

The Al-Gd (Aluminum-Gadolinium) System

By K.A. Gschneidner, Jr. and F.W. Calderwood
Iowa State University

Equilibrium Diagram

The Gd-rich part of the Gd-Al system was investigated by [64Cop], the Al-rich portion by [67Run], and the entire system by [65Bus1]. The assessed Gd-Al phase diagram (Fig. 1) is based essentially on the study by [65Bus1]. The melting point temperatures for Al and Gd and the $\alpha \leftrightarrow \beta$ transformation temperature for Gd are accepted from [86Gsc]. Because these temperatures were not given by [65Bus1], no adjustments were made to the various isotherms on the phase diagram.

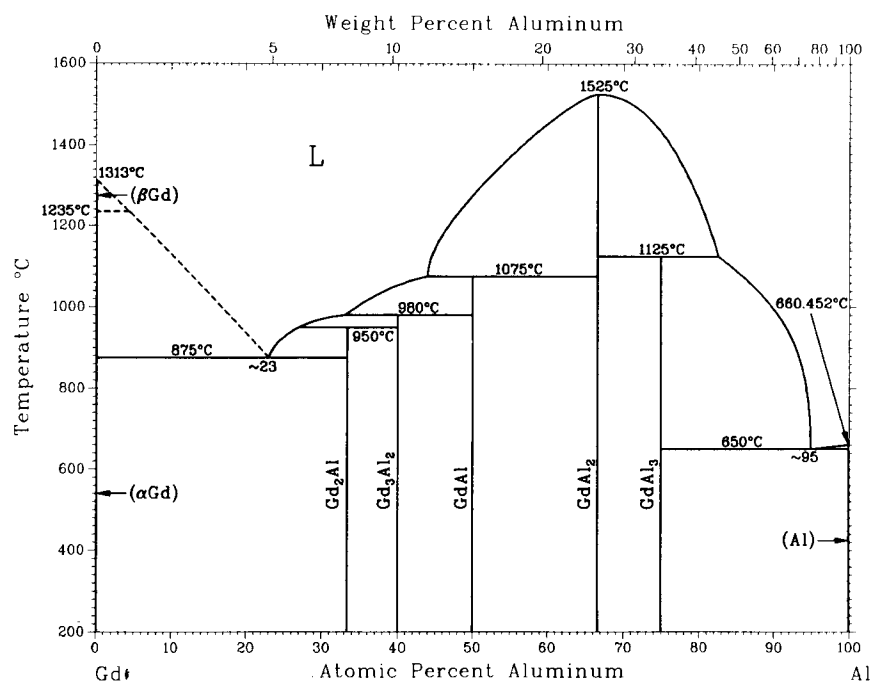
Although the phase diagram presented by [65Bus1] showed a eutectic between (Al) and $GdAl_3$ at 650 °C and a eutectic between Gd_2Al and (Gd) at 875 °C, the eutectic compositions were not stated specifically in his report. Scaling of his phase diagram indicated that the eutectic compositions are 95 at.% and ~23 at.% Al, respectively. No values were shown for the maximum solid solubility of either metal in the other. [67Bus] stated that whereas the solubility of Al in the RE metals is generally quite small, it seems to increase with decreasing RE radius.

[64Cop] were interested in the solubility of several nonlanthanide metals in (Sm), (Gd), (Dy), and (Er),

and from their study, they prepared phase diagrams over the composition range between the RE metal and the first lanthanide-rich compound or eutectic in each system, whichever occurred first (generally, the eutectic). Alloys were prepared from Al containing 10 to 100 ppm (weight?) Cu and from less pure Gd (100 to 1000 ppm each of Al and Si, 630 ppm oxygen, 10 to 100 ppm Cu, 70 ppm Fe, and 3 to 30 ppm B, probably on a weight basis). Alloys were melted under helium in an arc furnace, with a nonconsumable tungsten electrode and a water-cooled copper hearth, annealed by heating under vacuum in a resistance furnace to within 50 °C of the solidus temperature as determined by preliminary thermal analysis, then allowed to cool in the furnace. The annealed specimens were examined by thermal analysis and X-ray diffraction. [64Cop] reported that Gd_3Al undergoes a solid-state transformation at 645 °C. The melting temperature and the allotropic structures of this compound were not determined. They observed a eutectic at about 19.5 at.% (~4 wt.%) Al and 850 °C. Solubility was reported to be less than 1.16 at.% (0.2 wt.%) Al, but an exact value was not determined.

[67Run] using 99.99% + Al and 99.9% Gd (weight?), prepared alloys by dropping Gd metal into molten Al in a graphite crucible within an induction furnace. Liquid

Fig. 1 Assessed Gd-Al Phase Diagram



K.A. Gschneidner, Jr. and F.W. Calderwood, 1988.

Table 1 Gd-Al Crystal Structure Data

Phase	Composition, at.% Al	Pearson symbol	Space group	Strukturbericht designation	Prototype
(α Gd)	0	<i>hP2</i>	<i>P6₃/mmc</i>	A3	Mg
(β Gd)	0	<i>cI2</i>	<i>Im$\bar{3}m$</i>	A2	W
Gd ₂ Al	33.3	<i>oP12</i>	<i>Pnma</i>	C23	Co ₂ Si
Gd ₃ Al ₂	40	<i>tP20</i>	<i>P4₂/mnm</i>	...	Al ₂ Zr ₃
GdAl	50	<i>oP16</i>	<i>Pmma</i>	...	AlEr
GdAl ₂	66.7	<i>cF24</i>	<i>Fd$\bar{3}m$</i>	C15	Cu ₂ Mg
GdAl ₃	75	<i>hP8</i>	<i>P6₃/mmc</i>	D0 ₁₉	Ni ₃ Sn
(Al)	100	<i>cF4</i>	<i>Fm$\bar{3}m$</i>	A1	Cu

Table 2 Gd-Al Lattice Parameter Data

Phase	Composition, at.% Al	Lattice parameters, nm			Density, g/cm ³	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
(α Gd)	0	0.36336	...	0.57810	7.901	[86Gsc]
(β Gd)	0	0.405	7.86	[86Gsc]
Gd ₂ Al	33.3	0.6606	0.5146	0.9531	7.000	[63Mat]
Gd ₃ Al ₂	40	0.8339(5)	...	0.7620(23)	6.590	(c)
GdAl	50	0.5888	1.153	0.5656	6.375	[65Bus1, 65Bus2]
GdAl ₂	66.7	0.7900(1)	5.692	(b)
GdAl ₃	75	0.6331(5)	...	0.4600(3)	4.954	(a)
(Al)	100	0.40496	2.699	[Pearson2]

(a) [60Mor, 61Bae, 64Vuc, 65Bus1, 65Ian, 66Sta, 67Run, 75Can, 75Hav, 82Uml]. (b) [60Wer, 60Mor, 61Bae, 61Bec, 62Wer, 65Bus1, 65Har, 66Sta, 67Oes, 73Hid, 74Mac, 74Sch, 76Dor, 76Gro, 76Ngu, 77Bar, 77Mil, 78Sle1, 78Sle2, 78Sle3, 79Bes, 81Kon]. (c) [64Bae, 65Bus1, 65Bus2, 66Sta].

alloys were poured into water-cooled molds to provide casting, from which samples for heat treatment and thermal analysis were taken. It is quite possible that some carbon contamination could have been introduced into the alloys, due to the high affinity of Gd for carbon. Thermal analysis was carried out under vacuum in a tungsten resistance furnace. Temperatures were observed by means of a Pt/Pt-10% Rh thermocouple calibrated against the melting point of Al (660 °C) and of Au (1063 °C). Furnace temperatures were raised or lowered at a rate of 1 or 2 °C/per min. Both powder and single-crystal X-ray techniques were utilized.

[67Run] reported that on cooling at a rate of 1 °C/min, a thermal arrest at 643 °C indicated the eutectic solidification of (Al) and GdAl₃. This eutectic mixture contained ~98.1 at.% (~90 wt.%) Al. GdAl₃ was found to have hexagonal Ni₃Sn-type structure. They also reported finding GdAl₄, isotypic with UAl₄, which decomposes by a peritectoid reaction to form (Al) and GdAl₃ at about 400 °C.

[65Bus1] employed metallography, thermal analysis, and X-ray diffraction to prepare a phase diagram for this system. He reported five compounds (Gd₂Al, Gd₃Al₂, GdAl, GdAl₂, and GdAl₃), but not GdAl₄. His alloys were prepared by arc melting under argon 99.99% (weight?) pure Al and 99.9% pure Gd. Major impurities in the Gd, each less than 0.01%, were Cu, Fe, and Mn. X-ray patterns of the as-cast alloys indicated that only the GdAl₂ composition was a single-

phase alloy. After annealing, the X-ray patterns of the other intermetallic compound compositions indicated that each was a single phase.

[65Bus1] found the Gd-rich compound to be Gd₂Al not Gd₃Al, as reported by [64Cop]. In a later report, [67Bus] stated that cubic AuCu₃-type Gd₃Al can be stabilized by a small amount of carbon.

Gd₂Al (orthorhombic Co₂Si-type) decomposes peritectically at 950 °C to the melt and Gd₃Al₂ (tetragonal Zr₃Al₂-type). Gd₃Al₂ decomposes by a peritectic reaction at 980 °C to the melt and GdAl (orthorhombic ErAl-type). GdAl remains stable up to 1075 °C and then decomposes peritectically to the melt GdAl₂ (cubic Cu₂Mg type). GdAl₂ is the only Gd-Al compound to have a congruent melting point (1525 °C). GdAl₃ (hexagonal Ni₃Sn type) decomposes by a peritectic reaction at 1125 °C to the melt and GdAl₂.

Crystal Structures and Lattice Parameters

[65Bus1] attempted to confirm the existence of GdAl₄, which had been reported by [59Mor] (as cited by [61Lun]) and in an abstract by [63Run]. Annealing and quenching experiments at various temperatures failed to produce this compound. Because the starting materials used by [65Bus1] and [63Run] appeared to be of about the same purity, the difference in their findings may be due to the methods used in preparing their alloys. [63Run], using an induction furnace, first melted their Al in a graphite crucible in air at 1000 °C,

Al-Gd

then added the Gd. From their description of this process, it seems likely that carbon or oxygen contamination may have stabilized then GdAl₄ form. [65Bus1], on the other hand, prepared his alloys by arc melting under an inert atmosphere and was working, presumably, with more pure alloys.

[79Pop] reported a Gd₂Al₁₇ compound, which (if it exists as a stable equilibrium composition) would be the Al-rich compound in the Gd-Al system. These investigators reported a hexagonal structure of the Th₂Ni₁₇ type (space group *P6₃/mmc*), isotypic with Gd₂Ni₁₇ and having continuous solid solubility in the latter compound. Specimens were prepared by arc melting stoichiometric quantities of high-purity metals (99.9% Gd, 99.99% Al, weight?) in an argon atmosphere. X-ray diffraction was used to determine structure and lattice parameters. Inasmuch as no other investigators have reported this structure in the Gd-Al system (or for any of the neighboring RE metals with Al), the reviewers doubt its existence as an equilibrium intermetallic compound. In addition, [65Gsc] reported the existence of GdAl with orthorhombic CeAl-type structure. Because the *a* and *c* parameters are anomalously high, this form does not exist in the Ni-Al, Sm-Al, Tb-Al, or Dy-Al systems, and because the calculated volume of formation of this type of GdAl is positive, whereas those of LaAl, CeAl, and PrAl are negative, CeAl-type GdAl is not included in this evaluation.

Tables 1 and 2 list crystal structure and lattice parameter data for Gd-Al phases. See the "Crystal Structures and Lattice Parameters" section of "The Al-RE (Aluminum-Rare Earth) Systems," in this issue, for additional information.

Thermodynamics

For data on the thermodynamic properties of Gd-Al alloys, see the "Thermodynamics" section of "The Al-RE (Aluminum-Rare Earth) Systems," in this issue.

Effects of Pressure

[75Can] studied the effects of high pressure on the crystal structures of several REAl₃ compounds (see the "Effects of Pressure" section of "The Al-RE (Aluminum-Rare Earth) Systems," in this issue, for sample preparation details). When GdAl₃ with Ni₃Sn-type structure (100% hexagonal stacking) was treated at 41 kbar and 970 °C for 5 min, a partial conversion to BaPb₃-type structure (67% hexagonal stacking) took place. At the same temperature, but under 45 kbar, the transformation to BaPb₃-type structure was complete in 5 min. No further transformation occurred under high pressures (up to 65 kbar).

Amorphous Alloys

[79Sin] studied thin amorphous films prepared by reaction of a mixture of 99.99% (weight?) pure Gd and

99.9999% pure Al in a vacuum of $\sim 13 \times 10^{-5}$ Pa (10^{-7} Torr) at 500 °C. The films were studied in a transmission electron microscope and found to be amorphous as prepared. When pulsed by a focused electron beam (temperatures of ~ 500 °C were attained for pulses 30 to 40 s long), the films changed from amorphous to crystalline. Data collected from several single-crystal regions showed several polytypes to exist.

[80Bus] prepared various amorphous alloys of Gd with several metals including Al by arc melting, followed by melt spinning in a purified argon atmosphere. The thermal stability of the samples was determined by means of a differential scanning calorimeter. The recrystallization temperature for Gd₇₈Al₂₂ was determined to be 318 °C (591 K).

For additional reports on Gd-Al amorphous alloys, see the "Amorphous Alloys" section of "The Al-RE (Aluminum-Rare Earth) Systems," in this issue.

Cited References

- 59Mor:** J. Moriarty and N. Baenziger, prepublication data, University of Iowa, Iowa City (1959); cited by [61Lun].
- 60Mor:** J.L. Moriarty, Ph.D. thesis, University of Iowa, Iowa City; *Diss. Abst.*, 21, 1391 (1960).
- 60Wer:** J.H. Wernick and S. Geller, "Rare-Earth Compounds with the MgCu₂ Structure," *Trans. AIME*, 218, 866 (1960).
- 61Bae:** N.C. Baenziger and J.L. Moriarty, "Gadolinium and Dysprosium Intermetallic Phases. II. Laves Phases and Other Structure Types," *Acta Crystallogr.*, 14, 948 (1961).
- 61Bec:** R.L. Beck, Lackland Aircraft Reactor Rep. LAR-53, National Technical Information Service, U.S. Dept. of Commerce, Springfield, VA (Apr 1961).
- 61Lun:** C.E. Lundin, *The Rare Earths*, F.H. Spedding and A.H. Daane, Ed., John Wiley and Sons, New York, 350 (1961).
- 62Wer:** J.H. Wernick, S.E. Haszko, and D. Dorsi, "Pseudo-Binary Systems Involving Rare Earth Laves Phases," *J. Phys. Chem. Solids*, 23, 567 (1962).
- 63Mat:** B.T. Matthias, T.H. Geballe, and V.B. Compton, "Superconductivity," *Rev. Mod. Phys.*, 35, 1 (1963).
- 63Run:** O.J.C. Runnalls and R.R. Boucher, "Phase Equilibria in Aluminum-Rich Alloys of Aluminum-Gadolinium and Aluminum-Terbium," *J. Met.*, 15, 687 (1963).
- 64Bae:** N.C. Baenziger and J.J. Hegenbarth, "Gadolinium and Dysprosium Intermetallic Phases. III. The Structures of Gd₃Al₂, Dy₃Al₂, Gd₅Ge₃, Dy₅Ge₃ and DyAl₃," *Acta Crystallogr.*, 17, 620 (1964).
- 64Cop:** M. Copeland and H. Kato, *Physics and Material Problems of Control Rods*, IAEA, Vienna, 295 (1964).
- 64Vuc:** J.H.N. van Vucht and K.H.J. Buschow, "On the Binary Aluminum Rich Compounds of the Rare-Earth Elements," *Philips Res. Rep.*, 19, 319 (1964).
- 65Bus1:** K.H.J. Buschow, "Phase Relations and Intermetallic Compounds in the Systems Neodymium-Aluminum and Gadolinium-Aluminum," *J. Less-Common Met.*, 9, 452 (1965).
- 65Bus2:** K.H.J. Buschow, "Rare Earth-Aluminum Intermetallic Compounds of the Form RAl and R₃Al₂," *J. Less-Common Met.*, 8, 209 (1965).

- 65Gsc:** K.A. Gschneidner, Jr., "Crystal Structures of Some Equi-Atomic Gadolinium Compounds," *Acta Crystallogr.*, **18**, 1082 (1965).
- 65Har:** I.R. Harris, R.C. Mansey, and G.V. Raynor, "Cubic Laves Phases Formed with Aluminum and Cobalt," *J. Less-Common Met.*, **9**, 270 (1965).
- 65Ian:** A. Iandelli, AD-464643, National Technical Information Service, U.S. Dept. of Commerce, Springfield, VA (1965).
- 66Sta:** B. Stalinski and S. Pokrzywnicki, "Magnetic Properties of Gadolinium-Aluminum Intermetallic Compounds," *Phys. Status Solidi*, **14**, K157 (1966).
- 67Bus:** K.H.J. Buschow and J.H.N. van Vucht, "Systematic Arrangement of the Binary Rare-Earth-Aluminum System," *Philips Res. Rep.*, **22**, 233 (1967).
- 67Oes:** H. Oesterreicher and W.E. Wallace, "Studies of Pseudo-Binary Laves-Phase Systems Containing Lanthanides. I. Constitution and Magnetic Properties of $GdAl_2$ - $GdFe_2$, $GdAl_2$ - $GdCo_2$ and $ErCo_2$ - $ErAl_2$ Systems," *J. Less-Common Met.*, **13**, 91 (1967).
- 67Run:** O.J.C. Runnalls and R.R. Boucher, "Phase Equilibria in Aluminum-Rich Alloys of Aluminum-Gadolinium and Aluminum-Terbium," *J. Less-Common Met.*, **13**, 431 (1967).
- 73Hid:** M. Hidaka, M. Sakai, H. Hosokawa, and J. Sakurai, "The Paramagnetic Curie Temperature of the Alloys $Gd(Al_{1-x}Cu_x)_2$ and $Gd(Al_{1-x}Ni_x)_2$," *J. Phys. Soc. Jpn.*, **35**, 452 (1973).
- 74Mac:** E.S. Machlin, "Pair Potential Model of Intermetallic Phases - II," *Acta Metall.*, **22**, 109 (1974).
- 74Sch:** R.J. Schiltz, Jr. and J.F. Smith, "Elastic Constants of Some MA_2 Single Crystals," *J. Appl. Phys.*, **45**, 4681 (1974).
- 75Can:** J.F. Cannon and H.T. Hall, "Effect of High Pressure on the Crystal Structures of Lanthanide Trialuminides," *J. Less-Common Met.*, **40**, 313 (1975).
- 75Hav:** E.F. Havenga, "Influence of Repulsive Energy on Structural Parameters of Close-Packed Metal Structures," *J. Less-Common Met.*, **41**, 241 (1975).
- 76Dor:** E. Dormann and K.H.J. Buschow, "The Hyperfine Fields in Ferromagnetically Ordered Cubic Laves Phase Compounds of Gadolinium with Non-Magnetic Metals," *Phys. Status Solidi (b)*, **59**, 411 (1976).
- 76Gro:** R. Grössinger, W. Steiner, and K. Krec, "Magnetic Investigation of Pseudobinary SE (Fe,Al)₂ Systems (SE = Y, Gd, Dy, Ho)," *J. Magn. Magn. Mater.*, **2**, 196 (1976) in German.
- 76Ngu:** T.T. Nguyen, L.B. Chiu, P.R. Elliston, A.M. Stewart, and K.N.R. Taylor, "Electron Spin Resonance of $Gd_{1-x}Dy_xAl_2$," *J. Phys. F*, **6**, 1399 (1976).
- 77Bar:** B. Barbara, M.F. Rossignol, and M. Uehara, "Spontaneous Cell Distortion Due to the Crystal Field in Some Rare Earth- Al_2 Laves Phases," *Physica*, **86-88B**, 183 (1977).
- 77Mil:** P. Miles, M.A.A. Issa, K.N.R. Taylor, and G.J. Bowden, "Spin Adjustment in $(Gd,Dy)Al_2$," *J. Phys. F*, **7**, 2421 (1977).
- 78Sle1:** A. Slebarski and A. Chelkowski, "X-Ray Study of Ordering on Crystallographic Sites in Intermetallic Alloys $Gd(Al_{1-x}Mn_x)_2$," *J. Less-Common Met.*, **57**, 125 (1978).
- 78Sle2:** A. Slebarski, "Anomalous Change of the Curie Temperature of $GdAl_2$," *Phys. Status Solidi (a)*, **46**, K29 (1978).
- 78Sle3:** A. Slebarski, W. Zarek, D. Konopka, A. Winiarska, E. Derejczyk, and A. Chelkowski, *Transition Metals, 1977*, M.J.G. Lee, J.M. Perz, and E. Fawcett, Ed., Inst. Phys. Conf. Ser. No. 39, Bristol, United Kingdom, 393 (1978).
- 79Bes:** M.J. Besnus, A. Herr, and G. Fischer, "On the Magnetic Properties of $Gd(Fe_{1-x}Al_x)_2$ Compounds," *J. Phys. F*, **9**, 745 (1979).
- 79Pop:** I. Pop, N. Dihoiu, M. Coldea, and C. Hagan, "The Crystalline Structure of the Intermetallic Compounds $Gd_2Ni_{17-x}Al_x$," *J. Less-Common Met.*, **64**, 64 (1979).
- 79Sin:** A.K. Singh and O.N. Srivastava, "On the Occurrence of Polytypism in Gadolinium Aluminide Thin Films," *Jpn. J. Appl. Phys.*, **18**, 1603 (1979).
- 80Bus:** K.H.J. Buschow, H.A. Algra, and R.A. Heskens, "Magnetic Properties and Ferromagnetic Resonance in Amorphous Gd Alloys," *J. Appl. Phys.*, **51**, 561 (1980).
- 81Kon:** D. Konopka, M. Sobaszek, and T. Rendicki, "X-Ray Investigations of Laves Phase Intermetallic Compounds in the $Gd_{1-x}Er_xAl_2$ System for $0 \leq x \leq 0.6$," *J. Less-Common Met.*, **81**, 1 (1981).
- 82Uml:** E. Umlauf and E. Hess, "Anomalous Thermal Expansion of $CeAl_3$ Due to Valence Mixing," *Solid State Commun.*, **44**, 311 (1982).
- 86Gsc:** K.A. Gschneidner, Jr. and F.W. Calderwood, *Handbook of the Physics and Chemistry of Rare Earths*, Vol. 8, K.A. Gschneidner, Jr. and L. Eyring Ed., North-Holland Physics Publishing, Amsterdam (1986).

Al-Gd evaluation contributed by K.A. Gschneidner, Jr. and F.W. Calderwood, Rare-earth information Center, Ames Laboratory, Iowa State University, Ames, IA 50011. This work was supported by the Department of Energy through the Joint Program on Critical Compilations of Physical and Chemical Data coordinated through the Office of Standard Reference Data, National Bureau of Standards. Additional support was contributed by: Molycorp, Inc., Union Oil Co. of California, Los Angeles; Reactive Metals & Alloys Corp., West Pittsburg, PA; Ronson Metals Corp., Newark, NJ; and Santoku Metal Industry Co., Ltd., Kobe, Japan. Literature searched through 1982. Professor Gschneidner is the ASM/NBS Data Program Category Editor for binary rare-earth alloys.