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THE PHASE DIAGRAM OF THE Ce-Sn SYSTEM UP TO 50 AT.% Sn

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The phase diagram of the Ce-Sn system was investigated in the 0–50 percent tin composition range, using differential thermal, X-ray and metallographic analyses. Four intermediate phases were found in this range: Ce_3Sn (940 °C), Ce_5Sn_3 (1505 °C), Ce_5Sn_4 (1510 °C) and $Ce_{11}Sn_{10}$ (~1400 °C). One of them melts congruently: Ce_5Sn_4.

A eutectic and a eutectoid equilibrium were found at 725 °C, ~4 at.% Sn and 690 °C, ~2 at.% Sn, respectively.

The undercooling effects of the high temperature phases (5:3, 5:4 and 11:10) are pointed out. A slight solid state solubility was found for the Ce_5Sn_3 phase.

The rare earths (R) represent in the Periodic Table an outstanding family of elements with properties smoothly changing with the atomic number. The study of the rare earth intermetallic compounds represents an important part of the more general problem of the metallic phases. It is well known that R are usually present in the trivalent state; however, ionic compounds which contain lanthanides with valence 2 or 4 have been known for a long time. The anomalous valence states are due to the stability of certain 4f electronic configurations, namely $4f^0$, $4f^7$ and $4f^{14}$. In particular the different modifications of cerium metal exhibit the phenomenon of intermediate valence under various conditions of pressure and temperature, assuming the valence four at the pressure of about 5 GPa [1]. In the intermetallic compounds Ce may behave as a mixed valence element (i.e. with valence intermediate between 3 and 4) fixed or variable with temperature and pressure. One of the most studied mixed valence intermetallic compounds is $CeSn_3$ [2, 3]. In the oldest equilibrium phase diagram, where only three compounds of uncertain stoichiometry were detected, such a compound was not found [4]. At present nine different intermediate phases are known, but the crystal structure is not fully determined for all of them [5] and the phase diagram ought to be redetermined to account for the existence of the new phases. Moreover it would be interesting to examine completely the Ce–Sn phase diagram, beginning from the Ce-rich region in order to evidence possible differences in the constitution of this system in the

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thermal slope, stoichiometry or in the crystal structure of some phases with respect to those formed by the trivalent lanthanides.

In the present work, thermal, crystallographic and microhardness results obtained in the study of the phase diagram Ce–Sn up to 50 at.% Sn are reported.

Experimental

Cerium (Koch–Light; nominal purity 99.95%) and tin (Koch–Light; 99.999% pure) were used as starting materials. The samples (each consisting of about 1 g of a stoichiometric mixture of the elements) were sealed in molybdenum crucibles under pure argon and were melted a number of times in an induction furnace while being carefully shaken to ensure homogeneity.

Differential thermal analysis (DTA) was performed on both heating and cooling as described previously [6]. In some cases additional thermal treatments were applied.

The alloys were homogeneous and had a grey metallic lustre. They were extremely pyrophoric, oxidized readily in the whole range of composition studied and were brittle at tin contents of 20–50 at.% Sn. After conventional polishing under inert gas the sample were etched in air. The microhardness of the metallographic specimens was determined by the Vickers' method using a Leitz Durimet hardness tester (applied loads: 25 g and 50 g), allowing a first partial identification of the phases that were present.

The crystal structures of the phases were investigated by the X-ray powder method and by single-crystal analysis using Mo K_α, Cu K_α, and Fe K_α radiations. The intensity calculations for the powder patterns were performed using the Lazy Pulverix program [7].

Results and discussion

Figure 1 shows the partial (0–50 at.% tin) phase diagram of the Ce–Sn system derived from DTA, X-ray analysis and metallography. One eutectic equilibrium, one eutectoid equilibrium and four compounds are formed in this range of composition and the corresponding crystallographic and thermal data are listed in Table 1.

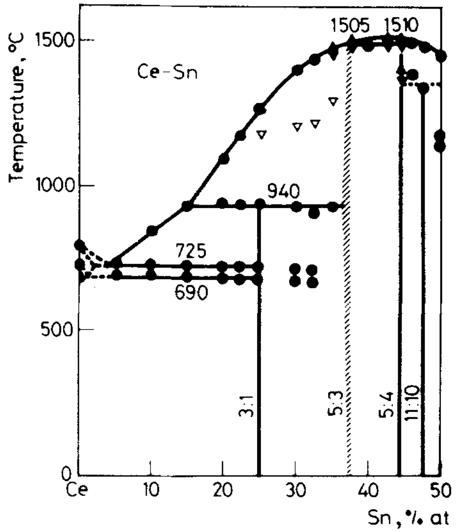

Fig. 1 The cerium-tin system from 0 to 50 at.% Sn: ▲, thermal effects observed on heating; ▼, thermal effects observed on cooling; ▽, faint thermal effects observed on cooling; ●, thermal effects observed on both heating and cooling

Table 1 Thermal, structural and microhardness data for Ce–Sn alloys

Composition	*T*, C	Structure type (Pearson's symbol)	Lattice parameters, Å* *a*	*b*	*c*	HV**, $kg_f mm^{-2}$	Ref.
Ce_3Sn	940	cP4 $AuCu_3$	4.927 (4)			170	t.w.
Ce_3Sn disordered?	—	cF4 Cu	5.01 (1)			—	t.w.
Ce_5Sn_3 h.T.	1505	hP16 Mn_5Si_3	9.330		6.790		8
Ce_5Sn_3 l.T.	—	tI32 Si_3W_5	12.599 (9)		6.179 (7)	330	t.w.
			12.591		6.174		11
Ce_5Sn_4	1510	oP36 Ge_4Sm_5	8.348 (9)	16.03 (2)	8.492 (9)	400	t.w.
			8.337	16.05	8.480		10
$Ce_{11}Sn_{10}$	1400	tI84 $Ge_{10}Ho_{11}$?	12.20		17.90	400	t.w.
$Ce_{.98}Sn_{.02}$	690	eutectoid				80	t.w.
$Ce_{.96}Sn_{.04}$	725	eutectic					t.w.

* Evaluated standard deviations are given in parentheses.

** Accuracy, 10%; applied loads, 25 g and 50 g.

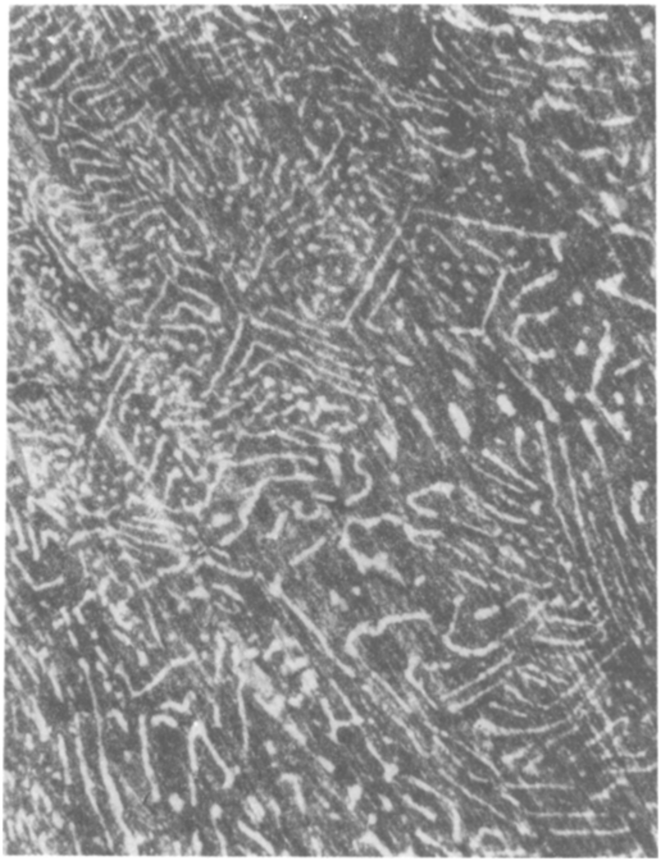

Fig. 2 Micrograph of a Ce–5 at.% Sn alloy after differential thermal analysis showing the eutectoid equilibrium between γ-Ce and Ce_3Sn (white areas). Etched in air. Magnification, 500 ×

Cerium rich alloys

The solid solubility of tin in γ-cerium is negligible (less than 0.5 at.% Sn) as the lattice constant of the pure metal does not change significantly on alloying with tin. The solubility of tin in δ-cerium was not investigated.

The addition of tin to cerium lowers its melting temperature to $725 \pm 5^\circ$ and the $\delta = \gamma$ transition temperature to $690 \pm 5^\circ$. The eutectic point occurs at 725° and ~4 at.% Sn (Figure 2).

Intermediate phases

Ce_3Sn forms peritectically at 940 ± 5°. No thermal effect was detected that could be ascribed to an order-disorder transformation of the Ce_3Sn and the anti $AuCu_3$ crystal structure is confirmed at room temperature on the stoichiometric composition. However, the powder photographs of samples of composition around 25 at.% Sn showed the presence of lines (not belonging to the adjacent phases) that can be inputed to a cubic phase (a = 5.01 Å) in agreement with that found by Borzone et al. [5]. Work is in progress to check if thermodynamic conditions exist under which such a disordered phase can be stabilized and obtained in pure form.

The Ce_5Sn_3 and Ce_5Sn_4 phases form at very similar temperatures so that it is quite difficult to decide only by DTA which of them forms peritectically.

Moreover, in this region of composition up to the $Ce_{11}Sn_{10}$ phase, large (a 50° undercooling effect was not uncommon) undercooling effects were observed.

However, the micrographic analysis suggests that Ce_5Sn_3 forms peritectically (1505 ± 5°) while Ce_5Sn_4 melts congruently (1510 ± 5°).

Although high-temperature Ce_5Sn_3 [8, 9] is confirmed on quenched samples by X-ray analysis, no clear thermal effect corresponding to the $\alpha \rightleftharpoons \beta$ transformation was observed. The thermal effects (V) detected only on cooling in the composition range 25–35 at.% Sn that could suggest a transformation, or an extended high temperature solid solution, or also a contamination due to the Mo crucible, are at present left unexplained. A slight solid solubility of low-temperature Ce_5Sn_3 was detected on X-ray powder patterns.

A peritectic equilibrium corresponding to the formation of the $Ce_{11}Sn_{10}$ phase was also detected at about 1400°. The crystal structure is certainly related to the $Ge_{10}Ho_{11}$ [10], but the indexing of the powder patterns on the basis of this structural type, although possible, is not satisfactory. We are performing a complete single crystal analysis to solve this problem. More work is in progress on pure phases to study their magnetic and electrical properties, in order to ascertain the valence state of Ce in intermetallic compounds with tin.

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Zusammenfassung — Das Phasendiagramm des Systems Ce—Sn wurde im Bereich von 0—50% Zinn mittels DTA, Röntgendiffraktometrie und metallographischer Analyse untersucht. Vier intermediäre Phasen wurden in diesem Bereich gefunden: Ce_3Sn (940 °C), Ce_5Sn_3 (1505 °C), Ce_5Sn_4 (1510 °C) und $Ce_{11}Sn_{10}$ (~1400 °C). Eine von diesen (Ce_5Sn_4) schmilzt kongruent. Ein eutektisches und ein eutektoides Gleichgewicht wurden bei 725 °C (4 Atom-% Sn) bzw. 190 °C (2 Atom-% Sn) festgestellt. Auf die Unterkühlungseffekte der Hochtemperaturphasen 5 : 3, 5 : 4 und 11 : 10 wird eingegangen. Eine sich in Grenzen haltende feste Lösung wurde in der Ce_5Sn_3-Phase gefunden.

Резюме — Используя дифференциальный термический анализ, рентгеноструктурный и металлографический анализы, исследована фазовая диаграмма системы Ce—Sn в области содержания олова 0—50%. Обнаружены четыре промежуточные фазы состава Ce_3Sn (940°), Ce_5Sn_3 (1505°), Ce_5Sn_4 (1510°) и $Ce_{11}Sn_{10}$ (~1400°), из которых третья конгруэнтно плавится. При 725° и около 4 атомных % олова, а также при 690° и около 2 атомных % олова установлено, соответственно, эвтектическое и эвтектоидное равновесия. Для высокотемпературных фаз (5 : 3, 5 : 4 и 11 : 10) отмечены эффекты переохлаждения, а для фазы 5 : 3 обнаружена еще незначительная твердотельная растворимость.