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CaF_2 solubility in NaC1-KC1 salt flux for aluminium recycling

A. SYDYKOV, B. FRIEDRICH, E. MILKE, and A. ARNOLD

IME Process Metallurgy and Metal Recycling, Technological University of Aachen, Germany

CaF_2 is often used as a fluoride addition to the chloride salt flux in the melting of aluminium scrap. The solubility of CaF_2 in the chloride salt system is limited. Dissolved CaF_2 is considered to improve the properties of salt fluxes. Experimental investigations indicated that the solubility of CaF_2 in 70 wt % NaCl/30 wt % KCl, German salt flux used in aluminium scrap melting, might be lower than expected according to literature data. The pseudobinary section CaF_2-(70 wt % NaCl-30 wt % KCl) was investigated by differential thermal analysis (DTA). The determined solubility of CaF_2 appeared to be considerably lower than presented in the literature. The pseudobinary section calculated using thermodynamic data partially confirmed the results. DTA allowed us also to determine the crystallization temperature interval of the two phase eutectic consisting of the solid solution NaCl-KCl and CaF_2.

Keywords: aluminium recycling, phase system, salt flux, CaF_2, NaCl, KCl, solubility

Introduction

Salt fluxes in recycling of aluminium scrap reduce metal losses by protecting the metal melt from oxidation and by adsorbing of surface contaminants. There are many salt flux compositions used in industry. Most of them are based on NaCl and KCl. A salt flux widely used in Germany for aluminium scrap remelting is based on a mixture of 70 wt% of NaCl and 30 wt% of KCl. As a fluoride addition calcium fluoride CaF_2 is used very often due to its satisfactory activity and low price. The concentration of CaF_2 in salt flux varies between 2 and 5 wt%[1].

CaF_2 and other fluoride salt additions in salt fluxes increase the metal yield by decreasing suspension of metal in the salt phase. Without fluoride salts the oxide layer on aluminium is stripped very slowly, which hinders the coalescence of metal droplets in salt. The mechanism of the effect of CaF_2 and other fluoride salts is still not clear. Possibly fluoride salts dissociate in molten salt fluxes and produce free fluoride ions, which act as a surface active component of the salt flux[2].

It is necessary to assume that only in salt flux can dissolved fluorides produce free fluoride ions. Beside dissociation reactions, it is important to know the solubility of fluorides in the salt flux. In this study the pseudobinary section of the ternary system NaCl-KCl-CaF_2 related to the salt flux based on 70 wt% NaCl and 30 wt% KCl was studied experimentally by DTA.

Experimental procedures

NaCl, KCl and CaF_2 (Table I) were dried during 24 h at 120°C under air atmosphere. Then samples containing 1, 2, 3, 5 wt% of CaF_2 were mixed and ground to 100 μm. The weight ratio NaCl to KCl in all samples was 70/30. The sample weight taken for DTA was 100 mg. Al_2O_3 was used as a reference. An argon gas flow (150 cm^3/min) was applied to carry the salt vapour from the DTA furnace. The temperature measurement accuracy was ±1°C. The weighing error of CaF_2 concentration was about ±0.02%. Heating and cooling rates were 20°C/min and 5°C/min respectively. The sample with 5 wt% CaF_2 was heated to 850°C and the other samples to 770°C in order to guarantee a complete dissolution of CaF_2.

Table I
Salts used for preparation of salt samples for DTA

Chemical (Producer)	NaCl (Fluka)	KCl (Fluka)	CaF_2 (Riedel-de Haën)
Main compound, %	≥ 99.5	≥ 99.0	≥ 99.5
	K ≤ 0.01%	Na ≤ 0.05%	Chlorides (Cl):≤ % 0.1
Sulphate (SO_4), %	≤ 0.01	≤ 0.01	≤ 0.005
Ca, Cd, Co, Cu, Fe, Ni, Pb, Zn, %	≤ 0.005	≤ 0.005	Pb ≤ 0.1; Fe ≤ 0.01; As ≤ 0.0005
pH (50 mg/ml H_2O, 25°C)	5.0-8.0	5.0-8.5	

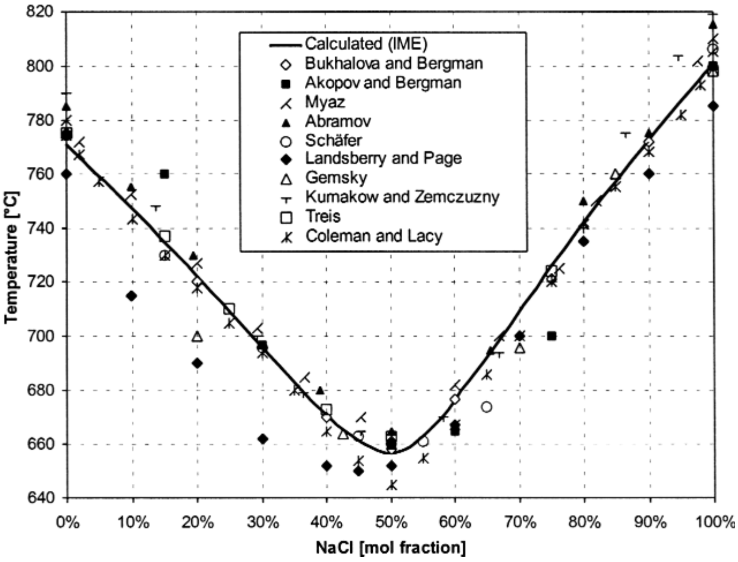

Figure 1. Liquidus line of the binary system NaCl-KCl

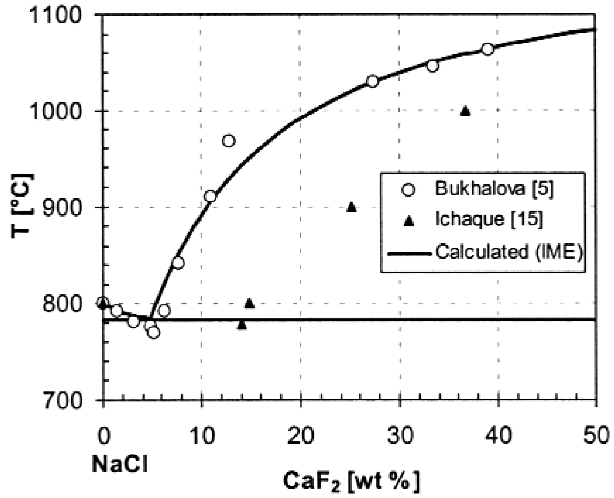

Figure 3. Binary system NaCl-CaF_2

Thermodynamical calculations

The thermodynamic calculations are carried out with the module 'Phase Diagram' of the software FactSage[3] on the basis of the thermodynamic data of binary systems NaCl-KCl, KCl-CaF_2, NaCl-CaF_2, as well the data from Barin, Knacke, and Kubaschewski [4]. The binary system NaCl-KCl was calculated by the Phase Diagram module using the databases Salt-liquid (FACT-SALT) and solution database AlkCl-ss (FACT-ACl). Gaseous, liquid and solid NaCl, KCl, as well $(NaCl)_2$ and $(KCl)_2$ solid were taken as possible phases. In the system NaCl-CaF_2 the possible liquid and solid phases were $CaCl_2$, CaF_2, NaCl, NaF, KF, and gaseous phases NaCl, $(NaCl)_2$, KCl, $(KCl)_2$, CaF_2, $CaCl_2$. The pseudobinary system CaF_2-(70 wt% NaCl-30 wt KCl) was calculated with the module 'Equlib' with the same possible species as for binary systems. The calculation of the system CaF_2-KCl at the CaF_2 concentrations was possible until about 15-20 wt%. At higher concentrations the calculations resulted in a possible immiscibility of CaF_2–rich and KCl-rich liquids[5], which should be verified experimentally as there are no published experimental data.

Results and discussions

The binary system NaCl-KCl was studied by many researchers (Figure 1 and Figure 2)[6, 7-15]. The minimum liquidus temperature is published to be between 645 and 665°C and corresponds to the equimolar composition. The phase transformation temperatures were determined by various methods: hot and cold stage microscope techniques, differential thermal analysis, and combined techniques. Some methods allow one to determine only the liquidus line. That explains why there are more experimental data for the liquidus line than for the solidus line.

Our caculated liquidus and solidus lines (using FactSage Database) lie between the published experimental points. The liquidus temperature of the composition 70 wt% NaCl (~75 mol. %) is between 690 and 712°C. The solidus temperature lies between 644 and 670°C. Calculated liquidus and solidus temperatures are respectively 709°C and 663°C.

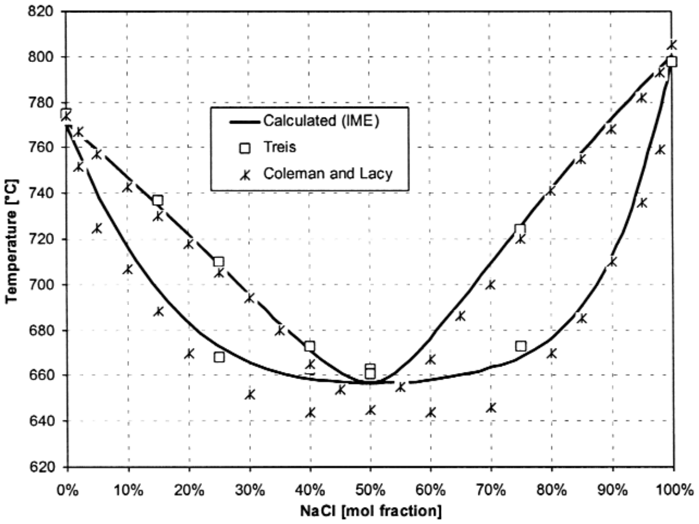

Figure 2. Binary system NaCl-KCl

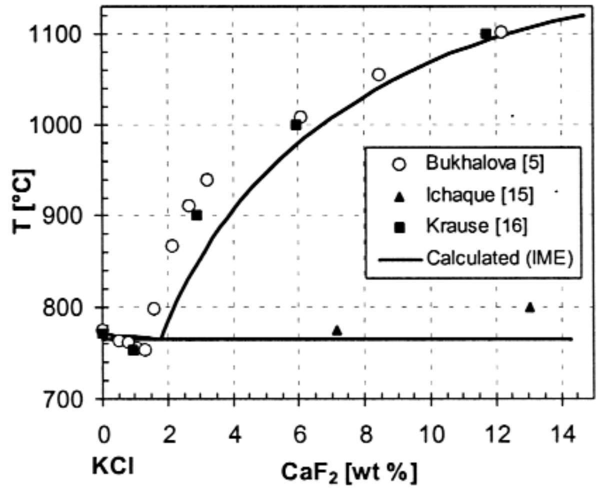

Figure 4. Binary system KCl-CaF_2

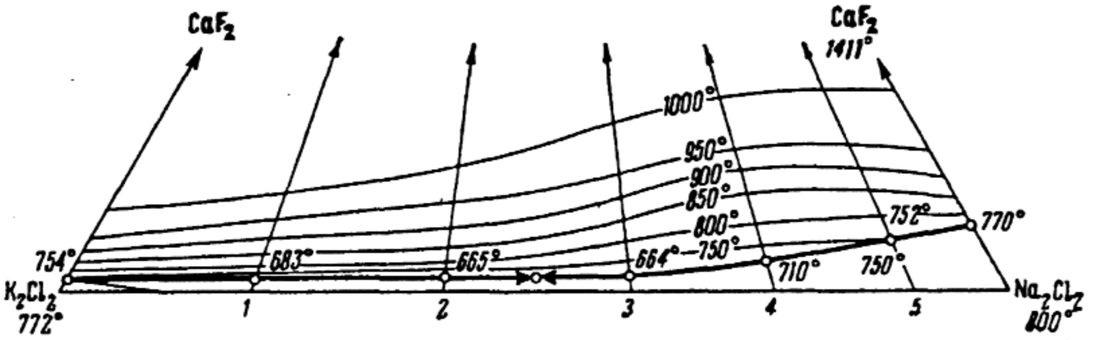

Figure 5. Ternary phase system Na_2Cl_2-K_2Cl_2-CaF_2 [6] (in mol. fraction)

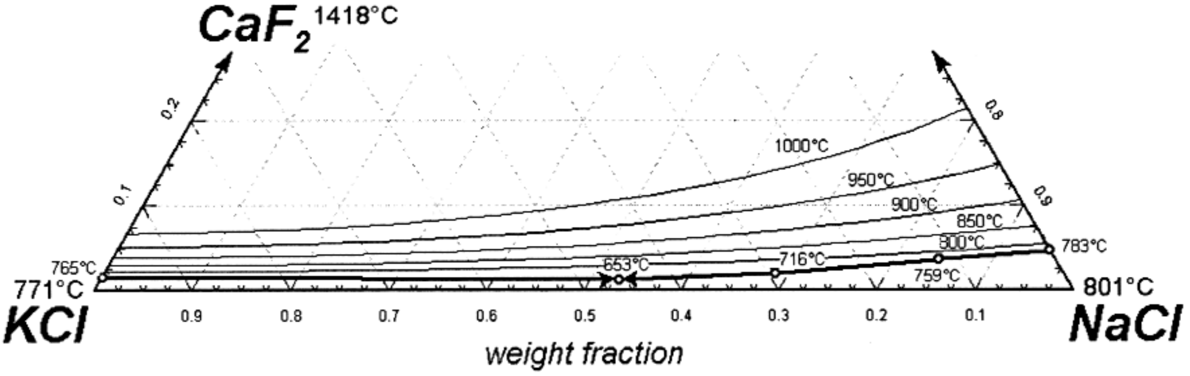

Figure 6. Calculated ternary system NaCl-KCl-CaF_2

Binary systems NaCl-CaF_2 and KCl-CaF_2: The differences between the experimental data of Ichaque[16] (DTA) and Bukhalova and Bergman[6], Krause and Bergman[17] (visual method) are over 100 degrees Celsius (Figure 3 and Figure 4). The calculated phase equilibrium lines are in better agreement with Bukhalova and Bergman than with Ichaque.

The ternary phase diagram NaCl-KCl-CaF_2 is given by Bukhalova and Bergman[6] as a section of a reciprocal system Ca,K, Na // Cl, F (Figure 5). The isothermal lines change their curvature to reverse on the right Na_2Cl_2-half, but there isn't any satisfactory explanation for that. This curvature change does not appear on the calculated ternary diagram (Figure 6). The calclulated minimum temperature of the eutectic line on the ternary liquidus surface is 653°C.

Pseudobinary section (70NaCl-30KCl)-CaF_2: First DTA measurements of the prepared salt samples showed that the salt evaporated very fast. Weight losses were above 50% after 30 min at 800–1000°C. Employing an alumina cover lid for the sample crucibles and reducing the maximal temperature decreased the evaporation to less than 1% for the samples with 1, 2 and 5% CaF_2 and about 4% for the sample with 3% CaF_2. By evaporation the decrease of the sum of calcium and fluor contents was about 0.02 wt%, potassium content didn't change, and the sodium content increase was about 0.17 % (calculated for evaporation 4 wt% of the initial weight)[18]. The phase transformation temperatures were plotted on Figure 7. The liquidus line appeared to be higher than according to Bukhalova and Bergman.

The calculated liquidus line is even higher than obtained by DTA. In the region of hypoeutectic compositions, the liquidus temperature difference between calculated and after Bukhalova and Bergman, is between 2 an 4°C. In hypereutectic compositions the differences between determined liquidus temperatures are much bigger, more than 100°C. Published results of centrifugation[19] and settling tests[20] are close to the calculated liquidus. Molten salt flux samples were filtered with a centrifugal technique at 800°C. The filter cakes were analysed for CaF_2. The CaF_2 concentration in the filter cake was higher than in the filtered melt where the CaF_2 concentration was above 3.8 wt%, which indicates undissolved CaF_2 in the salt flux. In the settling test molten salt flux was allowed to settle up to 110 min. Clear salt samples from the top of the melt were taken and analysed for CaF_2. In the coalescence tests[2] 5 wt.% of CaF_2 addition into the 70NaCl-30KCl salt flux at 830°C resulted in undissolved CaF_2 particles in the melt, but with 3 wt.% no undissolved CaF_2 was observed in the melt.

Under the liquidus line in the hypoeutectic range there is an area of crystallization of NaCl-KCl solid solution. On the hypereutectic side during cooling CaF_2 crystals precipitate first until 708–709°C. Then a binary freezing starts: the binary eutectic consisting of NaCl-KCl solid solution and CaF_2 crystallizes. The solidification ends at 676-679°C (Figure 7).

Pseudobinary section CaF_2-equimolar (NaCl-KCl)

A thermodynamically calculated liquidus line is in good agreement with the pseudobinary section corresponding to the equimolar NaCl-KCl graphically calculated using the data of Bukhalova and Bergman[6] (Figure 8). The calculated minimum is at 652°C and 0.91 wt% CaF_2. An extrapolation based on data of Bukhalova and Bergman gave the minimum at 655°C and 0.87 wt.%CaF_2. According to the calculated liquidus, the solubility of CaF_2 is about 2.7 wt% at 800°C.

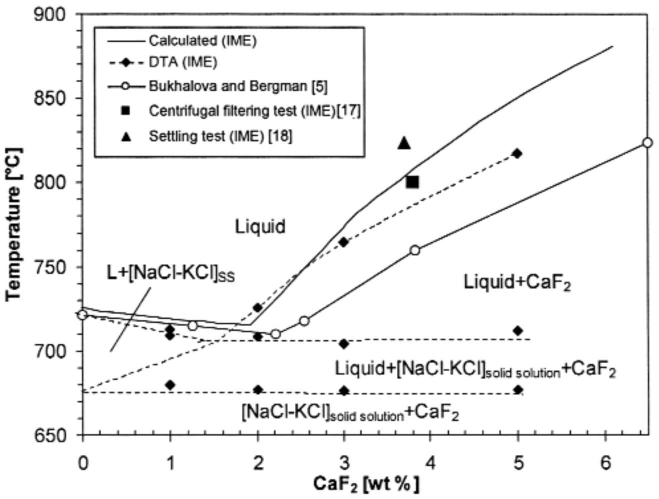

Figure 7. Pseudobinary section CaF_2-[70 %NaCl-30% KCl] of the ternary phase system

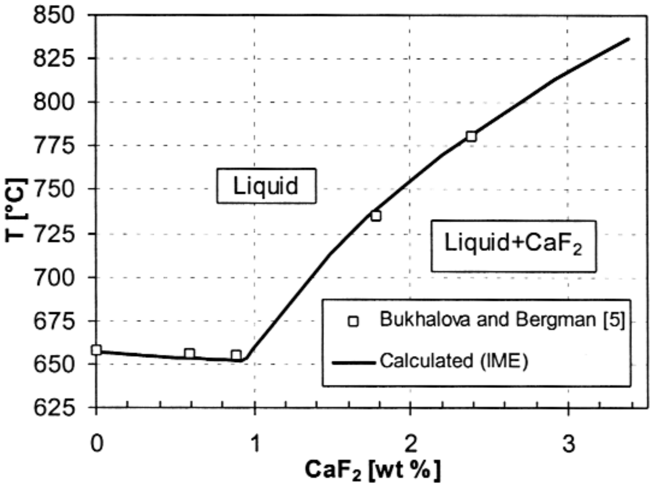

Figure 8. Pseudobinary section (equimolar NaCl-KCl)-CaF_2 of the ternary system NaCl.KCl-CaF_2

Conclusions

Experimental results, literature data and the thermodynamical calculations indicated that the solubility of CaF_2 in the salt flux (70 wt.% NaCl-30 wt.% KCl), used in Germany in aluminium scrap remelting, is lower than according to the only available ternary phase diagram NaCl-KCl-CaF_2 of Bukhalova and Bergman[6]. The knowledge of the CaF_2 solubility allows one to avoid its unnecessary overconsumption, which lead, to metal losses by increasing the viscosity of the salt flux, and additional residues after the water leaching of the salt slags. A thermodynamic calculation of the pseudobinary section resulted in even lower solubilities a result, which is in better agreement with recently published works. It is recommended not to add more than 3.5 wt% CaF_2 to the salt flux based on 70 wt% NaCl-30 wt% KCl and 2.7 wt% to the equimolar NaCl-KCl at the operation temperature of 800°C.

Acknowledgements

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