Evgeniya Il'ina[1], Svetlana Pershina[1], Alexey Vylkov[1], Alexander Chuikin[1], Alexander Kataev[1], Alexey Rudenko[1], Alexander Redkin[1], Yurii Zaikov[1,2]
[1]Institute of High Temperature Electrochemistry, Ural Branch of the Russian Academy of Sciences, Ekaterinburg,
[2]Ural Federal University named after the first President of Russia B.N.Yeltsin, Ekaterinburg

PHASE TRANSITIONS AND THERMAL EXPANSION OF CRYOLITE BASED EUTECTIC MIXTURES IN SOLID STATE

Molten cryolites are widely used as electrolytes for production of aluminium. The properties of molten electrolytes are well known [1] but the properties of solid cryolites and their mixtures with some additive such as aluminium oxide and calcium fluoride have not been investigated especially at temperatures close to melting point. Besides, low temperature cryolite mixtures are of interest for some industrial applications [2]. The properties of solid compounds are also important due to electrolyte feeezing on the walls of electrolytic cell.

Some eutectic mixtures of sodium cryolite with Al_2O_3 and CaF_2 as well as some low melting eutectic mixtures were under investigation. The phase transformations were studied by using STA 449F1 Jupiter. The Netzsch DIL 402C was used for thermal expansion determination. The results obtained manifest several transition points for sodium cryolite based mixtures. Most common point is $\alpha \rightarrow \beta$ cryolite transition. This point is also seen on linear expansion dependence on temperature (Figure 1a). The second DSC peak was observed at 1080 K for samples containing essential amounts of calcium fluoride. This peak also corresponds to linear expansion shift.

The results shed light the fact that all phase transitions manifest themselves in thermal expansion. The value of thermal expansion is relatively small in comparison with liquid state. The density of solid cryolites at temperatures on 100 degrees below melting point on 30% higher that of liquid. It means the significant change of structure during melting. The investigation of melting process is also objective of our work. Thus we can trace all changes that take place in cryolite-alumina mixtures up to appearing liquid phase.

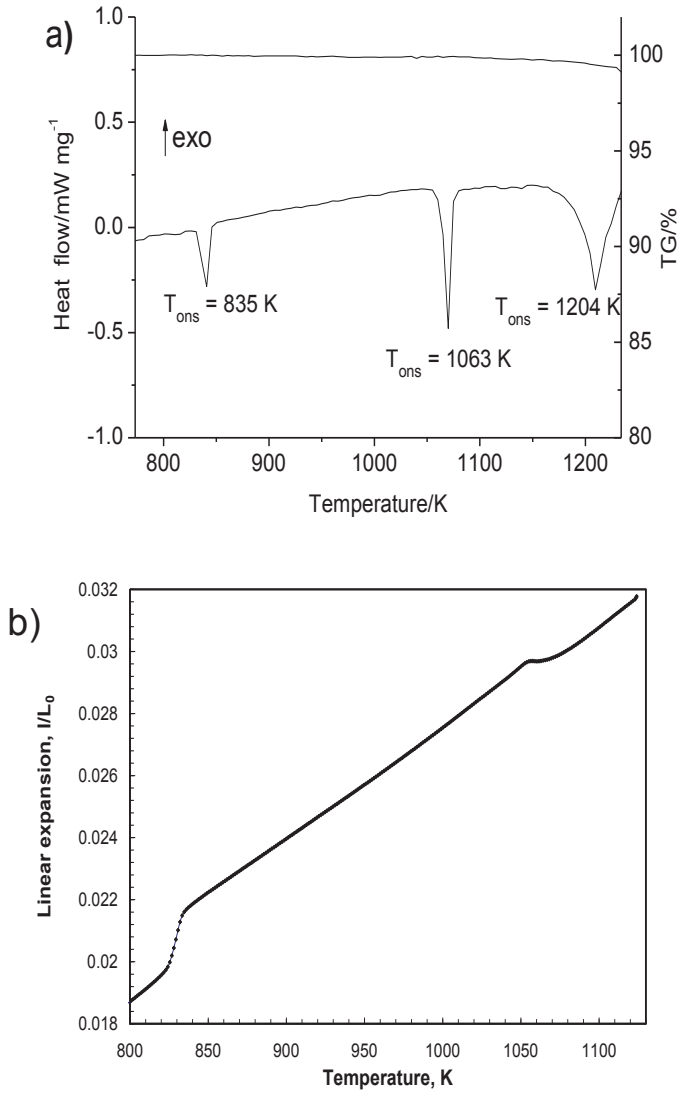

Figure 1 – DSC curve (a) and linear expansion (b) of the eutectic mixture 0.66 NaF-0.185AlF_3-0.102 CaF_2-0.017 Al_2O_3.

Acknowledgments
The work was supported by RFBR. Grants No 18-03-00785 A.

REFERENCES

1. J.Thonstad, P.Fellner et al. Aluminium Electrolysis. 3 rd Edition. – Aluminium- Verlag, Dusseldorf, 2001.
2. Yu. Zaikov, A. Khramov, V. Kovrov et. al. Electrolysis of aluminum in the low melting electrolytes based on potassium cryolite. Light metals 2008 Edited by: David H. DeYoung TMS (the Minerals, Metals & Materials Society), 2008, p. 505-508.