THERMODYNAMICS OF FORMATION OF GERMANIDES OF THE HEAVY RARE EARTH METALS

Sidorko V.R.
I.M. Frantsevich Institute for problems of material sciences NAN Ukraine
03680, Kiev-142, Krzhyzhanovskii str. 3, Ukraine, E-mail: korniy@ipms.kiev.ua

The thermodynamics properties of alloys of heavy rare earth with germanium are studied insufficiently comparing with the corresponding phase diagrams data. Liquid alloys in the R–Ge systems have been studied only for the germanium rich composition (exceptionally the Y–Ge system). For the systems with known concentration dependences of the thermodynamic functions (Y, Gd, Ho, Er)–Ge, when going toward the compounds with highest content of R–element the negative values of $\Delta_f G^o$ ($\Delta_f H^o$) increase steadily, reaching extremal values at 5:3 ratio. For these systems the R_5Ge_3 compounds have the highest melting temperatures and are the only congruently melting ones. The known formation enthalpy data for the same formula germanides R_5Ge_3 are approximately the same for the compounds of cerium group metals, whereas for the yttrium group there is a marked increasing of the heat effects along the row from Gd to Lu [1]. The formation enthalpy value for the Y_5Ge_3 is close to the same value for the Ho_5Ge_3 (Table 1). Apparently, the $\Delta_f H$ (298,15 k) for the germanides Gd_5Ge_3 and Tb_5Ge_3 seem to be slightly lower.

Table 1

Formation enthalpies of lowest germanides the rare earth of Y-group

Germanide	$-\Delta_f H^o$(298,15 K), kJ/mol of at.
Y_5Ge_3	89,8 ± 5,0
Gd_5Ge_3	82,0 ± 2,6
Tb_5Ge_3	81,7 ± 2,7
Dy_5Ge_3	92,4 ± 2,3
Ho_5Ge_3	91,8 ± 1,7
Er_5Ge_3	95,6 ± 2,0
Tm_5Ge_3	91,3 ± 1,9
Lu_5Ge_3	93,1 ± 2,2

The thermodynamic characteristics of formation of highest germanides of the rare earth of the Y-group by calorimetric methods have not been studied; however, for the systems Ge–(Y, Gd, Ho, Er) these data were obtained by us by the electromotive forces method [1-3]. The values of $\Delta_f H^o$ for the compounds RGe_m, being in equilibrium with the solid germanium one can compute from limiting enthalpies of dissolution of the rare earth in liquid germanium. if one suggest the $\Delta\overline{H}_R$ in the two-phase field [RGe_m + Ge] is equal to $\Delta\overline{H}^{\infty}_R$ in liquid germanium. The values of $\Delta_f H$ for highest germanides of the rare earth of Y-group, calculated by this way, are listed in Table 2.

Table 2

Formation enthalpies of highest germanides of the rare earth of Y-group

R	$-\Delta\overline{H}^{\infty}_{R(Ge)}$ kJ/mol of at [4]	RGe_m	$-\Delta_f H(RGe_m)$, kJ/mol of at.	
			calculated	experiment
Y	258±13 176±6	$YGe_{1,7}$ $YGe_{1,7}$	95,6±4,8 65,2±2,2	77,8±3,4
Gd	241±15	$GdGe_{1,63}$	91,6±5,7	82,9±3,4
Tb	232±16	$TbGe_2$	76,6±5,3	
Dy	214±14	$DyGe_{2,7}$	57,8±3,8	
Ho	196±14	$HoGe_{2,7}$	52,9±3,8	53,8±1,3
Er	213±11	$ErGe_{2,5}$	60,9±3,1	59,6±0,9
Tm	200±15	$Tm_{0,9}Ge_2$	62,1±4,7	
Lu	190±7,4	$LuGe_{1,8}$	67,8±2,6	

For Tm metal the value $\Delta\overline{H}^{\infty}_{Tm(Ge)}$ is not measured in experiments, so, it was estimated by interpolation. The calculated formation enthalpies for compounds $HoGe_{2,7}$ and Er_2Ge_5 are very close to the experimental data, and are in agreement for the $GdGe_{1,63}$ within estimated error bars. Significant discrepancies of the experimental $\Delta\overline{H}^{\infty}_{Y(Ge)}$ data does not allow to conclude a degree of agreement between the experimental and calculated $\Delta_f H^o$ value for the germanide $YGe_{1,7}$.

[1] Сидорко В.Р., Буланова М.В., Мелешевич К.А. // Современные проблемы физического материаловедения. – Киев: ИПМ НАН Украины, 2005. – С. 28-41.
[2] Гончарук Л.В., Сидорко В.Р., Обушенко И.М. // Порошковая металлургия. – 2012. – № 5/6. – С. 100-105.
[3] Сидорко В.Р., Гончарук Л.В. // Порошковая металлургия. – 2008. – № 11/12. – С. 99-104.
[4] Сидорко В.Р., Полоцкая Р.И. // Термодинамика металлических сплавов. – Киев: ИПМ НАН Украины, 1994. – С. 71-102.