Solid−Liquid and Liquid−Vapor Equilibria in the Zr(Hf)Cl_4−$KAlCl_4$ Systems: A Basis for the Extractive Distillation Separation of Zirconium and Hafnium Tetrachlorides

Lev A. Niselson,*,[†] Egor A. Egorov,[†] Elena L. Chuvilina,[†] Oksana A. Arzhatkina,[‡] and Vladimir D. Fedorov[‡]

State Research and Design Institute for the Rare-Metals Industry, Bol'shoi Tolmachevskii per. 5, Moscow, 119017 Russia, and All-Russia Research Institute of Chemical Technology, Kashirskoe sh. 33, Moscow, 115230 Russia

The relative volatility $\alpha_{HfCl_4/ZrCl_4}$ in molten potassium chloroaluminate, $KAlCl_4$, has been determined using equilibrium Rayleigh vaporization from mixtures containing a 36 % mass fraction of $ZrCl_4$ + 1.4 % $HfCl_4$. At these component concentrations and at a temperature near 450 °C, the $ZrCl_4$ + $HfCl_4$ vapor pressure over the melt is close to atmospheric pressure. According to preliminary results, $\alpha_{HfCl_4/ZrCl_4} \approx 1.29 \pm 0.04$. The $ZrCl_4$−$KAlCl_4$ and $HfCl_4$−$KAlCl_4$ systems have been studied by visual thermal analysis. The results confirm that they are simple binary eutectic systems. According to our data, the eutectic temperature in the $ZrCl_4$−$KAlCl_4$ system is 519 K, and the eutectic is located at a $ZrCl_4$ mole fraction of 0.08. The $HfCl_4$−$KAlCl_4$ system has a eutectic at an $HfCl_4$ mole fraction of 0.171 with a melting point of 507.5 K.

Zirconium−hafnium separation via direct distillation of zirconium and hafnium tetrachlorides is possible only at elevated pressures, on the order of (2.5 to 3) MPa, in the relatively narrow liquid range of the tetrachlorides.[1,2] This is a major impediment to the practical use of this potentially attractive process. A possible alternative to the direct separation of $ZrCl_4$ and $HfCl_4$ is extractive distillation, a process that utilizes a low-melting solvent with a relatively low vapor pressure. Selecting an appropriate solvent and optimizing tetrachloride distillation conditions enables the separation process to be run at near atmospheric pressure.

To date, a variety of extractive distillation solvents have been proposed ($ZnCl_2$, $SnCl_2$, Na(K,Li)$AlCl_4$, Na(K,Li)$FeCl_4$, Na(K)$_2ZrCl_6$, other chlorides and their mixtures), and more than 50 patents related to the extractive distillation separation of zirconium and hafnium tetrachlorides have been issued. The most widely used solvent for the distillation separation of these chlorides is potassium chloroaluminate, $KAlCl_4$. In practice, the $KAlCl_4$−KCl eutectic, which is very close in composition to $KAlCl_4$ ($AlCl_3$/KCl = 1:1.04), is commonly used instead of pure $KAlCl_4$.

Despite the large number of related patents, the physicochemical aspects of the extractive distillation separation of zirconium and hafnium tetrachlorides have not yet been studied in sufficient detail, and some of the literature data are contradictory. In particular, various data have been reported for the single-stage separation factor or relative volatility, α, a key characteristic of the system. For example, $\alpha_{HfCl_4/ZrCl_4}$ in $KAlCl_4$ as the solvent is 1.5 according to Tangri et al.[3] and 1.18 according to Delons et al.[4]

The overall separation factor, A, for a distillation column is known to be a power-law function of relative volatility. At total reflux (reflux ratio $R = \infty$), the overall separation factor is $A = \alpha^N$, where N is the number of equilibrium stages (theoretical plates).

Let us compare the overall separation factors for the above α values. Taking $N = 25$, we obtain $A = 25\,250$ for $\alpha = 1.5$ and $A = 63$ for $\alpha = 1.18$. Therefore, even a small difference in α leads to a 400-fold increase in the separation factor. Clearly, at a finite reflux ratio, for example, at the optimal ratio R_{opt}, the difference in the separating power of the column will be smaller but nevertheless significant.

The above led us to undertake systematic studies of phase equilibrium in systems of Zr(Hf)Cl_4 with $KAlCl_4$-based solvents.

Materials and Methods

Special attention was paid to the purity and moisture protection of the chlorides. The volatile compounds $AlCl_3$, $ZrCl_4$, and $HfCl_4$ are very hygroscopic and readily hydrolyze. The chlorides were purified by distillation and then resublimed in tubes sealed off under vacuum. The $AlCl_3$ purity was 99.999 % on the basis of the metal content. The $HfCl_4$ content of the $ZrCl_4$ was below 0.003 %, and the $ZrCl_4$ content of the $HfCl_4$ was 0.008 %. We used compact pieces of the sublimates with as small a specific surface as possible. Potassium chloride (extra pure grade) was dried at (550 to 600) °C in a vacuum of (0.7 to 1.3) Pa. We synthesized $KAlCl_4$ and the $KAlCl_4$−KCl eutectic by melting appropriate chloride mixtures, and they were purified by directional solidification in tubes sealed off under vacuum while being heated. The inner diameter of the tubes was 16 mm, the melt height was about 120 mm, and the solidification rate was (2 to 2.5) $cm \cdot h^{-1}$. This purification process allowed us to obtain the exact compositions of $KAlCl_4$ and the $KAlCl_4$−KCl eutectic.

After purification and other preparation steps, the chlorides were stored in sealed glass tubes. All manipulations were carried out in glove boxes or polyethylene glove bags under dry nitrogen produced by liquid nitrogen evaporation from a Dewar.

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* Corresponding author. E-mail: lanhit@girmet.ru. Fax: +7-499-788-9964.

[†] State Research and Design Institute for the Rare-Metals Industry.

[‡] All-Russia Research Institute of Chemical Technology.

10.1021/je800299y CCC: $40.75

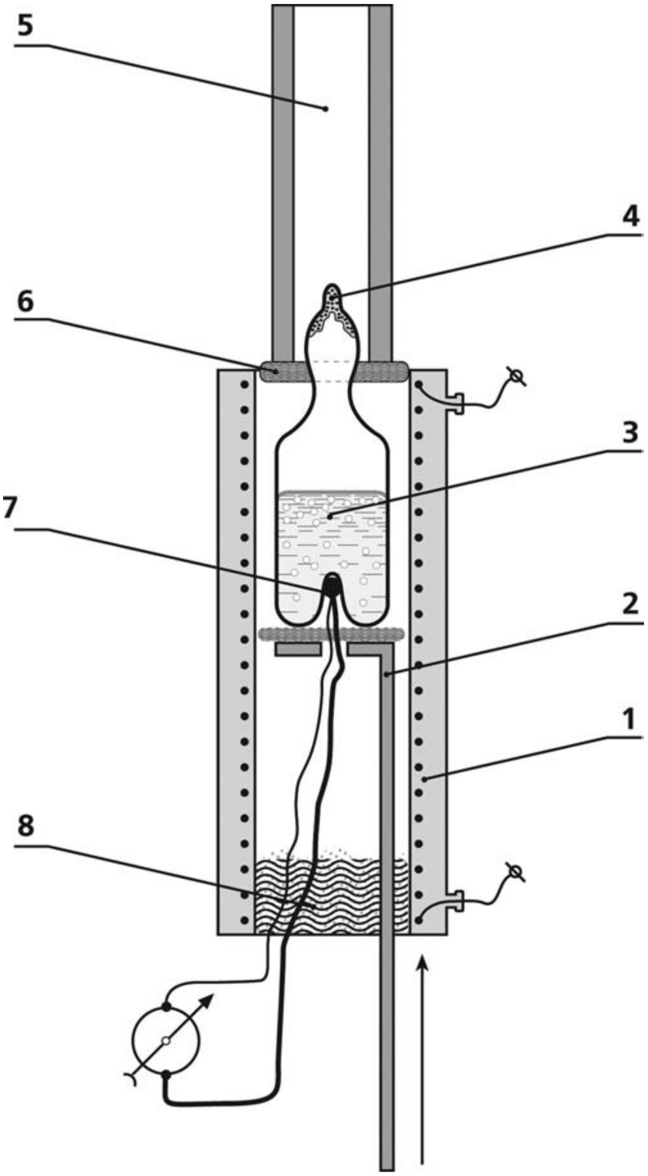

Figure 1. Schematic of the apparatus used to determine the relative volatility of $HfCl_4$ to $ZrCl_4$ in molten $KAlCl_4$: 1, tubular electric furnace; 2, ampule-translation rod; 3, ampule containing a mixture of $KAlCl_4$ and $ZrCl_4$ + 1.4 % $HfCl_4$; 4, $ZrCl_4$ sublimate enriched in $HfCl_4$; 5, aluminum cylinder; 6, heat-insulating gasket; 7, thermocouple; 8, mineral wool plug.

Relative Volatility of $HfCl_4$ to $ZrCl_4$ in Molten $KAlCl_4$

There are several techniques for determining the relative volatility of components. Details and critical evaluation of the existing techniques can be found elsewhere.[5]

The type of system under consideration is uncommon for vapor−liquid equilibrium because vaporization occurs from a liquid phase (melt), *L*, and the vapor, *V*, condenses to a solid phase (sublimate), *S*. Therefore, we deal with an $L \leftrightarrow V \rightarrow S$ process that ensures near-equilibrium Rayleigh distillation conditions. In addition, it offers technological advantages, simplifying experiments and eliminating countercurrent effects.

Figure 1 shows a schematic of the apparatus we used to determine $\alpha_{HfCl_4/ZrCl_4}$ for the vaporization of zirconium and hafnium tetrachlorides from the $KAlCl_4$ solvent. An ampule (3) charged with a chloride mixture and sealed off under vacuum was first mounted in a vertical tubular electric furnace having narrow slit windows on opposite sides for visual observation. After the chlorides had melted and the desired temperature had been reached, the melt was held for 1.5 h. Initially, we planned to use a nickel stirrer rotated by a magnetic field, but, after the addition of several milligrams of Al_2O_3, we observed sufficiently active convection in the melt, so there was no need for stirring. After holding, the ampule was lifted to a cold thick-walled aluminum cylinder (5) through a loose asbestos gasket by a rod (2). The ampule translation rate was about 1 $cm \cdot h^{-1}$, and the tetrachloride deposition time was (20 to 30) min. In a typical experiment, an ampule (13 to 14) mm in inner diameter, having a cylindrical body about 25 mm in length and a total volume on the order of 4 cm^3, was charged with (6 to 7) g of a mixture of $KAlCl_4$ and $ZrCl_4$, the latter containing ~ 1.4 % $HfCl_4$. We prepared the mixture by melting the chlorides, (100 to 120) g, in another ampule. To ensure chemical homogeneity of the mixture, the melt was cooled as rapidly as possible, and additional care was taken to prevent phase segregation.

Table 1. Liquidus Temperatures of Systems $ZrCl_4$−$KAlCl_4$ and $HfCl_4$−$KAlCl_4$ with Different Mass Fraction of $ZrCl_4$ ($HfCl_4$)

mass fraction of $ZrCl_4$ percent	temperature °C	mass fraction of $HfCl_4$ percent	temperature °C
0	256	0	256
3.64	253	8.20	251
6.83	249.5	13.6	246.6
7.20	245.8	19.4	242.0
12.2	258.5	25.0	235.8
17.7	288	29.1	254.6
27.5	322.5	34.4	278.0
38.9	346	43.3	307
54.5	385	52.7	335
66.2	397	66.8	373
72.5	411	74.5	390
85.7	423	83.3	406
100	438	100	432.0

In the first series of experiments, we used a eutectic $AlCl_3$ + KCl mixture (1:1.04 molar ratio) to which a 36 % mass fraction of $ZrCl_4$ + 1.4 % $HfCl_4$ was added. At this $ZrCl_4/KAlCl_4$ ratio, the tetrachloride vapor pressure reached 10^5 Pa at ~ 450 °C. It was at this temperature that we determined the relative volatility of zirconium and hafnium tetrachlorides in molten $KAlCl_4$. After each experiment, the ampule head, containing (0.15 to 0.2) g of the sublimate, was broken away from the ampule body. The tetrachloride sublimate and an average sample of the bottom residue were analyzed for Zr and Hf. To this end, samples were dissolved in (0.1 to 0.2) % HCl, and the Zr/Hf ratio was determined on a Varian Vista-PRO ICP-OES spectrometer.

Note that because the relative volatility calculation from analytical data utilizes the Zr/Hf ratio in the bottoms fraction divided by that in the sublimate there are special requirements on analytical accuracy. Systematic errors that remain unchanged in a given series of analyses do not distort the final result. The $ZrCl_4$ balance calculation indicated that in our experiments (6 to 8) % of the $ZrCl_4$ passed from the starting mixture to the overhead fraction (sublimate). This may have a significant effect on the Hf/Zr ratio in the bottom residue and was taken into account in the evaluation of the relative volatility of zirconium and hafnium tetrachlorides. From the results of six independent determinations, we obtained $\alpha_{HfCl_4/ZrCl_4} \approx 1.29 \pm 0.04$.

Liquidus Diagrams of the Zr(Hf)Cl_4−$KAlCl_4$ Systems

Phase diagram data are of key importance in devising new processes for mixture separation and processing. The liquidus relations in the $AlCl_3$−KCl system have been extensively studied[6] and have been described in at least eight independent reports. Most of the data agree reasonably well. In our opinion, the most reliable results have been obtained by Fisher and

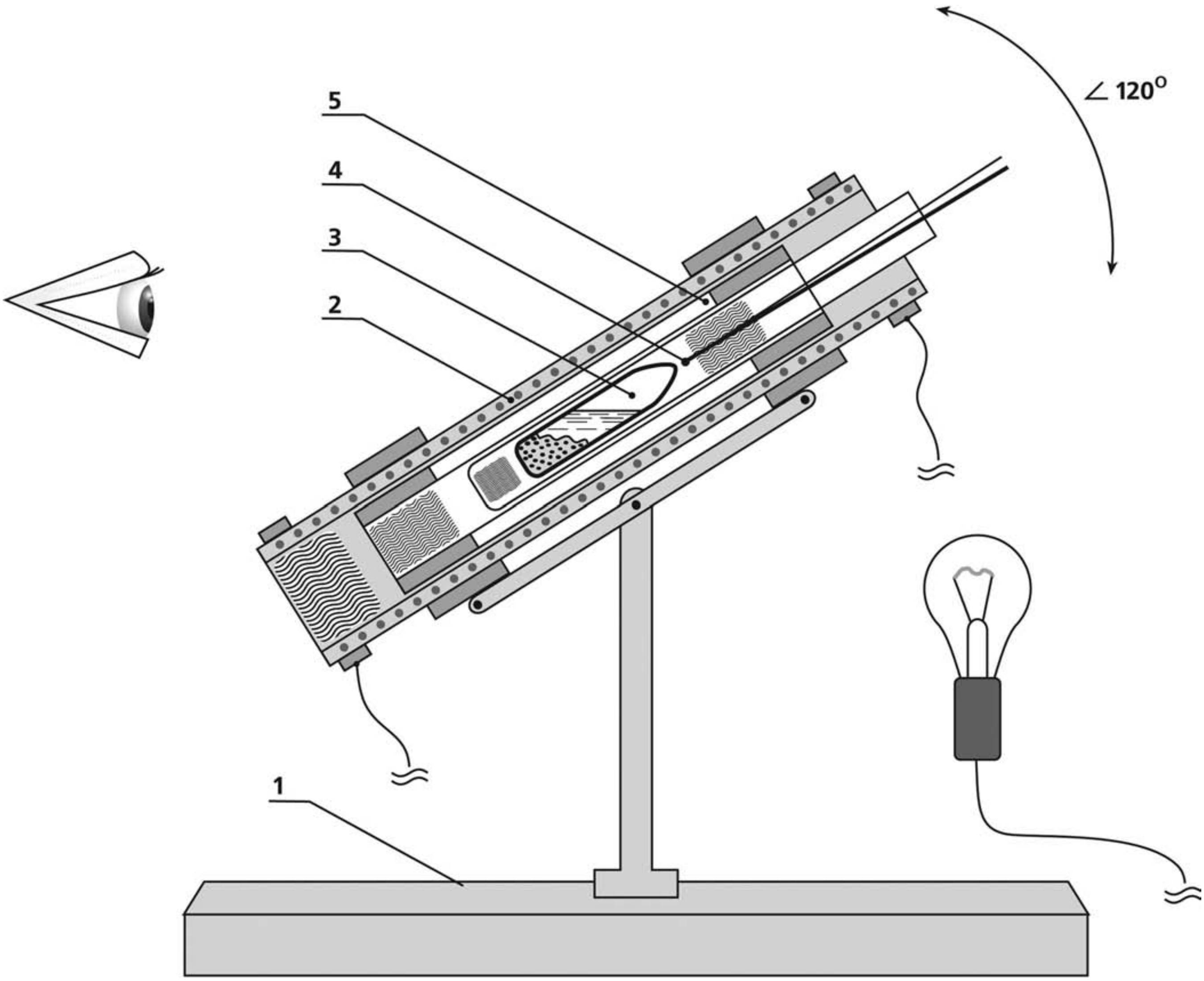

Figure 2. Schematic of the apparatus used to study the liquidus relations in the $ZrCl_4-KAlCl_4$ system: 1, support; 2, tubular electric furnace; 3, ampule containing a chloride mixture; 4, thermocouple; 5, aluminum cylinder.

Simon.[7] They noted a pronounced tendency for molten $KAlCl_4$ to supercool, which led them to supplement classic thermal analysis with visual observation of the melting behavior of the crystalline phase during heating. We studied the $Zr(Hf)Cl_4-KAlCl_4$ systems using visual thermal analysis. Note that this method, which is applicable in the case of transparent melts with low color intensity, gives near-equilibrium liquidus temperatures. This condition is met by almost all inorganic chlorides. Figure 2 shows a schematic of the apparatus used. An ampule (3) charged with a chloride mixture was introduced to a massive aluminum cylinder (5) having longitudinal slit windows for visual observation during heating and cooling. The cylinder was mounted in a transparent electric furnace (2) made of quartz tubes. The furnace was rocked 90° to 120° about the horizontal at a rate of 8 to 12 cycles per minute by an electric motor (not shown in Figure 3). The current through the furnace heater was thyristor-controlled so that the temperature could be varied at a rate as slow as 1 °C over (15 to 20) min or even slower. Coupled to melt agitation (via rocking), this ensured high accuracy in the obtained liquidus temperatures. $Zr(Hf)Cl_4-KAlCl_4$ samples were contained in evacuated Pyrex ampules of (9 to 10) mm in outer diameter and (1 to 1.2) mm in wall thickness, having a cylindrical body of (35 to 40) mm in length. An important point is that ampules of such dimensions withstand internal pressures above 10 MPa.

The liquidus relations in the binary systems $Zr(Hf)Cl_4-KAlCl_4$were recently studied by Trifonov and Medvedev.[8] In accordance with their results, the $ZrCl_4-KAlCl_4$ and $HfCl_4-$ $KAlCl_4$ systems were found in this study to be simple binary eutectic systems. At the same time, there are marked differences in quantitative characteristics between their and our results, as seen in Figure 3, which compares the $ZrCl_4-KAlCl_4$ phase diagram obtained in this study and that obtained by Trifonov and Medvedev.[8] In their phase diagram, the eutectic is located at a $ZrCl_4$ mole fraction of ~ 0.35 and melts at 453 K, whereas we obtained a $ZrCl_4$ mole fraction of ~ 0.08 and eutectic temperature of 519 K. Therefore, the difference in eutectic temperature between the two independent studies is 66 K, and the $ZrCl_4$ contents of the eutectic differ by a factor of almost 4.5. The differences are considerable for the binary system $HfCl_4-KAlCl_4$, too. According to Trifonov and Medvedev,[8] the eutectic is located at an $HfCl_4$ mole fraction of ~ 0.45 and melts at 476 K, whereas we obtained an $HfCl_4$ mole fraction of ~ 0.171 and eutectic temperature of 507.5 K. We suppose that these large discrepancies originate from the pronounced tendency for

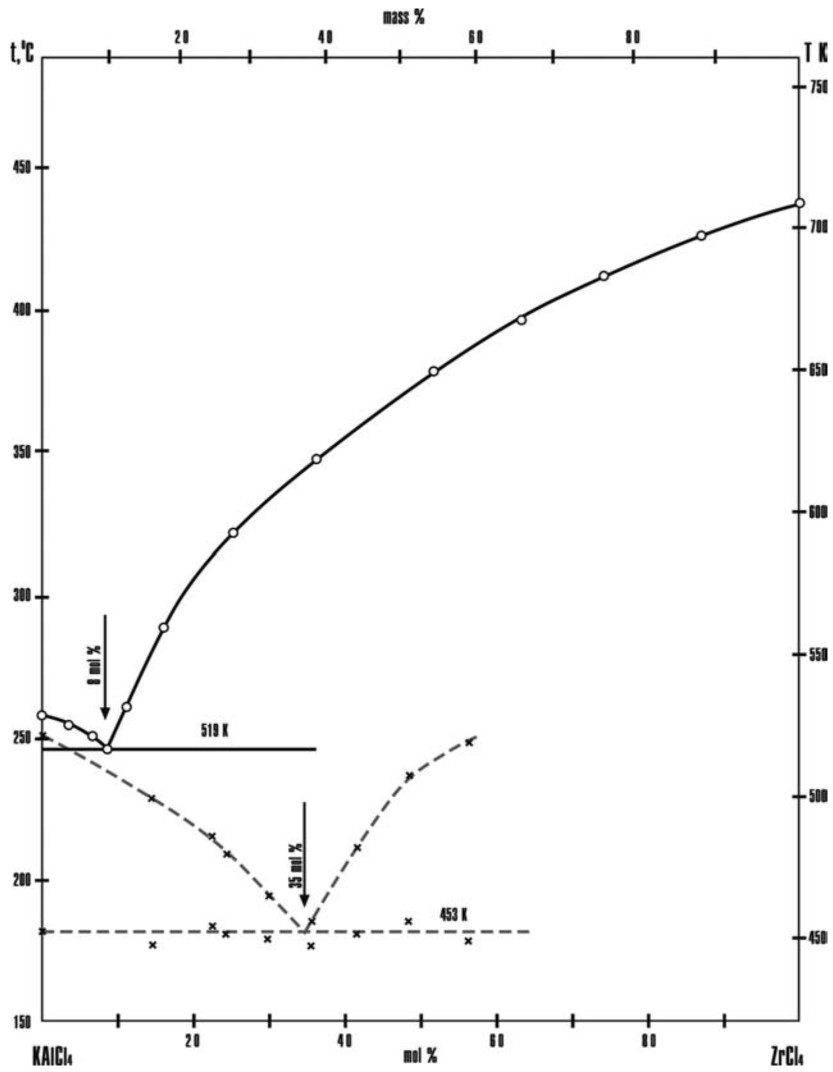

Figure 3. Liquidus diagram of the $ZrCl_4-KAlCl_4$ system. ○, this work; ×, ref 8.

liquid $KAlCl_4$ and $KAlCl_4$-containing melts to supercool. In the previous study,[8] the melt was superheated, and liquidus relations were inferred from cooling curves rather than from heating curves so that the supercooling effect was probably very strong.

Conclusions

The relative volatility, α, of hafnium and zirconium tetrachlorides in molten potassium chloroaluminate, $KAlCl_4$, was determined at about 450 °C and at a tetrachloride vapor pressure on the order of 10^5 Pa using equilibrium Rayleigh vaporization from a mixture containing a 36 % mass fraction of $ZrCl_4$ + 1.4 % $HfCl_4$. According to preliminary results, $\alpha_{HfCl_4/ZrCl_4} \approx 1.29 \pm 0.04$.

The $ZrCl_4-KAlCl_4$ and $HfCl_4-$ $KAlCl_4$ systems were studied by visual thermal analysis. The results confirm that they are simple binary eutectic systems. According to our results, the eutectic temperature in the $ZrCl_4-KAlCl_4$ system is 519 K, and the eutectic is located at a $ZrCl_4$ mole fraction of 0.08. The $HfCl_4-KAlCl_4$ system has a eutectic at an $HfCl_4$ mole fraction of 0.171 with a melting point of 507.5 K. In our studies, we took into account the pronounced tendency for liquid $KAlCl_4$ and $KAlCl_4$-containing melts to supercool.

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Received for review June 2, 2008. Accepted November 30, 2008.

JE800299Y