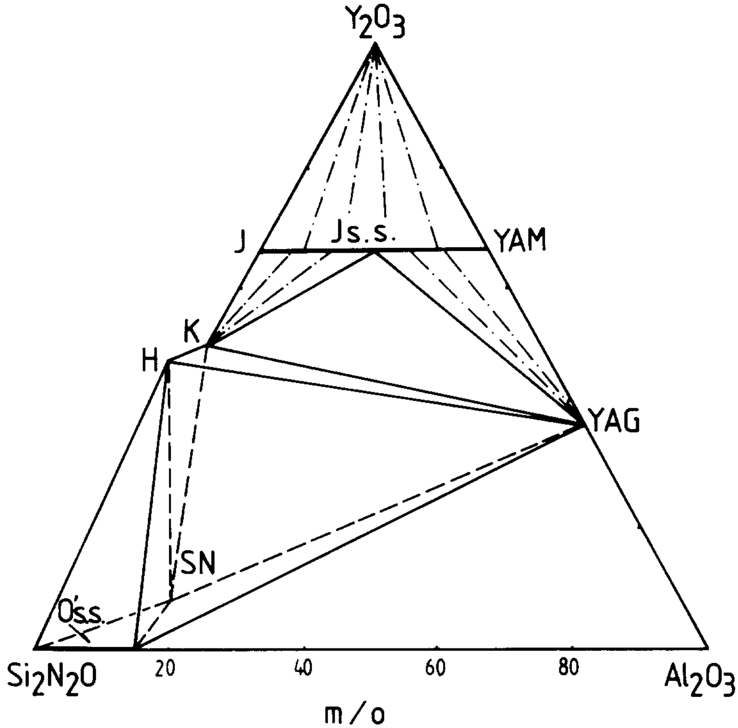

Fig. 1. Sub-solidus diagram of the Si_2N_2O–Al_2O_3–Y_2O_3 system. J = $2Y_2O_3 \cdot Si_2N_2O$; SN = Si_3N_4; YAM = $2Y_2O_3 \cdot Al_2O_3$; K = $Y_2O_3 \cdot Si_2N_2O$; H = $Y_{10}(SiO_4)_6N_2$; YAG = $3Y_2O_3 \cdot 5Al_2O_3$.

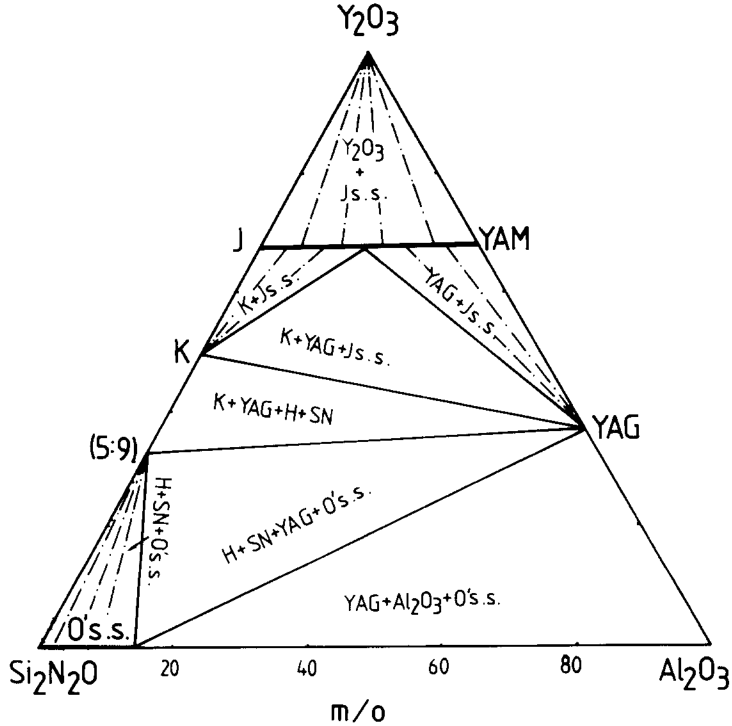

Fig. 2. Sub-solidus diagram of the Si_2N_2O–Al_2O_3–Y_2O_3 system. (5:9) Si_3N_4 and $Y_{10}(SiO_4)_6N_2$.

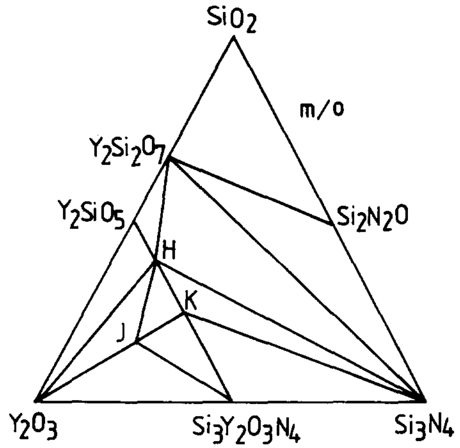

Fig. 3. Phase diagram of the Si_3N_4–SiO_2–Y_2O_3 system reported by Lange *et al.*[8]

of the Si_2N_2O–Y_2O_3 system, so in the Si_2N_2O-rich area of the Si_2N_2O–Al_2O_3–Y_2O_3 system several quaternary compatibility areas are formed:

H–Si_3N_4–$Y_2O_3 \cdot Si_2N_2O$–$3Y_2O_3 \cdot 5Al_2O_3$

H–Si_3N_4–$3Y_2O_3 \cdot 5Al_2O_3$–O′ ss

H–Si_3N_4–O′ ss–Si_2N_2O

H–$Y_2O_3 \cdot Si_2N_2O$–$3Y_2O_3 \cdot 5Al_2O_3$–$4Y_2O_3 \cdot Si_2N_2O \cdot Al_2O_3$

3.3. Review of the Si_3N_4–SiO_2–Y_2O_3 phase diagram

In the Si_3N_4–SiO_2–Y_2O_3 phase diagram previously reported,[8–10] Si_3N_4 is considered to be compatible with $Y_2O_3 \cdot 2SiO_2$ (Fig. 3). However, our experimental results in connection with the Si_2N_2O–Y_2O_3 system showed the contrary. Using either silicon oxynitride or a mix of silicon nitride and silicon dioxide, several samples in the composition range of

TABLE 2
Compositions Studied and X-ray Analysis Results for the Si_2N_2O–Y_2O_3 System

No.	Y_2O_3	Si_2N_2O	Si_3N_4	SiO_2	*Phases present*[a]
1	5	9	0	0	SN; H
2	5	0	4·5	4·5	SN; H
3	1	3	0	0	SN; H; Si_2N_2O
4	2	0	3	3	SN; H; Si_2N_2O

[a] For key see Fig. 1.

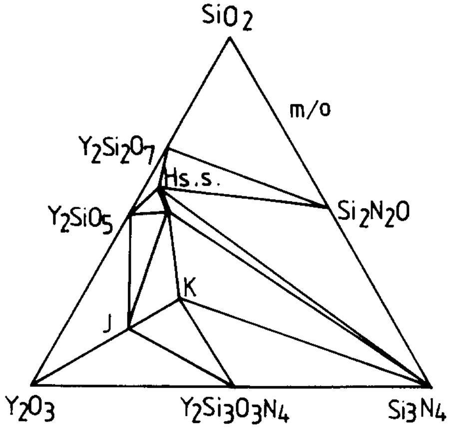

Fig. 4. Phase diagram of the Si_3N_4–SiO_2–Y_2O_3 system reported by Jack.[11]

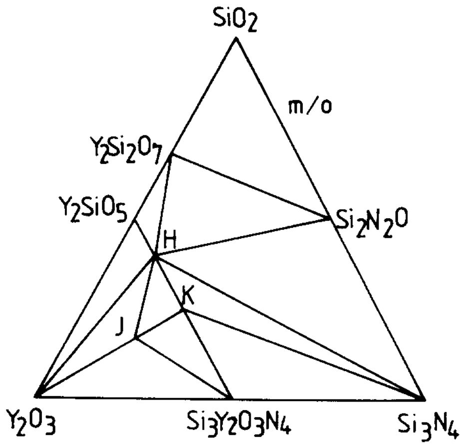

Fig. 5. Phase diagram of the Si_3N_4–SiO_2–Y_2O_3 system obtained in the present work.

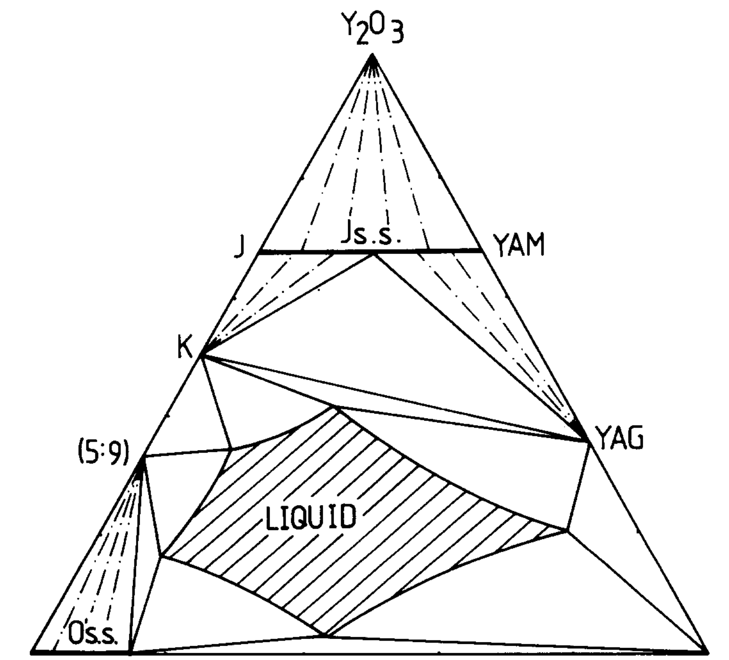

Fig. 6. Isothermal section at 1550 °C in the Si_2N_2O–Al_2O_3–Y_2O_3 system. $T_{eu} = 1450$ °C.

$Si_2N_2O:Y_2O_3 > 9:5$ were prepared and their phase analyses were performed. The results (Table 2) show that under a pure nitrogen atmosphere only $Y_{10}(SiO_4)_6N_2$ (H-phase) can be compatible with Si_3N_4, not $Y_2O_3 \cdot 2SiO_2$. This contradiction may be caused by the different experimental conditions used. The sub-solidus reaction immediately gave the H-phase. However, $Y_2O_3 \cdot 2SiO_2$ was only detected by the devitrification of glass,[8,9] indicating the difficulty of crystallization of a nitrogen-containing phase. This result is similar to that of Jack[11] (Fig. 4). The phase diagram of the Si_3N_4–SiO_2–Y_2O_3 system, based on the above results, is also presented (Fig. 5).

3.4. The isothermal section at 1550 °C of the Si_2N_2O–Al_2O_3–Y_2O_3 system

Using the melting method, a very large liquid-phase area at 1550 °C was identified near the Si_2N_2O–Al_2O_3 side in this system (Fig. 6). The small liquid-phase area in the Si_3N_4–SiO_2–Y_2O_3 system[10] is greatly enlarged with the addition of Al_2O_3. The eutectic in this liquid-phase area was detected to be $Y_2O_3:2Al_2O_3:2Si_2N_2O$ with $T_{eu} \sim 1450$ °C by means of DTA and high temperature microscopy observation. This liquid-phase formation phenomenon may have a considerable effect on the sintering of O′-sialon-containing ceramics.

4. CONCLUSIONS

1. The sub-solidus phase diagram of the Si_2N_2O–Al_2O_3–Y_2O_3 system is presented, in which no new compound has been found. The extent of solid solubility of Al_2O_3 in Si_2N_2O is defined as 15 m/o. For the Si_2N_2O–Y_2O_3 system all compositions of $Si_2N_2O:Y_2O_3 > 1:1$ decompose at high temperatures, forming Si_3N_4 and $Y_{10}(SiO_4)_6N_2$. As a result, four quaternary phase regions are formed in the Si_2N_2O–Al_2O_3–Y_2O_3 system.
2. In the Si_3N_4–SiO_2–Y_2O_3 system, Si_3N_4 was found to be compatible with $Y_{10}(SiO_4)_6N_2$, but not $Y_2O_3 \cdot 2SiO_2$, contrary to what was previously reported.
3. The isothermal section at 1550 °C of the Si_2N_2O–Al_2O_3–Y_2O_3 system is also presented, in which a large liquid-phase area near the Si_2N_2O–Al_2O_3 side was determined. It may have a considerable effect on the sintering of O′-sialon-containing ceramics.

REFERENCES

1. Huang, Z. K., Greil, P. and Petzow, G., *Ceramics International*, **10**(1) (1984) 14–17.

2. Levin, E. M., Robbins, C. R. and McMurdia, H. F., *Phase Diagrams for Ceramists*, American Ceramic Society, Columbus, Ohio, 1969, Fig. 2344.
3. Bertaut, F. and Mareschal, J., *Compt. Rend.*, **257** (1963) 867–70.
4. Naik, I. K. and Tien, T. Y., *J. Am. Ceram. Soc.*, **62** (1979) 642–3.
5. Naik, I. K., Gauckler, L. J. and Tien, T. Y., *J. Am. Ceram. Soc.*, **61** (1978) 332–5.
6. Sekercioglu, I. and Wills, R. R., *J. Am. Ceram. Soc.*, **62** (1979) 590–3.
7. Sun, W. Y., Huang, Z. K. and Cheng, J. X., *Trans. Brit. Ceram. Soc.*, **82** (1983) 173–5.
8. Lange, F. F., Singhal, S. C. and Kurnicki, R. C., *J. Am. Ceram. Soc.*, **60** (1977) 249–52.
9. Wills, R. R., Holmquist, S., Wimmer, J. M. and Cunningham, J. A., *J. Mat. Sci.*, **11**(7) (1976) 1305.
10. Gauckler, L. J., Hohnke, H. and Tien, T. Y., *J. Am. Ceram. Soc.*, **63**(1/2) (1980) 35.
11. Jack, K. H., in *Nitrogen Ceramics*. Ed. F. L. Riley, Noordhoff International, Reading, Mass., 1977, 109–28.

Received 10 April 1985; amended version received and accepted 29 October 1985