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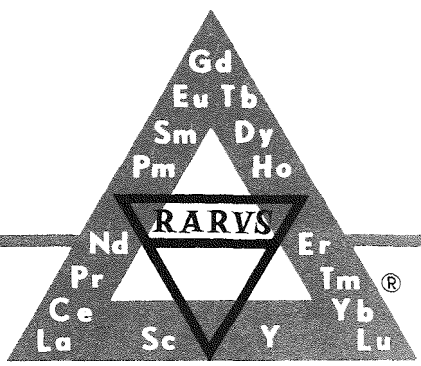

SELECTED CERIUM PHASE DIAGRAMS

Karl A. Gschneidner, Jr. and Mary E. Verkade

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INTRODUCTION

Considerable work has been accomplished on the phase relationships of cerium alloys since the 1950's. The results, however, are generally widely scattered through the technical literature and often do not appear in suitable form for metallurgical use.

This report represents a compilation of cerium alloy phase equilibria data based on the most reliable information available. The binary systems selected are those of cerium with each of the following twenty-nine elements which might be commonly found in steels: Al, Sb, As, Bi, Ca, C, Cr, Co, Cb (Nb), Cu, Fe, Pb, Mg, Mn, Mo, Ni, N, O, P, Se, Si, Ag, S, Te, Sn, Ti, W and Zn. A brief discussion, a summary of crystal lattice parameters where applicable, and a list of references is included for each element surveyed.

PHASE DIAGRAMS

Where the equilibrium relationships have been reasonably well established, the phase diagram is presented in two forms — temperature in °C vs. atomic percent and weight percent, respectively. The Ce-rich portions of the diagrams have been adjusted to reflect the most accurate melting point and $\gamma \rightarrow \delta$ transformation temperatures of cerium currently available.[801] When this correction has exceeded 5°C, an explanatory note is included in the discussion.

Based on our experience, rare earth phase diagrams determined prior to World War II are, for the most part, unreliable. In as much as these data can, in many instances, lead to erroneous conclusions, we believe that to include them in this critical review would be a disservice to the scientific community. However, for completeness, references to the earlier work or to pertinent reviews are included in the bibliography.

CRYSTAL DATA

When two or more references have been cited for a given alloy structure, the crystal lattice parameters represent an average value and the error limits indicate the maximum observed deviation from the average value. Lattice constants containing less than three significant figures to the right of the decimal were generally not included in the averages except when they represented the greatest degree of accuracy available. Error limits should be interpreted as follows:

$$6.078 \pm 8 \equiv 6.078 \pm 0.008$$

$$6.165 \pm 10 \equiv 6.165 \pm 0.010$$

REFERENCES

The reference numbers used herein correspond to those of the Molycorp referencing system.

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CERIUM – ALUMINUM

PHASE DIAGRAM

Buschow and van Vucht[802] examined the Ce-Al system between 60 and 100 a/o Al (22 and 100 w/o Al) by means of thermal, metallographic and X-ray analyses using 99.99% pure Al and 99.9% pure Ce. The Ce contained primarily La, Pr and Nd as impurities. In Figures 1a and 1b, their results are combined with previously published data for alloys of 0 to 60 a/o Al (0 to 22 w/o Al) as reviewed by Gschneidner.[803] Of the five compounds identified, Ce_3Al and $CeAl_2$ form congruently, CeAl and Ce_3Al_{11} form peritectically, and $CeAl_3$ forms peritectoidally. The aluminum-rich compound which was previously reported to have the $CeAl_4$ stoichiometry[803-4] actually has the Ce_3Al_{11} composition.[805] The $\alpha \rightleftarrows \beta$ transformation observed for Ce_3Al at 250°C is further confirmed by electrical resistance techniques.[802] Buschow and van Vucht[805] have noted that C, but not

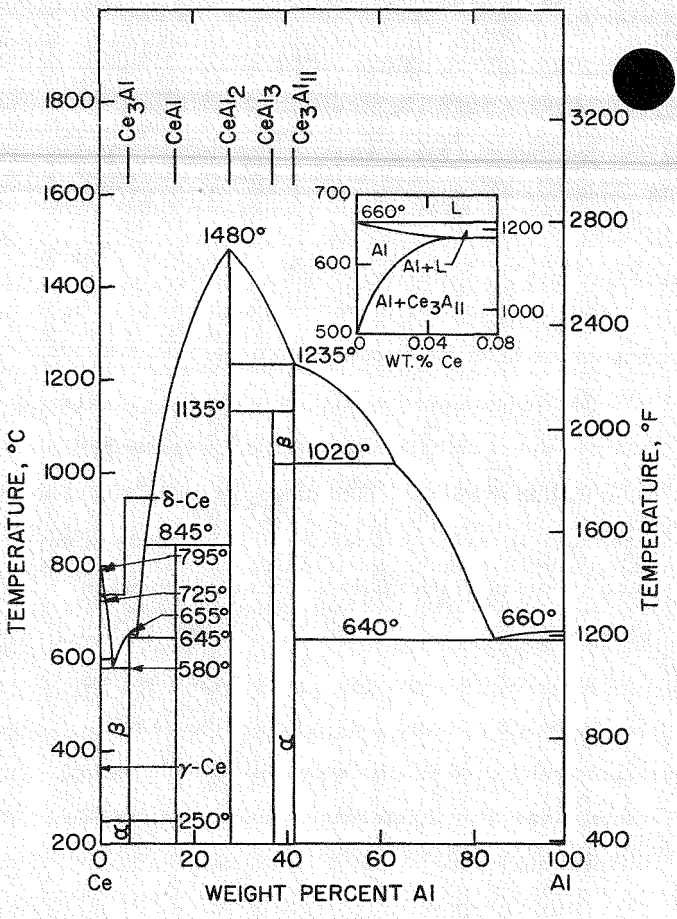

Fig. 1a. Ce-Al Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
α-Ce_3Al	hex.	7.042±2	-	5.450±1	803-4
β-Ce_3Al	cubic	4.998±16	-	-	803-4
CeAl	ortho.	9.270	7.680	5.760	803, 806-8
$CeAl_2$	cubic	8.054±29	-	-	802-4, 812-14
$CeAl_3$	hex.	6.543±2	-	4.610±1	802, 815-6
α-Ce_3Al_{11}	ortho.	4.392±3	13.018±7	10.082±10	802, 805, 817
β-Ce_3Al_{11}	tetr.	4.377±3	-	10.030	802-4

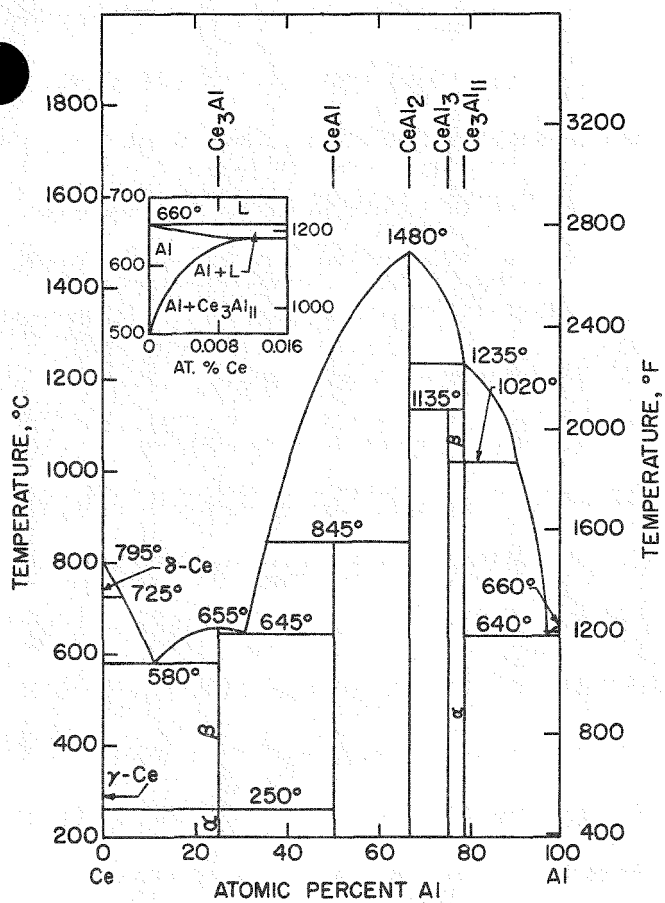

Fig. 1b. Ce-Al Phase Diagram (in a/o).

N or O, stabilizes the β-Ce_3Al form. A polymorphic transformation was also indicated at 1020° C for Ce_3Al_{11}. Two crystalline forms of the monoaluminide have been reported — orthorhombic[803, 806-8] and cubic.[809-10] Attempts to reproduce the preparation of the cubic form have been unsuccessful,[806-8] and it is doubtful that this phase is a true equilibrium in the pure Ce-Al binary system. Bécle and Lemaire[806-7] noted that the CeAl orthorhombic prisms are analogous with the semi-lattice of the cubic structure. Three eutectic reactions occur — L ⇄ Ce + β-Ce_3Al at approximately 11 a/o Al (2.3 w/o Al), L ⇄ β-Ce_3Al + CeAl at 30 a/o Al (7.7 w/o Al) and L ⇄ Al + α-Ce_3Al_{11} at about 96 a/o Al (84 w/o Al). A maximum solubility of 0.01 a/o Ce (0.05 w/o Ce) in Al at the 640° C eutectic temperature has been extrapolated from the lower temperature solid solubility data of Drits et al.[811] (see insertions in Figures 1a and 1b).

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CERIUM — ANTIMONY

PHASE DIAGRAM

No temperature-composition data is available for the Ce-Sb system.

CRYSTAL DATA

Two compounds — Ce_2Sb and Ce_3Sb_2 — have been reported[818] in addition to the four intermediate phases for which structure data is available (see Table). From the results of Olcese,[818] CeSb appears to exist over a composition range from at least $CeSb_{0.94}$ to about $CeSb_{1.00}$. Ce_4Sb_3 forms peritectically.[819]

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Compound	Crystal Class	Lattice Parameters Å a	b	c	References
Ce_5Sb_3	hex.	9.302±9	-	6.514±5	820
Ce_4Sb_3	cubic	9.520±9	-	-	819, 821
CeSb	cubic	6.420±9	-	-	803, 818, 822-3
$CeSb_2$	ortho.	6.295±6	6.124±6	18.21±2	824

CERIUM – ARSENIC

PHASE DIAGRAM

There is not sufficient phase relationship data available to prepare a diagram.

CRYSTAL DATA

X-ray crystallographic studies[825] made on alloys prepared at temperatures of 500 - 900° C indicate the formation of Ce_4As_3, CeAs and $CeAs_2$ stoichiometries. On the basis of samples prepared between 1100 and 1400° C, Olcese[818] reported that CeAs exists in equilibrium with Ce and $CeAs_2$ over a solid solution range from $CeAs_{<1.00}$ to $CeAs_{\sim 1.00}$. It is quite likely that the Ce_4As_3 found by Ono[825] decomposes to Ce and CeAs between 900 and 1100° C.

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Compound	Crystal Class	Lattice Parameters Å a	b	c	References
Ce_4As_3	cubic	9.052±1	-	-	825-6
CeAs	cubic	6.078±8	-	-	803, 818, 822, 827-8
$CeAs_2$	mono.[a]	4.165	6.871	10.561	825

[a] The oblique angle, β, is equal to 106.72°.

CERIUM — BISMUTH

PHASE DIAGRAM

Some phase equilibria data were determined prior to the 1950's, but are not reliable and thus are not included here. The earlier diagram is given in Gschneidner's 1961 review.[803] X-ray data have confirmed the existence of Ce_4Bi_3 and CeBi.

On the basis of studies of the other rare earth systems (Pr-Bi,[829] Y-Bi,[830] Nd-Bi,[831] Gd-Bi,[819, 832] and Dy-Bi[819]) and the similarities expected for rare earth-bismuth systems, the following properties are anticipated for the Ce-Bi alloys:

1. The CeBi phase is probably the highest melting compound with a congruent melting point estimated to be >1700°C.
2. Ce_4Bi_3 is expected to melt peritectically around 1600°C.
3. The Bi-rich phase — probably $CeBi_3$ — melts peritectically at 910°C.[833]
4. A eutectic on the Ce-rich side probably occurs.

The solubility of cerium in liquid bismuth has been determined by Pleasance[833] from 271 to 910°C and by Schweitzer and Weeks[834] from 300 to 450°C. The results of the two investigations are in fair agreement with each other. Since the data of Pleasance covers a wider temperature range their parameters are given here:

$$\log (\text{ppm Ce}) = 7.74 - \frac{3030}{T}$$

where T is in °K.

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	References
Ce_4Bi_3	cubic	9.656±16	819, 821
CeBi	cubic	6.497±10	803, 818, 822, 835

REFERENCES

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CERIUM – CALCIUM

PHASE DIAGRAM

The diagrams shown here are based on the known equilibria data as reviewed by Gschneidner.[803] The general form of the phase diagram illustrates the limited mutual solubility of cerium and calcium in both the liquid and solid forms. The Ce-rich and Ca-rich ends of the diagram are shown in Figures 2a and 2b.

CRYSTAL DATA

No compounds are formed between cerium and calcium.

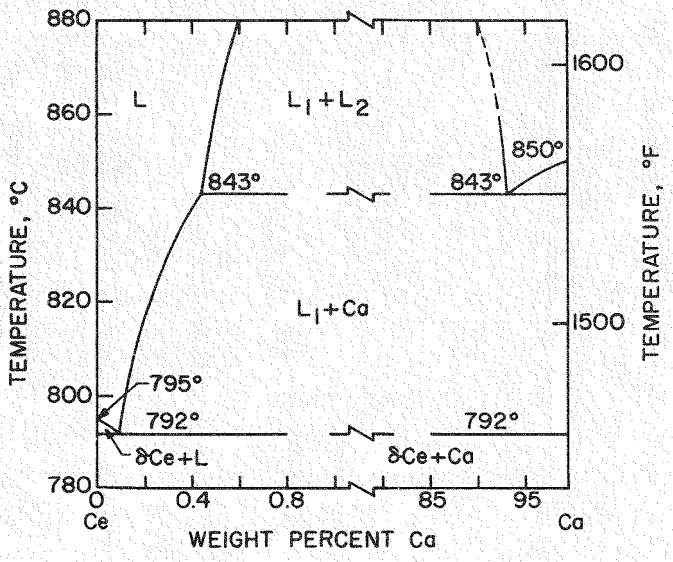

Fig. 2a. Ce-Ca Phase Diagram (in w/o).

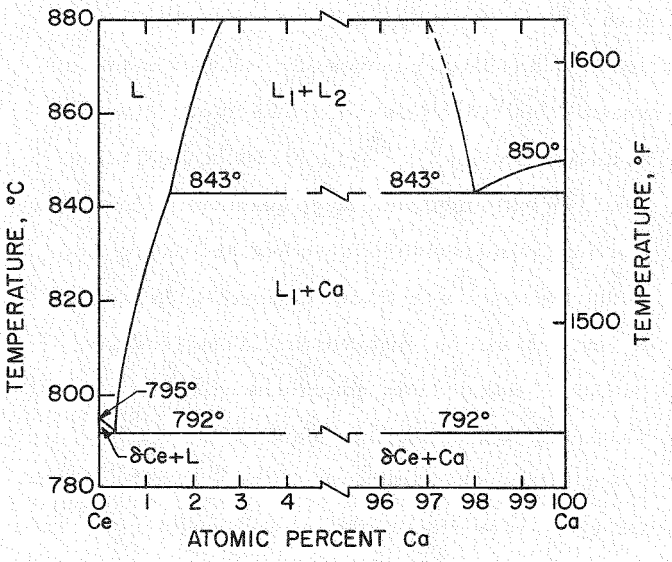

Fig. 2b. Ce-Ca Phase Diagram (in a/o).

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CERIUM — CARBON

PHASE DIAGRAM

Figures 3a and 3b indicate tentative phase diagrams as originally proposed by Stecher et al.,[836] but also incorporate modifications based on several researches. Three compounds — CeC,[837] Ce_2C_3 and CeC_2 — have been reported, although the existence of CeC is dubious. Since rare earth carbides with 3:1 and 1:1 stoichiometries are methanides, production of large amounts of methane would be expected from hydrolysis of Ce_3C and CeC. However, hydrolytic studies[838-40] of a series of Ce-C alloys produced little methane, large quantities of hydrogen, and moderate amounts of acetylene and ethane indicating the absence of these compounds. In addition, X-ray, thermal and metallographic analyses have confirmed that no other compounds exist between Ce and Ce_2C_3 (0 and 60 a/o or 0 and 11 w/o C).[836, 838-9] From a thorough examination of the X-ray, hydrolytic and visual properties of the Ce-C-N system, Anderson et al. conclude that the suggested CeC form is probably CeN_xC_y.[838-9]

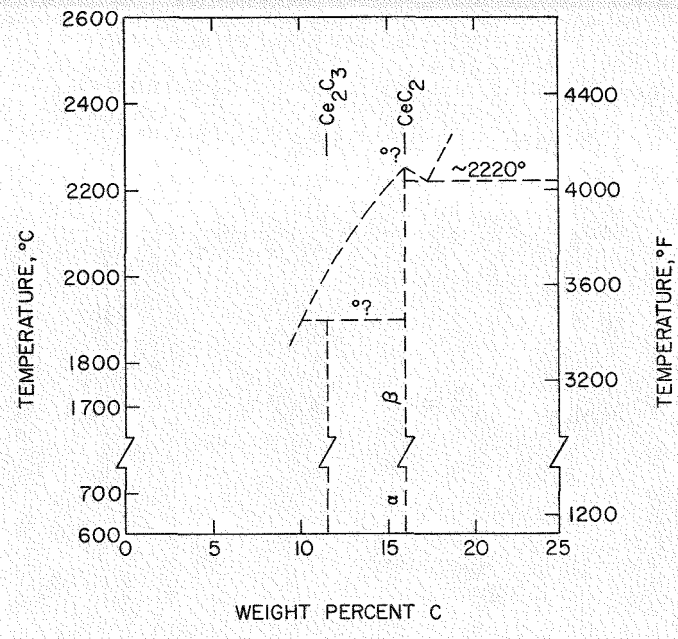

Fig. 3a. Ce-C Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	c	References
Ce_2C_3	cubic	8.446±5	—	803, 836, 838-9, 845-8
α-CeC_2	tetr.	3.878±7	6.484±8	803, 836, 839, 841-3, 845, 848-51
β-CeC_2	cubic	5.939±2	—	843

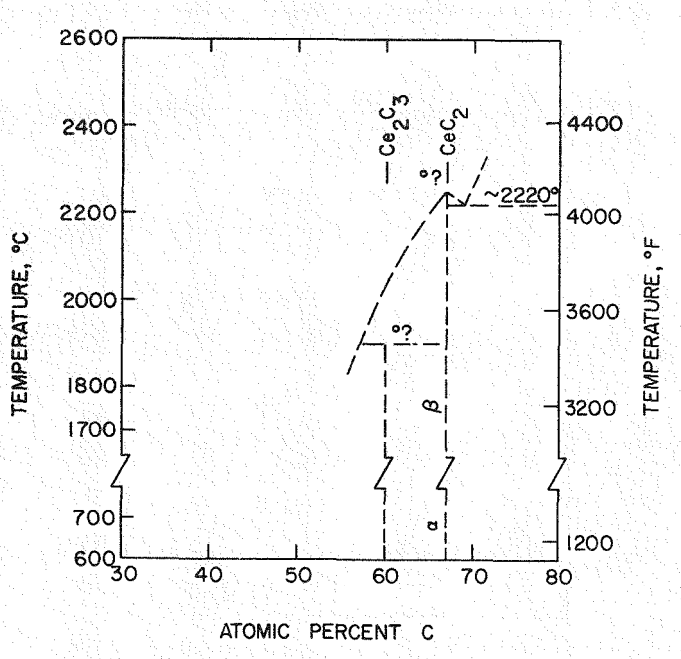

Fig. 3b. Ce-C Phase Diagram (in a/o).

The congruent melting point of the dicarbide, the 69 a/o C (16 w/o C) eutectic, and the Ce_2C_3 peritectic horizontal are not well established. Stecher and associates reported that Ce_2C_3 melts incongruently above 1700°C, although their proposed diagram shows the peritectic horizontal at approximately 1900°C.[836] They also indicate that CeC_2 melts congruently somewhere above 2000°C[836] and Faircloth et al.[841] found the melting point to be 2250±20°C. The diagram has been adjusted to reflect the latter. Stecher and co-workers[836] observed a eutectic reaction, $L \rightleftharpoons CeC_2+C$, at approximately 2150°C. Others report the same eutectic at 2245±20°C[842] and 2270±20°C.[843] An average of these temperatures (2220°C) was selected for the diagrams. Several investigations[842-4] also reveal an allomorphic transition for CeC_2 around 1050°C. A liquidus temperature of 2270°C was reported[841] for an alloy with the $CeC_{2.34}$ stoichiometry (70 a/o C or 17 w/o C).

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CERIUM – CHROMIUM

PHASE DIAGRAM

Kobzenko and co-workers[852-4] have published several versions of the cerium-chromium system based on thermal, X-ray, metallographic and hardness analyses using 99.98% pure Cr and 99.27% pure Ce. The tentative diagrams of Figures 4a and 4b, representing their results, are in good agreement with previously published work as reviewed by Gschneidner.[803] However, the melting point and the polymorphic transition temperature for pure Ce reported by Kobzenko et al. are 20 to 30° lower than the accepted values. In the diagrams, these have been corrected to 798°C and 725°C, respectively, and the corresponding eutectic and eutectoid transformations have been raised by similar amounts (i.e. from 765 to 785°C for the eutectic temperature and from 685 to 715°C for the δ-Ce ⇌ γ-Ce + Cr eutectoid transition). The 98.15 a/o Cr (95.17 w/o Cr) monotectic composition and the maximum solubilities of Ce in Cr at the monotectic temperature (1.25 a/o Ce or 3.30 w/o Ce) and at 1260°C (0.25 a/o Ce or 0.67 w/o Ce) are taken from the latest paper,[852] which is presumably the most reliable version.

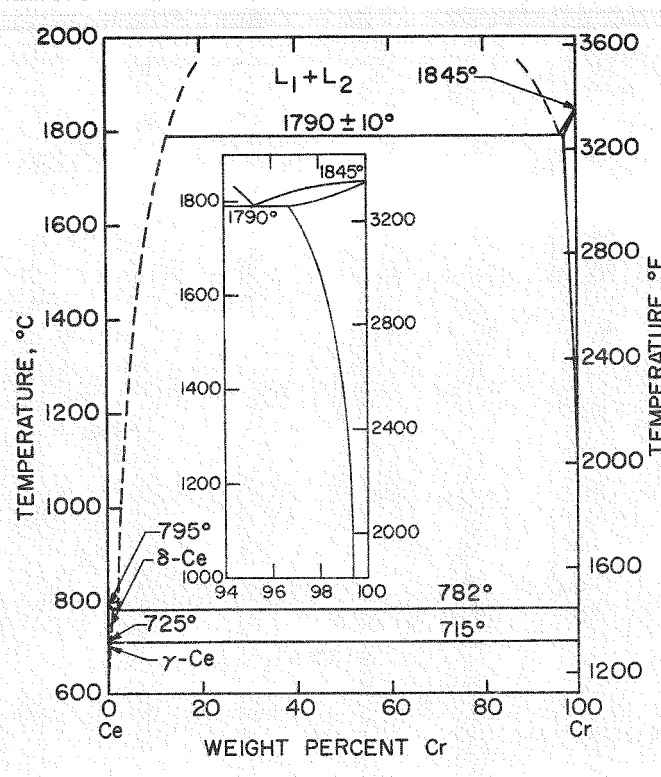

Fig. 4a. Ce-Cr Phase Diagram (in w/o).

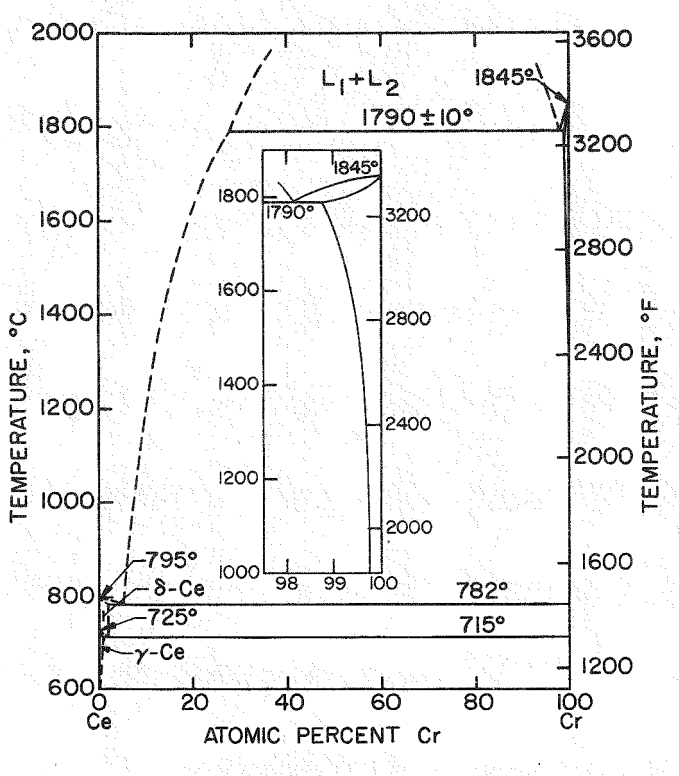

Fig. 4b. Ce-Cr Phase Diagram (in a/o).

CRYSTAL DATA

No compounds are formed between cerium and chromium.

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CERIUM — COBALT

PHASE DIAGRAM

Ray et al.[855] and Buschow[856] examined the Ce-Co system by means of thermal, metallographic and X-ray analyses. 99.97% pure Ce and 99.94% pure Co were used by the former authors while the latter employed 99.99% pure Ce and 99.9% pure Co. The diagrams of Figures 5a and 5b, representing the results of both researches, are also in good agreement with the earlier work of Ellinger et al.[857] on the Ce-rich portion (0 to 50 a/o, 0 to 30 w/o Co). In addition to the five cobalt-rich peritectic compounds identified by Buschow[856] — $CeCo_2$, $CeCo_3$, Ce_2Co_7, $CeCo_5$ and Ce_2Co_{17} — Ray and co-workers[855] detected a sixth alloy, Ce_5Co_{19}, melting peritectically at 1134°C, the temperature at which Ce_2Co_7 was formerly[858] thought to form. The 1130°C thermal arrest previously[858] attributed to a polymorphic transformation of Ce_2Co_7 is instead the formation temperature of that compound.[855]

A single Ce-rich alloy, $Ce_{24}Co_{11}$, forms congruently. The peritectic temperatures of Buschow[856]

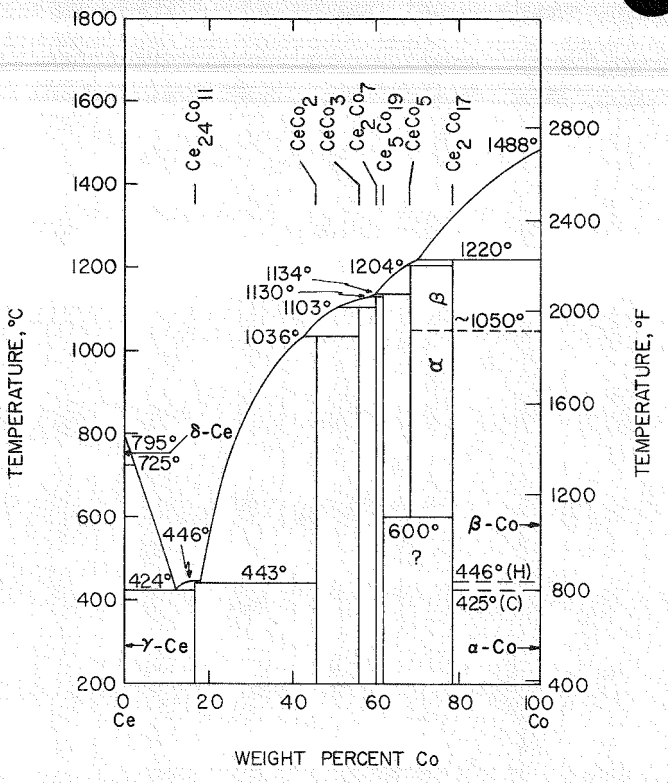

Fig. 5a. Ce-Co Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	c	References
$Ce_{24}Co_{11}$	hex.	9.587±2	21.825±10	855, 860
$CeCo_2$	cubic	7.161±3	—	803, 812-4, 855, 861-4
$CeCo_3$	rhomb.	4.968±26[a]	24.784±7[a]	855-6, 865-6
Ce_2Co_7	hex.	4.944±5[b]	24.47 ±1	855-6, 858
Ce_5Co_{19}	rhomb.	4.939±1[a]	48.71±4[a]	855
$CeCo_5$	hex.	4.920±17	4.019±7	803, 867-71
α-Ce_2Co_{17}	rhomb.	8.364±28[a]	12.189±36[a]	855, 872-5
β-Ce_2Co_{17}	hex.	8.369±34	8.124±22	855, 870, 872-6

[a] Lattice parameters are for the hexagonal unit cell.

[b] The value of the a parameter reported by Ray and Hoffer,[858] which deviated significantly (>10%) from the other data for this compound, has not been included in the calculation of the mean.

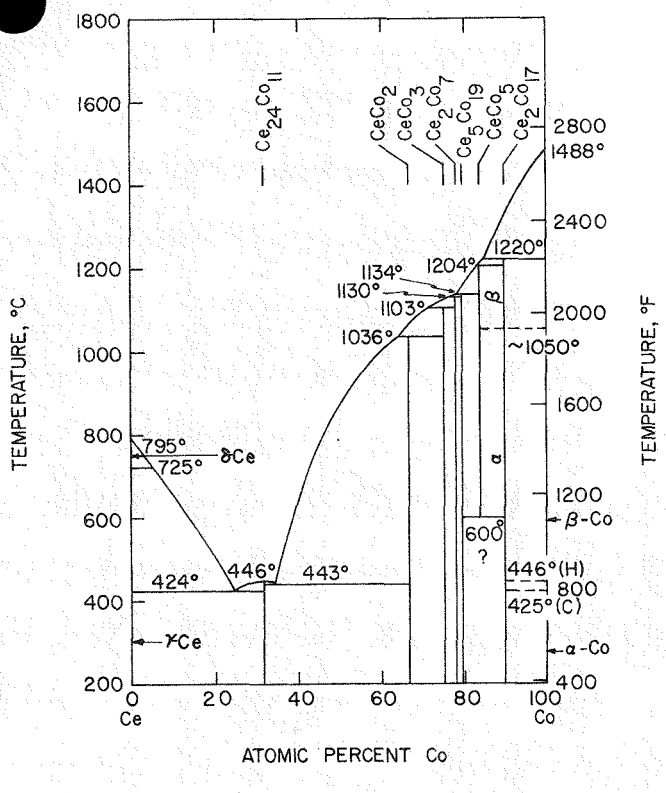

Fig. 5b. Ce-Co Phase Diagram (in a/o).

are 21 to 27°C higher than those of Ray et al.[855] Average values were used to construct the graph, except for the Ce_2Co_7 and Ce_5Co_{19} temperature horizontals. In as much as Buschow[856] did not detect the Ce_5Co_{19} phase, we have employed the results of Ray et al.[855] for these compositions.

A polymorphic transformation of the Ce_2Co_{17} stoichiometry is indicated by X-ray diffraction patterns which reveal the presence of only the hexagonal (β) form at 1100°C and only the rhombohedral (α) form at 1000°C.[855] Two eutectic reactions occur: $L \rightleftarrows Ce_{24}Co_{11} + Ce$ at ~24 a/o Co (~12 w/o Co) and $L \rightleftarrows Ce_{24}Co_{11} + CeCo_2$ at ~34 a/o Co (~18 w/o Co). Buschow[859] reported that alloys of 83.3 a/o Co (67.7 w/o Co) decompose eutectoidally to the two adjacent compositions when cooled below 600°C. However, Ray and co-workers,[855] using differential thermal analysis, metallographic, electron microscopy and electron microprobe techniques, found no evidence of instability of the $CeCo_5$ phase.

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CERIUM – COLUMBIUM (NIOBIUM)

PHASE DIAGRAM

The tentative phase diagrams of Figures 6a and 6b are taken from the review by Gschneidner.[803] A monoeutectic occurs at approximately 99 a/o Cb (98 w/o Cb). No intermediate phases are formed. There is little or no solid solubility of Ce in Cb; the solubility limits at the Ce-rich end are unknown.[803] Cb reportedly raised the melting point of Ce by 5 to 7°C and lowered the allotropic transformation temperature of Ce by 20 to 25°C.[803] The Ce-rich end shown in Figs. 6a and 6b is a schematic representation of the phase relationships and, thus, the peritectic and eutectoid concentrations and solubilities are probably greatly exaggerated.

CRYSTAL DATA

No solid compounds are formed.

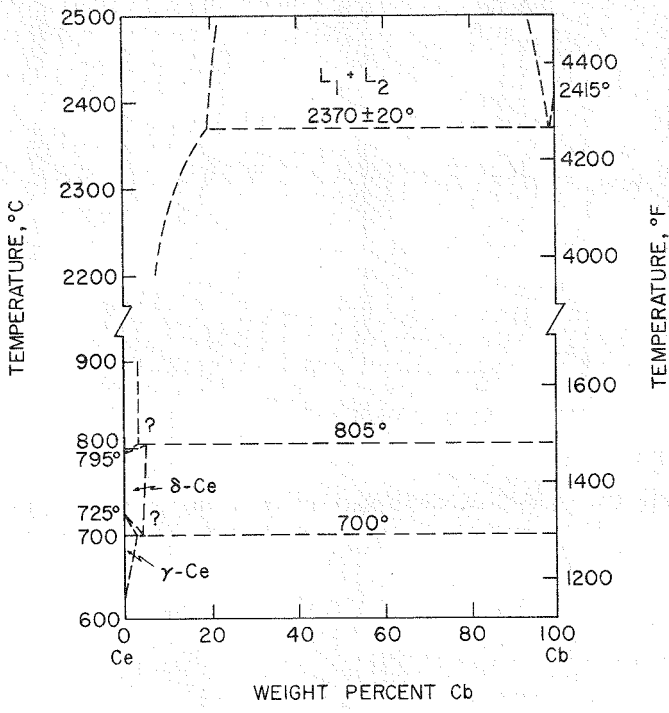

Fig. 6a. Ce-Cb Phase Diagram (in w/o).

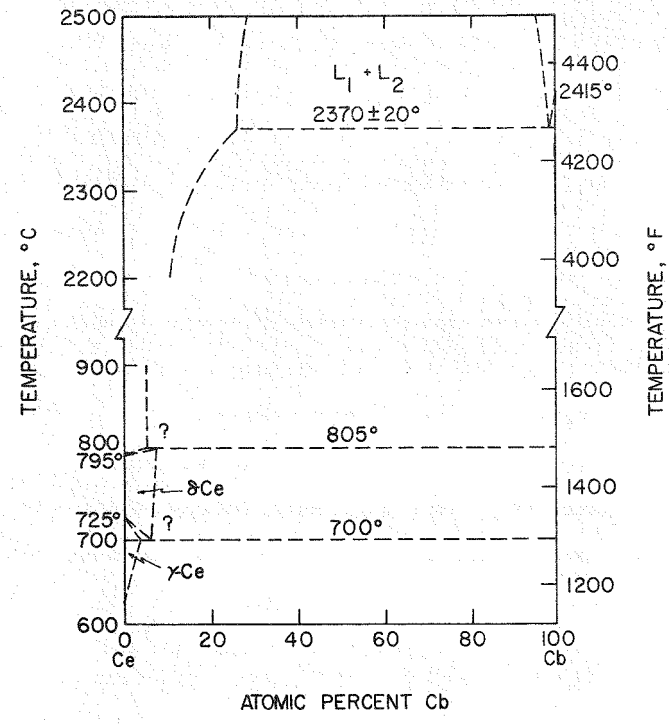

Fig. 6b. Ce-Cb Phase Diagram (in a/o).

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CERIUM – COPPER

PHASE DIAGRAM

The phase diagrams of Figures 7a and 7b are those of Rhinehammer and co-workers[877] as established by analysis of thermal, metallographic, microhardness and X-ray data. Although generally in good agreement with previously published results as reviewed by Gschneidner,[803] the diagrams of Rhinehammer et al. indicate the formation of an additional compound, $CeCu_5$. Prior attempts to identify the compound(s) melting in the 80 to 85 a/o Cu (64 to 72 w/o Cu) range were inconclusive. An alloy with $Ce_{1.2}Cu_{4.8}$ stoichiometry, but resembling the structure of $CaZn_5$ had been assigned the $CeCu_4$ formula.[803] However, subsequent examination of single crystals[877] revealed the existence of both $CeCu_4$ and $CeCu_5$ melting incongruently at a temperature interval of only 2° C. It is likely that earlier measurements of alloys cooling in this region contained significant amounts of $CeCu_5$ and $CeCu_4$ which led to erroneous results.

A total of five compounds have been identified. $CeCu_2$ and $CeCu_6$ form congruently; CeCu, $CeCu_4$ and $CeCu_5$ form peritectically. Three eutectic reactions occur – $L \rightleftarrows \gamma\text{-Ce} + CeCu$ at 28 a/o Cu (15 w/o Cu), $L \rightleftarrows CeCu_2 + CeCu_4$ at 74 a/o Cu (56 w/o Cu), and

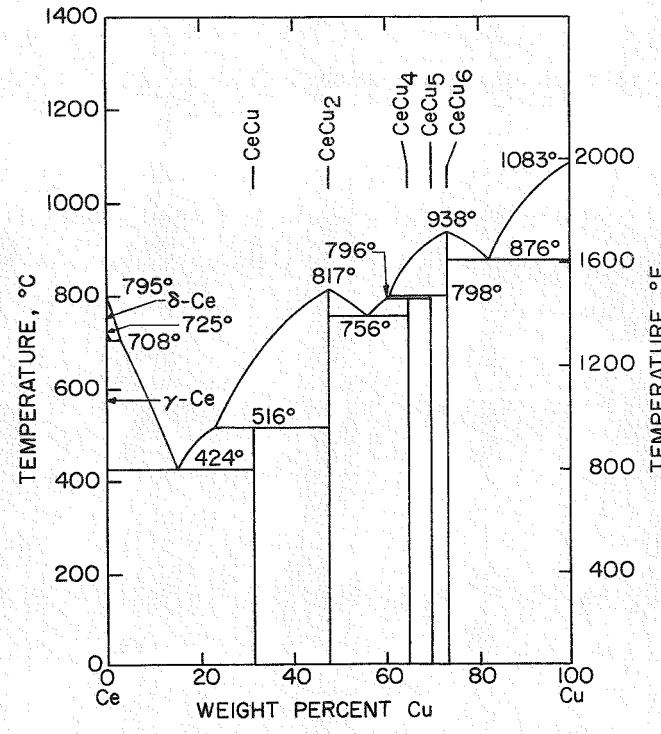

Fig. 7a. Ce-Cu Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
CeCu	ortho.	7.370[a]	4.623[a]	5.648[a]	879-81
$CeCu_2$	ortho.	4.425±5	7.057±5	7.475±5	803, 882
$CeCu_4$	ortho.	4.54±1[a]	8.10±1[a]	9.19±1[a]	877, 883
$CeCu_5$	hex.	5.148±2	-	4.108	871, 877, 884
$CeCu_6$	ortho.	8.108	5.02	10.160	885

[a]Due to significant deviations in the reported parameters, only the set of values considered to be most accurate are reported here.

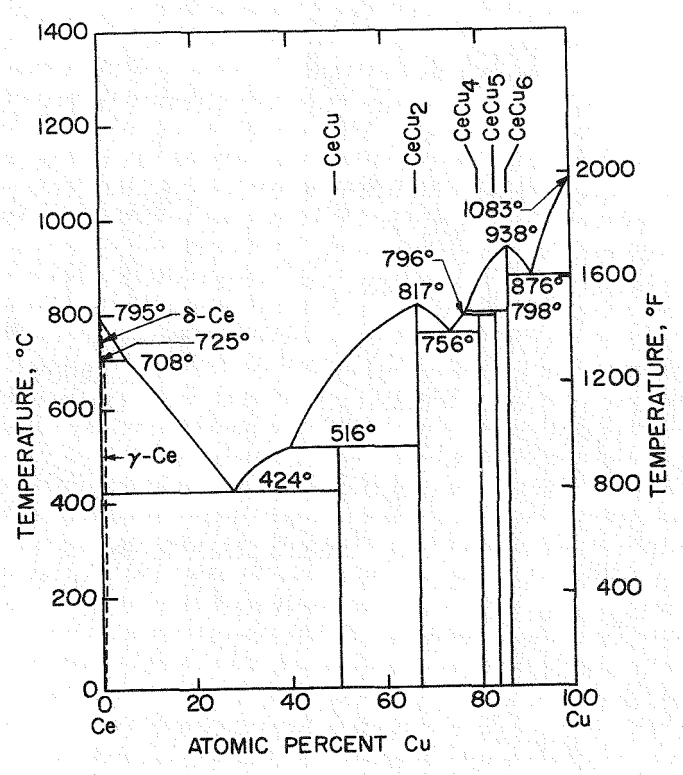

Fig. 7b. Ce-Cu Phase Diagram (in a/o).

$L \rightleftarrows CeCu_6 + Cu$ at 91 a/o Cu (82 w/o Cu). Data of Gschneidner[803] and Rhinehammer et al.[877] indicate a maximum solubility of Cu in Ce of approximately 1 a/o Cu (0.45 w/o Cu). The maximum solubility of Ce in Cu is <2 a/o Ce (<1 w/o Ce).[878]

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CERIUM – IRON

PHASE DIAGRAM

Buschow and van Wieringen[886] have redetermined the phase relationships for the cerium-iron system by analysis of thermal, metallographic, X-ray and magnetic properties using 99.94% pure Fe. (The purity of the Ce stocks were not reported. However, both melted at 800° C and one was said to contain 0.2% metallic impurities.) Their results, which deviate somewhat from earlier data as reviewed by Gschneidner[803] and the investigations of Gebhart and co-workers,[887] are shown in Figures 8a and 8b.

Only two compounds – $CeFe_2$ and Ce_2Fe_{17} – both of which form peritectically, exist in this system. The iron-rich phase was confirmed as Ce_2Fe_{17} and not the previously reported $CeFe_5$[803] or $CeFe_7$[887-8] stoichiometries. Although Gebhart et al.[887] noted a small solid solubility range for both $CeFe_2$ and Ce_2Fe_{17} ($CeFe_7$), Buschow and van Wieringen,[886] after searching for solid solution regions, concluded that $CeFe_2$ and Ce_2Fe_{17} are line compounds. The transition temperature for Ce_2Fe_{17} has not been established, but 89.5 a/o Fe (77.3 w/o Fe) alloys

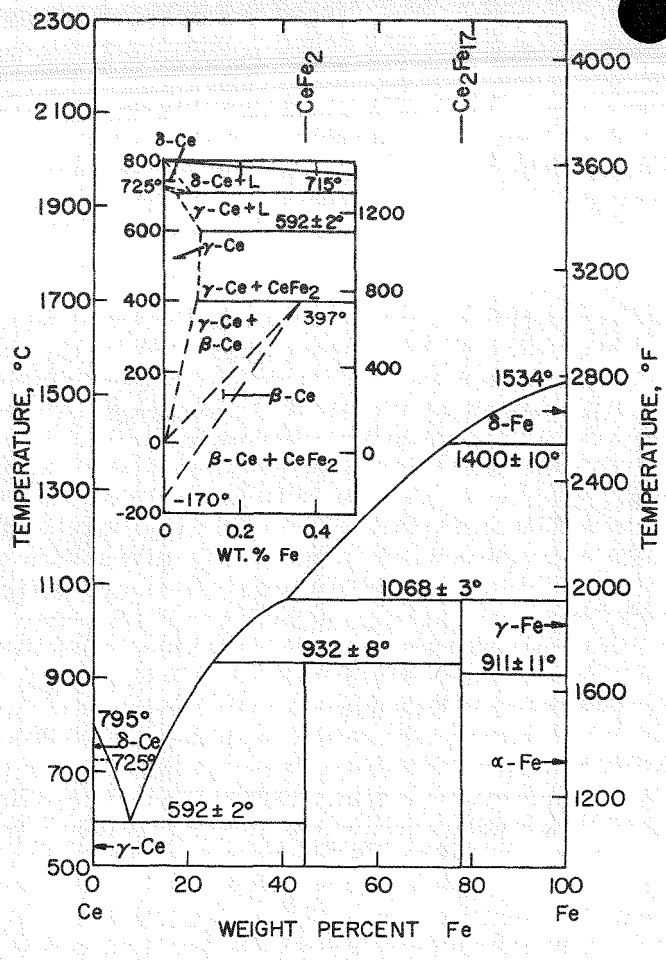

Fig. 8a. Ce-Fe Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	c	References
$CeFe_2$	cubic	7.302±2	–	803, 812, 814, 861-2, 886, 890-1
α-Ce_2Fe_{17}	hex.	8.490	8.281	886
β-Ce_2Fe_{17}	rhomb.	8.493±19[a]	12.409±41[a]	874, 876, 886, 888, 891-2

[a]Lattice parameters are for the hexagonal unit cell.

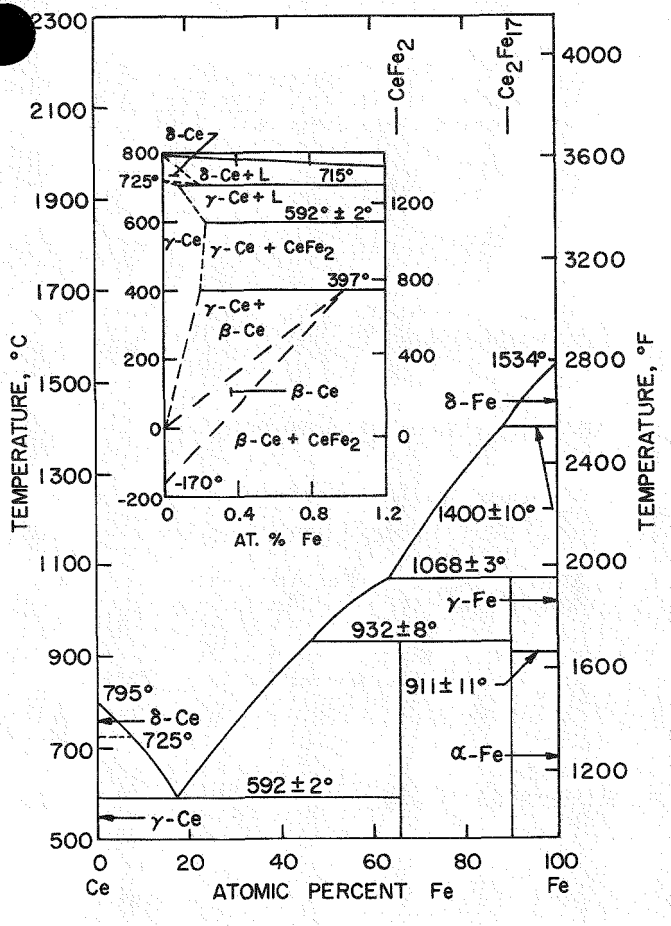

Fig. 8b. Ce-Fe Phase Diagram (in a/o).

quenched from 1025°C yield only the β (rhombohedral)-form.[886] Buschow and van Wieringen[886] also observed that excess iron stabilizes the β-form regardless of heat treating and quenching temperatures. A single eutectic reaction — $L \rightleftarrows CeFe_2 + Ce$ — occurs at 17 a/o Fe (7.5 w/o Fe).

Tucker et al.[889] have deduced the character of the Ce-rich portion of the phase diagram from their investigation of the Ce-Fe-Pu system. (See insertions in Figs. 8a and 8b.) The temperature horizontals are reasonably well established and the stabilization of β-Ce by ~0.2 a/o Fe (0.08 w/o Fe) at room temperature is confirmed. The solid solubility limits are not, however, adequately substantiated in this study.

The addition of Ce appears to raise the $\alpha \rightleftarrows \gamma$ transition temperature of Fe from 910 to 922 ± 3°C.[803, 886] In contrast, however, the results of Gebhart et al.[887] indicate that it is lowered to 900°C.

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CERIUM — LEAD

PHASE DIAGRAM

Some phase equilibria data were determined prior to the 1950's, but the results are probably not too reliable and are not included here. The earlier diagram is given in Gschneidner's 1961 review.[803] Reliable X-ray data have confirmed the existence of Ce_3Pb, Ce_5Pb_3, Ce_5Pb_4 and $CePb_3$. On the basis of the investigations of McMasters et al.[893-4] of the light lanthanide-lead systems, the Ce phases, Ce_3Pb_4 and $CePb_2$, probably also exist, but no phase of the Ce_4Pb_3 stoichiometry is formed. Furthermore, Ce_5Pb_3 is probably the highest melting phase in the system with an estimated melting point of 1450° C. $CePb_2$ has an estimated incongruent melting point of 1100° C, and $CePb_3$ is expected to melt congruently at 1150° C. (All estimates are thought to be within ± 25° C.)

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CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
Ce_3Pb	cubic	4.964	-	-	895
Ce_5Pb_3	hex.	9.473±4	-	6.825±2	896
Ce_5Pb_4	ortho.	8.435±6	16.15±1	8.571±6	897
$CePb_3$	cubic	4.885±20	-	-	803, 898-9

CERIUM – MAGNESIUM

PHASE DIAGRAM
(For discussion and diagrams see pages 24 and 25).

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PHASE DIAGRAM

Figures 9a and 9b are based on a composite of available information for the Ce-Mg system. The region from 0 to 82 a/o Mg (0 to 44 w/o Mg) is essentially as reviewed by Gschneidner.[803] Wood and Cramer[900] examined the Ce-Mg system between 82 and 100 a/o Mg (44 and 100 w/o Mg) by means of thermal, metallographic and X-ray analyses using 99.99% pure Mg and 99.5% pure Ce. The cerium contained primarily 0.4% Fe as impurity. The region from 82 to 100 a/o Mg (44 to 100 w/o Mg) represents primarily their results with modifications as suggested by subsequent research.

Ten compounds have been reported in the literature, but only five appear to be unequivocally identified. Only $CeMg_3$ forms congruently. CeMg, $CeMg_2$, Ce_5Mg_{41} and $CeMg_{12}$ form incongruently. Johnson and Smith[901-2] have determined by means of single crystal methods that the alloy tentatively assigned a $CeMg_{8.25}$ stoichiometry by Wood and Cramer[900] has the formula, $Ce_5Mg_{41}(CeMg_{8.2})$.

Johnson and Smith[903] have also examined, by single crystal techniques, the phase previously designated Ce_2Mg_{17}.[900, 904-7] Their results indicate the existence of a compound with the Th_2Ni_{17}-type structure (hexagonal), but with a $CeMg_{10.3}$ composition. The powder pattern reported for Ce_2Mg_{17} by Crosby and Holman[904] was confirmed to be that of Ce_5Mg_{41}.[901] Johnson and Smith[903] also observed that the powder pattern for a Ce_2Mg_{23} alloy identified by Crosby and Holman[904] agrees well with crystal data for the $CeMg_{10.3}$ stoichiometry. The compound(s) occurring in this region (89.5 to 92 a/o Mg or 59.7 to 67 w/o Mg) exist only over a 10°C range.[900] In

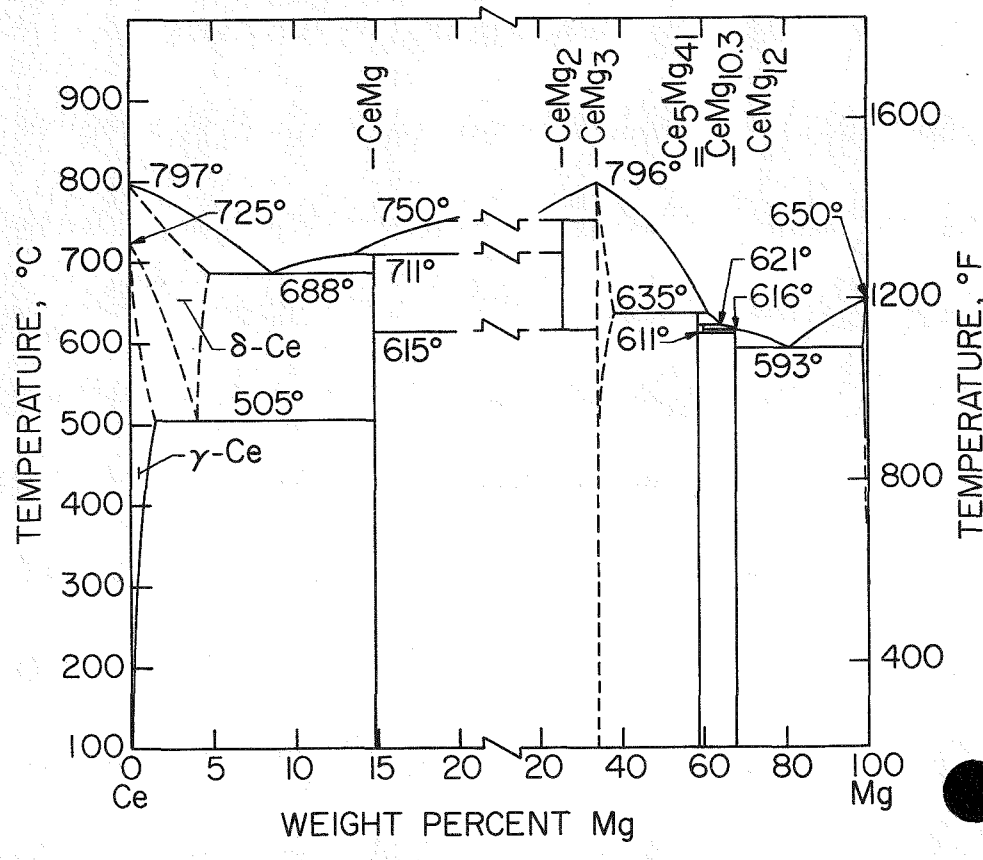

Fig. 9a. Ce-Mg Phase Diagram (in w/o).

addition, the powder pattern of the alleged $CeMg_9$[803, 908] stoichiometry is in good agreement with the calculated pattern for $CeMg_{12}$.[901]

Two eutectic reactions occur — $L \rightleftarrows CeMg + \delta\text{-Ce}$ at 35 a/o Mg (8.5 w/o Mg) and $L \rightleftarrows CeMg_{12} + Mg$ at 95.8 a/o Mg (80.6 w/o Mg).

A maximum solid solubility of 8.2 a/o Mg (1.5 w/o Mg) in Ce at 505°C has been determined.[909] The maximum solubility of Ce in Mg is 0.166 a/o Ce (0.98 w/o Ce) at 590°C,[910] which is slightly higher than the value one obtains from Rohklin's data (0.13 a/o Ce, 0.74 w/o Ce).[911]

REFERENCES (See page 23.)

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	c	References
CeMg	cubic	3.900±1	—	803, 912
$CeMg_2$	cubic	8.733	—	803
$CeMg_3$	cubic	7.412	—	803
Ce_5Mg_{41}	tetr.	14.66±12	10.36±8	900-2
$CeMg_{10.3}$	hex.	10.33	10.25	903
$CeMg_{12}$	tetr.	10.34±1	5.96	900, 913-4

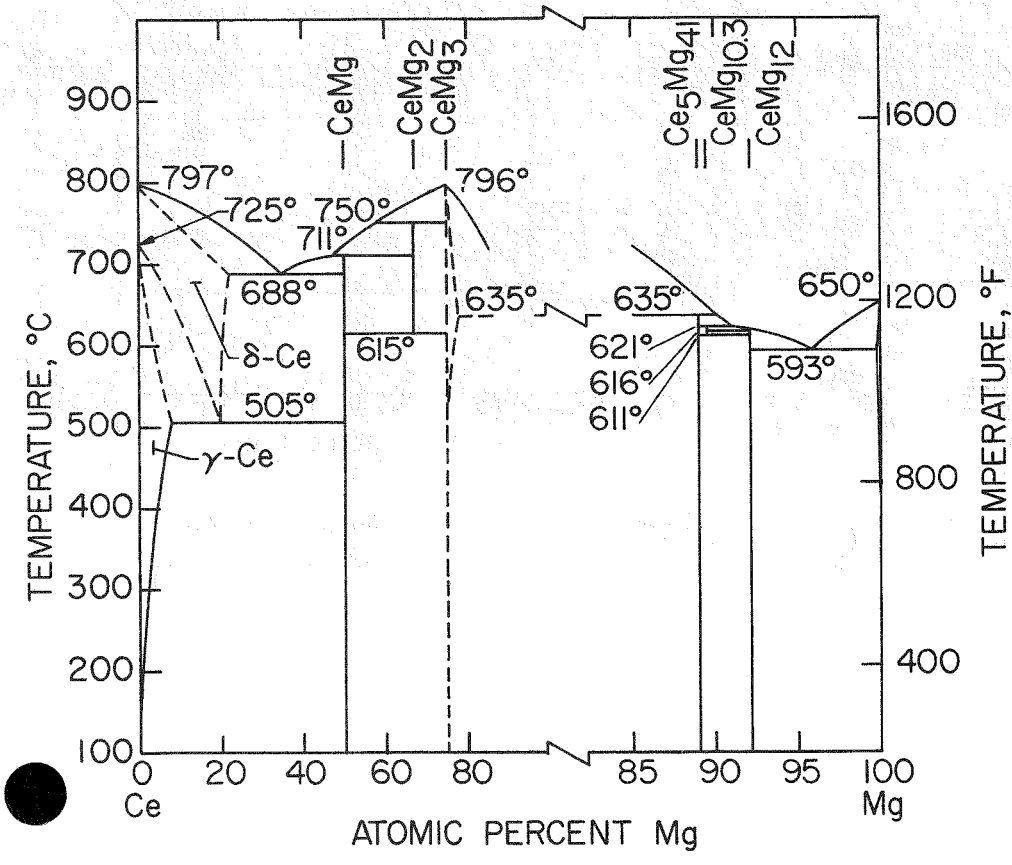

Fig. 9b. Ce-Mg Phase Diagram (in a/o).

CERIUM – MANGANESE

PHASE DIAGRAM

B. J. Thamer[915] examined the Ce-Mn system from 0 to 20 a/o Mn (0 to 9 w/o Mn) by means of thermal and metallographic analyses using 99.96% pure Mn and 99.7% pure Ce. The cerium contained 0.1% other rare earth metals as major impurities. In Figures 10a and 10b, his results are combined with previously published data as reviewed by Gschneidner.[803] Many of the questions raised previously by Gschneidner have not been resolved, especially at Mn concentrations >20 a/o Mn (>9 w/o Mn).

The 622°C eutectic temperature — L ⇄ γ-Ce + Mn (α ?) at 16.1 a/o Mn (7.0 w/o Mn) - observed by Thamer is almost midway between the 612°C reported by Iandelli[916] and the 635°C of Mirgalovskaya and Strel'nikova.[917] A β-Mn ⇄ α-Mn + γ-Ce eutectoid reaction may account for the 625°C temperature horizontal, but the interpretations of the 996 and 1087°C horizontals remain unresolved. The 996°C horizontal was thought to be due to the formation of immiscible liquids between 68 and 82 a/o Mn (45 and 64 w/o Mn) by Iandelli.[916] However, Mirgalovskaya and Strel'nikova[917] interpreted this horizontal to be due to the inverted peritectic reaction — γ-Mn ⇄ L+β-Mn — with an unusually flat liquidus curve between 68 and 82 a/o Mn (45 and 64 w/o Mn). Details are also lacking with regard to the influence of Ce on the allotropic transformations of Mn. The maximum solid solubilities of Mn in γ-Ce and δ-Ce are, respectively, 2 ± 1 a/o Mn (0.8 ± 0.5 w/o Mn) and 5 ± 1 a/o Mn (2 ± 0.5 w/o Mn) at 638°C.[915]

CRYSTAL DATA

No solid compounds exist in this system.[803, 918-9]

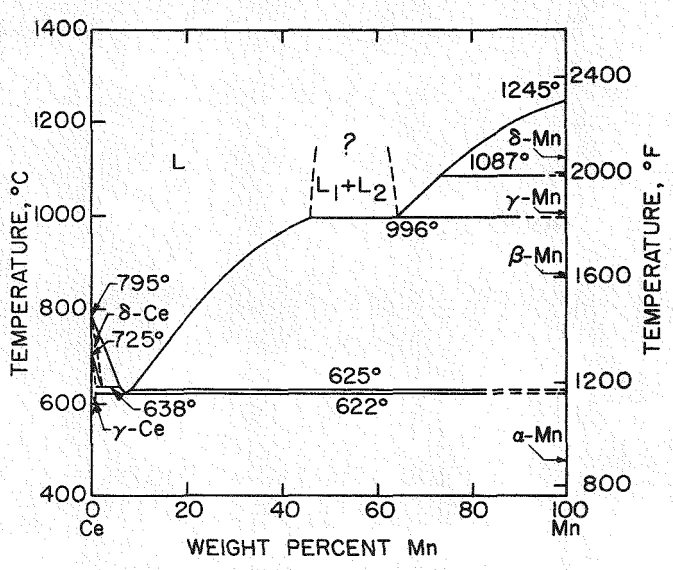

Fig. 10a. Ce-Mn Phase Diagram (in w/o).

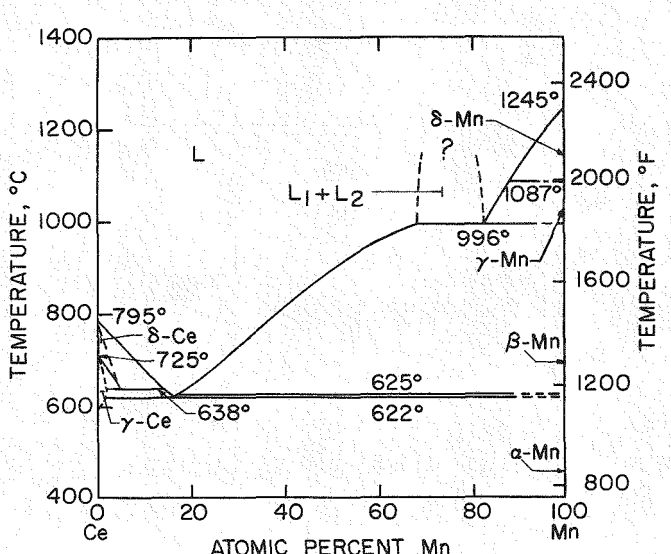

Fig. 10b. Ce-Mn Phase Diagram (in a/o).

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CERIUM – MOLYBDENUM

PHASE DIAGRAM

Only a limited amount of phase equilibria data is available on the Ce-Mo system. The solid solubility of Ce in Mo was reported to be < 0.07 a/o Ce (< 0.1 w/o Ce).[920] Gaume-Mahn and Blanchard[921-2] and Madej[923] have studied the behavior of Mo in contact with liquid Ce, but liquid solubility cannot be derived from their data. Their results would suggest, however, that the solubility of Mo in liquid Ce is small.

CRYSTAL DATA

No solid compounds are known in the Ce-Mo system.

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CERIUM – NICKEL

PHASE DIAGRAM

The cerium-nickel phase diagrams of Figures 11a and 11b are based on the research of Gebhart et al.[887] Their results largely confirm previously published data as reviewed by Gschneidner.[803] The 477, 495 and 655° C temperature horizontals and the melting points of CeNi and $CeNi_5$ are from 7 to 45° C higher than those reported earlier. Also, the compound formerly designated Ce_3Ni[803] does not exist,[924-5] but an additional Ce-rich alloy, Ce_7Ni_3 (30.0 a/o or 15 w/o Ni) has been identified.[925-8] The latter is close to the Ce_5Ni_2 composition (28.6 a/o Ni or 14.4 w/o Ni) reported by Gebhart et al.[887]

Of the six intermediate phases in this system, three form congruently – Ce_7Ni_3, CeNi and $CeNi_5$ –

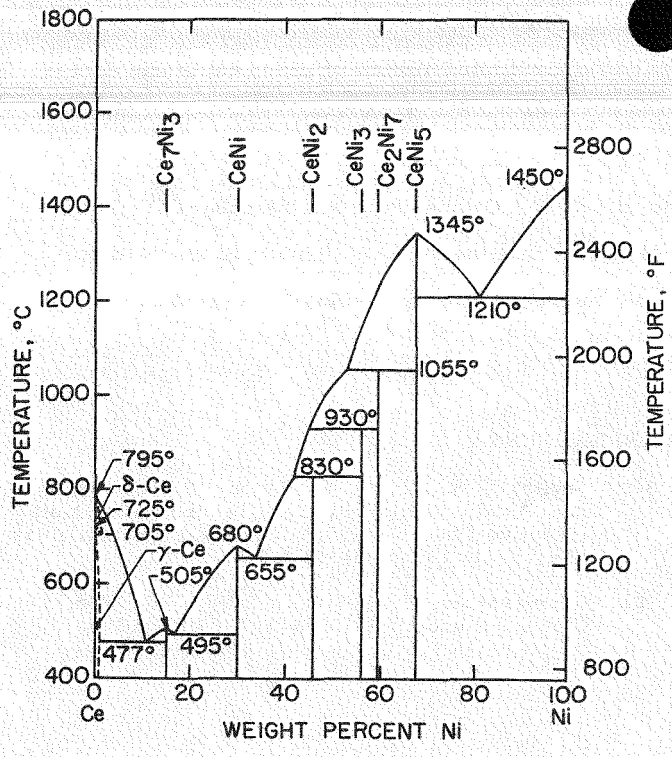

Fig. 11a. Ce-Ni Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
Ce_7Ni_3	hex.	9.916±11	-	6.316±5	926-8
CeNi	ortho.	3.782±7	10.456±100	4.339±53	864, 927, 930-3
$CeNi_2$	cubic	7.211±13	-	-	803, 812, 814, 861-2, 890
$CeNi_3$	hex.	4.945±5	-	16.48±1	934
Ce_2Ni_7	hex.	4.93[a]	-	24.28±10	803, 934-5
$CeNi_5$	hex.	4.887	-	4.003	871

[a] Value taken from Ref. 935, which is consistent with earlier data summarized by Ref. 803. Ref. 934 erroneously gave a = 4.095Å.

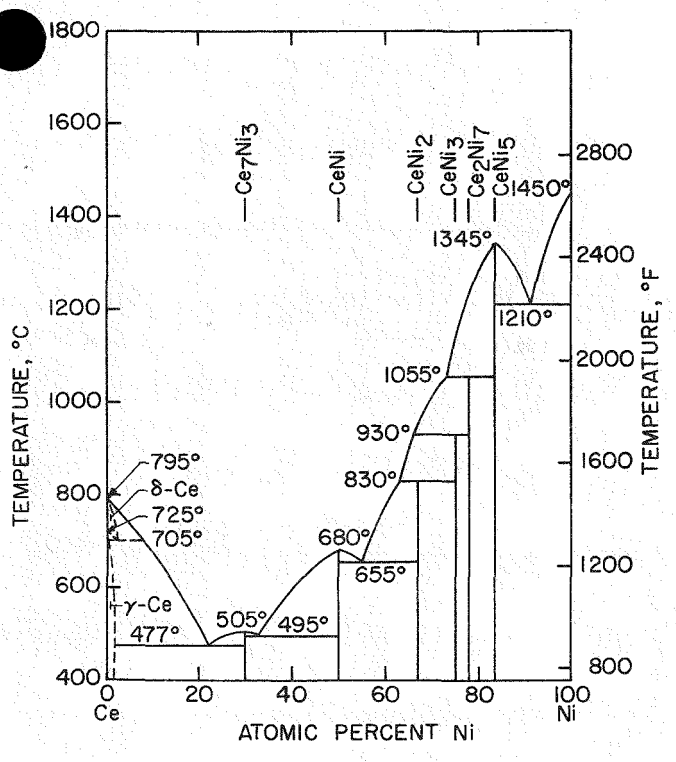

Fig. 11b. Ce-Ni Phase Diagram (in a/o).

and three form peritectically — $CeNi_2$, $CeNi_3$ and Ce_2Ni_7. Isothermal breaks at 1080, 1095 and 1120°C may indicate additional compounds between 78 and 83 a/o Ni (60 and 67 w/o Ni).[887] Four eutectic reactions occur — $L \rightleftarrows Ce + Ce_7Ni_3$ at 22 a/o Ni (11 w/o Ni), $L \rightleftarrows Ce_7Ni_3 + CeNi$ at 33 a/o Ni (17 w/o Ni), $L \rightleftarrows CeNi + CeNi_2$ at 55 a/o Ni (34 w/o Ni), and $L \rightleftarrows CeNi_5 + Ni$ at 91 a/o Ni (81 w/o Ni).

The wide variation in the b and c lattice parameters of CeNi suggests a range of solid solubility. Metallographic examination of Ni-rich alloys quenched from temperatures of 500, 900 and 1200°C revealed a maximum solubility of Ce in Ni of 0.052 a/o Ce (0.125 w/o Ce).[929]

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CERIUM – NIOBIUM

See Cerium - Columbium, p. 17.

CERIUM – NITROGEN

PHASE DIAGRAM

Kobzenko and Ivanchenko[936] examined the cerium-nitrogen system between 0 and 50 a/o N (0 and 9.1 w/o N) by means of thermal, X-ray, metallographic and dilatometric analyses. Figures 12a and 12b contain tentative, partial phase diagrams based on their results. The reported melting point and transition temperatures (760 and 680° C, respectively) of the cerium stock are significantly lower than those of the high purity metal indicating that the cerium contained much more than 0.7% impurities as stated by the authors. In Figs. 12a and 12b these temperatures have been adjusted to reflect the most accurate data currently available. As a result the 770°C peritectic and 705°C peritectoid temperatures reported by Kobzenko and Ivanchenko have been increased to 805 and 750°C, respectively.

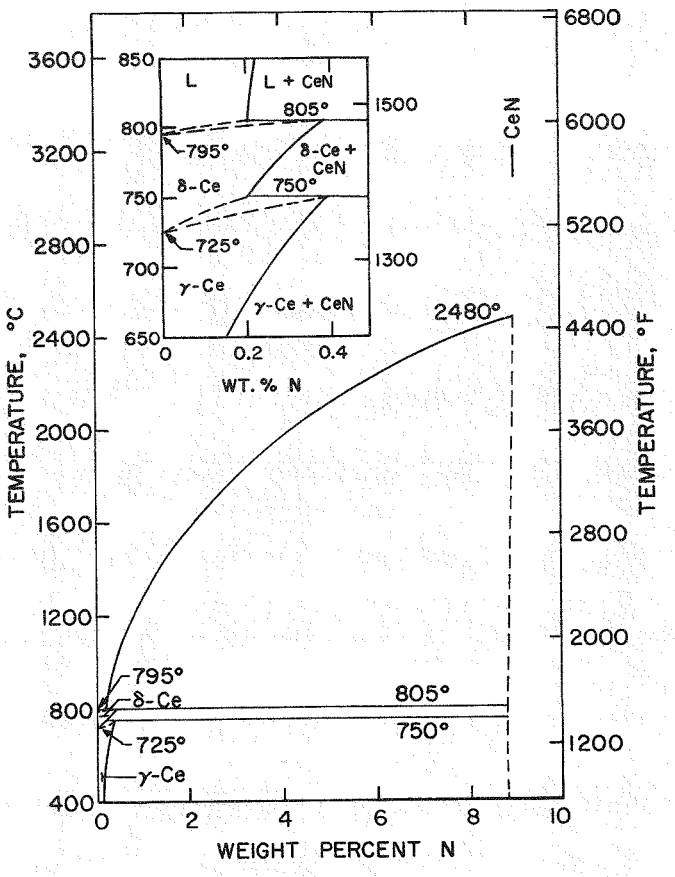

Fig. 12a. Ce-N Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	References
CeN	cubic	5.023±3	803, 837, 939-44

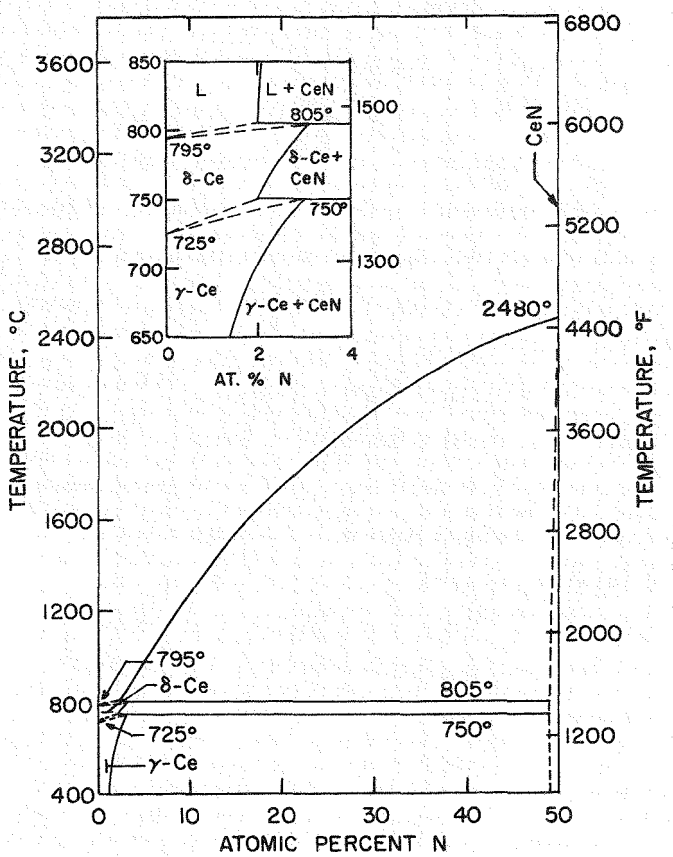

Fig. 12b. Ce-N Phase Diagram (in a/o).

CeN, the only intermediate phase detected at normal pressures, forms congruently. The melting point of CeN was reported by O'Dell and Hensley[937] as a function of N_2 pressure, and reported to be 2575±20°C at 5±1 atm. pressure. Using their equation we calculate the melting point to be 2480°C. This value was used rather than the 2600°C given by Kobzenko and Ivanchenko.[936] CeN appears to be substoichiometric with a solid solubility range as indicated by the phase diagram of Kobzenko and Ivanchenko.[936]

Kieffer and co-workers[938] report the formation of CeN_2 at pressures between 30 and 300 atm. Very little additional information is known about this high pressure phase.

The solubilities of N in γ-and δ-Ce are approximate. (See insertions in Figures 12a and 12b).

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CERIUM – OXYGEN

PHASE DIAGRAM

A great deal of information is known about the cerium-oxygen system in the range Ce_2O_3 to CeO_2 (60 to 66 a/o O; 15 to 18 w/o O),[803, 945] but essentially nothing is known at lower oxygen concentrations. This is unfortunate, since the emphasis of this report is on metallurgical systems and, thus, the main interest in the cerium-oxygen phase relationships would be between pure cerium and the first cerium-rich compound, probably Ce_2O_3.

The best we can do at the present time is speculate about the cerium-oxygen phase diagram between 0 and 60 a/o O (0 and 15 w/o O). The Ce_2O_3 phase is known to exist.[803, 945] Two widely variant values for the melting point of Ce_2O_3 have been reported, 1690°C[803] and 2140°C.[951] In view of the melting points of the other rare earth sesquioxides, the higher value would appear to be more reasonable. From examinations of the Ce_2O_3 phase by means of mass effusion and mass spectrometric analyses, Ackermann and Rauh[946] have reported the existence of substoichiometric Ce_2O_{3-x} compositions with x varying from 0.32 at ~1710°C to near zero at ~1240°C. This represents a composition range from 57.2 to 60 a/o O (13.2 to 15 w/o O), respectively. A slightly superstoichiometric phase also was observed between ~1730°C and 2030°C.[946]

CeO has been reported to exist in the vapor state[946, 949-50] but it is very doubtful that the monoxide phase exists in the solid state, except possibly when stabilized by a large amount of a second nonmetallic element. Vapor pressure measurements of Ce-Ce_2O_3 mixtures further confirm the non-existence of solid CeO between 1277 and 1777°C.[946]

From an analogy to the Y-O system,[947-8] an extensive terminal solid solubility range — up to 25 a/o O (3.7 w/o O) or more — in δ-Ce might be expected near the melting point with solubility in γ-Ce probably decreasing to 1 a/o O (0.1 w/o O) or less at room temperature. Futhermore, oxygen would be expected to raise the melting point of cerium, but lower the transformation point.

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	c	References
Ce_2O_3	hex.	3.888±1	6.062±8	803, 952

REFERENCES

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CERIUM – PHOSPHORUS

PHASE DIAGRAM

Phase equilibria data for the Ce-P system have not been determined. At least three phases, in addition to the well-characterized monophosphide, have been noted in the literature.[953-4] Schmid and Hahn[954] give the stoichiometries as $CeP_{1.7-2.4}$, $CeP_{3.5-6.5}$ and $CeP_{6.5-9.0}$. Olcese[818] reported a phase with CeP_2 stoichiometry, which is probably the same as Schmid and Hahn's[954] $CeP_{1.7-2.4}$ phase. Ono[953] found a cerium phosphide at the CeP_5 composition, and it is quite likely that this phase corresponds to Schmid and Hahn's[954] $CeP_{3.5-6.5}$ alloy. We cannot rule out the possibility, however, that Olcese's CeP_2 and Ono's CeP_5 phases are distinctly different from those found by Schmid and Hahn.

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	References
CeP	cubic	5.923±28	803, 818, 822, 827, 955

REFERENCES

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CERIUM — SELENIUM

PHASE DIAGRAM

Insufficient phase equilibria data are available to construct a constitutional diagram. Guittard and Flahaut,[956] reviewing the rare earth-selenium phase diagrams, report that the phases CeSe, Ce_2Se_3-Ce_3Se_4 solid solution, Ce_4Se_7 and $CeSe_2$ exist. $CeSe_2$ apparently has three polymorphic modifications (see Table below) and possibly may form a selenium deficient solid solution region, although the data of Yarembash and Eliseev[957] suggest a distinct phase $CeSe_{2-x}$ ($x \leq 0.2$). Yarembash[958] reported that both Ce_2Se_3 and Ce_3Se_4 melt congruently at 1750 and 1800° C, respectively, while $CeSe_2$ melts incongruently at 750° C.[959] The melting modes of the remaining two compounds — CeSe and Ce_4Se_7 — are unknown.

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
CeSe	cubic	5.988±4	-	-	803, 822, 956, 960-1
Ce_3Se_4[a]	cubic	8.973	-	-	803, 962
Ce_2Se_3[a]	cubic	8.970±10	-	-	958-9, 961, 963-6
Ce_4Se_7	mono.[b]	8.375	8.375	8.487	967
$CeSe_{2-x}$ ($x \leq 0.2$)	tetr.	4.22	-	8.51	957
$CeSe_2$	mono.[c]	8.420±5	4.210±5	8.482±5	968
$CeSe_2$	tetr.	8.430±9	-	8.486±4	825, 959, 969; 969 rept. compd. to have mono. structure in later publ. (968).
$CeSe_2$	hex.	8.45	-	8.51	803

[a] This compound is the terminal composition of a solid solution region between 57.2 and 60.0 a/o Se (43.0 and 45.8 w/o Se).

[b] The oblique angle, β, is approximately equal to 90°.

[c] The "oblique" angle, β, is equal to 90°.

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CERIUM – SILICON

PHASE DIAGRAM

Benesovsky et al.[970] examined the Ce-Si system by means of thermal, X-ray and metallographic analyses using 99.5% pure Ce and 99.7% pure Si. No analysis of the impurities contained in either stock was reported. Although based primarily on their results, Figures 13a and 13b also incorporate data of other researchers. Ten different compositions for intermediate phases have been reported in the literature, but Benesovky et al.[970] indicated only six of these on their phase diagram – congruently formed Ce_2Si, Ce_3Si_2, $Ce_{\sim 1.2}Si$ (Ce_6Si_5), CeSi, and $CeSi_2$ plus a single incongruently forming compound, $CeSi_{<2}$. In a later paper, Benesovsky and co-workers[971] report that Ce_2Si (33.3 a/o, 9.1 w/o Si) actually has the Ce_5Si_3 composition (37.5 a/o, 10.7 w/o Si) with the Cr_5B_3 type structure. Also, $Ce_{\sim 1.2}Si$ (45.5 a/o, 14.3 w/o Si) is reported[971] to have instead

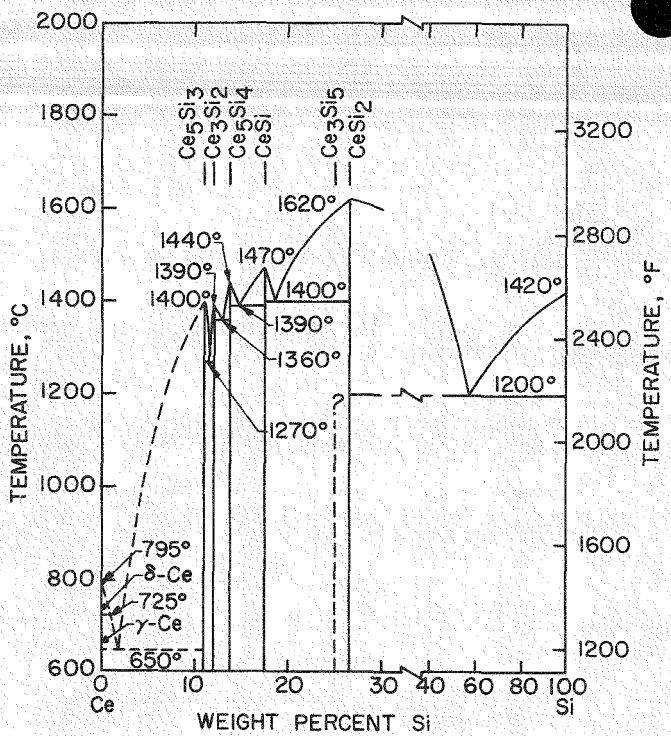

Fig. 13 a. Ce-Si Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
Ce_5Si_3[a]	tetr.	7.886±5	-	13.75±6	971, 974-7
Ce_3Si_2	tetr.	7.802±18	-	4.323±26	970-1, 974, 978
Ce_5Si_4	tetr.	7.93	-	15.04	976
CeSi	ortho.	8.287±47	3.957±15	5.984±33	803, 970-1, 974 979-80
Ce_3Si_5	ortho.	4.180±5	4.100±5	13.82±1	974
$CeSi_2$	tetr.	4.177±27	-	13.876±28	803, 899, 971, 974, 981-2

[a]Some older and preliminary information as summarized by Gschneidner[803] indicated another structure for this compound, but in view of the more recent data it is doubtful that the earlier reported hexagonal structure is correct.

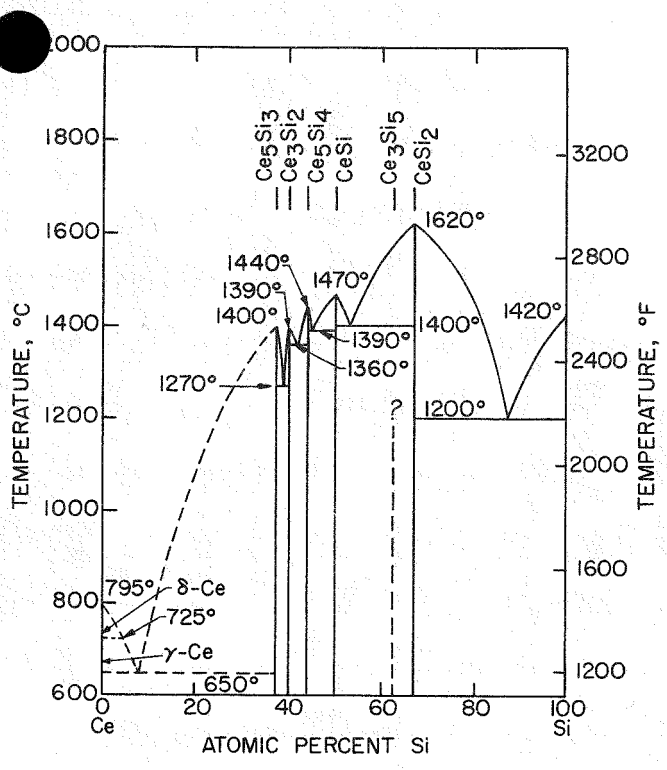

Fig. 13b. Ce-Si Phase Diagram (in a/o).

the Ce_5Si_4 (44.4 a/o, 13.8 w/o Si) stoichiometry with the Zr_5Si_4 type structure. Structure type and composition suggest that $CeSi_{<2}$, and also the $CeSi_{1.7-2.0}$[972] and $CeSi_{2-x}$[973] stoichiometries reported by others, are probably equivalent to Ce_3Si_5.[974] It is quite likely that $CeSi_{\sim 1.3}$ ($\sim Ce_3Si_4$)[972] is also the same phase as Ce_3Si_5.

Six eutectic reactions occur —

$L \rightleftarrows Ce + Ce_5Si_3$ at 8 a/o Si (1.7 w/o Si)

$L \rightleftarrows Ce_5Si_3 + Ce_3Si_2$ at 38.5 a/o Si (11.1 w/o Si)

$L \rightleftarrows Ce_3Si_2 + Ce_5Si_4$ at 42 a/o Si (13 w/o Si)

$L \rightleftarrows Ce_5Si_4 + CeSi$ at 46 a/o Si (15 w/o Si)

$L \rightleftarrows CeSi + Ce_3Si_5$ (?) at 53 a/o (18 w/o Si).

$L \rightleftarrows CeSi_2 + Si$ at 87 a/o Si (57 w/o Si).

The original diagram given by Benesovsky and co-workers has been modified to incorporate their more recent data. The solid solubilities of Ce in Si and Si in Ce are unknown.

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CERIUM – SILVER

PHASE DIAGRAM

Five different compound stoichiometries have been identified: CeAg,[803, 983-6] $CeAg_2$,[803, 987] $CeAg_3$,[803, 988] $CeAg_{3.6}$[989] and $CeAg_5$.[989-90] An X-ray and metallographic study by McMasters and coworkers[989] clearly showed that the $CeAg_3$ stoichiometry is actually $CeAg_{3.6}$. The phase relationships as reviewed by Gschneidner[803] are based on a study made before 1943, and assuming these are reasonably correct except for the region between 70 and 85 a/o Ag (64 and 81 w/o Ag), the results are presented in Figures 14a and 14b. Between 70 and 85 a/o Ag we have changed the $CeAg_3$ composition to $CeAg_{3.6}$, but assumed the melting point to be reasonably correct.

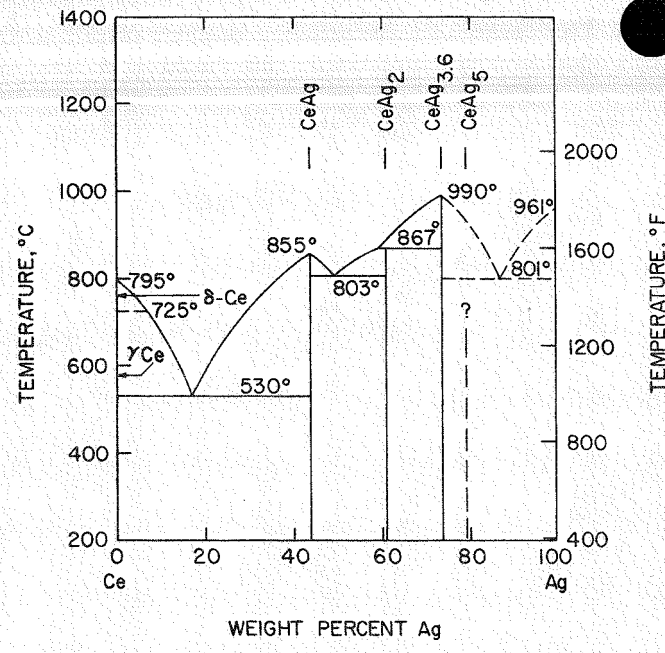

Fig. 14a. Ce-Ag Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
CeAg	cubic	3.754±8	-	-	803, 983-6
$CeAg_2$	ortho.	4.800	7.090	8.205	987
$CeAg_{3.6}$	hex.	12.831±52	-	9.438±18	988-9

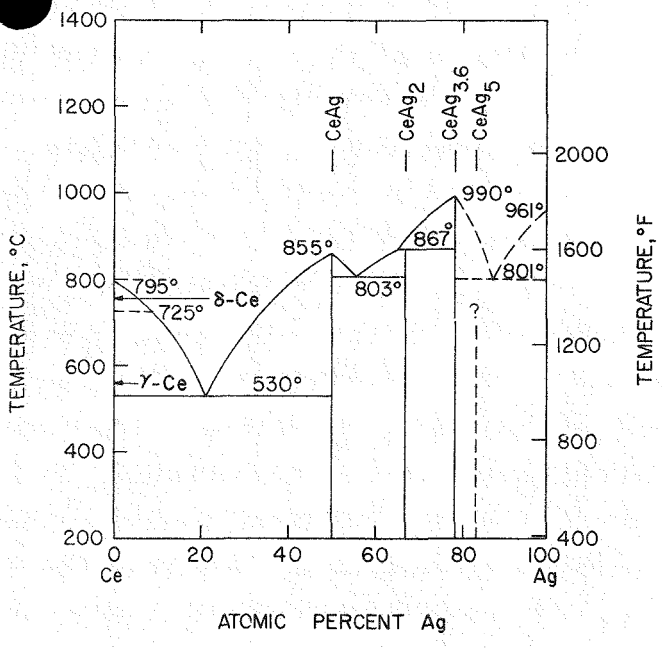

Fig. 14b. Ce-Ag Phase Diagram (in a/o).

The mode of formation of $CeAg_5$ is unknown and thus the exact phase relationships between 79 and 85 a/o Ag (74 and 81 w/o Ag) need to be determined. The high temperature form of $CeAg_5$ is reported to be related to the Laves phase type compound.[989]

A maximum solid solubility of Ce in Ag of 0.04 to 0.06 a/o Ce (0.05 to 0.08 w/o Ce) was extrapolated from lattice parameter values of the two-phase alloys by Gschneidner et al.[990] They also confirmed the 801°C Ag-rich eutectic temperature. Three eutectic reactions occur – $L \rightleftarrows Ce + CeAg$ at 21 a/o Ag (17 w/o Ag), $L \rightleftarrows CeAg + CeAg_2$ at 56 a/o Ag (49 w/o Ag), and $L \rightleftarrows CeAg_5(?) + Ag$ at 90 a/o Ag (?) (87 w/o Ag).

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CERIUM – SULFUR

PHASE DIAGRAM

The partial phase diagrams of Figures 15a and 15b are based primarily on the available equilibria data as reviewed by Gschneidner.[803] Five intermediate phases exist – congruently forming CeS, Ce_3S_4 and Ce_2S_3; the peritectoidally forming compound Ce_5S_7; and CeS_2, for which the mode of formation has not been determined. Three polymorphic forms of Ce_2S_3 have been reported in the literature,[803, 969, 991-5] but according to Besancon et al.,[996] the Ce_5S_7 stoichiometry more accurately represents the phase previously identified[969] as the β-form of Ce_2S_3. Klinvex and Berger[997] report that CeS, Ce_3S_4, Ce_5S_7 and Ce_2S_3 all exist from 600 to 1300° C and that γ-Ce_2S_3 exists above 1100° C. Between 1800 and 1300° C, the phase relationships for alloys of 55 to 70 a/o S (22

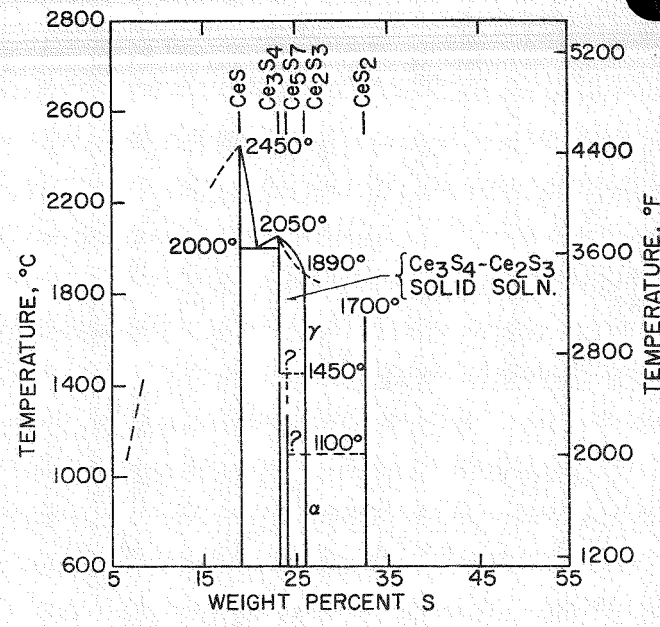

Fig. 15a. Ce-S Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
CeS	cubic	5.769±4	-	-	803, 822, 960, 994, 998
Ce_3S_4[a]	cubic	8.628±3	-	-	803, 994, 997
Ce_5S_7	tetr.	15.19	-	20.19	991, 996
α-Ce_2S_3	ortho.	7.513	4.091	15.715	803, 969, 991-3
γ-Ce_2S_3[a]	cubic	8.630±1	-	-	803, 969, 994-5
CeS_2	cubic	8.115±5	-	-	803, 969

[a] These two phases form a complete series of solid solutions at high temperature.

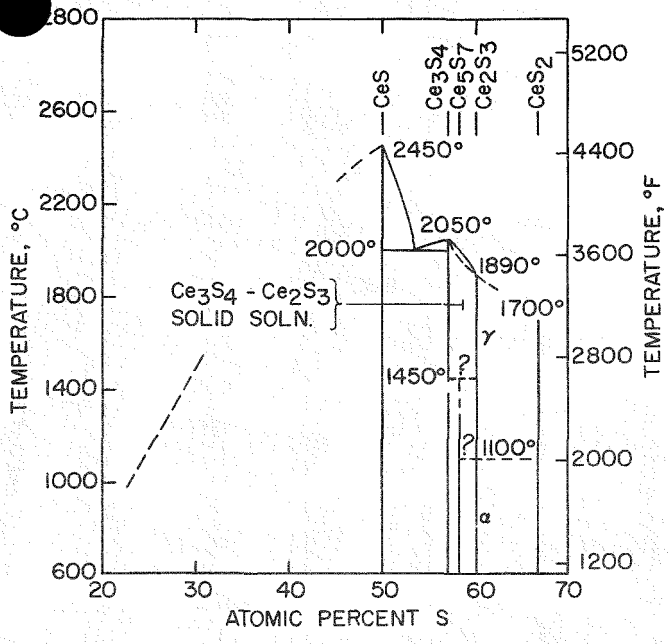

Fig. 15b. Ce-S Phase Diagram (in a/o).

to 35 w/o S) are not well established and need to be verified.

Earlier data indicated phase transformations at 1150 and 1450°C for the Ce_2S_3 stoichiometry,[803] but the results of Klinvex and Berger[997] suggest that the 1150°C temperature horizontal might be due to the $\alpha \rightleftarrows \gamma$ transformation of Ce_2S_3. The 1450°C temperature could be associated with the formation of Ce_5S_7. Klinvex and Berger[997] also give liquidus points for Ce-rich alloys as: 1300°C and 25 a/o S (7.2 w/o S) and 1115°C and 27 a/o S (8.0 w/o S). Although the liquidus compositions seem to be inverted for the two temperatures, the steep rise in the liquidus curve could lead to such experimental inaccuracies. A eutectic reaction — $L \rightleftarrows CeS + Ce_3S_4$ — occurs at 53.4 a/o S (20.8 w/o S).

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CERIUM — TELLURIUM

PHASE DIAGRAM

Chukalin et al.[999,1000] studied the Ce-Te system by means of X-ray, metallographic and thermal analyses using 99.5% pure Ce and 99.99% pure Te. However, the reported Te-rich eutectic temperature (455° C) is appreciably higher than the accepted melting point of Te (449.6° C), indicating that the purity of the Te stock was probably much lower than stated. This would especially affect the Te-rich portion of the diagram. From an examination of this system between 65 and 100 a/o Te (63 and 100 w/o Te) by means of X-ray and thermal analyses, Pardo and co-workers[1001-3] suggest that the Te-rich eutectic occurs instead at 435° C and 99 a/o Te (99 w/o Te). It is thought that the results of Pardo et al. for the Te-rich end are more accurate, and their data are used in Figures 16a and 16b between 70 and 100 a/o Te (68 and 100 w/o Te). The remaining portion of the diagram is based on the results of Chukalin and co-workers.[999, 1000]

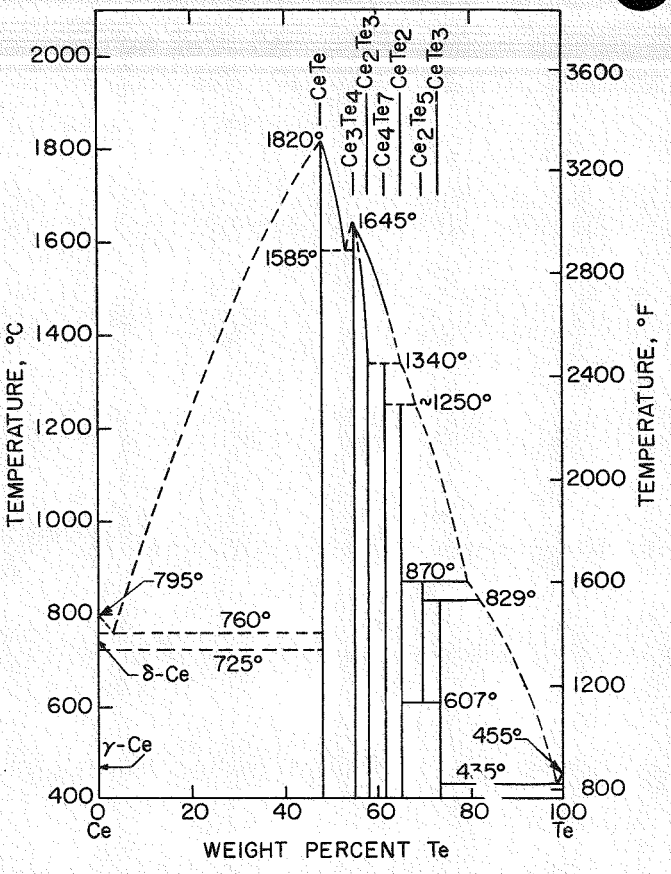

Fig. 16a. Ce-Te Phase Diagram (in w/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
CeTe	cubic	6.350±9	-	-	803, 822, 961 1000
Ce_3Te_4[a]	cubic	9.549±17	-	-	803, 1000, 1004
Ce_2Te_3[a]	cubic	9.536±6	-	-	1000, 1004-7
Ce_4Te_7	tetr.	8.988	-	9.167	1000
$CeTe_{1.9-2.0}$[b]	tetr.	4.47-4.54	-	9.10-9.12	803, 1008-9
Ce_2Te_5	ortho.	4.444±10	4.444±10	44.35	1000-2
$CeTe_3$	ortho.	4.398±5	4.398±5	25.99±3	1000-1, 1003

[a] These two compounds represent the terminal members of a solid solution region which occurs between 57.1 and 60.0 a/o Te (54.8 and 57.7 w/o Te).

[b] Compound exists over a solid solution range. Lattice parameters vary over range listed.

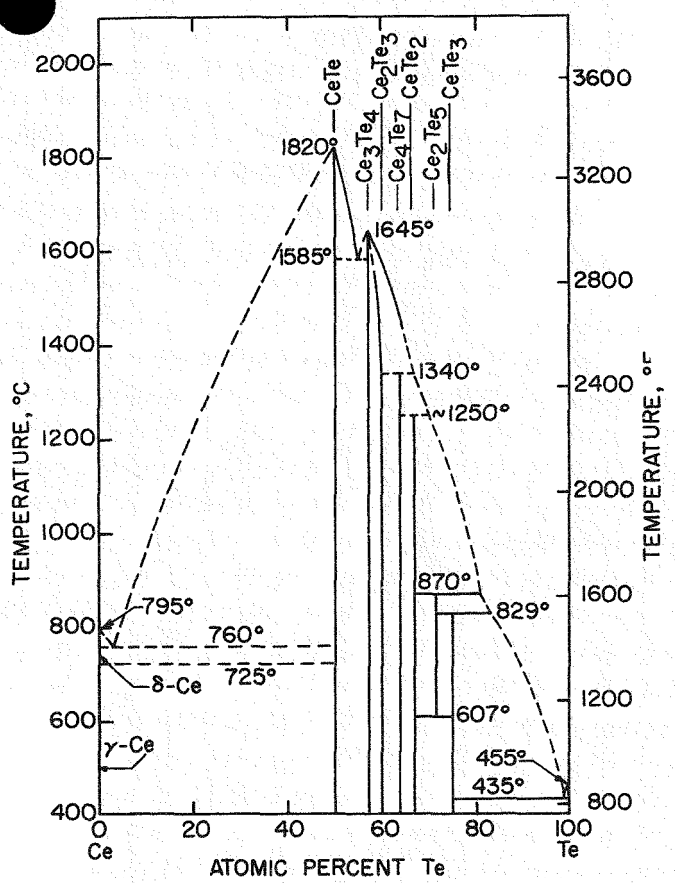

Fig. 16b. Ce-Te Phase Diagram (in a/o).

Seven intermediate phases have been identified, two of which form congruently — CeTe and Ce_3Te_4. The five incongruently melting compounds are Ce_2Te_3, Ce_4Te_7, $CeTe_2$, Ce_2Te_5 and $CeTe_3$. Chukalin et al.[1000] report that solid solutions exist from Ce_3Te_4 to Ce_2Te_3 (57.1 to 60.0 a/o Te; 54.8 to 57.7 w/o Te) and from $CeTe_{1.94}$ to $CeTe_{2.0}$ (66.0 to 66.67 a/o Te; 63.9 to 64.56 w/o Te). According to Pardo and Flahaut,[1001] Ce_2Te_5 exists only from 607 ± 19°C to 870°C. Three eutectic reactions occur — $L \rightleftarrows Ce$ + CeTe at 3 a/o Te (3 w/o Te),[1000] $L \rightleftarrows CeTe + Ce_3Te_4$ at 55 a/o Te (53 w/o Te),[1000] and $L \rightleftarrows CeTe_3$ + Te at 99 a/o Te (99 w/o Te).[1001]

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CERIUM – TIN

PHASE DIAGRAM

Some phase equilibria data were determined prior to the 1950's, but the results are not reliable and thus are not included here. The earlier diagram is given in Gschneidner's 1961 review.[803] X-ray data have confirmed the existence of Ce_3Sn, Ce_5Sn_3, Ce_5Sn_4 and $CeSn_3$ (see below). An X-ray and metallographic study of the tin-rich end has also revealed the existence of Ce_3Sn_7 (70.0 a/o, 66.4 w/o Sn) and Ce_2Sn_5 (71.4 a/o, 67.9 w/o Sn), but the structures of these phases were not determined.[1010]

On the basis of studies of the Sm-Sn[1011] and Y-Sn[1012] systems and the similarities expected for the R-Sn and R-Pb systems, the Ce_5Sn_3 phase is probably the highest melting intermetallic compound in the Ce-Sn system, with a melting point estimated to be in excess of 1400° C. The $CeSn_3$ compound is expected to melt congruently with a melting point near 1150° C.

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
Ce_3Sn	cubic	4.929	-	-	895
Ce_5Sn_3	hex.	9.328±5	-	6.788±5	1013; 1014 reptd. unable to prepare
Ce_5Sn_4	ortho.	8.337	16.05	8.480	1015
$CeSn_3$	cubic	4.720±3	-	-	803, 898-9, 1016

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CERIUM – TITANIUM

E DIAGRAM

Figures 17a and 17b combine the results of Savitskii and Burkhanov[1017] with data reviewed earlier by Gschneidner.[803] The solid solubility limits of Ce in Ti, as given by Savitskii and Burkhanov, appear to be high. Thus, compositions around the $\alpha \rightleftarrows \beta$ Ti transition are based on the earlier results.[803] The $\alpha \rightleftarrows \beta$ Ti transformation temperature for alloys saturated with Ce is a mean value as is the monotectic temperature. According to Savitskii and Burkhanov's diagram,[1017] Ti lowers the melting point and the $\delta \rightleftarrows \gamma$ Ce transformation temperature. The solid solubility limits for the Ce-rich end are unknown and probably greatly exaggerated in the diagram. A eutectic and monotectic reaction occur — $L_1 \rightleftarrows \alpha\text{-Ti} + \delta\text{-Ce}$ and $L_2 \rightleftarrows \beta\text{-Ti} + L_1$, respectively.

CRYSTAL DATA

No solid compounds exist in the Ce-Ti system.

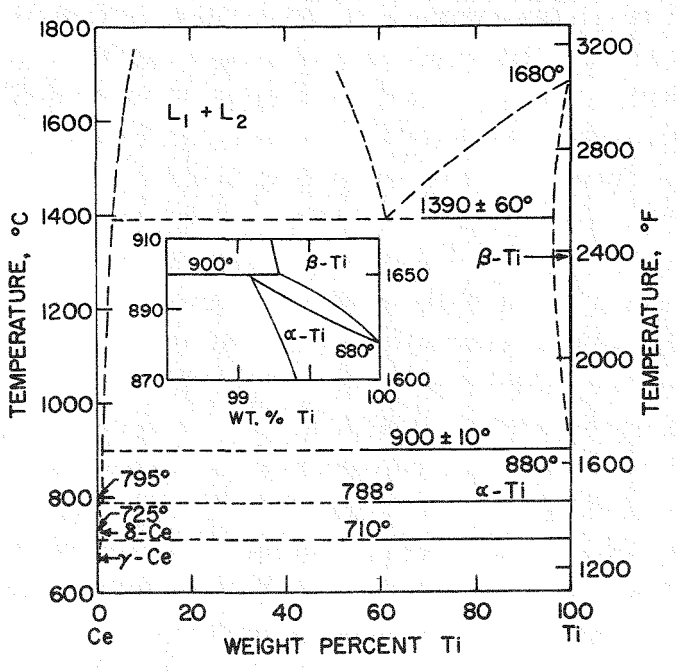

Fig. 17a. Ce-Ti Phase Diagram (in w/o).

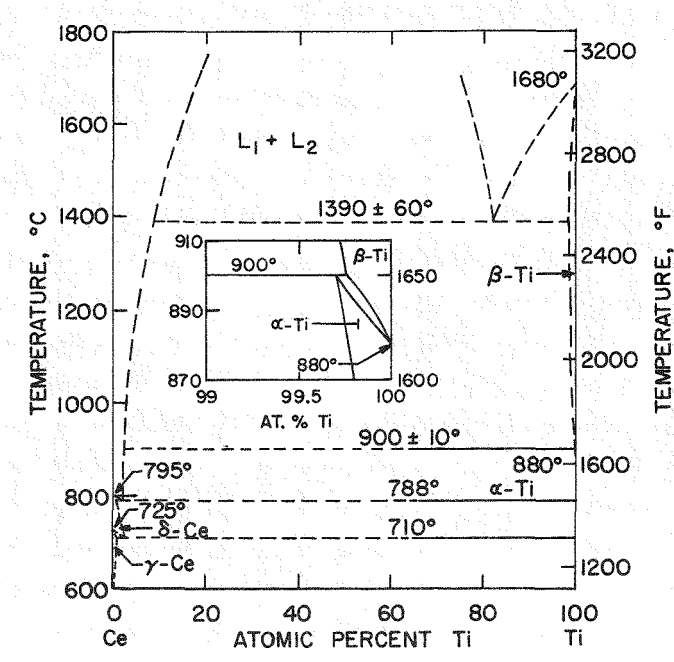

Fig. 17b. Ce-Ti Phase Diagram (in a/o).

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CERIUM – TUNGSTEN

PHASE DIAGRAM

Insufficient phase equilibria data are available on the Ce-W system. Two peritectically forming compounds, one of which is probably CeW_2, – have been reported.[1018] A eutectic was observed near pure cerium.[1018] The solubility of tungsten in liquid Ce was determined by Dennison and co-workers[1019] to increase from 0.0242 a/o W (0.0317 w/o W) at 1537°C to 0.1238 a/o W (0.1624 w/o W) at 2077°C, obeying the usual log concentration vs. 1/T equation:

$$\log N = -\frac{5.418}{T} - 0.588$$

where N is the concentration in atomic fraction of W and T is in °K.

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CERIUM – VANADIUM

PHASE DIAGRAM

Figures 18a and 18b are based primarily on an examination of the vanadium-rich alloys in the Ce-V system by Savitskii et al.[1020] using 99.77% pure V and 98.8% pure Ce. The authors report a monotectic at 99.89 to 99.93 a/o V (99.7 to 99.8 w/o V) and 1885 ± 15°C, approximately the same temperature as the melting point of vanadium. The immiscible liquids formed by the two metals[803, 1021] exhibit a critical point, which was calculated to be 2480°C and 75 a/o V (52 w/o V).[1022] Komjathy and co-workers[1021] observed little or no solubility of Ce in V and Savitskii et al.[1020] reported only 0.036 a/o Ce (0.1 w/o Ce) in V at all temperatures with no observable changes in the lattice parameters of V containing Ce additions. However, Efimov[1022] found that 0.11 a/o Ce (0.30 w/o Ce) dissolves at 1885°C and a significant increase in solubility in liquid V was observed at 2000°C (1.90 a/o or 5.02 w/o Ce).

A confusing picture exists for the solubility of V in liquid Ce. Komjathy and co-workers[1021] reported that 13 to 23 a/o V (5 to 10 w/o V) is dissolved at the monotectic temperature, but Efimov[1022] found a solubility of 1.6 a/o V (0.57 w/o V) in liquid Ce at the monotectic and 2.0 a/o V (0.72 w/o V) at 2000°C. Savitskii et al.[1020] noted that V raises the melting point of Ce 5-7°C and lowers the $\delta \rightleftarrows \gamma$ transition temperature by 20-25°C, but exact data were not reported.

CRYSTAL DATA

No solid compounds exist in the cerium-vanadium system.

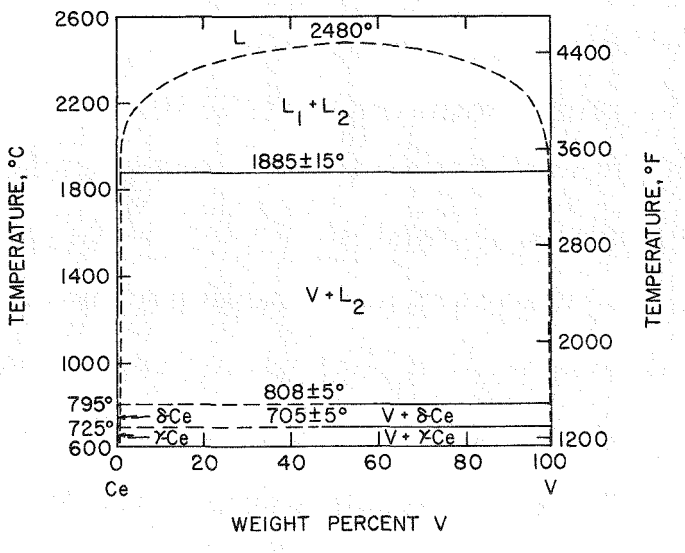

Fig. 18a. Ce-V Phase Diagram (in w/o).

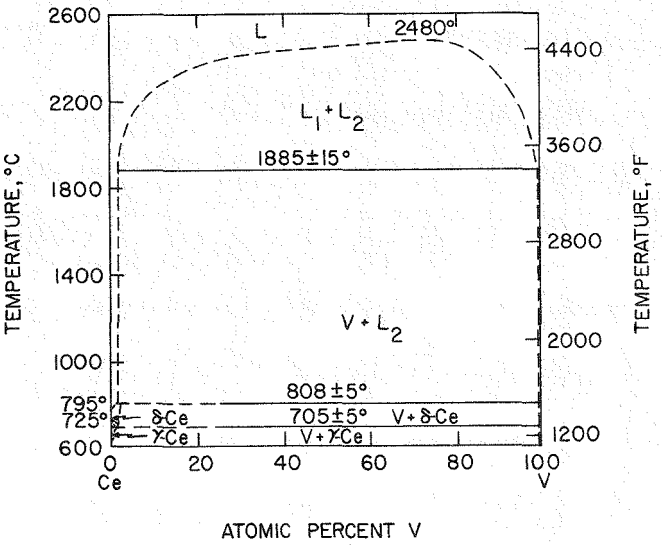

Fig. 18b. Ce-V Phase Diagram (in a/o).

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CERIUM – ZINC

PHASE DIAGRAM

Chiotti and Mason[1023] examined the Ce-Zn system by means of metallographic, thermal, X-ray and vapor pressure analyses under constrained vapor conditions using 99.99% pure zinc and 99.7% pure cerium. The cerium stock contained Mg, Fe, Si and O as the major impurities. Figures 19a and 19b are based on their results. Of the nine compounds identified, three form congruently – CeZn, $CeZn_2$ and $CeZn_{8.5}$ The remaining six form peritectically – $CeZn_3$, $CeZn_{3.67}$, $CeZn_{4.5}$, $CeZn_{5.25}$, $CeZn_7$ and $CeZn_{11}$. A composition range of 83.6 to 84.1 a/o Zn (70.4 to 71.1 w/o Zn; $CeZn_{5.1}$ to $CeZn_{5.3}$) has been determined for the $CeZn_{5.25}$ stoichiometry from X-ray diffractometer patterns and a c/a versus composition plot. $CeZn_{\sim 5}$ and $CeZn_5$ (83.2 a/o Zn, 69.8 w/o Zn) alloys reported by other researchers[803, 1024-5] lie close to this solid solubility region. Examination of the microstructure of ~87.5 a/o Zn (~76.6 w/o Zn) compositions indicates that the true stoichiometry of the $CeZn_7$ alloys is actually richer in Zn than the formula suggests.[1023, 1026] Thus, Ce_3Zn_{22}[1027] and $CeZn_7$ are probably equivalent. Two structural forms of Ce_2Zn_{17} ($CeZn_{8.5}$) have been observed,[1026, 1028-9] but the $\alpha \rightarrow \beta$ allotropic transformation is not reversible.[1028] Excess zinc appears to stabilize the α-form.[1028]

Three eutectic compositions exist – γ-Ce + CeZn at 19.2 a/o Zn (10 w/o Zn), CeZn + $CeZn_2$ at 55.7 a/o Zn (37 w/o Zn), and $CeZn_2$ + $CeZn_3$ at 73.2 a/o Zn (56 w/o Zn). From X-ray diffractometer patterns,

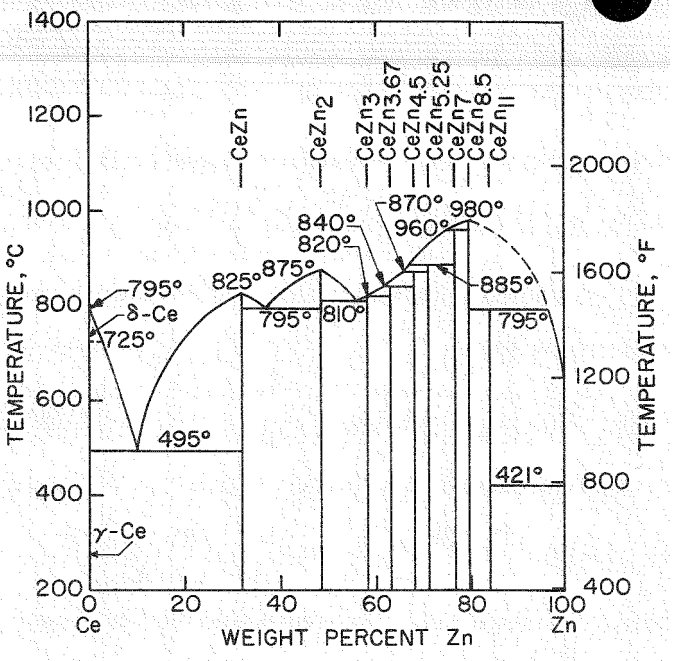

Fig. 19a. Ce-Zn Phase Diagram (in w/o).

Chiotti and Mason[1023] conclude that the solubility of Zn in Ce is << 2 a/o Zn (<< 1 w/o Zn) at 540°C. The solubility of Ce in liquid Zn has been reported[1030] to obey the usual log X vs. 1/T relationship over the 500-795°C temperature range:

$$\log X = 4.634 - \frac{6.952}{T}$$

where X is the mole fraction of Ce and T is in °K. These values are in good agreement with earlier results,[803, 1] but cover a wider temperature range. The solid solubility limit of Ce in Zn has been given as 0.0056 a/o Ce (0.012 w/o Ce).[1032]

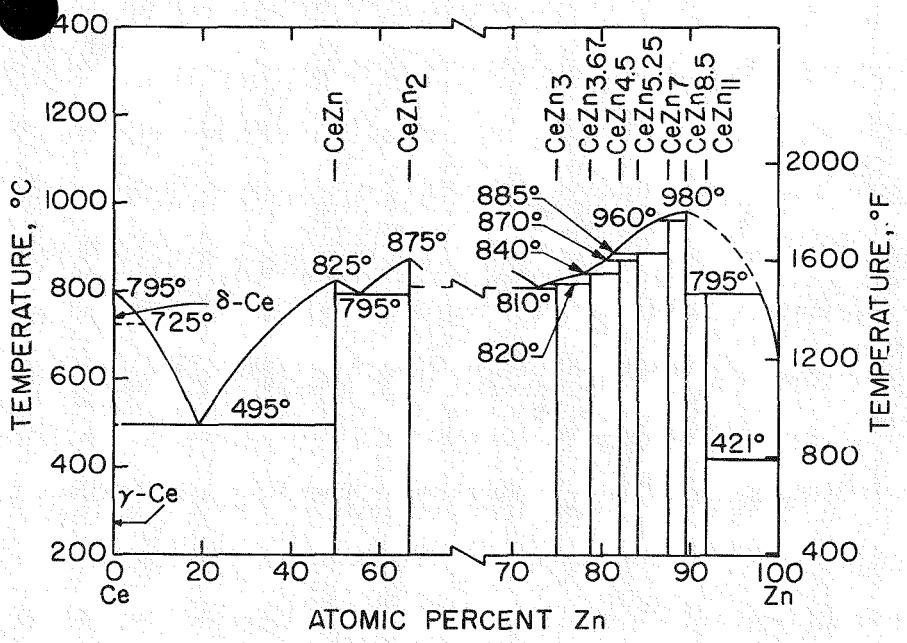

Fig. 19b. Ce-Zn Phase Diagram (in a/o).

CRYSTAL DATA

Compound	Crystal Class	Lattice Parameters Å a	b	c	References
CeZn	cubic	3.708±5	-	-	803, 1025
$CeZn_2$	ortho.	4.633	7.538	7.499	1023, 1026, 1029
$CeZn_3$	ortho.	4.620	10.440	6.640	1023, 1026
$CeZn_{3.67}$	ortho.	4.5215	8.8855	13.463	1023, 1026
$CeZn_{\sim 4.5}$	hex.	14.600	-	14.110	1023, 1026
$CeZn_{5.25}$[a]	hex.	5.404±13	-	4.264±7	810, 1024-6
Ce_3Zn_{22}	tetr.	8.94±1	-	21.33±5	1027
$CeZn_{8.5}$ or α-Ce_2Zn_{17}	rhomb.	9.079±9[b]	-	13.287±3[b]	1026, 1028
β-Ce_2Zn_{17}	hex.	9.086±3	-	8.860±4	1028-9
$CeZn_{11}$	tetr.	10.66	-	6.855	803, 1025

[a]Variation in lattice parameters is due to the existence of a range of solid solutions (see text).

[b]Lattice parameters are for the hexagonal unit cell.

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