INTERACTION OF RARE-EARTH FLUORIDES WITH ZIRCONIUM AND LEAD-SODIUM ALLOYS IN MOLTEN MIXTURES OF ALKALY METAL FLUORIDES

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This communication presents the results of studying the interaction of rare-earth halides (rare-earth elements (REE) – La, Pr, Nd, Gd, Dy and Yb) with zirconium and lead-sodium alloys in molten alkali halide mixtures. The investigation, have been carried out using differential thermal (DTA), X-ray phase and chemical analysis with thermodynamic assessment of the interaction of REE halides with reducing metals. The reducing metals (zirconium, sodium) react at elevated temperatures with the atmosphere, the rate of this interaction depending on temperature, the purity of the metal, the state of its surface and its fineness. For example, powdered zirconium begins to react with oxygen at a temperature as low as 180 °C and oxidizes at a high rate in the range 450-800 °C. Therefore, the DTA of reaction mixtures was performed in evacuated Stepanov quartz vessels or corundum crucibles using special protective fluxes or inert gases (arson, carbon dioxide). The investigation carried out showed that sodium metaphosphate-vanadium oxide mixture and zirconium dioxide-carbon mixture passes good protective properties. The protective flux $NaPO_3$-V_2O_5 has a low melting point (360 °C), protects well the original reaction mixture from atmospheric oxygen and does not react with its components. This is supported by DTA results. In the temperature range 400-680 °C, the reaction mixture retains a constant mass, and the DTA curves exhibit no effects of interaction with the components of the system under investigation. The protective mixture ZrO_2-C can be used in a wider temperature in investigation, which rule the DTA method.

It has been found by chemical analysis methods, that metallic zirconium interacts with REE fluorides, as a results of which the metal is reduced from its fluorides. 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. It has been found that the initial zirconium-REE fluoride, interaction temperature increases in a symbate manner with rising REE fluoride melting temperature. An exception among the fluorides investigated is praseodymium fluoride. 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 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:MF_3 ratio (where M=REE) 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%. Unlike fluorides, there is practically no interaction of zirconium with REE chlorides (up to 850 °C).

The reduction of REE fluorides by lead-sodium alloys begins in the range 145-170 °C. Lead-sodium alloys were fabricated by the electrolysis of molten sodium hydroxide on the lead cathode. Nickel was used as the anode.

It was noted that as in the case of reduction of REE fluoride by zirconium, the temperature at the onset of interaction with lead-sodium alloys rises with the MF_3 melting temperature.

The degree of reduction depends on the sodium content of the alloy and is the higher, the higher the sodium concentration.

Same characteristics of the reduction of REE fluorides by zirconium are listed in Table 1 and Table 2 .

Table 1

Results of the reduction of REE fluorides by zirconium and sodium at the ratio Zr:MF_3=1,5:1 (mol), and Na:MF_3(mol)=4:1, Na content of lead-sodium alloy 9%

Compound	*Melting tempera-ture, °C*	*Initial reduction temperature, °C*	
		Reduction by zirconium	*Reduction by sodium*
LaF_3	1390	490	170
PrF_3	1373	485	165
NdF_3	1413	475	160
GdF_3	1380	475	160
DyF_3	1360	470	155
YbF_3	1330	465	150

Table 2

Degree of the reduction of REE fluorides by zirconium and sodium at the ratio Zr:MF_3=1,5:1 (mol), and Na:MF_3(mol)=4:1, Na content of lead-sodium alloy 9%

Compound	*Degree of reduction,%*	
	By zirconium	*By sodium*
LaF_3	34.7	84.2
PrF_3	33.2	83.6
NdF_3	34.1	84.5
GdF_3	35.0	85.2
DyF_3	34.3	83.2
YbF_3	33.6	84.1