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HEAT TREATING OF ALUMINA CABLES

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SLIP CAST COATING OF ALUMINA CRUCIBLES

BY

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ABSTRACT

The development of a process for coating alumina crucibles with MgO protective coat in a two-step slip casting operation is described. The best milling conditions for the alumina used were wet ball milling for 24 hr. MgO had to be calcined at 1200 °C to minimize hydration. Optimum slip casting conditions for alumina and magnesia were found to be L/S 1 and pH 3-6 or 9-11 for the former, and L/S 3 (alcohol) and pH 8.5-10 for the latter. Sintering of Al₂O₃ and MgO in the temperature range 1150-1500 °C was investigated. Additions of NiO and MgO lowered the sintered densities at lower temperatures, but improved the densification at 1500 °C. Near theoretical density Al₂O₃ and MgO crucibles were obtained. A two step slip casting technique was developed to coat Al₂O₃ with MgO. Certain slow firing schedules could eliminate the otherwise observed coat-crucible separation and cracks.

INTRODUCTION

The reactivity of molten uranium has dictated the development and use of special-and sometimes novel-refractory materials and techniques. In the calciothermic reduction either sintered (1,2) or rammed CaF_2 crucibles are used while tamped MgF_2 slag (3-2) or dolomite (6-7) are the lining materials in the magnesiothermic process. More stringent requirements are imposed on crucibles used for melting uranium and its alloys. Graphite crucibles for induction melting have to be coated to avoid the heavy carbon contamination. Coating techniques included brushing (8-10) flame spraying (9-12) dipping in--followed by decomposition of nitrates of thorium, zirconium or beryllium (13) dipping in molten Zr, Ti or Nb to form carbides (14) and halide vapor coating (40,46). Flame spraying of MgZrO_3 yielded a better protective coat than brushed MgO or Al_2O_3 --flame sprayed coats (9,15). Comparing Al_2O_3 , MgO , ThO_2 , BeO and ZrO_2 ; the latter three (and particularly ZrO_2) appeared to be best protective while Al_2O_3 worst (16). In selecting a suitable material, considerations other than chemical contamination has also to be coped with. These include the high temperature strength, thermal shock resistance and heat transfer. In this respect, Al_2O_3 has outstanding properties. However, chemical incompatibility with uranium necessitates some sort of coating. Since alumina crucibles are normally produced by slip casting, it was considered appropriate to coat it before firing; using a slip of another oxide that does not contaminate uranium e.g. MgO . If properly developed this technique would be simpler, cheaper and easier to control than flame spraying. The theory behind this technique has been developed by one of us (18).

Preliminary development of slip casting of both Al_2O_3 and MgO was carried out before in this department (I7) In the present report development of the MgO-coated slip cast alumina process will be described.

EXPERIMENTAL TECHNIQUES

I- Raw powders

The starting source of alumina was a pure grade of Gibbsite obtained via El-Naar Co. for Ceramics and Porcelain-Cairo, This was calcined in a muffle furnace in air at 1100 C for 1 hr, to yield calcined alpha alumina, The analysis of gibbsite as well as the resulting alumina was according to the Bureau of Chemistry Ministry of Industry-as

follows:

	Al_2O_3	CaO	Na_2O	MgO	Fe_2O_3	SiO_2
Gibbsite	67.8	0.3	0.43	---	----	---
Alumina	99.6	0.4	----	---	----	---

Magnesia analysing 99.26% +0.7% CaO+0.04% Fe_2O_3 (light grade- Prolabo, France) was calcined in a muffle furnace at 1200C for 4 hr to obtain the starting MgO Power.

2- Powder Processing

Particle size distributions were adjusted through through in a 4.5 litres porcelain ball mill 40% filled with porcelain balls and running at 100 r.p.m. Both dry and wet milling were attempted, and the void to solid ratio was varied

3- Powder characterization:

The average particle sizes were determined using a Fisher subsieve sizer. The partial size distributions were determined both optically and by sedimentation

3- Powder Characterization

The average particle sizes were determined using a Fisher subsieve sizer. The particle size distributions were determined both optically and by sedimentation in an Andreasén's pipette. The dispersant used was 0.3% sodium phosphate tribasic aqueous solution. The apparent powder density was determined by a simple specific gravity bottle.

4- Slip Casting

Slips were mixed by a propeller in a beaker for 20 mins. The pH was adjusted by adding HCl or NH_4OH additions. Crucibles were prepared by drain casting in plaster of paris moulds. The latter were prepared by thorough mixing of 60% plaster + 40% water and pouring in plastic case moulds, setting and air drying for 3 hr.

5- Heat Treatments

All crucibles were air dried for 24hr followed by oven drying at 120 C for 1 hr. Sintering was carried out in a laboratory constructed silicon carbide heated tubular furnace. Temperatures were measured through a Pt-Pt18Rh thermocouple calibrated with the aid of a Honeywell potentiometer. The heating and cooling rates were 10 C/minute.

6- Density measurements

Unfired crucible (green) densities were measured geometrically using a travelling microscope. The fired densities were determined by three techniques i.e. geometrically, by mercury displacement in a mercury hydrometer and by oil displacement in a Jolly balance. The means of these three measurements were taken

RESULTS AND DISCUSSION

1- Powders Processing

The average particle size of as-calcined alumina was found to be 7.6 μm . This was considered rather coarse for slip casting. A series of milling experiments were carried out both dry (solid to void ratio 1/1 or 2/1) and wet (solid to void ratio 1/1 or 1.5/1), and for various lengths of time. The results are shown in figure 1 from which the best milling conditions were selected as: wet milling for 24 hr using a solid to void ratio 1/1. The cumulative particle size distribution is shown in fig. 2.

Calcined MgO had an average particle size of 1.9 μm . It was subsequently milled in absolute ethyl alcohol for 6 hr. The resulting powder has an average size 0.85 μm , and a powder density of 3.42 gm/ml.

2- Slip Casting

Alumina slips of liquid to solid ratios 1/2, 2/3 and 1/1 at pH 3-6 were prepared and drain cast. Except at the last L/S ratio cracks, foaming and bad drainage were observed. Similarly, fixing L/S at 1/1 and increasing the pH to 6-8, 9-II or 12 led to cracks and sedimentation except at pH-II. Hence sound and uniform crucibles could be cast using L/S 1/1 and pH of either 3-6 or 9-II. The casting rate and drainage properties were reasonable; although somewhat better in the alkaline rather than in the acidic range.

Similarly slip casting of MgO at pH 8.5-10 (as prepared) using L/S ratios 1/1, 2/1 and 3/1 was carried out. Only the highest L/S ratio could produce sound uniform crucibles, although the mould release time was rather long i.e. 20 min

Attempts to decrease the pH necessitates the use of an acid e.g. HCl, with larger amounts being used for the lower pH values. However, it was found that large compositional changes could have occurred in MgO by this pH adjustments. These were indicated by the large weight changes (up to 40%) on calcining (1100 C- 1hr) the filtered dried slips. Similarly, attempts to slip cast MgO using water instead of alcohol-as a vehicle- failed due to hydration (indicated e.g. by weight loss 22% for MgO powder soaked for only 15 min in water). Hence slip casting conditions of MgO were set as : vehicle absolute ethyl alcohol of 1/3 3/1 without pH adjustment.

Preparation of MgO- coated Al_2O_3 crucibles was performed using the optimized conditions for Al_2O_3 and MgO respectively. Drain casting of Al_2O_3 to the desired thickness was followed by pouring MgO slip into the formed Al_2O_3 crucible, and draining the excess liquid. Using this technique, sound and uniform composite crucibles were prepared. No defects were observed on drying prior to firing.

In all these experiments, crucible dimensions were:
Diameter 10mm, Height 10 mm and Thickness 1.5 mm

3- Sintering Of The Components And The Composites:

Densification of Al_2O_3 is depicted in fig. 3-5. Compared to a green porosity of 67.4%, it is obvious that some densification has already occurred during heating up to the sintering temperature. An end point density has been reached for each temperature. Additions (0.25%) of either NiO or MgO lowered the densification rates at the lower temperatures employed (1150 - 1400 C). However, at 1200 C these additions could aid in the attainment of near theoretical density. Several mechanisms have been proposed to explain the beneficial effects of these additives (19-25). It has been shown

by one of us (26) that the most probable mechanism is a modification of pore surface energy and hence, pore kinetics; such as to drag the pores with the migrating grain boundaries instead of being isolated inside grains.

Densification of MgO is shown in fig.6 High end point densities were obtained at 1400 C and 1500 C i.e. 98.3 and 98.8% theoretical, respectively. However, at both temperatures, crucibles exhibited a bloating period followed by further densification to the end point densities. Bloating has been noted before in copper (27), Al_2O_3 (28) and UO_2 (29). It has been attributed to the inability of gases in closed pores to diffuse out. Hence gas is either transferred from the smaller (high pressure) pores to larger pores, or pores coalesce during grain growth.

In a preliminary work, slip cast coated crucibles I.4/I (i.e. I.4mm alumina coated with I mm magnesia) were fired at 1400 C for 4hr. This led to complete separation. Firing at 1500 C instead of 1400 C resulted in cracks in alumina as well as separation. Sintering for the same length of time at the lower temperatures did not solve the separation problem. By this time, a procedure has been developed for estimating the stresses in the crucibles and coats. This indicated that decreasing the relative coat/crucible thickness ratio would decrease the stresses. Hence, the MgO thickness was reduced to 0.2 mm. Also, since spinel formation at the Al_2O_3 MgO interface is possible, with an accompanying volume change (30), the firing schedule was modified such as to hold the bodies at steps of temperature for long times. This would allow the body to adjust slowly to spinel formation as well as to sintering shrinkage. Four schedules were employed to

fire Al_2O_3 (0.25% MgO) coated with MgO (thickness ratio \sim 0.1). These schedules are shown in fig.7. All have led to production of sound coated crucibles. Other configurations and sizes could change the stresses in both crucible and coat in different ways (18).

CONCLUSIONS

- 1 - Wet milling is more effective than dry milling for milling Al_2O_3 . The solid to void ratio should be 1/1. Milling for 24 hr could produce a powder of average particle size 0.4 μm , and suitable slip casting tendencies.
- 2 - Optimum slip casting conditions for this Al_2O_3 powder is liquid to solid ratio 1/1 and pH 3-6 or 9-11.
- 3 - Optimum slip casting conditions for MgO- prepared by calcining prolabo light MgO at 1200°C for 4 hr and milling in absolute alcohol for 2 hours alcohol to solid ratio 3/1 and pH (as received) 8.5-10. Slip casting from aqueous slips or HCl - added lower pH slips failed due to hydration.
- 4 - Additions of 0.25% MgO or NiO allow Al_2O_3 to densify to near theoretical density, although they lower the sintering rate at lower temperatures (less than 1500 C).
- 5 - MgO crucibles could be sintered to more than 98% theoretical density, in air at 1400 or 1500 C although some bloating was observed.
- 6 - Slip cast coating of Al_2O_3 with MgO is possible.

- 7 - Small coated crucibles could be sintered soundly if the coat/ crucible thickness ratio is small enough, and if the heating schedule is in gradual steps.
- 8 - Further work is necessary using larger sizes and other configurations in order to optimize the heating schedules..

REFERENCES

- 1-R. Golin et al, UN CONF. PUAE., P/179, Geneva, 1958
- 2-J. Decrop et al, *ibid.*, P/1252.
- 3-F. W. Melvanin, *ibid.*, P/602
- 4-H. E. Thayer, *ibid.*, P/602
- 5-T. O. Anderson, NYO -1348.
- 6-T. O. Anderson, UN CONF. PUAE. P/1399, 1958
- 7-R. Riper and A. E. Ruchle, NYO -1333, 1952
- 8-W. A. Oppold, ECW- 29 , 1957. 2-0
- 9-O. R. Magoteaux et al, TID-6287 1960
- 10-O. R. Magoteaux et al, TID-6286, 1959.
- 11-O. R. Magoteaux et al, NLCO- 759, 1958
- 12-Anon, NLCO-760, 1958.
- 13-G. Moister U.S. Pat. 2,76632, Oct. 9, 1956.
- 14-M. A. Steinberg, U.S. Pat. 2,929, 741, Mar, 22, 1960
- 15-O. R. Magoteaux, NLCO-759, 1958
- 16-H. K. Feder, et al, ANL-5765, 1957.
- 17-N. A. Haroun and G. I. Orabi, ARB AEB Rep-164, 1973
- 18-N. A. Haroun, unpublished.
- 19-R. L. Coble, J. appl. Phys., 32,793-9, 1961
- 20-P. J. Jorgensen, and J. W. Westbrock, J. Amer. Ceram. Soc.,
43,332-B, 1964
- 21-P. J. Jorgensen, J. Amer. Soc. 48,207-210, 1965
- 22-K. O. Warman and D. W. Budworth, Trans. Brit. Ceram. Soc. 66,
253-264, 1967.
- 23-W. C. Johnson and R. L. Coble, J. Amer. Ceram. Soc., 61, 110-4,
1978
- 24-M. Harner et al, Trans. Brit Ceram. Soc., 76, 22-25, 1979.
- 25-A. H. Heuer. J. Amer. Ceram. Soc., 62, 317-8, 1979
- 26-N. A. Haroun, In press.

- 27-F..N.Rhines et al, Trans AIME, I88, 378, I950
- 28-N.A.L.Mansour and J.White, Powder Met, I2, I08-2I, I963
- 29-M.O.Warman and D.W.Budworth, Trans. Brit. Ceram. Soc.,
66, 265, -27I, I967.
- 30-ERykewitch, Oxide Ceramics, Academic Press, I960.

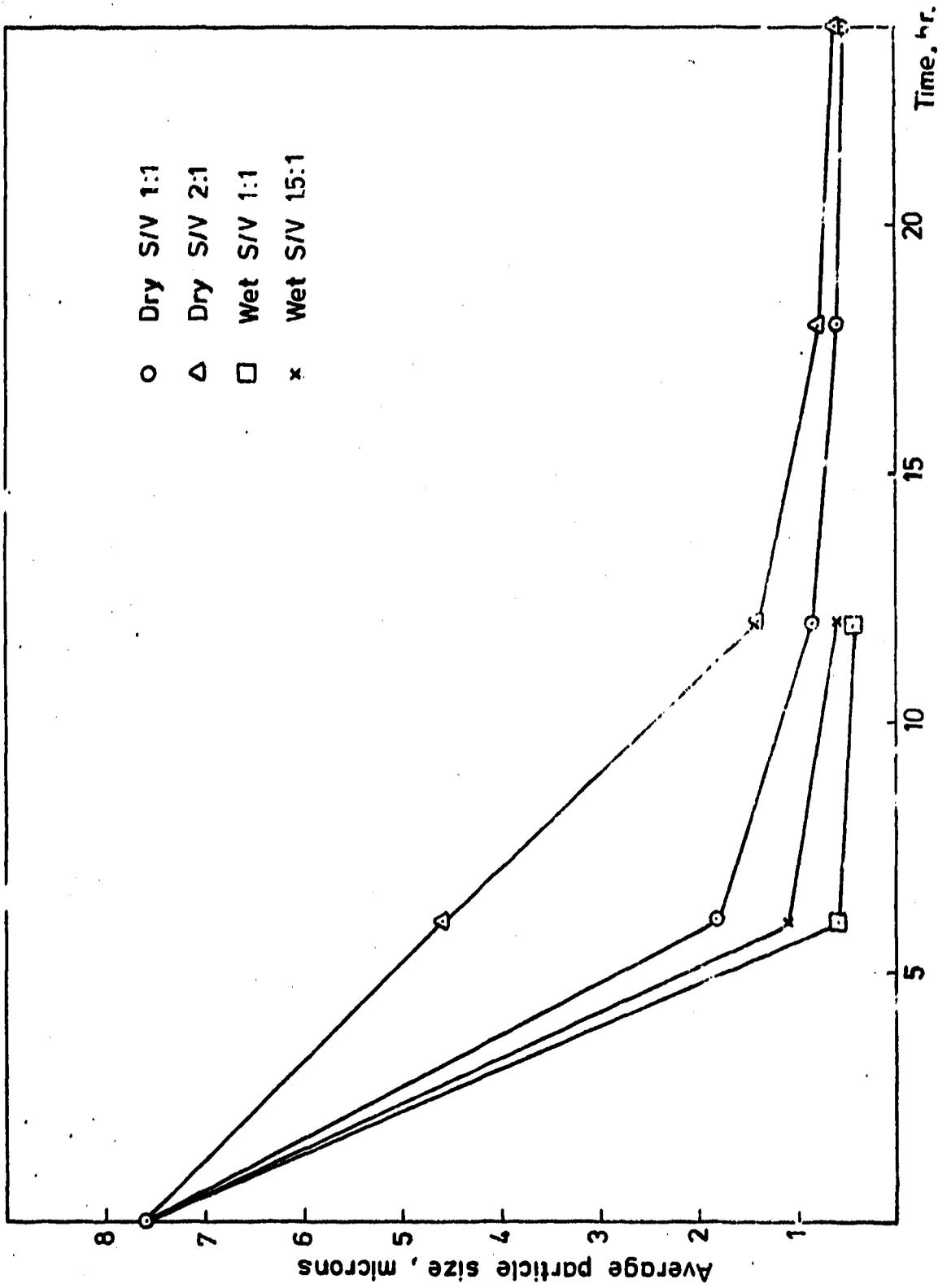


Fig.1.

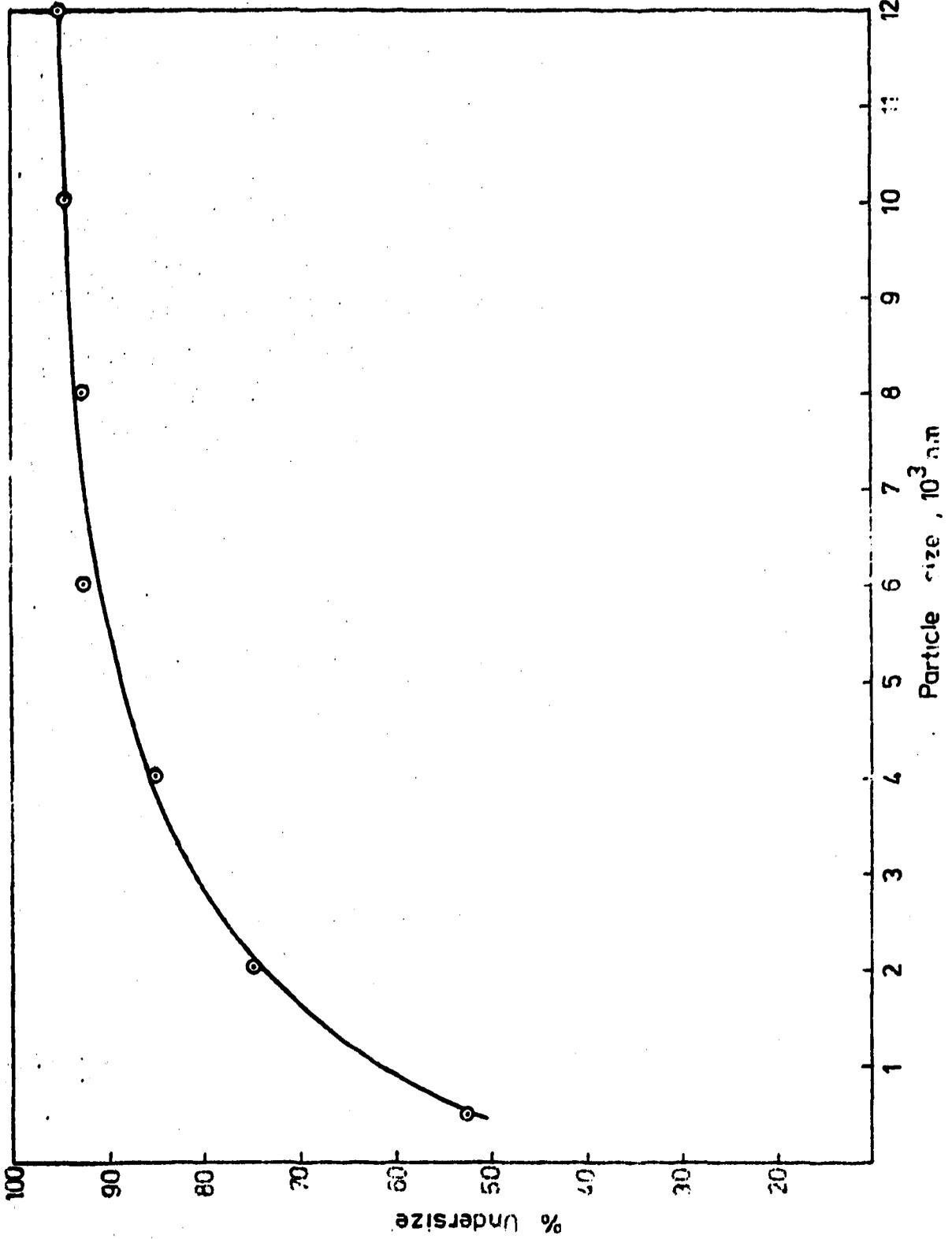


Fig. 2.

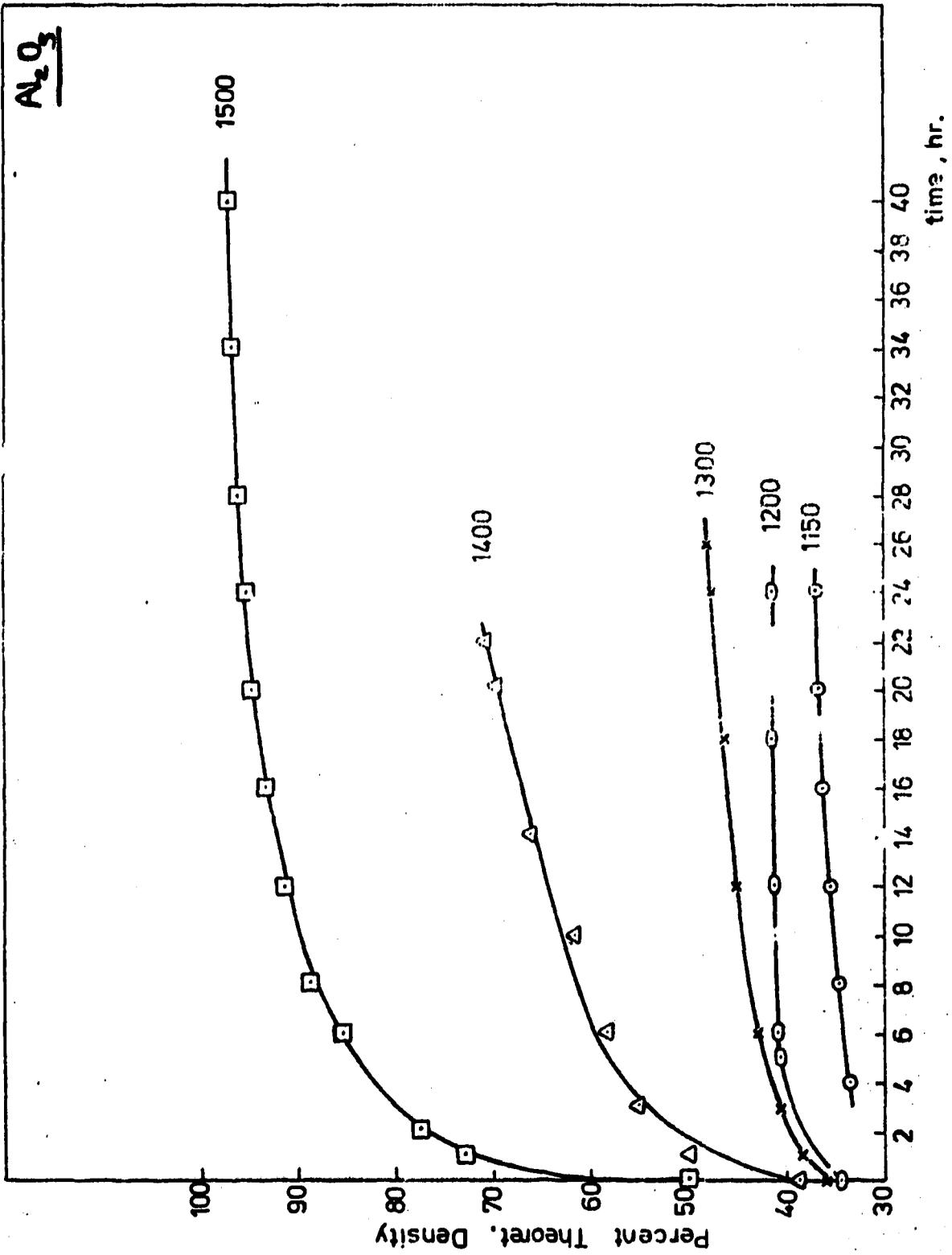


Fig. 3.

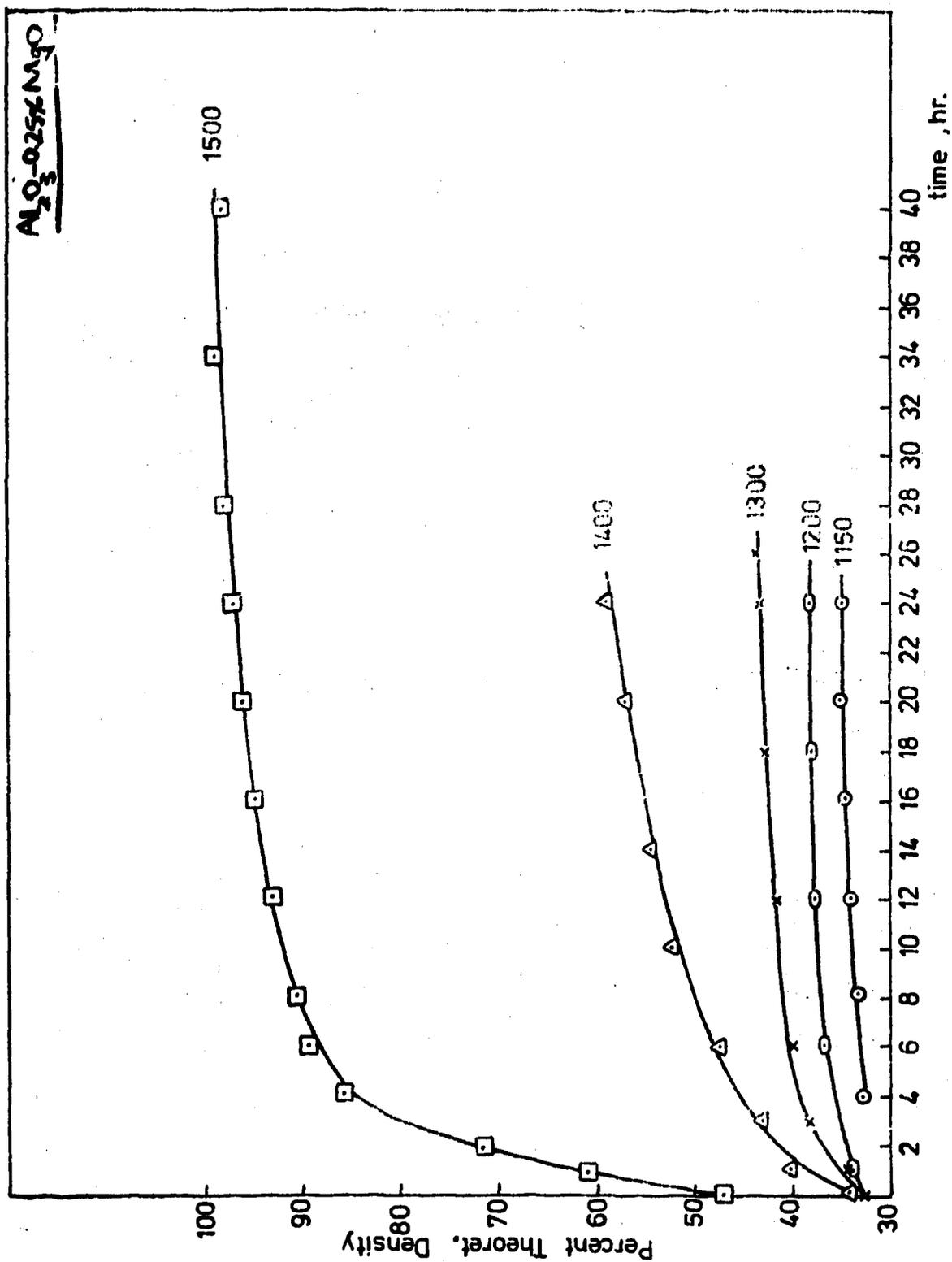


Fig. 4.

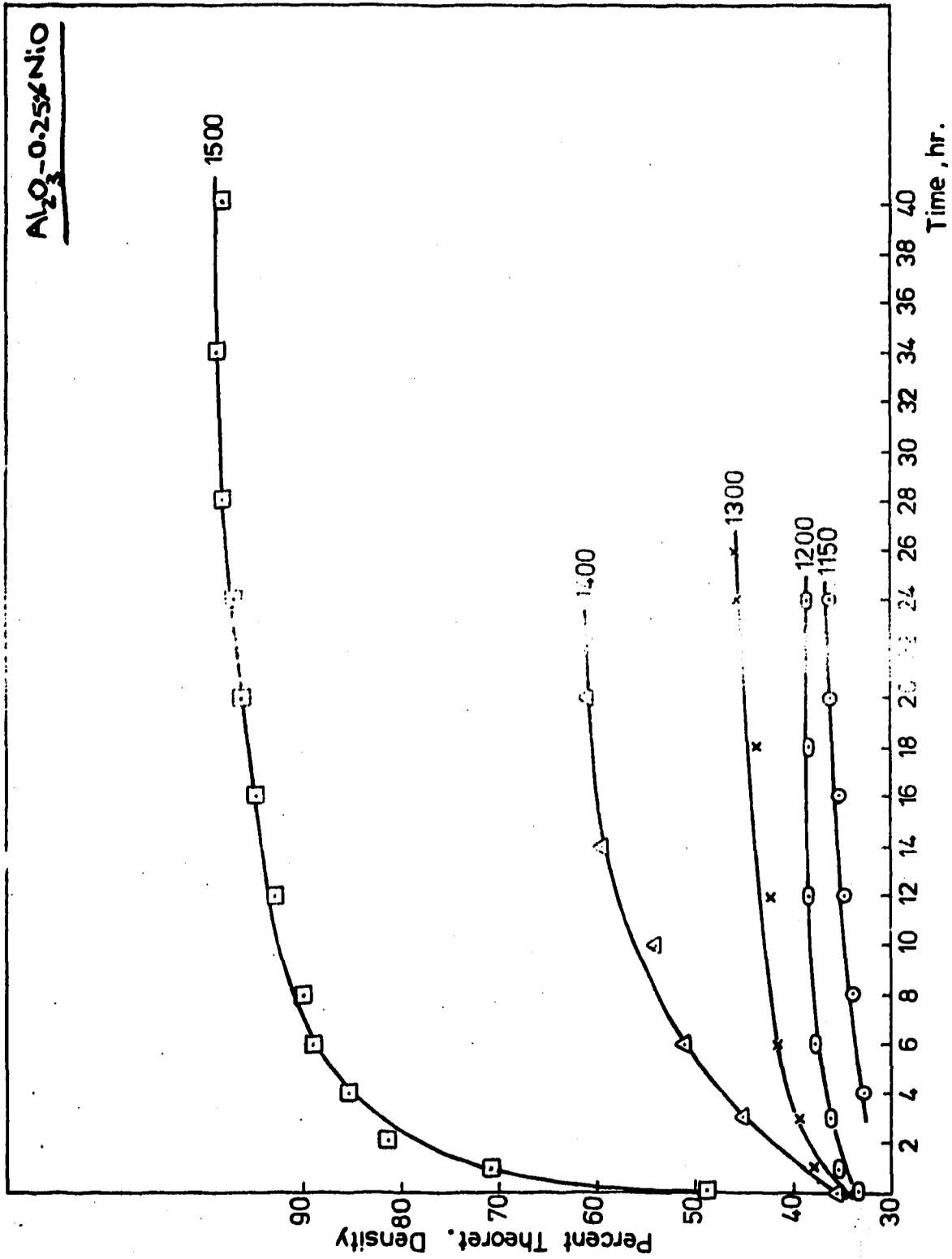


Fig. 3

MgO

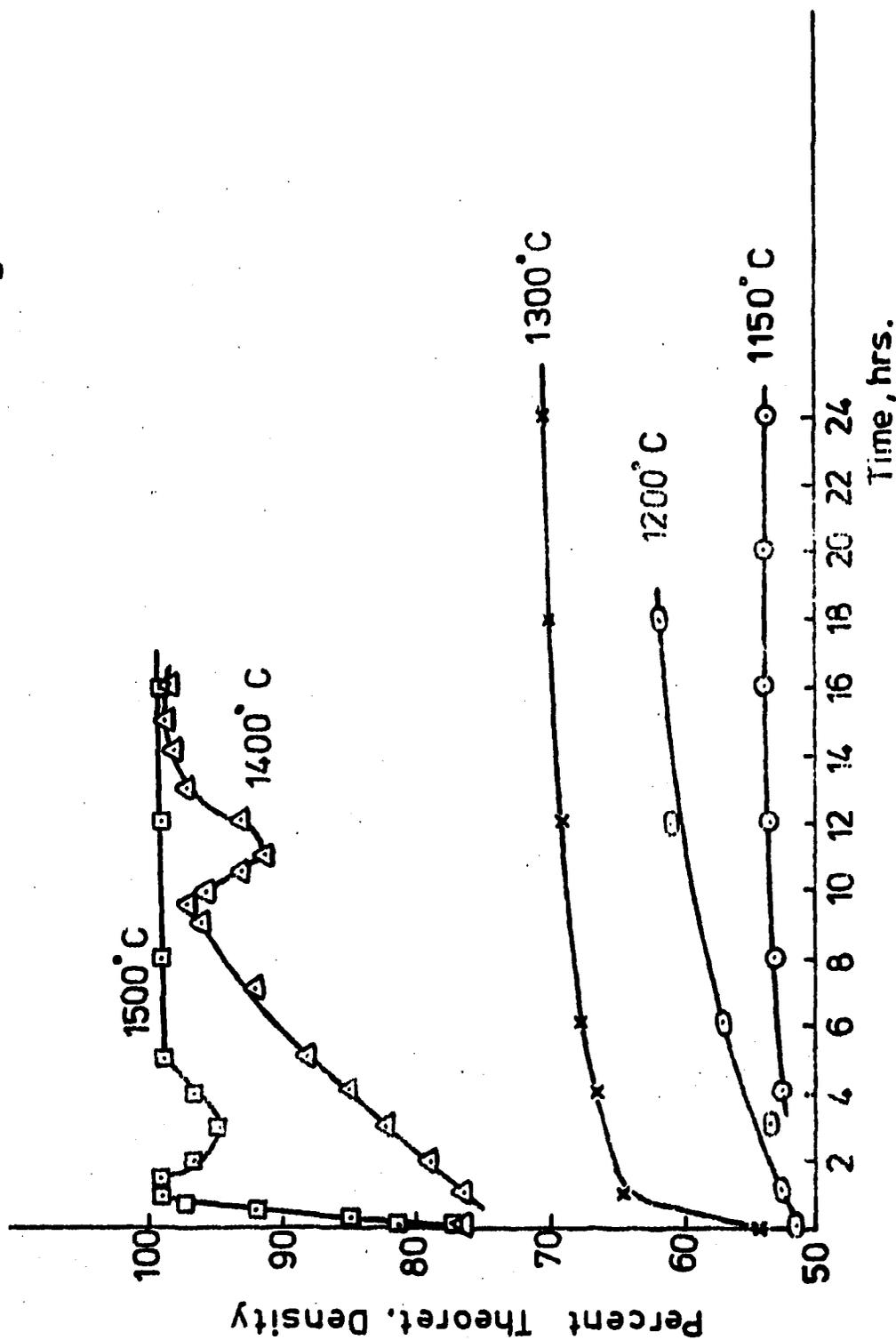


Fig. 6.

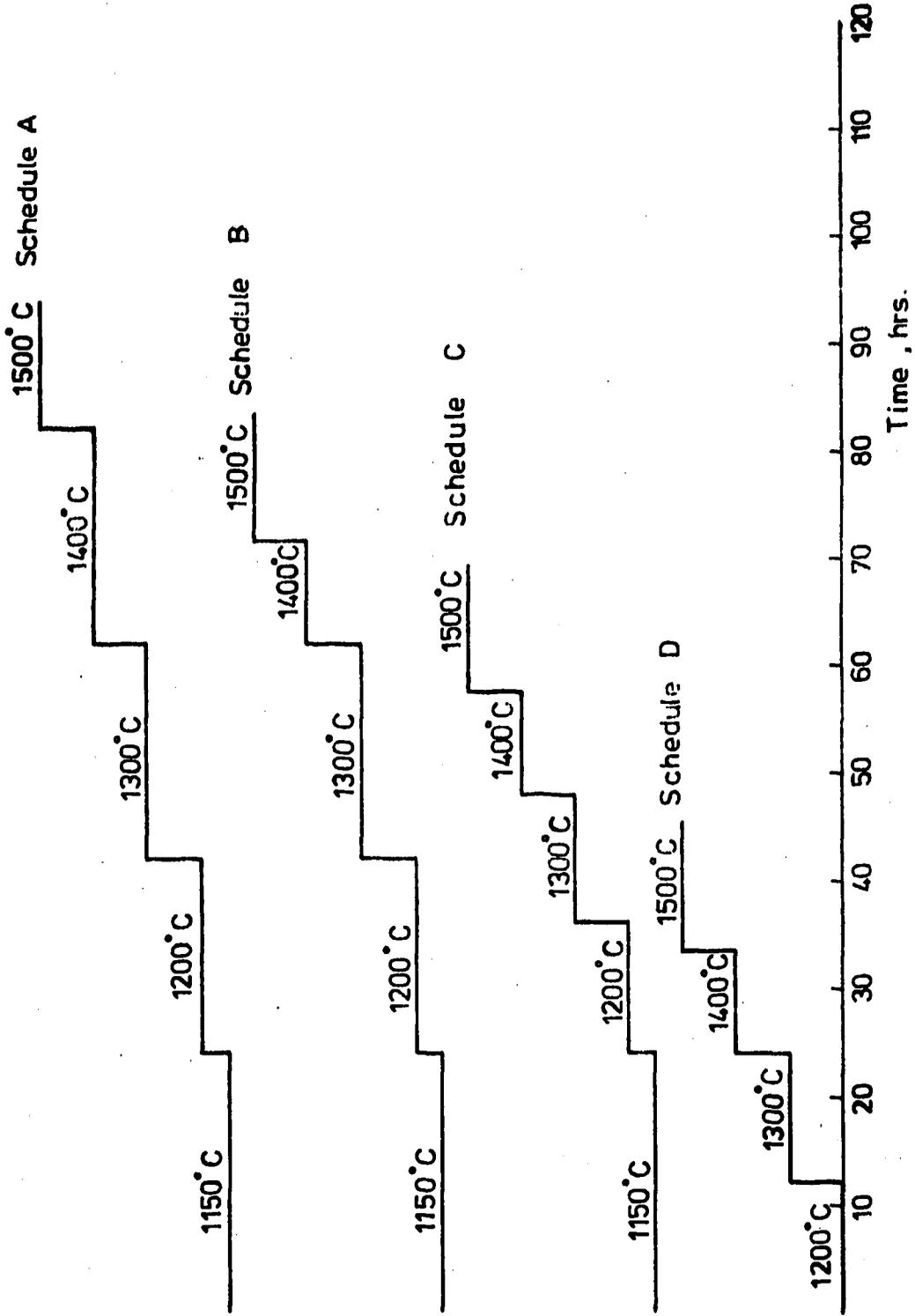


Fig. 7.