Investigation Of Behaviour Of Zirconium – Rare-Earth Metal Fluoride Mixture In Molten Fluoride

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Reactions between metals and molten salts are of great scientific and commercial importance. They are used for the preparation of zirconium, hafnium, titanium, and several rare-earth elements, and for the purification metals and molten salts and their mixtures. Information on the reaction of metals with molten salts is also necessary for choosing construction materials and ensuring their compatibility with salt fluxes.

The results of investigation of the molten fluoride systems NaF|LiF – LnF_3 – Zr and NaF|ZrF_4 –LnF_3 – Zr (were Ln = La, Pr, Nd, Gd, Dy, Yb) have been present in this abstract. The researches have been carried out using differential thermal (DTA), X-ray phase, IR-spectroscopy and chemical analysis with thermodynamic assessment. Differential thermal analysis (DTA) was carried out on a Q–1500 derivatograph. The heating rate was 10 K/min. Calcined alumina served as a standard. X-ray powder diffraction experiments were carried out on a DRON-UM diffractometer using Cu K_α radiation. IR spectra were recorded on a Specord M–80 spectrophotometer as a potassium bromide pellets.

At research of behaviour of REE fluoride – zirconium systems in fused mixtures NaF (0.39) – LiF (0.61) and NaF (0.51) – ZrF4 (0.49) the dehydrated and remelted mixtures on a technique circumscribed utilised earlier beforehand [1].

Using the chemical analysis methods, it has been found, that metallic zirconium interacts with REE fluorides, as results of which the metal is reduced from its fluorides. In the system based on NaF(0.39)–LiF(0.61) compounds of zirconium in the oxidation state +4 have been identified in the interaction products. The reduction takes place in the temperature range 470–680 °C (Fig. 1).

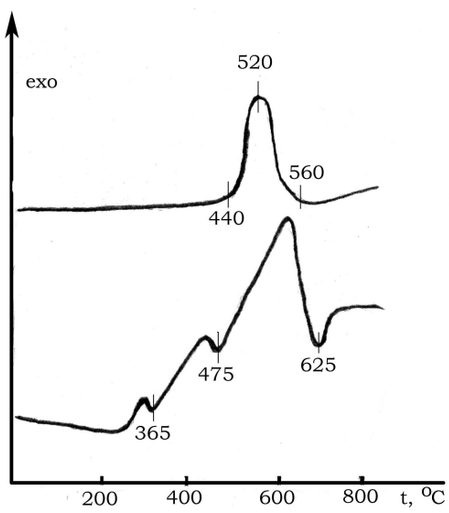

Fig 1. DTA curves for ZrF_4 – Zr (1) and Na,Li|F – GdF_3 – Zr (2).

It should be noted that the complete reduction of metals (REE's) from their fluorides is not observed even when the reductant is in 4-fold excess. Increasing the Zr:LnF_3 ratio decreases the initial interaction temperature. For example, at the ratio Zr:MF_3(mol)=4:1, the degree of reduction of REE fluorides is not over 35%. It has been found that the initial zirconium–REE fluoride, interaction temperature increases in a symbate manner with rising REE fluoride melting temperature:

Compounds	LaF_3	GdF_3	DyF_3	YbF_3
Melting temperature, ℃	1390	1380	1360	1330
Initial reduction temperature, ℃	490	475	470	460

The interaction rate depends on zirconium fineness and is the higher, the higher the fineness of the reducing metal, in which the components of the original reaction mixture are in the unmelted state.

It was shown that in case molten NaF–ZrF_4 systems the REE and zirconium in the oxidation state +2 presented in the interaction products. The reduction takes place in the temperature range 450–540 °C. Rare-earth and alkali metal fluoride compounds of the composition $MLnF_4$ (M = Na, Li; Ln = La, Pr, Nd, Gd, Dy, Yb), sodium fluorozirconates of variable composition: Na_2ZrF_6, Na_3ZrF_7, $Na_5Zr_2F_{13}$, and ZrF_2 have been identified in interaction products by physico-chemical analysis methods. The phases: $Yb(La)_{1-x}Zr_xF_{3+x}$ (were $0{,}03 \le x \le 0{,}18$), $NaYb(La)F_4$, Na_3YbF_6, have been found in NaF/ZrF_4–LnF_3–Zr sample.

The Gibbs energy change of the reaction between rare-earth metal fluorides and zirconium estimated using shows that the reaction described by the equation

$$4LnF_3 + 3Zr \rightarrow 4Ln + 3ZrF_4 \quad (1)$$

is impossible because the ΔG of this reactions are positive. According to thermodynamic calculations the is possible the following reactions:

$$ZrF_4 + Zr \rightarrow 2ZrF_2, \quad (2)$$

$$2LnF_3 + 3Zr \rightarrow 2Ln + 3ZrF_2. \quad (3)$$

Taking into account reaction (1)–(3), it may conclusion that the most probable process can describe equation

$$6LnF_3 + 7Zr \rightarrow 6Ln + 2ZrF_4 + 5ZrF_2 \quad (4)$$

The Gibbs energy ΔG for reaction (4) change at 500 °C is estimated at –1612.4…–1558.4 kJ/mol

References

1. Savchuk R.N., Omelchuk A.A., Kompanichenko N.M. and Nagorniy P.G. // *Russian Journal of Inorganic Chemistry.* – 2003, – Vol. 48, no.10, - *pp.*1454–1458

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