Chapter III

Experimental part

3.1 Description and scope

Description of experiments

A study was designed using raw materials and base glass batch compositions to study the effect of particle size and heating rate by differential thermal analysis (DTA) and resistivity measurement. The study can be classified into 6 steps: preparation of equipment and tools, sample preparation, DTA measurement, resistivity measurement, oxygen activity measurement and hot-stage XRD test. The following chart shows the details.

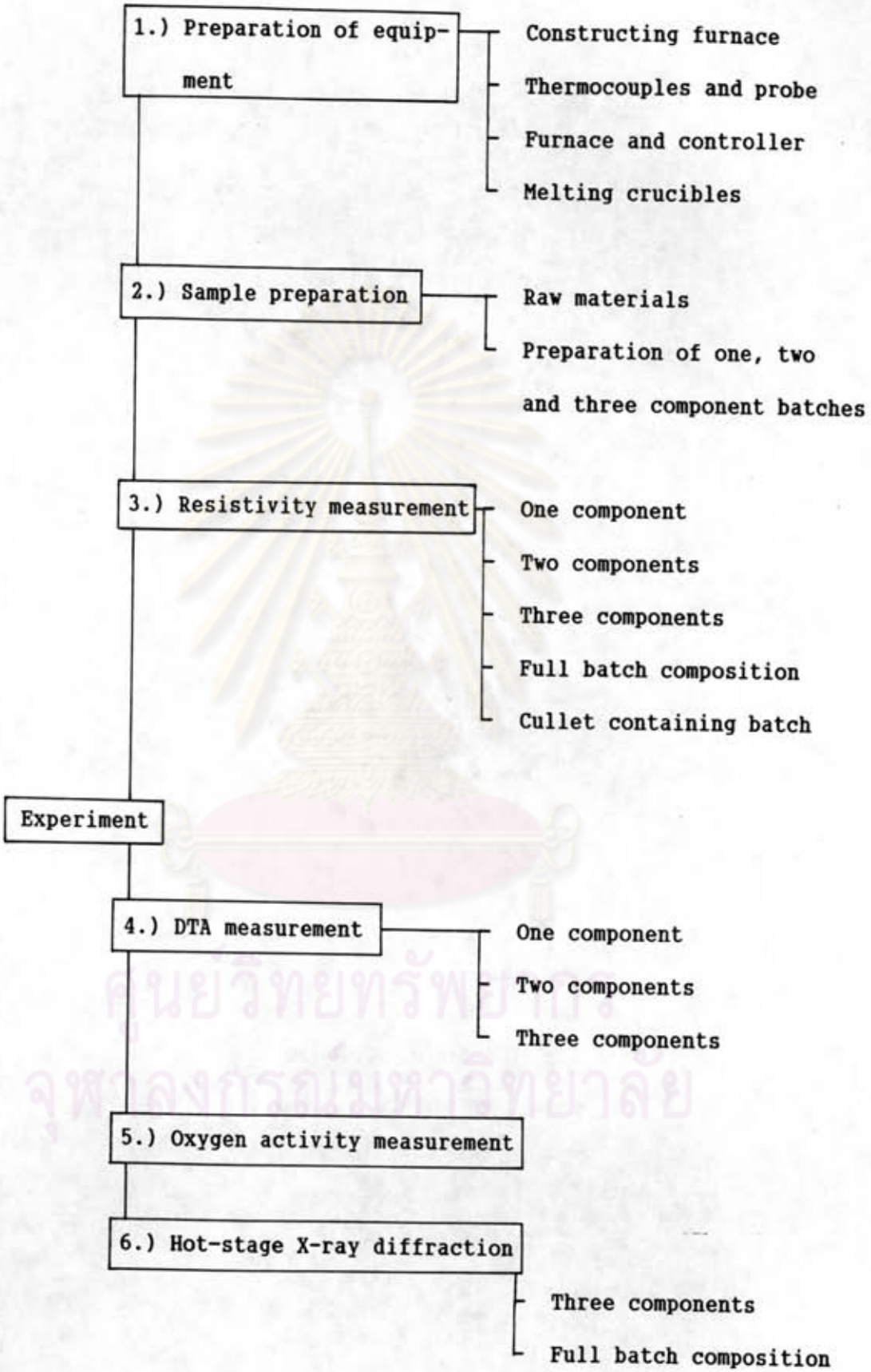

Figure 3.1 Chart of experiments

3.2 Preparation of equipment and tools

Constructing Furnace

A small study furnace was constructed using light alumina brick (C-1 type with 7.5 cm thickness) and Kanthal wire (Ni-Cr, 1.6 in diameter) as a heating coil. Total resistance for the heating coil is about 5 ohm. The inner area of the furnace is 6 x 6 inches. For the top stopper and the shape of the opening, several designs were required for different tests. Figure 3.2 shows a sketch of furnace and the top stopper.

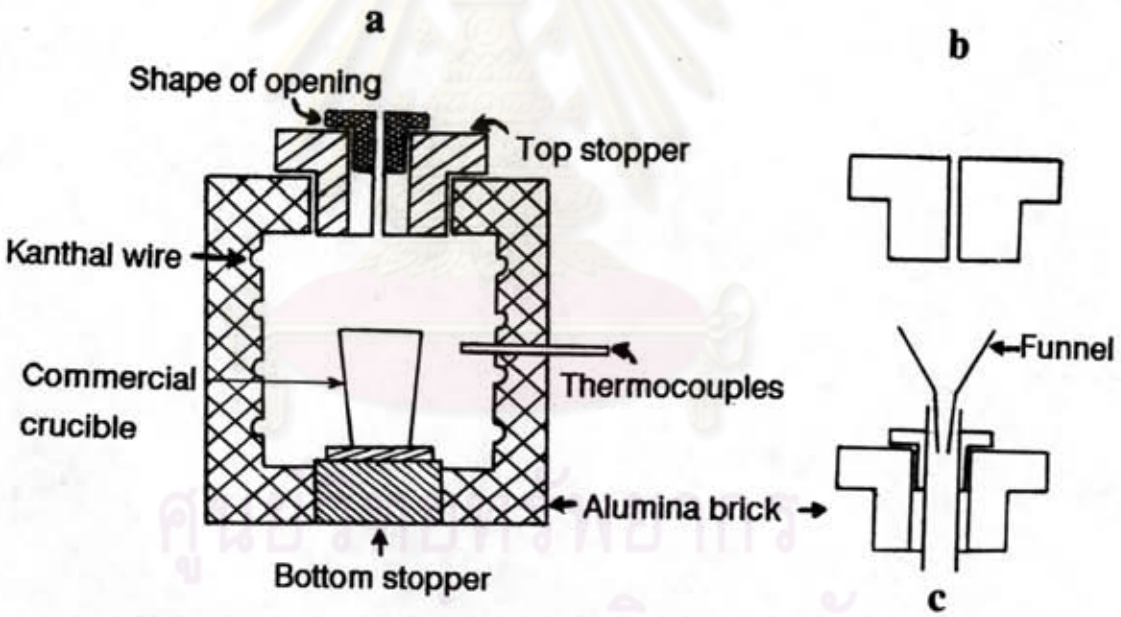

Figure 3.2 Small study furnace a), top stopper b), and shape of the opening c).

Thermocouple and probe

The resistivity and temperature probe is made by inserting type K thermocouple (NiCr-Ni, diameter 0.6mm) wires into sintered alumina tubes with (6 mm, 1.5 mm) two inner bores. The

resistivity parts of the probe are made of two NiCr wires and the free lower terminals of the NiCr wires in the length of 7 cm are wound up in the shape of short solenoids to make a pair of electrodes. Their distance and effective surface area are approx. 1 cm and 1 cm^2 respectively. The temperature parts are made of NiCr-Ni, pairs twisted and squeezed together at the lower ends of the sintered alumina tubes. A sketch of the probe is shown in figure 3.3.

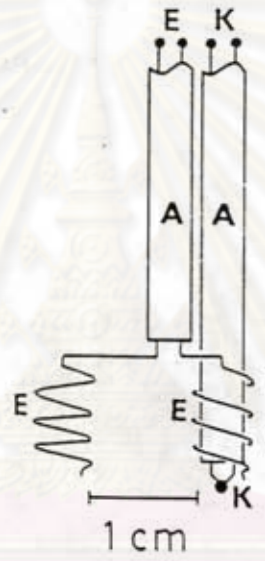

Figure 3.3 Sketch of probe

Furnace and controller

The temperature profile and process controller model CPS was selected to control the heating rate in the small study furnace. Figure 3.4. shows the construction and figure 3.5 shows the external wiring of the controller.

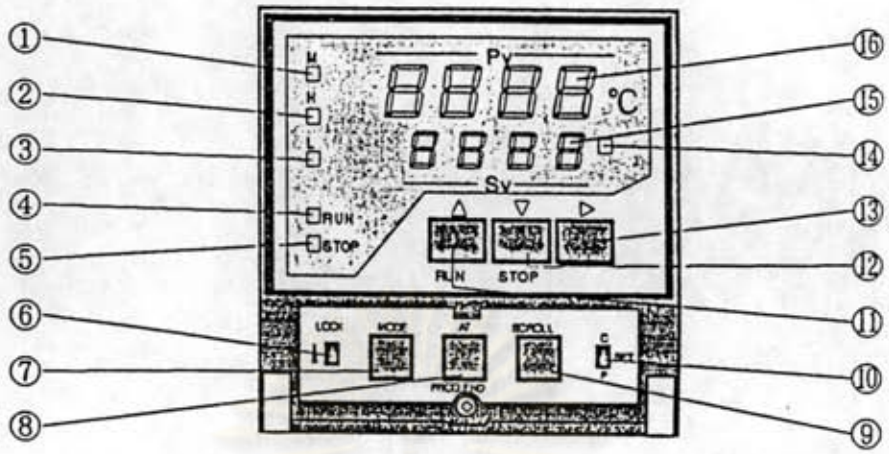

Figure 3.4 Consi ..t controller.

1). LED for main control

2). LED for high alarm

3). LED for low alarm

4). LED for run mode

5). LED for stop mode

6). Lock switch

7). Key for mode changing

8). Key for auto-tuning start or stop

9). Scroll Key
Key for checking and parameter setting

10). SET switch
C:Setting for control parameters
P:Setting for programming pattern

11). Key to run and increase digit

12). Key to stop and decrease digit

13). Shift key

14). LED for auto-tuning

15). Indication of operation data

16). Indication of process value
indication of setting items

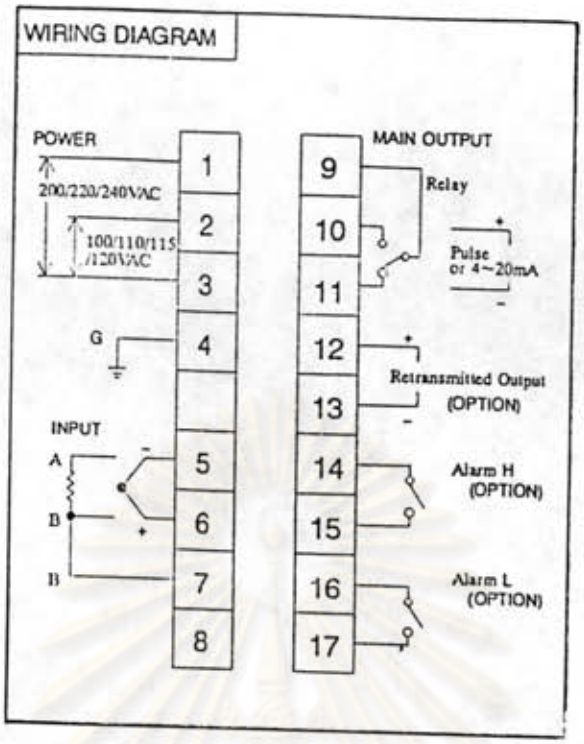

Figure 3.5 External wiring of the controller.

Under full load, the heating coil pulls 25 A. Since the CPS controller operates as an on/off switch, this leads to a heavy load change of the coil and hence, to its rapid wear. Therefore, the following set-up (see figure 3.6) was selected for the power supply.

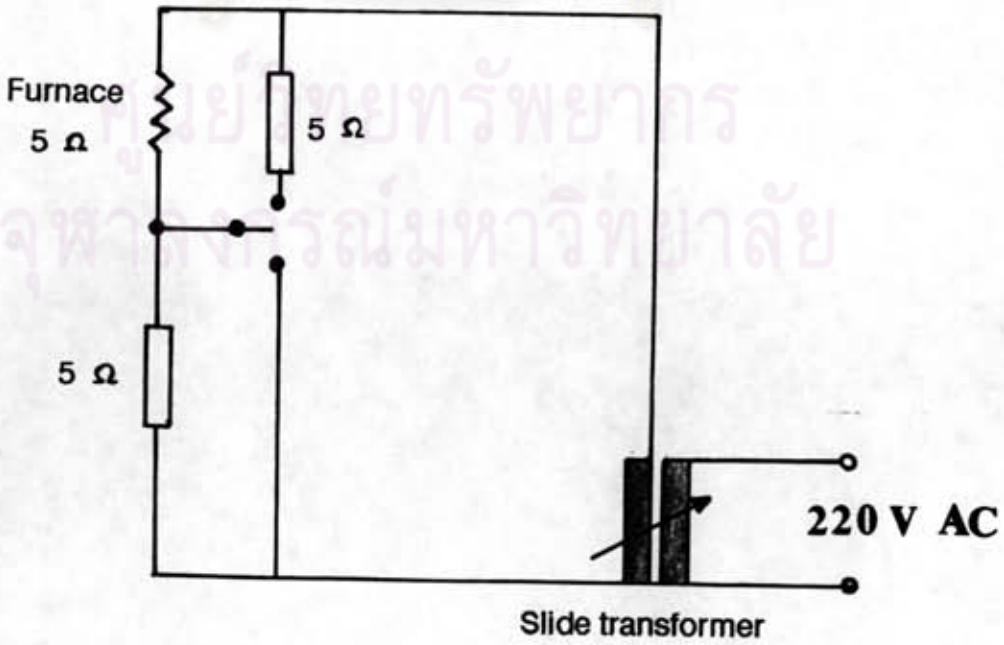

Figure 3.6 Power circuit of small study furnace

It allows to operate the furnace between ground and peak load, and never cuts off the current to zero (thereby also suppressing the electrical "noise" in the lab).

Melting crucible

For the oxygen activity measurement 7cm wide and 10 cm high melting crucibles and a specifically designed reference tube were prepared; see figure 3.7. The compositions of the clay body is shown in table 3.1. Before mixing, raw materials were ground in a porcelain dish and passed through sieve no. 40 mesh, then mixed in a ball mill for about 3h. After that, a slip was prepared and cast into plaster molds (plaster of paris at a gypsum to water ratio of 70 %). The objects were dried in air for 2 days, and in an oven for 24h at 120^{o}C, then bisquit fired at 950 ^{o}C and sintered at 1200 ^{o}C.

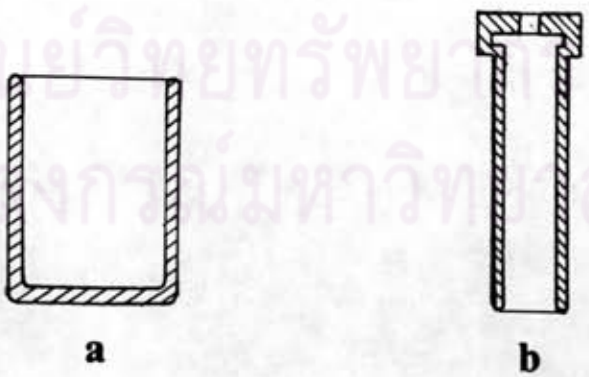

Figure 3.7 The sketch of clay crucible a). and reference tube b).

Table 3.1. Composition of clay crucible.

batch composition	(%)
Kaolin (Ranong)	20
Ball Clay	40
Alumina	40

3.3 Sample preparation

Raw materials

Raw materials used in this research work were soda ash, sand, dolomite, limestone, cullet, sulfate, coal, and NaCl. Table 3.2. lists the chemical composition of the first for major raw materials, used in one, two and three components batches. Three different redox numbers of batches were set by combining coal and sulfate, eventually adding NaCl as accelerants. The base glass batches are listed in Table 3.3.

Table 3.2. Chemical Compositions of Raw Batch Materials

	composition(%)						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Sand	99.23	0.152	0.032	0.026	0.012	0.03	0.035
Limestone	0.82	0.18	0.06	54.200	0.7	0.1	0.1
Dolomite	0.25	0.07	0.06	32.00	20.20	0.01	-
Soda ash	-	-	-	-	-	58.2	-
Cullet	72.4	1.6		6.9	4.5	14.2	-

Table 3.3 Glass Batch Composition by Weight

	Composition (g)				
Raw materials	R=+20	R=-20	R=+20 (1 % NaCl)	R=-20 (1 % NaCl)	R=-20 (0.3 % NaCl)
Sand	61.59	61.48	61.59	61.48	61.48
Calcite	14.80	14.83	14.86	14.83	14.83
Soda ash	20.93	20.90	20.02	19.90	20.62
Sodium sulfate	2.46	2.46	2.46	2.46	2.46
Coal	0.15	0.34	1.00	1.003	0.488

Preparation of one, two, and three component batches

For DTA measurement, particle sizes of raw materials were chosen only in the range of (0.032-0.063 mm) for all components. The raw materials, ratios and heating rate are listed in the table 3.4.

Table 3.4 Raw materials, ratios and heating rate for DTA measurement; total amount is 200 mg.

components	raw materials	ratio	heating rate 10 K/min	heating rate 100 K/min
one	soda		✓	✓
	sand		✓	✓
	limestone		✓	✓
	dolomite		✓	✓
two	soda + sand	1:1	✓	✓
	soda + limestone	1:1	✓	✓
	Soda + dolomite	1:1	✓	✓
three	soda + sand + limestone	1:1:1	✓	

For resistivity measurements, raw materials were separated by size via dry sieving into four different size ranges (in mm) before mixing them, as listed in table 3.5.

Table 3.5 Different particles size of raw materials in mm.

	Coarse	Medium	fine	Flint
Sand	0.350-0.500	0.185-0.250	0.063-0.125	<0.063
Limestone	1.000-2.000	0.350-0.500	0.185-0.250	
Dolomite	"	"	"	
Cullet	5	2-3	1-2	<0.063

For one-component systems, only industrial grade size distribution was selected. Table 3.6. shows the raw materials, the ratio used in a combination of selected raw materials, and the heating rate.

Table 3.6 Raw materials, ratios and heating rate used in resistivity measurement; total amount is 180 g.

components	raw materials	ratio	heating rate 10 K/min	heating rate 80 K/min
one	soda		✓	
	sand		✓	
	limestone		✓	
	dolomite		✓	
	cullet		✓	
two	soda + sand*	1:1	✓	
	soda + limestone*	1:1	✓	
	soda + dolomite*	1:1	✓	
	cullet + soda*	9:1	✓	
	cullet + limestone*	9:1	✓	
	cullet + dolomite*	9:1	✓	
three	soda + sand + limestone*	1:1:1	✓	✓
	soda + sand + dolomite*	1:1:1	✓	✓
	soda + sand + limestone	1:1:1	✓	
	soda + sand + dolomite	1:1:1	✓	

* varied size as showed in table 3.5.

3.4 Resistivity measurement

Slow heating rate

The mixtures prepared as listed in table 3.6. were loaded into a commercial crucible and exposed to the small study furnace. The resistivity and temperature probe was placed in the middle of samples. The immersion depth was approx. 5 cm in the batch. When cullet was used together with other components in a ratio of 9:1, a small amount of distilled water had to be added to the mixtures to make them homogeneous. These mixtures were dried in an oven at 100 ^{o}C for 3h before being exposed to the furnace. The probes were connected to a computer which recorded both resistivity and temperature of the batch, and the temperature of the furnace, in intervals of 1 s.

High heating rate

For high heating rate experiments, an empty crucible and the probe were positioned in the cold furnace. The furnace was heated up until the temperature reached 1200 ^{o}C. Then, the opening in the top stopper of the furnace was opened and the sample was charged through a metal funnel as quickly as possible. The opening was closed, and resistivities and temperatures were recorded as in 3.4.1.

3.5 DTA measurement

After mixing raw materials as listed in table 3.6 samples weighed to approx. 200 mg were loaded into platinum crucibles, with alumina powder as a reference. Samples were exposed to a 10 K/min (slow heating) and 100 K/min (fast heating), respectively.

3.6 Oxygen activity measurement

Pre-test

Firstly, the commercial oxygen activity sensor had to be dismantled, because it was too big for the small study furnace (see figure 3.8). Even its parts were hard to handle. So, a balancing mechanism with a counter weight was designed. Figure 3.9 shows the sketch of the set-up.

To understand the oxygen sensor, pre-tests were needed. A commercial table ware glass was selected for pre-tests, weighed in charges of about 300g into the self-made crucible, and exposed to the furnace. The oxygen sensor was positioned above the sample in the cold furnace, and heated up in the furnace until 1200^{o}C. Then, the sensor was moved down until it contacted the surface of the glass melt. The computer was started to record data for four channels, which were: temperature of the atmosphere (i.e. furnace temperature), temperature of the platinum, and both the platinum and zirconia side of the sensor (e.m.f.). When the sensor contacted the glass surface for a while, different gases was flushed into the furnace through an alumina tube, (see figure 3.9). The effect of the different gases on the e.m.f was studied.

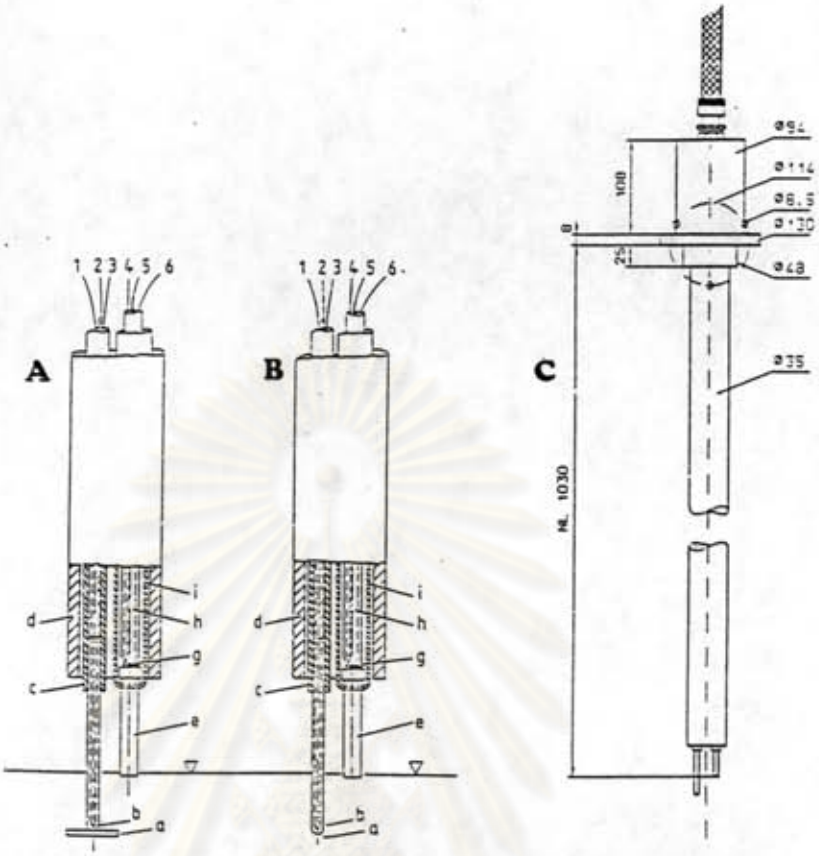

Figure 3.8 Sketch of yttria-stabilized zirconia solid electrolyte oxygen sensors for measurement in glass melt;
A: pilot design for measurement in stationary melt
B: pilot design for measurement in flowing melt
C: commercial realization

electrical terminals:

1: PtRh10 thermowire
2: Pt thermowire
3: working electrode
4: PtRh10 thermowire
5: Pt thermowire
6: reference electrode

constituents of the probes;

a: Pt electrode
b: thermocouple junction, melt
c: alumina tube
d: sillimanite tube
e: zirconia solid electrolyte
g: thermocouple junction, ref.
h: capillary tube
i: alumina tube

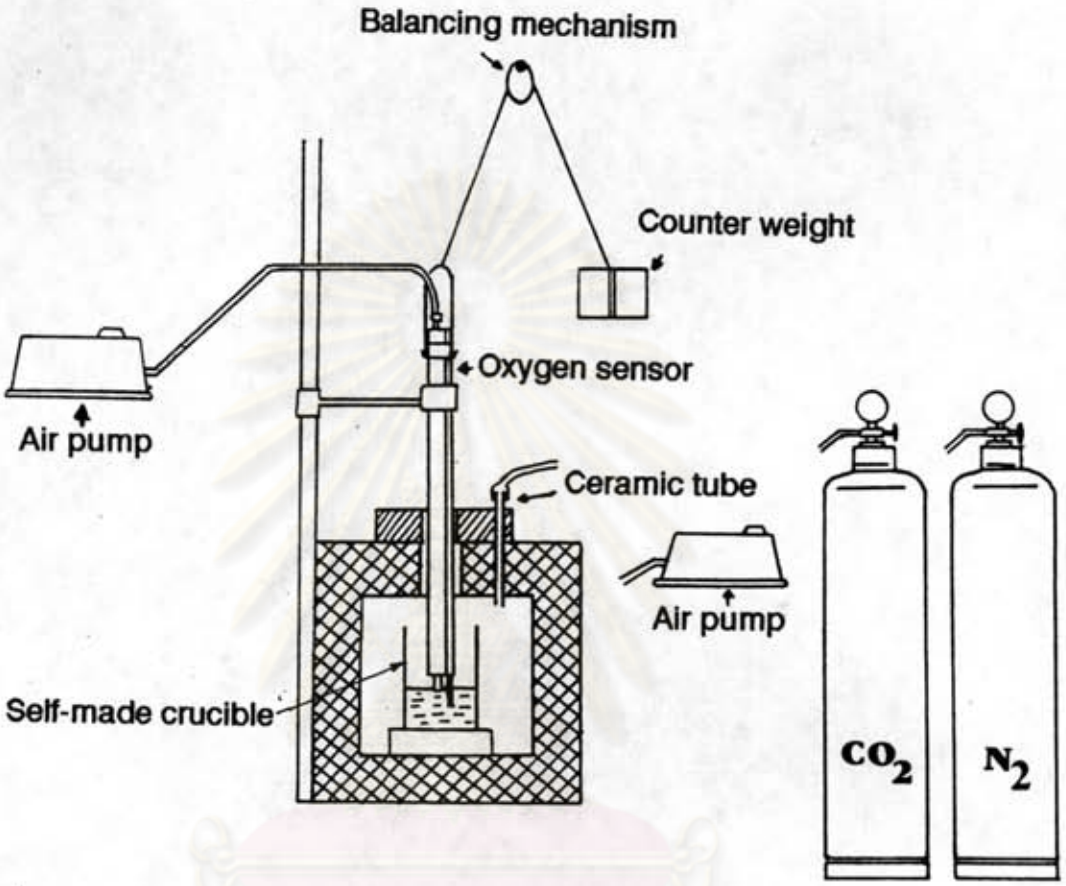

Figure 3.9 The setting of oxygen sensor with furnace

Glass batch measurement

A commercial insulation fiber glass which reaches a low viscosity at 1200 ^{o}C already was selected for the following test. This should enhance oxygen mobility and stabilize the e.m.f. reading. When the temperature reached 1200^{o}C, the sensor was moved down to contact the surface of the glass melt. Before the batch was charged onto the glass melt, the alumina tubes of the sensor were shielded by a refractory tube to prevent damage.

3.7 Hot-stage X-ray diffraction measurement

Batches with different redox number R and NaCl contents (R=-20, R=-20 + NaCl (1 wt. %) and soda-lime-sand in the ratio of 1:1:1) were selected. Samples of 500mg were weighed, placed in platinum pans, and heated at 10 K/min.