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Thermochromatographic studies of heavy actinides in metal columns

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Abstract

The adsorption of californium, einsteinium, and ferminium on polycrystalline titanium, iron, niobium, molybdenum, and tantalum was studied by the thermochromatographic technique. The adsorption behaviour of the actinides under study varied in dependence on the adsorbent metal. Enthalpies of adsorption evaluated from the experimental data are in correspondence with partial molar enthalpies of adsorption, which were calculated with a semi-empirical method.

1. Introduction

Since the heavy actinides beyond Es are available only in trace amounts, their predicted metallic state properties can be verified only indirectly. It has been found that the thermochromatographic deposition temperature and the enthalpy of adsorption evaluated from the data of thermochromatographic experiments correlate with the macroscopic heat of sublimation for many elements and several classes of compounds [1]. Using this correlation, the metallic divalency and information on the position of the f level of Fm and Md were deduced from the data of thermochromatographic experiments [2]. For more quantitative conclusions the extent of experimental data compiled up to now is not sufficient.

However, an exact theoretical description of the adsorption on metal surfaces would be necessary. To our knowledge, there exists no quantitative microscopic theory which aims at calculating the interaction between actinide adatoms and transition metal surfaces within quantum theory. Therefore we have applied the semi-empirical Miedema method for estimating the heats of formation of binary intermetallic compounds [3] to the adsorption of adatoms on metals [4, 5]. In the present work the adsorption of Cf, Es, and Fm on polycrystalline Ti, Fe, Nb, Mo, and Ta was studied by the thermochromatographic method. From the experimental data enthalpies of adsorption were evaluated and compared with partial molar enthalpies of adsorption which were calculated with the semi-empirical method.

2. Calculation of enthalpies of adsorption

The semi-empirical method for calculating enthalpies of adsorption [4] is based on the concept that the partial molar enthalpy of adsorption of a metal atom A on an adsorbent metal B at zero coverage, $\Delta\bar{H}_a$, is a function of the desublimation enthalpy of the adsorbed metal, ΔH_D°, and the partial molar net adsorption enthalpy $\Delta\bar{H}_{net}$. The net adsorption enthalpy can be deduced from the partial molar enthalpy of solution of A in B at infinite dilution, $\Delta\bar{H}_{Ls}$, and the displacement energy $\Delta\bar{H}_{displ}$ which is necessary for the formation of the solid solution. The displacement energy is a function of the vacancy formation energy in B and the effective atomic volumes of A and B in their solution. Empirical relations to the melting temperature were used to evaluate the vacancy formation energy. To evaluate the enthalpy of solution the semi-empirical Miedema method [3] was used.

An actual summary of input data and a detailed description of the method of calculation are given elsewhere [6].

3. Experimental details

The setup for thermochromatographic experiments and the procedure were very similar to those described earlier [2].

The actinides under study were obtained from the heavy actinide fraction of experiments carried out at the Unilac accelerator of the Gesellschaft für Schwerionenforschung to further investigate the chemical prop-

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erties of element 105 [7]. A few thousand atoms of ^{248}Cf, ^{252}Es, and ^{255}Fm, which were obtained among others by bombarding ^{249}Bk with ^{18}O ions, were used as the indicatory isotopes.

Nitric acid solutions of the actinides were evaporated in a tantalum boat. La was added as a reductant and up to 10% Al to lower the melting point. Then the boat was inserted into the chromatographic column in the starting position.

High-purity He 5.0 was used as a carrier gas. Immediately before flowing into the column the gas was purified by a Zr getter operating at 1200 K.

The inner surface of the open tubular thermochromatographic quartz columns with an inner diameter of 3 mm was lined with 25–50 μm thick foils of the adsorbent metals. In order to prevent reactions of the adsorbent metals with silica and oxygen from the quartz a Ta foil lining was placed between the quartz and the absorbent metal. The columns were conditioned by heating in He at 1400 K for 10 min.

A sharp chromatographic starting position was achieved by evaporating the actinides into a pre-column made out of Ti. At 1275 K the evaporated actinide atoms entered the thermochromatographic columns with the carrier gas.

The columns were held at working temperature for 30 min. The average temperature gradient was 21.7 K cm^{-1} and the linear gas velocity 28 cm s^{-1} at normal pressure and temperature. The distribution of the actinides along the thermochromatographic columns was measured off-line by alpha spectrometry in 1 cm sections.

4. Results and discussion

The thermochromatographic distribution of the actinides under study in Fe, Nb, and Ti columns are shown in Figs. 1–3 respectively. Table 1 summarizes thermochromatographic deposition temperatures, enthalpies of adsorption evaluated from the experimental data, and for comparison enthalpies of adsorption calculated for both the adsorption of actinide atoms ($\Delta \bar{H}_{a(M)}$) and the adsorption of actinide monoxides ($\Delta \bar{H}_{a(MO)}$) [8].

For a number of adsorbate/adsorbent combinations only lower limits are given, indicating that the actinides were adsorbed at the first contact with the column surface. In these cases the column temperature was too low for the desorption of the adsorbed actinides. But of course, reversibility of adsorption is a precondition for a chromatographic transport and hence the determination of thermodynamic functions from chromatographic data.

The strong and nearly uniform adsorption of Cf, Es, and Fm on Fe as shown in Fig. 1 we attribute to an

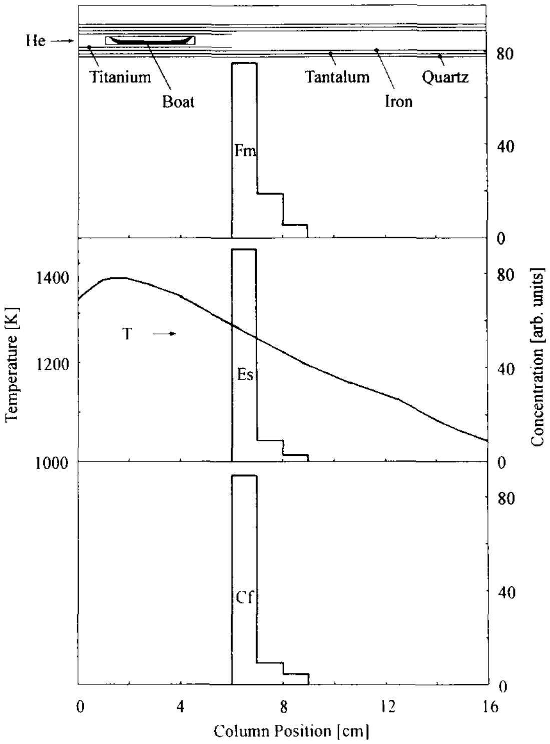

Fig. 1. Thermochromatograms of Cf, Es, and Fm in an iron column.

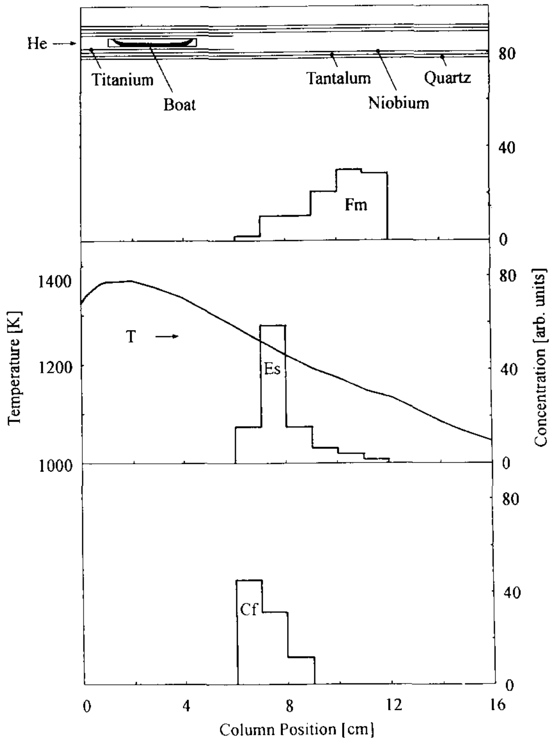

Fig. 2. Thermochromatograms of Cf, Es, and Fm in a niobium column.

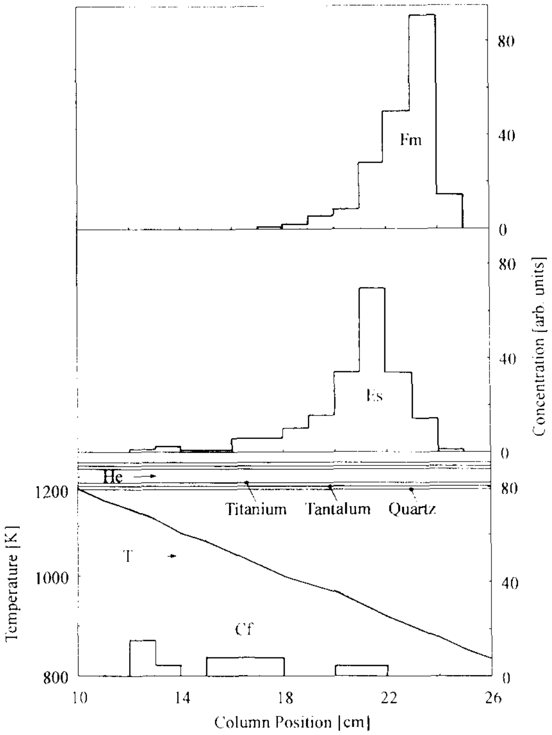

Fig. 3. Thermochromatograms of Cf, Es, and Fm in a titanium column.

oxide layer at the Fe surface. The surfaces of Mo, Nb, Ta, and Ti should remain metallic under the experimental conditions due to thermal desorption of surface contaminants or formation of solid solutions of oxygen. The actinides are expected to evaporate as free atoms from the molten La/Al alloy and to enter the chromatographic column in the atomic state. Therefore the actinide adsorption on Mo, Nb, Ta, and Ti can be considered as interaction between transition metal surfaces and actinide atoms. As seen from Fig. 2 and Fig. 3 for the case of Nb and Ti the actinides under study differ from each other in their adsorption behaviour. The interaction energy decreases from Cf to Fm. As follows from the experimental data, Nb in particular is a good column material for the gas chromatographic separation of the heavy actinides. In Ti columns the minimal temperature for the chromatographic transport of Es and Fm is lower. But the diffusion of Cf into the bulk of Ti is a disadvantage. Such behaviour has not been observed for Es and Fm. In former experiments using Ti modified with Ca only Am was lost by diffusion, whereas Cf was transported chromatographically with high yields. Cf was deposited at 760 K, at a lower temperature than Ca. This result was taken as evidence for the divalency of Cf in the metallic state [2]. The diffusion of Cf into the bulk of Ti under Ca-free conditions is not consistent with the divalency of Cf. Divalent Cf would be too large for this behaviour. The diffusivity of Cf in Ti indicates a volume contraction of Cf due to charge transfer from the Cf atoms to the Ti host under formation of trivalent Cf. There is further experimental evidence for the position of Cf at the borderline between di- and trivalent actinide metals.

On Ta and Mo the actinides are adsorbed much more strongly than on Nb and Ti. Therefore Ta and Mo are well suited for the preparation of thin alpha radiation sources by vapour deposition at high temperatures.

TABLE 1. Deposition temperatures of actinides in thermochromatographic metal columns and enthalpies of adsorption

Actinide (adsorbate)	Transition metal (adsorbent)	Deposition temperature, T_a (K)	Enthalpy of adsorption				
			Experimental $-\Delta\bar{H}_{a,exp}$ (kJ mol^{-1})	Calculated			
				$-\Delta\bar{H}_{a,(M)}$	(kJ mol^{-1})	$-\Delta\bar{H}_{a,chemis(MO)}$	(kJ mol^{-1})
				M(II)	M(III)	MO(II)	MO(III)
Cf	Ti	Diffusion	$(^{1}268,\ ^{2}162)$	283.4	206.9	462.4	385.9
	Fe	⩾1260	⩾309.5	351.4	285.9	320.4	254.9
	Nb	⩾1250	⩾298.2	349.4	372.8	468.4	491.8
	Mo	⩾1260	⩾308.2	403.6	442.2	464.6	503.2
	Ta	⩾1260	⩾302.3	360.0	380.5	509.5	671.1
Es	Ti	930	219.5	214.7		641.7	
	Fe	⩾1260	⩾309.5	288.2		505.2	
	Nb	1230	289.5	282.9		649.9	
	Mo	⩾1250	⩾301.6	340.8		649.8	
	Ta	⩾1260	⩾302.4	294.1		671.1	
Fm	Ti	890	210.3	210.4		610.4	
	Fe	⩾1255	⩾305.9	271.1		461.1	
	Nb	1160	269.5	265.8		605.8	
	Mo	1225	291.0	313.6		595.6	
	Ta	1200	277.5	275.1		625.1	

As seen from Table 1 in the case of reversible adsorption there is a good agreement between experimental and theoretical enthalpies of adsorption calculated for the case of adsorption of actinide atoms ($\Delta \bar{H}_{a(M)}$). The limiting values for the adsorption on Fe, which are distinctly higher as the calculated $\Delta \bar{H}_{a(M)}$ values, suggest an adsorption of actinide monoxides. This corresponds to the interpretation given above on the basis of macroscopic properties. In all other cases the limiting values may be interpreted with both the adsorption of actinide atoms and the adsorption of monoxides.

Of course, without confirmation the experimental enthalpies of adsorption cannot be used to verify the results of the semi-empirical calculations. Unfortunately, experimental data on the adsorption of actinides on metal surfaces available up to now are very limited. More experimental actinide adsorption studies are needed. It would be interesting to conduct thermochromatographic experiments at higher temperatures. Complementary methods like thermal desorption spectroscopy should be applied to confirm the results of the thermochromatographic studies.

However, the results presented here show again that thermochromatography in metal columns is a promising technique for the fast separation of heavy actinides and the characterization of their metallic state properties.

Acknowledgments

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