

DTA determination of liquidus temperatures and Al_2O_3 and AlF_3 content in cryolitic melts¹

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Abstract

Differential thermal analysis (DTA) of $\text{Na}_3\text{AlF}_6\text{-}4\text{CaF}_2\text{-}n\text{AlF}_3\text{-}m\text{Al}_2\text{O}_3$ (with $5 \leq n \leq 14$ and $2 \leq m \leq 5$) has been performed in closed nickel crucibles. Charts are constructed from the DTA curves, which allow the determination of the liquidus temperature and the composition of the sample.

INTRODUCTION

The mixture $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-Al}_2\text{O}_3\text{-CaF}_2$ is the so-called “classical electrolyte” used in the electrolytic Hall–Héroult process. All the phase equilibrium diagrams of importance to the aluminium industry have been thoroughly studied [1, 2]; in particular the quaternary system mentioned above was established by Craig and Brown [3]. Figure 1 represents the subsolidus portion of this diagram; the Hall–Héroult cell compositions are situated in the high-cryolite corner, where the primary phase upon crystallisation is cryolite solid solutions.

The knowledge of the liquidus temperature and of the concentration of Al_2O_3 and AlF_3 is useful for the process control of the electrolysis; these two compounds are consumed during the process and must be complemented continuously in order to maintain the optimum conditions. DTA is the method most widely used to determine the liquidus temperature [4, 5]; several chemical and instrumental methods have been used to obtain the concentrations of Al_2O_3 and AlF_3 (generally expressed as the cryolite ratio CR (mol NaF/mol AlF_3)) [6, 7].

The aim of this study is to check the possibilities of determining by DTA

¹ Dedicated to Hans Georg Wiedemann.

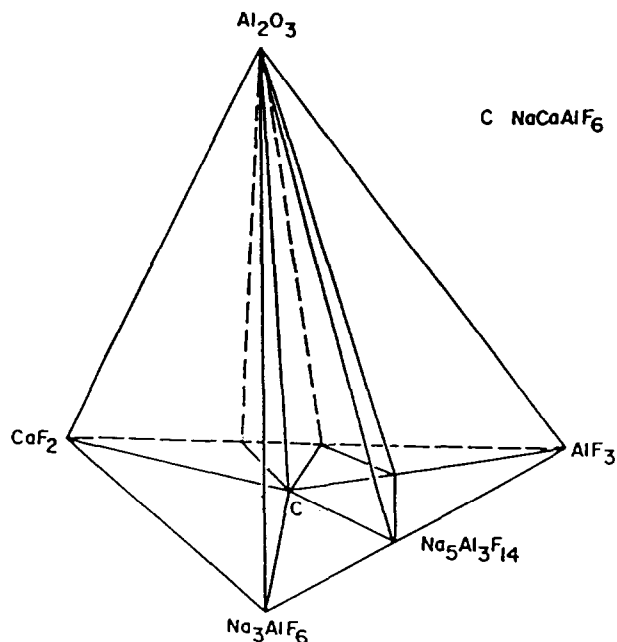


Fig. 1. Subsolidus portion of the diagram $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-Al}_2\text{O}_3\text{-CaF}_2$.

the concentration of Al_2O_3 and AlF_3 and the liquidus temperature in melts of the quaternary mixtures $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-Al}_2\text{O}_3\text{-CaF}_2$.

EXPERIMENTAL PART

Sample preparation

We have studied 45 mixtures of $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-Al}_2\text{O}_3\text{-CaF}_2$ within the following limits: AlF_3 , 5–14 wt.% (expressed as the excess with regard to cryolite) (notation 5 AF–14 AF); Al_2O_3 , 2–5 wt.% (notation 2 AO–5 AO); CaF_2 , 4 wt.% (notation 4 CF); Na_3AlF_6 , difference to 100% (notation K).

The mixtures were prepared by grinding in acetone the pure compounds Na_3AlF_6 (natural cryolite, m.p. 1009.5°C), AlF_3 (Cerac Inc., purity greater than 99.5%), Al_2O_3 (Alusuisse-Lonza, dried at 300°C) and CaF_2 (Merck Suprapur, dried at 300°C). The purity of AlF_3 was tested by mixing with NaF in 1 to 3 molar proportion and measuring the melting point of the cryolite; we have obtained a melting point of 1010°C.

Samples ((55 ± 3)mg) were introduced in a nickel crucible of laboratory manufacture, closed by argon arc. As reference we used 5.07 mg of LiF in a similar crucible; the peak corresponding to the melting of LiF (847°C) does not interfere with the sample peaks and allows us to calibrate continuously the temperature and the calorimetric sensitivity of the device.

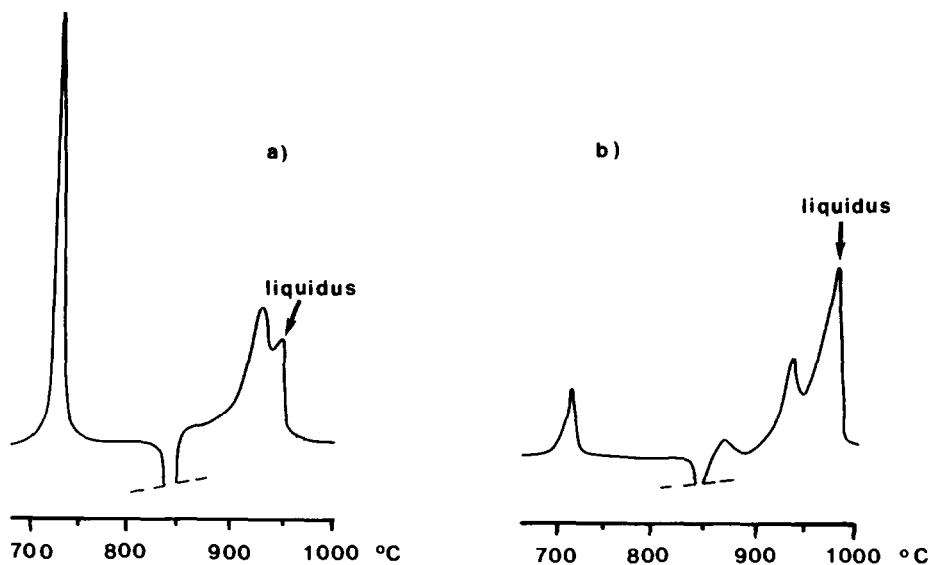


Fig. 2. Examples of DTA curves. Reference: 5.07 mg LiF; heating rate, $5^{\circ}\text{C min}^{-1}$. Samples: (a) 53.28 mg K-4CF-10AF-5AO; (b) 55.17 mg K-4CF-5AF-2AO.

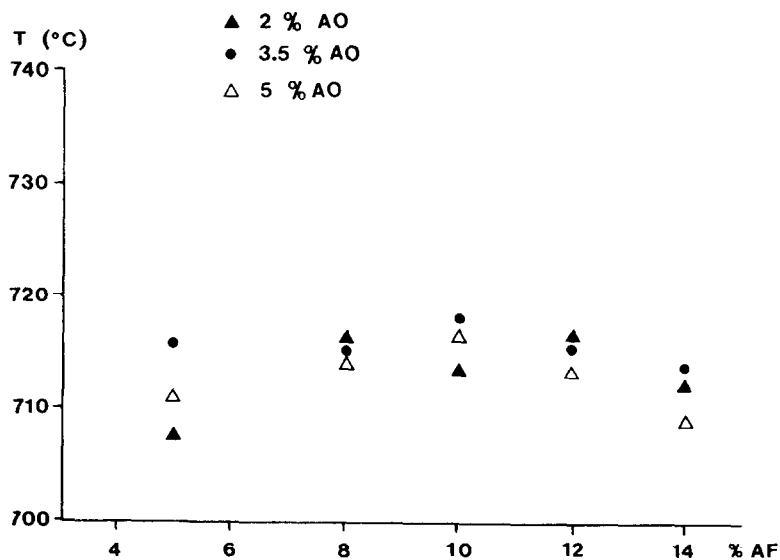


Fig. 3. Solidus temperature as a function of Al_2O_3 and AlF_3 . CaF_2 , 4%; Na_3AlF_6 , diff. to 100%.

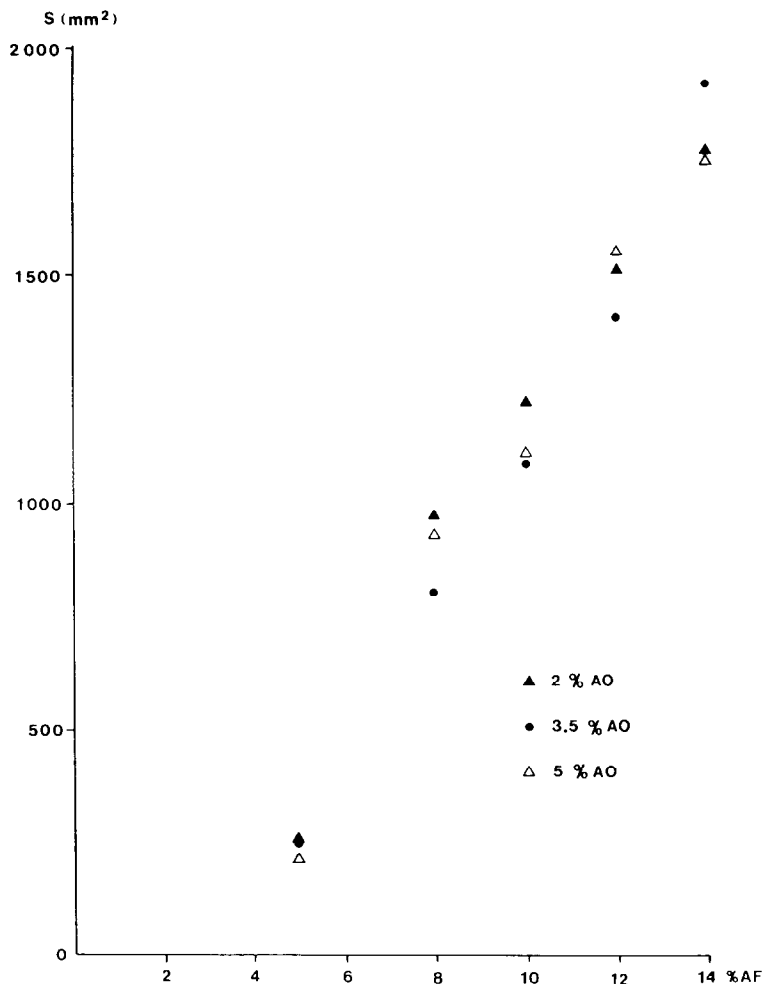


Fig. 4. Solidus peak area as a function of Al_2O_3 and AlF_3 .

Apparatus

The DTA apparatus was developed in our laboratory; it comprise a crucible holder in alumina, with two NiCr/Ni thermocouples for the DTA and a Pt/PtRh 10% thermocouple for the temperature. The crucible holder is introduced into a quartz tube flushed with argon, to prevent oxidation. The quartz tube is surrounded by a 1600 W furnace; the temperature of the furnace is measured with a Pt/PtRh 10% thermocouple and controlled by a Setaram RT 3000 programmer; a heating rate of 0.05 mV min^{-1} was used. The DTA signal was amplified $40\times$ with a Setaram NV 274 amplifier and either recorded graphically, or stored with a Wavetek 51 acquisition device. The thermocouple used for temperature measurements was calibrated with transitions and melting points of NaCl, Na_2SO_4 , NaF and K_2SO_4 .

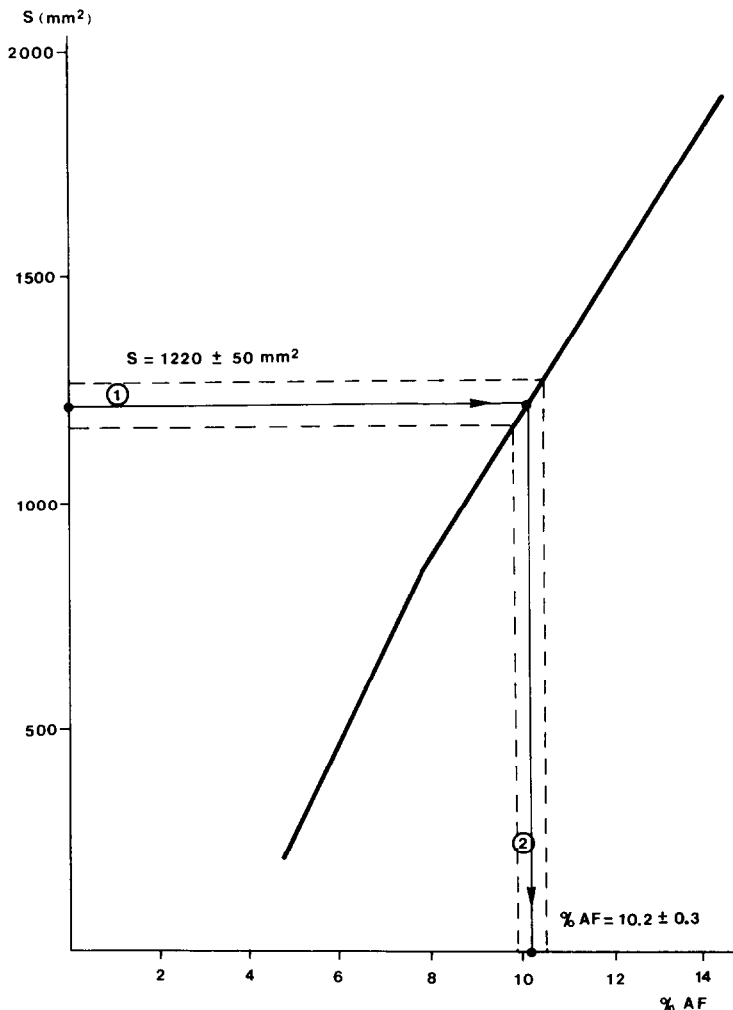


Fig. 5. Chart to determine the AlF₃ concentration from the solidus peak area.

RESULTS AND DISCUSSION

Figure 2 shows two examples of DTA; all the samples studied gave similar curves: a solidus peak at around 715°C and a complex set of peaks at higher temperature. The top of the last peak correspond to the liquidus temperature. The solidus peak occurs at approximately the same temperature for all compositions (Fig. 3), but the area of the peak increases appreciably with the quantity of AlF₃ present in the sample, and is almost independent of the Al₂O₃ content (Fig. 4).

Statistical evaluation of three measurements done for each composition results in the chart presented in Fig. 5, which allows us to determine the AlF₃ content from the area of the solidus peak.

The liquidus temperature is measured at the top of the last peak observed on the DTA curves (Fig. 2); as has already been noted [4, 5], a deep trough occurs in the liquidus surface with the change of composition.

Figure 6 shows a linear depression of the liquidus temperature with the increase of Al_2O_3 ; an average value of 6.1°C per 1% of Al_2O_3 is calculated from the slopes at each AlF_3 concentration.

The depression of the liquidus temperature versus AlF_3 concentration is shown in Fig. 7; by a linear interpolation between each concentration studied, an average value of the depression is calculated for each concentration interval, as indicated in Fig. 7.

Figure 8 has been constructed from the average depression values; the slope of the lines corresponds to 6.1°C per 1% of Al_2O_3 , and the distance between each line is determined by the average values indicated in Fig. 7. Knowing the liquidus temperature and the AlF_3 content enables the concentration of Al_2O_3 to be determined, as indicated on the graph.

CONCLUSIONS

DTA of cryolitic melts performed in closed crucibles provides sufficiently reproducible results to allow the determination of the liquidus temperature and the composition of the mixture with an acceptable accuracy.

This study has been limited to the quaternary mixture Na_3AlF_6 – CaF_2 – AlF_3 – Al_2O_3 . The main advantages of the method described are its rapidity and ease of use, and the low cost of the apparatus. However it cannot be used to analyse melts containing LiF ; in that case, only the liquidus temperature can be determined. Application to the analysis of industrial mixtures was performed; the method described here is simpler than those proposed by Lee [4] and Ballard [5], due to the fact that we consider the CaF_2 concentration to remain constant at 4%. As a matter of fact, calcium fluoride is seldom added intentionally; because of a small amount as impurity in the alumina, it reaches a steady state concentration between 3 and 8% in the melt. At this level, calcium is codeposited with aluminium and emitted in the evolved gas at a rate equal to its introduction. The procedure described in this paper was applied to mixtures with CaF_2 concentrations of 3 and 5%, and afforded the same accuracy for the determination of the concentration of AlF_3 and Al_2O_3 .

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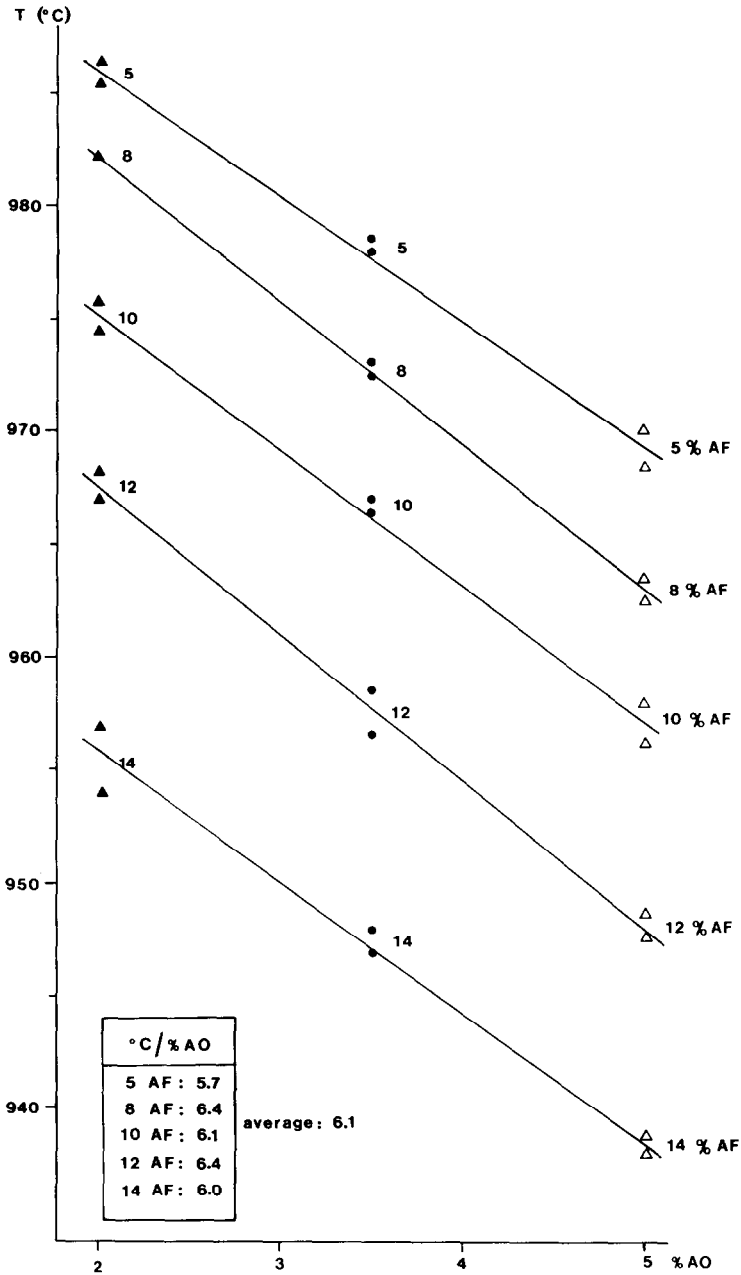


Fig. 6. Liquidus temperature as a function of Al_2O_3 at fixed AlF_3 concentrations. CaF_2 , 4%; Na_3AlF_6 , diff. to 100%.

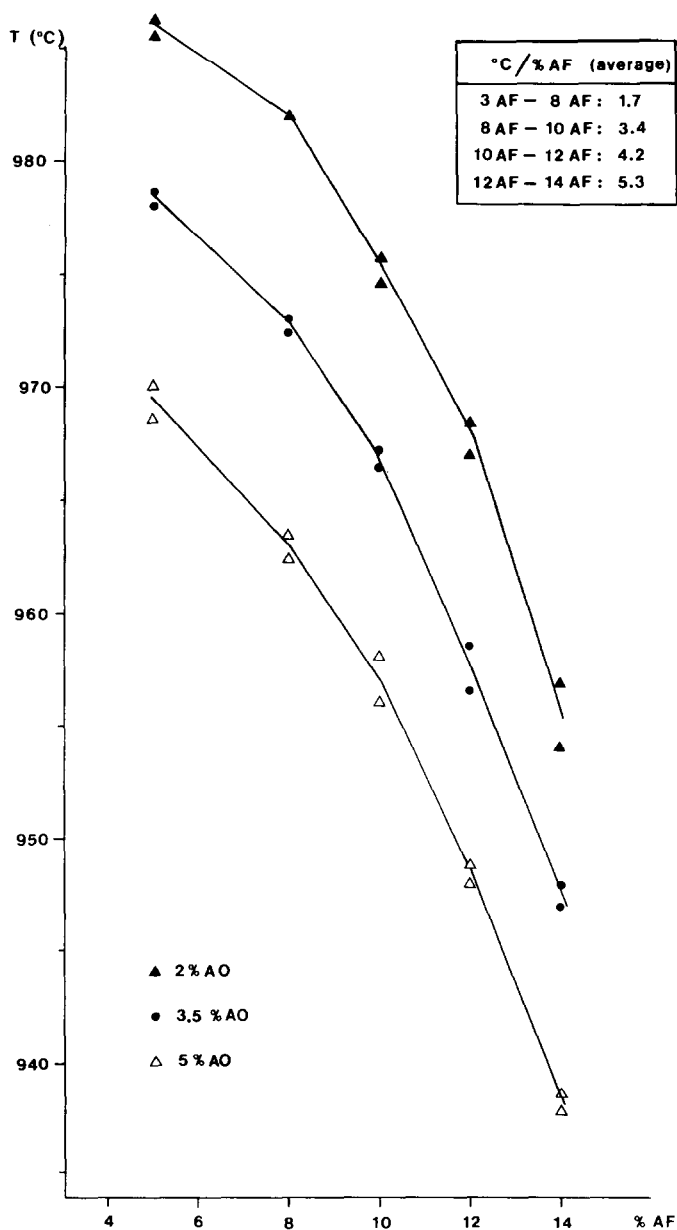


Fig. 7. Liquidus temperature as a function of AlF_3 at fixed Al_2O_3 concentrations. CaF_2 , 4%; Na_3AlF_6 , diff. to 100%.

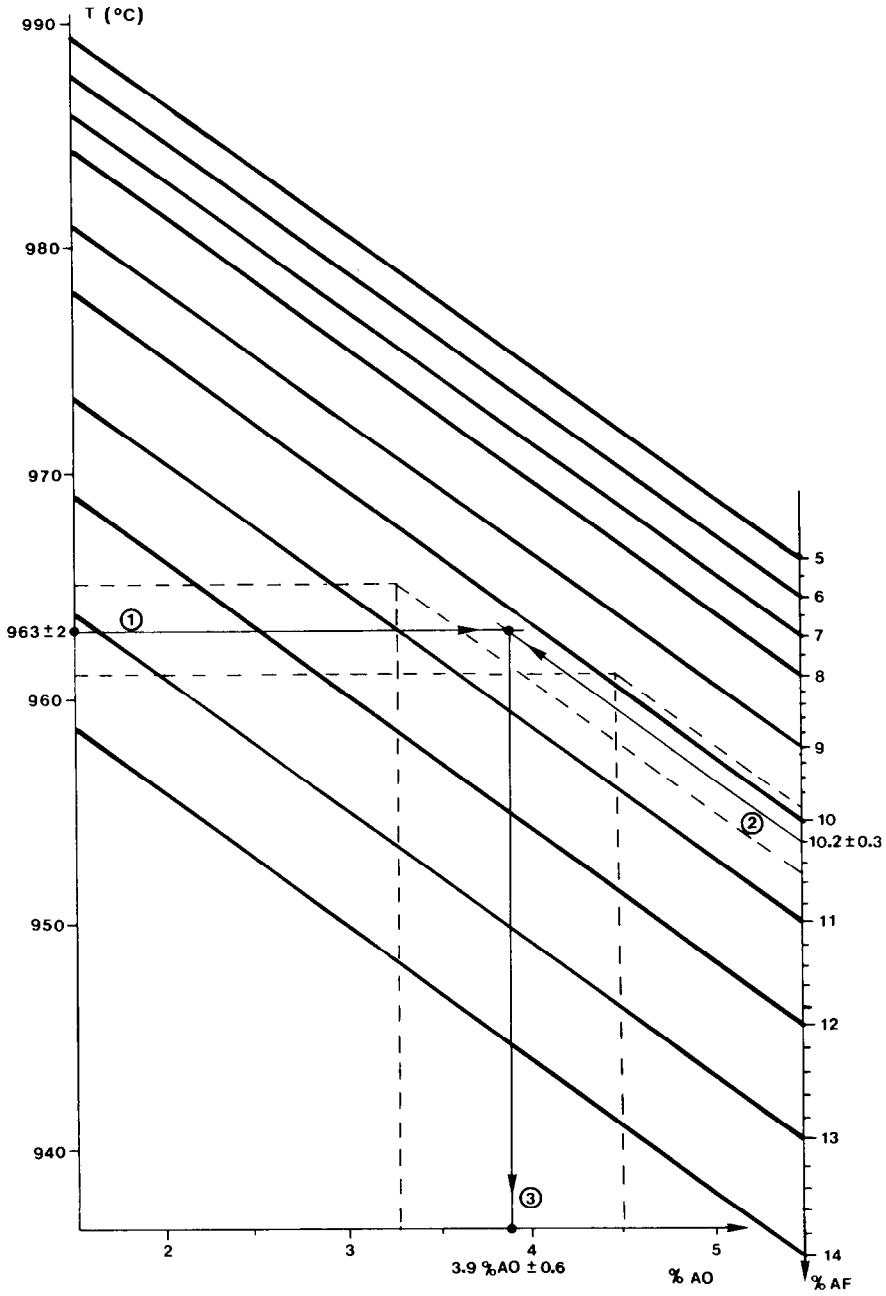


Fig. 8. Chart to determine the Al_2O_3 concentration from liquidus temperature and AlF_3 concentration.

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