INVESTIGATION OF BEHAVIOUR OF ZIRCONIUM – RARE–EARTH METAL FLUORIDE MIXTURE IN MOLTEN FLUORIDE

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ABSTRACT

The present communication presents results of an investigation of the interaction rare–earth metal fluorides (rare–earth elements (REE): La, Pr, Nd, Gd, Dy, Yb) with zirconium in molten alkali halide and molten sodium fluoride–zirconium tetrafluoride mixtures. The investigation has been carried out by differential thermal analysis (DTA), X-ray phase analysis (XPA), IR spectroscopy, and chemical analysis. It has been found that the metallic zirconium reduce rare–earth fluoride in the temperature range where the constituents of reaction mixture are in solid phase to form compounds of zirconium in lower oxidation states and rare–earth metals. The dependence of the temperature at the commencement of exchange reactions on the chemical nature of rare–earth halide has been established: increase in the melting point of rare–earth fluoride leads to a rise of initial interaction temperature. The degree of reduction of rare–earth fluorides by reducing metals depends on the ratio of the constituents of the original reaction mixture.

INTRODUCTION

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 salt is also necessary for choosing construction materials and ensuring their compatibility with salt fluxes.

The research carried out in recent years showed that one of the promising methods for the destruction of radioactive wastes accumulated by operation nuclear power station and by the production of weapon plutonium is the accelerator–driven transmutation of long–lived nuclides, and that a suitable reaction medium is molten salt composition. According to the existing infrastructure of a nuclear power system, spent fuel is fluorinated to extract uranium (1), zirconium tetrafluoride, with is part of fuel element jackets, forming the basis of fluorination products. If sodium fluoride is added to fluorination products (ZrF₄) in a 1:1 (mol.) ratio, the composition formed, NaF–ZrF₄, will conform to the criteria for choosing fuel mixtures for nuclear reactors and will be a good carrier of nuclear transmutation products.
Whereas the nuclear transmutation that are possible to date are exhaustively studied in terms of theoretical physics, the chemistry of molten salt blanket is at the initial stage of investigation. In view of this, the investigation of chemical processes occurring in melts, which form the basis of fuel mixtures in reactors–transmuters, is topical and is of not only scientific, but also practical interest.

The results of investigation of the molten fluoride system Na[LiF–LnF3–Zr and Na[ZrF4–LnF3–Zr (were Ln = La, Pr, Nd, Gd, Dy, Yb) have been present in this paper. The researches have been carried out by differential thermal analysis (DTA), X-ray phase analysis (XPA), chemical analysis, and IR spectroscopy. A thermodynamic evaluation of the interaction the components of a number systems has been performed.

EXPERIMENTAL

The DTA was made on a Q–1500D derivatograph of system F. Paulik, J. Paulik and L. Erdey in corundum crucibles for DTG investigations under dry argon since the reducing metals and rare–earth fluorides are oxidised by atmospheric oxygen (2, 3). The heating rate of the samples under investigation was 5–10 deg-min⁻¹. Aluminium oxide was used as a standard. For a more reliable protection of samples from air oxidation, they were coated with a molten NaPO₃–V₂O₅ mixture. According to the results of (4), the presence of a protective coating of the composition (wt.%) NaPO₃ (75)–V₂O₅ (25) does not interfere in the identification of thermoeffects which are observed between the constituents of reaction mixtures: moreover, this coating has good protective properties in thermographic investigations.

The XPA was made on a DRON–UM diffractometer with CuKα radiation by the powder methods. The IR spectra were recorded in a frequency range of 3800–200 cm⁻¹ by means of a Specord–80M device on pelleted samples with potassium bromide.

Analytically pure and extra pure reagents and sublimed zirconium tetrafluoride of monoclinic system, which was obtained by dehydration and simultaneous fluorination of ZrF₄·xHOH (5).

The interaction between rare–earth fluorides and reducing metals was investigated in a previously prepared (mol %) NaF (39)–LiF (61) and NaF (51)–ZrF₄ (49) mixtures. The rare–earth fluoride content of this mixture was varied from 4 to 20 wt.%; the ratio Zr:MF₃ (mol.%) (M=La, Yb) was varied from 10:1 to 4:1. The samples were prepared by procedure described earlier (6).

The investigations carried out showed the solvent melt NaF (39 mol.%)–LiF, in which the reduction of REE fluorides by zirconium was studied, to melt at 700 °C. Thermograms exhibit only one endotherm, which corresponds to the melting of this mixture. Addition of REE fluorides to this melt lowers its melting temperature on an average by 80–70 °C (Fig.1).
The heating curves for a NaF (51 mol.%)–ZrF$_4$ (49 mol.%) mixture exhibit only one thermoeffect at 525 ± 5 °C, which is characteristic of the melting of a eutectic mixture in the NaF–ZrF$_4$ system and is in satisfactory agreement with literature data (7). It should be noted that alloys of the system NaF–ZrF$_4$ are characterised by supercooling. Indeed, the cooling curves for a NaF (51 mol.%)–ZrF$_4$ (49 mol.%) mixture exhibit an effect of solidification of sodium fluoride–zirconium fluoride melt at 490°C (Fig. 2).

A compound of the composition 7NaF·6ZrF$_4$ has been identified by an XPA (Fig. 3). The results of the XPA of a NaF (51 mol.%)–ZrF$_4$ (49 mol.%) mixture show that a fraction is formed at the top of the melt; the fraction shows a texture, due to long soaking, which is manifested in diffractograms by a group of strong reflections from crystallographic plane with $d = 0.5077$ nm. At the bottom of the melt is a fraction, whose basis is formed by a phase with fcc lattice ($a_0 = 0.543$ nm).

Figure 1. The typical thermograms for molten NaF–LiF–LnF$_3$ (were Ln = REE) flux.
Figure 2. The typical DTA heating (a) and cooling (b) curves of NaF–ZrF₄ mixtures (51–49 mol.%)

Figure 3. Diffractogram of the NaF (51 mol %)–ZrF₄ (49 mol %) mixture

The NaF–LiF–LnF₃–Zr and NaF–ZrF₄–LnF₃–Zr systems, were Ln = La, Pr, Nd, Gd, Dy, Yb (REE), were investigated on samples of 1.5–3.5 g mass. Pounded mixtures were poured into a glassy carbon crucible, which was placed in a hermetically sealed metallic reactor (Fig. 4). The samples were first subjected to vacuum degassing at 200 and 300°C and then heated under dry oxygen-free argon. The temperature in investigations did not exceed 600–650 °C.
The rare-earth metal concentration in the salt phase after the occurrence of exchange reaction was determined by complexometric titration in the presence of eriochrome black T and by gravimetric method by precipitating the rare-earth metal with oxalic acid (8). The fluoride ion content of the reaction mixture was determined by means of fluorine-selective electrode (9).

RESULTS AND DISCUSSION

A characteristic of the interaction between rare-earth fluorides and reducing metals is free Gibbs energy ($\Delta G$). The exchange reaction between the constituents of the mixtures under investigation may be schematically represented as follows:

$$6\text{LnF}_3 + 7\text{Zr} \rightarrow 2\text{ZrF}_4 \text{ + 6Ln + 5ZrF}_2$$
$$\text{LnF}_3 + 3\text{Na} \rightarrow \text{Ln} + 3\text{NaF},$$

where Ln is REE. The calculations that have been made on the basis of the data obtained in (10) give ground to consider the interaction between rare-earth fluorides and reducing metals to be possible on the whole since a noticeable decrease in the $\Delta G$ quantity is observed.

**Investigation of the NaF–LiF–LnF$_3$–Zr.** The reduction of lanthanum, praseodymium, neodymium, gadolinium, dysprosium, and ytterbium fluorides by zirconium metal is characterised by a broad exotherm in the range 465–625°C. The DTA and TG curves show similar trends for all mixtures; only the exotherm shifts when changing the rare-earth fluoride. Therefore, a representative DTA curve for the NaF–LiF–GdF$_3$–Zr system is shown in Fig. 5 to exemplify the interaction between the components. It was found that the reaction between the components of the systems begins
in the 450–490°C range, where all components of the reaction mixture are solid, and ends in the endotherm due to flux melting (625°C). It is noteworthy that the initial temperature of the interaction between the components increases with the melting point of the rare-earth fluoride and decreases with increase in zirconium content (Table 1).

Figure 5. The typical DTA curve of the system NaF–LiF–GdF₃–Zr

Table 1. DTA results of the reduction of REE fluorides by zirconium in the NaF (39 mol.%)–LiF mixture.

| Compound | Melting point (°C) | Initial reduction temperature (°C) |
|----------|-------------------|----------------------------------|
|          |                   | MF₃:Zr(mol)=1:1.5 | MF₃:Zr(mol)=1:6 |
| LaF₃     | 1390              | 490                 | 475              |
| PrF₃     | 1373              | 485                 | 460              |
| NdF₃     | 1413              | 475                 | 455              |
| GdF₃     | 1380              | 475                 | 450              |
| DyF₃     | 1360              | 470                 | –                |
| YbF₃     | 1330              | 465                 | –                |

The X-ray diffraction analysis of the products shows ZrF₄, ZrF₂, and the unreacted initial rare-earth fluoride. This provides evidence that reduction at the chosen feed ratios is incomplete. Among the products, the complexes NaLnF₄ and LiLnF₄ (Ln = La, Pr, Nd, Gd, Dy, Yb) are also found by X-ray diffraction. Chemical analysis showed that the degree of reduction of rare-earth fluoride by zirconium is independent of the position of the rare-earth element in the periodic table or of the zirconium content of the feed (even...
though it is in excess). The degree of reduction (Table 2) was determined as an average value of 2–3 replicate experiments.

Table 2. Degree of REE fluoride reduction by zirconium in a sodium and lithium fluoride melts.

| Compound | Degree of reduction at the constituent ratio in the original mixture (%) |
|----------|-------------------------------------------------------------------------|
|          | MF₃:Zr(mol)=1:1.5 | MF₃:Zr(mol)=1:6 |
| LaF₃     | 34.7 ± 0.3        | 34.9 ± 0.3        |
| PrF₃     | 35.2 ± 0.3        | 34.3 ± 0.3        |
| NdF₃     | 34.2 ± 0.3        | 34.6 ± 0.3        |
| GdF₃     | 35.0 ± 0.3        | 35.2 ± 0.3        |
| DyF₃     | 34.3 ± 0.3        | –                 |
| YbF₃     | 33.6 ± 0.3        | –                 |

Investigation of the NaF–ZrF₄–LnF₃–Zr. The reduction of lanthanum and ytterbium fluorides by metallic zirconium in a molten sodium fluoride–zirconium fluoride mixture takes place in a temperature range of 440–580 °C, the rate of the exchange reaction depending on the fineness of reducing metal and being the higher, the higher its fineness. The differential heating curves exhibit a number of thermoeffect: endotherms of the melting of NaPO₃–V₂O₅ mixture (365±5 °C) and the solvent melt NaF–ZrF₄ (520±5 °C); an exotherm with an initial interaction temperature of 440–460°C, whose maximum is overlapped by the endotherm of the melting of a eutectic sodium fluoride–zirconium fluoride mixture. These exotherm and the thermoeffects at 460 ± 5°C and 490 ± 5°C may be assigned to exchange reactions between metallic zirconium and rare–earth fluoride and zirconium tetrafluoride with the formation of compounds of zirconium in lower–oxidation states and rare–earth metal. Since the trend of the DTA and TG curves for the samples under investigation is practically the same, a typical DTA curve for the NaF–ZrF₄–LaF₃–Zr system is shown in Fig. 6 as an example.
The results of an XPA of interaction products showed that zirconium (IV) and (II) compounds: Na$_2$ZrF$_6$, Na$_7$Zr$_5$F$_{31}$, Na$_5$Zr$_2$F$_{13}$, ZrF$_2$; complicated compounds comprising rare-earth fluorides and sodium fluoride, and reduced lanthanides are present in the samples under investigation. The unit cell parameters have been calculated for the identified compounds by means of a computer program; they are in satisfactory agreement with those given in publications. It should be noted that the parameters of the compound ZrF$_2$, which crystallizes in orthorhombic system with $a = 0.40425$ nm, $b = 0.49537$ nm, $c = 0.65801$ nm, have same deviations from literature data ($a = 0.409$ nm, $b = 0.491$ nm, $c = 0.656$ nm), which may be due to the different stoichiometry of this compound (Table 3) (11, 12).

Thus the interaction in the system NaF–ZrF$_4$–LnF$_3$–Zr (were Ln = La, Yb) may be represented by the following equations:

\[ 4\text{LaF}_3 + 3\text{Zr} \rightarrow 4\text{La} + 3\text{ZrF}_4 \]  
\[ \text{Zr} + \text{ZrF}_4 \rightarrow 2\text{ZrF}_2 \]  
\[ 2\text{LaF}_3 + 3\text{ZrF}_2 \rightarrow 2\text{La} + 3\text{ZrF}_4 \]

i.e. exchange reactions [1] is paralleled by the interaction of metallic zirconium with tetrafluoride to form zirconium difluoride [2], which then also takes part in the reduction of rare-earth fluoride to metal [3].
Table 3 A fragment of diffractogram for the interaction products of the system NaF–ZrF₄–Zr

| Experimental data | Literature data |
|-------------------|-----------------|
| Sample            | ZrF₂            |
|                   | d Å° | I/I₀, % | d Å° | I/I₀, % |
| 4.077             | 59   |        | 4.065| 60     |
| 3.453             | 20   |        | 3.448| 30     |
| 3.285             | 28   |        | 3.279| 60     |
| 2.942             | 14   |        | 2.933| 10     |
| 2.779             | 67   |        | 2.762| 100    |
| 1.918             | 57   |        | 1.923| 10     |
| 1.731             | 15   |        | 1.739| 10     |
| 1.654             | 24   |        | 1.664| 60     |
| 1.545             | 20   |        | 1.541| 30     |
| 1.479             | 20   |        | 1.484| 60     |
| 1.378             | 32   |        | 1.377| 60     |
| 1.319             | 19   |        | 1.316| 30     |

CONCLUSIONS

Thus, as a result of the research carried out, it has been found that the interaction of zirconium with rare-earth fluorides begins in the temperature range where the constituents of reaction mixtures are in the solid state. Zirconium (IV) and (II) compounds: Na₂ZrF₆, Na₂Zr₂F₁₃, ZrF₂; complicated compounds comprising rare-earth trifluoride and sodium and lithium fluoride (MLnF₄, were M = Na, Li), and reduced lanthanides have been identified in the interaction products by physico-chemical methods of analysis. It has been found that the degree of reduction of rare-earth fluorides depends on metallic zirconium concentration in initial composition.

Comparison of the results of the work with the data shows that the change of the cationic composition of reaction mixtures (NaF–LiF, NaF–ZrF₄) influences the stepwise character of exchange reactions between rare-earth fluorides and metallic zirconium. In the system NaF–ZrF₄, zirconium reduces not only rare-earth fluorides but also zirconium tetrafluoride. Compounds of zirconium in lower oxidation states also show reducing ability with respect to rare-earth fluorides.

An interaction takes place between rare-earth fluorides and sodium and lithium fluorides to form complex compounds of the composition MLnF₄ (were M = Li, Na). Increase in the atomic number of rare-earth element does not affect the composition of these compounds.

REFERENCES

1. C.D. Bowman. Sustained Nuclear Energy without Weapons or Reprocessing Using Accelerator–Driven System, Proceedings of the III Intern. Confer. of

858  Electrochemical Society Proceedings Volume 2004-24
2. V.P. Tolstoi. B.S. Zhuchkov. and I.V. Murin. Investigation of compounds of group III A and III B metals in the case of their air storage, Zhurn. Neorg. Mater., 36, 99–100, (2000).

3. A.J. Popov. G.E. Knudson. Preparation and Properties of the Rare Earth Fluorides and Oxyfluorides, JACS, 76, 3921–3922, (1954).

4. R.M. Savchuk. P.G. Nagornyi. N.M. Kompanichenko. and A.O. Omelchuk. Use of the molten NaPO₃ - V₂O₅ mixture in the differential thermal analysis of the interaction of rare-earth fluorides with zirconium, Ukr. Khim. Zhurn., 69, 71–74, (2003).

5. R.M. Savchuk. P.G. Nagornyi. N.M. Kompanichenko. and A.O. Omelchuk. Formation of compounds of zirconium in lower oxidation states in the Zr–ZrF₄ system, Ukr. Khim. Zhurn., 69, 26–29, (2003).

6. R.N. Savchuk. P.G. Nagornyi. N.M. Kompanichenko. and A.A. Omelchuk. Reduction of Rare–Earth Fluorides with Zirconium, Rus. J. Inorg. Chem., 48, 1454–1458, (2003).

7. K.A. Sense. C.A. Alexander. R.E. Bowman. R.B. Filbert. Jr. Vapor Pressure and Derived Information of the Sodium Fluoride–Zirconium fluoride System. Description of a Method for the Determination of Molecular Complexes Present in the Vapor Phase, J. Phys. Chem., 61, 337–344, (1957).

8. V.V. Serebrenikov. Chemistry of Rare–Earth Element. Vol. 2. (in Russian). University of Tomsk Publishers. Tomsk. (1961).

9. Ion–Selective Electrodes. (edited by R. Darts). (in Russian). Mir. Moscow. (1972).

10. W.J. Hamer. M.S. Malmberg. B. Rubin. Theoretical Electromotive Force for Cell Containing a Single or Molten Fluoride. Bromide or Iodide, J. Electrochem. Soc., 112, 750–754, (1965).

11. Powder Diffraction File Completed by the Joint Committee on Powder Diffraction Standards, American Society for Testing Materials (ASTM), Philadelphia, (1989).

12. F. Basile. E. Chassaing. G. Lorthioir. Synthesis of ZrCl₃. ZrCl₂. and ZrF₂: Non–Stoichiometry of ZrF₂, J. Less Com. Met., 98, 1–10, (1984).