Thermodynamic properties of Pt₅La, Pt₅Ce, Pt₅Pr, Pt₅Tb and Pt₅Tm intermetallics

K T JACOB¹* and Y WASEDA²

¹Department of Metallurgy, Indian Institute of Science, C V Raman Avenue, Bangalore 560012, India
²Institute of Mineral Dressing and Metallurgy (SENKEN), Tohoku University, Sendai 980, Japan

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Abstract. The Gibbs' energies of formation of Pt₅La, Pt₅Ce, Pt₅Pr, Pt₅Tb and Pt₅Tm intermetallic compounds have been determined in the temperature range 870–1100 K using the solid state cell:

Ta, M + MF₃/CaF₂/Pt₅M + Pt + MF₃, Ta.

The reversible emf of the cell is directly related to the Gibbs' energy of formation of the Pt₅M compound. The results can be summarized by the equations:

\[ \Delta G_f^{\circ} (\text{Pt}_5\text{La}) = -373,150 + 6.60T \pm 300 \text{ J mol}^{-1} \]
\[ \Delta G_f^{\circ} (\text{Pt}_5\text{Ce}) = -367,070 + 5.79T \pm 300 \text{ J mol}^{-1} \]
\[ \Delta G_f^{\circ} (\text{Pt}_5\text{Pr}) = -370,540 + 4.69T \pm 300 \text{ J mol}^{-1} \]
\[ \Delta G_f^{\circ} (\text{Pt}_5\text{Tb}) = -372,280 + 4.11T \pm 300 \text{ J mol}^{-1} \]
\[ \Delta G_f^{\circ} (\text{Pt}_5\text{Tm}) = -368,230 + 4.89T \pm 300 \text{ J mol}^{-1} \]

relative to the low temperature allotropic form of the lanthanide element and solid platinum as standard states. The enthalpies of formation of all the Pt₅M intermetallic compounds obtained in this study are in good agreement with Miedema's model. The experimental values are more negative than those calculated using the model. The variation of the thermodynamic properties of Pt₅M compounds with atomic number of the lanthanide element is discussed in relation to valence state and molar volume.

Keywords. Platinum–lanthanide intermetallic compounds; Gibbs' energy of formation; enthalpy of formation; entropy of formation; systematics.

1. Introduction

The platinum-rich intermetallic compounds of lanthanide elements are of interest from the practical as well as the theoretical point of view. It is known (Bronger 1967) that the oxides of most lanthanide elements can be reduced in the presence of platinum by dry hydrogen or ammonia at temperatures above 1473 K resulting in the formation of Pt₅M compounds, where M represents a lanthanide element. This points to the very high stability of the intermetallic phases. Based on the experimental observation of Bronger (1967), Wengert and Spanoudis (1974) have estimated the upper limit on the Gibbs' energy of formation of some Pt₅M compounds. It is possible to recover some lanthanide metals from the Pt₅M intermetallics by sublimation at higher temperatures. In order to compute the optimum temperatures for the recovery of the lanthanides more accurate thermodynamic data are required.

*For correspondence.
All the rare earth elements except perhaps Ce can be described by a localized $4f$ (core) electron model. Except for the elements Eu and Yb which are divalent in their elementary metallic state, other rare earth metals are trivalent. They can be treated as having three conduction electrons per atom and $M^{3+}$ ionic cores. Platinum forms a series of intermetallic compounds with each lanthanide metal (Iandelli and Palenzona 1981; Moffatt 1985; Massalski 1986). The compound with the highest concentration of Pt has the formula $Pt_3M$ for $M$ ranging from La to Tm. For Yb and Lu the compound having the highest concentration of Pt is $Pt_3M$, which has the $Cu_3Au$ structure (Bronger 1967; Moffatt 1985; Massalski 1986). $Pt_3M$ compounds containing the lighter lanthanides crystallize in the hexagonal $CaCu_3$ structure (Bronger 1967). For $M=Sm$, Eu and Gd the structure is similar, but the powder pattern contains more reflections. The structure has rhombic symmetry (Bronger 1967). A further small change in structure occurs at Tb. The lanthanide contraction is manifested by the shrinkage in the $a$- or the $a$- and $b$-axes, whereas the $c$-axis becomes larger. The crystal structures of $Pt_5M$ compounds containing the heavier rare earth metals have not been fully elucidated.

Since the literature does not contain any report about thermodynamic measurements on $Pt_5M$ compounds containing lanthanides, solid state galvanic cell measurements were undertaken on systems containing La, Ce, Pr, Tb and Tm in the temperature range 870–1100 K. The galvanic cell had the configuration represented by

$$Ta, M + MF_3/CaF_2/Pt_5M + Pt + MF_3, Ta \quad (\text{cell 1}).$$

Single crystal $CaF_2$ was used as the solid electrolyte and Ta wire as the electrical lead to the electrodes. The emf of cell I directly gives the Gibbs' energy of formation of $Pt_5M$ without the use of any auxiliary data. The Gibbs' energies of formation of $Pt_5M$ compounds ($M=Nd, Sm, Eu, Gd, Dy, Ho, Er$) have been measured recently (Jacob and Waseda 1990).

2. Experimental

2.1 Materials

The purity of the starting materials was 99-9% for the lanthanide metals and 99-99% for Pt. The $Pt_5M$ intermetallic compounds were prepared both by arc melting on a water-cooled copper hearth ($M=\text{Tb}, \text{Tm}$) and by solid state reaction of powders under prepurified argon ($M=\text{La}, \text{Ce}, \text{Pr}$). High purity argon was further dried over $P_2O_5$ and deoxidized by passage through granules of Ti at 1173 K. The alloy buttons were remelted two or three times to ensure homogeneity. Weight losses were found to be negligible. The final composition of the compounds were confirmed by chemical analysis. In the powder technique synthesis, an intimate mixture of metal powders in the required ratio was pressed into pellets and sealed under high purity argon in a molybdenum crucible. The crucible was heated under argon to a temperature of 1000 K. The reactions were exothermic. The intermetallic compounds were annealed under high vacuum at 1100 K for 300 ks. Formation of the $Pt_5M$ compounds was confirmed by X-ray diffraction. Single crystals of $CaF_2$ of 99-999% purity were obtained from the Harshaw Chemical Company. The lanthanide fluorides used in the electrodes were of 99-9% purity.