

# *Molar Volume Modeling of Ti-Al-Nb and Ti-Al-Mo Ternary Systems*

**Jun Zhu, Chuan Zhang, Weisheng Cao, Shuanglin Chen, Fan Zhang, Joon Sik Park & Seonghoon Yi**

**JOM**

The Journal of The Minerals, Metals & Materials Society (TMS)

ISSN 1047-4838

JOM

DOI 10.1007/s11837-015-1493-6



**Your article is protected by copyright and all rights are held exclusively by The Minerals, Metals & Materials Society. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at [link.springer.com](http://link.springer.com)".**



# Molar Volume Modeling of Ti-Al-Nb and Ti-Al-Mo Ternary Systems

JUN ZHU,<sup>1,4</sup> CHUAN ZHANG,<sup>1</sup> WEISHENG CAO,<sup>1</sup> SHUANGLIN CHEN,<sup>1</sup>  
FAN ZHANG,<sup>1</sup> JOON SIK PARK,<sup>2</sup> and SEONGHOON YI<sup>3</sup>

1.—CompuTherm, LLC, Madison, WI 53719, USA. 2.—Department of Materials Science and Engineering, Hanbat National University, Daejeon 305-719, Republic of Korea. 3.—Materials Science and Metallurgical Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea. 4.—e-mail: junzhu@compuTherm.com

Molar volume modeling was performed for both Ti-Al-Nb and Ti-Al-Mo ternary systems based on the thermodynamic modeling of these two systems. Comparison between the calculated phase equilibria and the experimental data proved the accuracy of thermodynamic modeling. With the calculated density contour curves superimposed on the equilibrium phase diagram, it provides a map for alloy developers to identify the promising alloy compositions that satisfy both the phase stability and density requirements and rule out those that fail to meet the requirements.

## INTRODUCTION

The outstanding thermo-physical properties of the TiAl-based alloys have attracted considerable interest among aerospace, automotive and other applications. The multiphase TiAl-based alloys exhibit low density, promising high-temperature strength, and good resistance against oxidation and corrosion when compared to conventional titanium alloys.<sup>1–5</sup> These alloys consisting of  $\gamma$ -TiAl (L1<sub>0</sub> structure),  $\alpha_2$ -Ti<sub>3</sub>Al (D0<sub>19</sub> structure) and  $\beta_0$ -TiAl (B2 structure), can be used at temperatures below 750°C. At higher temperatures,  $\alpha_2$  disorders to  $\alpha$ -Ti(Al) (A3 structure),  $\beta_0$  disorders to  $\beta$ -Ti(Al) (A2 structure) and only  $\gamma$  phase keeps its ordered state until dissolution. Such phase transformations limit their applications in turbine engines used in high-temperature and severe environments.

Considerable efforts have been devoted to improve the mechanical properties of TiAl-based alloys in view of both the chemical modifications and microstructure control over the last two decades. Nb is one of the most important additions to TiAl alloys due to several beneficial affects, including improving room temperature ductility, high-temperature oxidation resistance and strength. The effects of different Nb additions on the phase stabilities and mechanical properties of TiAl-based alloys have been investigated through experiments<sup>6–9</sup> and theoretical calculations.<sup>10–15</sup>

Microstructure control of the TiAl-based alloys can be improved by quenching and retaining the  $\beta$  phase solid solution at room temperature and producing the  $\gamma$ -TiAl +  $\alpha_2$ -Ti<sub>3</sub>Al or other beneficial microstructures on aging. Mo is known as a strong  $\beta$ -stabilizer. Addition of Mo may improve the quenching ability of the  $\beta$  phase. Investigations of Mo effects on the  $\beta$  phase stability and microstructural evolution have been carried out by both experimental<sup>16–18</sup> and thermodynamic modeling.<sup>19</sup>

Both Nb and Mo, being heavy elements, will greatly affect the most important characteristics of the light weight of the Ti alloys. In addition to the microstructural control issue, the densities of the alloys are also important when exploring the best interests of Nb and Mo additions during alloy design. In this paper, molar volume (reciprocal of density) modeling is developed together with the thermodynamic modeling for the two ternaries, Ti-Al-Nb and Ti-Al-Mo. With the calculated density contour curves superimposed on the phase equilibrium data, researchers may immediately eliminate certain composition areas without any experimental effort and focus only on the compositions that are promising. The purpose of this paper is to demonstrate the benefit of combining phase diagrams with property diagrams in the search of optimal alloy compositions which satisfy both phase stability and density requirements.

## MOLAR VOLUME MODELING

In general, the molar volume  $V_m$  of nonmagnetic materials can be expressed as a function of temperature  $T$ :

$$V_m = V_0 \exp \left( \int_{T_0}^T 3\alpha dT \right) \quad (1)$$

where  $V_0$  is the molar volume at the reference temperature  $T_0$  and  $\alpha$  is the coefficient of thermal expansion (CTE) of the phase in its nonmagnetic state. For an Hcp phase,  $\alpha$  should be the average linear thermal expansion of the polycrystalline phase.

The nonmagnetic volumetric expansivity,  $3\alpha$ , can be well represented as a simple polynomial function of temperature in the experimental data range, usually between room temperature (298.15 K) and the melting temperature:

$$3\alpha = a + bT + cT^2 + dT^{-2} \quad (2)$$

where the coefficients are obtained from experimental data.

For magnetic materials, the magnetic contribution is usually treated in a separate term. With all the elements in the current study being nonmagnetic, the magnetic contribution will not be discussed here.

When a phase has a solubility range, the molar volume may vary with respect to the change of compositions. A simple assumption is made such that the excess molar volume behaves similarly to the other excess thermodynamic properties such as excess Gibbs energy with respect to compositions. Thus, the molar volume of a solid solution phase  $\varphi$  can be expressed as:

$$V_m^\varphi = \sum_i x_i V_m^i + \sum_i \sum_{j \neq i} x_i x_j L_{ij} \quad (3)$$

where  $x_i$  is the molar fraction of element  $i$  in the phase,  $V_m^i$  is the molar volume of element  $i$  in the same crystal structure as phase  $\varphi$ , and  $L_{ij}$  is the interaction parameter between elements  $i$  and  $j$ .

And the molar volume of an intermetallic phase described using a sublattice model such as  $(A,B,\dots)_x(C,D,\dots)_y$  can be expressed similarly as:

$$V_m^\varphi = \frac{1}{x+y} \left( \sum_i \sum_j y'_i y''_j V_{ij} + \sum_j \sum_i \sum_{k \neq i} y'_i y'_k L_{i,k;j} \right. \\ \left. + \sum_i \sum_j \sum_{l \neq j} y''_j y''_l L_{i,j;l} \right) \quad (4)$$

where  $y'_i$  and  $y''_j$  are the site fractions of  $i$  and  $j$  on sublattice 1 and 2,  $V_{ij}$  is the molar volume of a hypothetical compound  $i_x j_y$ , and  $L_{i,k;j}$  and  $L_{i,j;l}$  are

the interaction parameters between the elements on first and second sublattice.

The density of an alloy, which may consist of multiple phases, can be calculated as:

$$\rho = \frac{\sum_i x_i M_i}{\sum_\varphi f^\varphi V_m^\varphi} \quad (5)$$

where  $x_i$  is the molar fraction of element  $i$  in the alloy,  $M_i$  is the Molar mass of element  $i$ ,  $f^\varphi$  is the phase fraction of phase  $\varphi$ , and  $V_m^\varphi$  is the molar volume of phase  $\varphi$ .

To calculate the density of an alloy with multiple phases, an alloy developer needs to know the molar volume and the fraction of every constituent phase simultaneously. Thermodynamic modeling is very important to obtain accurate phase fractions given an alloy chemistry and temperature. The thermodynamic modeling is usually performed via the CALPHAD (CALculation of PHase Diagrams) approach,<sup>19</sup> in which the excess Gibbs energies of all the phases are expressed as polynomials with model parameters optimized from available experimental data and the phase equilibrium can be calculated by minimizing the total Gibbs energy of the system at a given alloy composition and temperature. The technical details of CALPHAD approach can be found elsewhere in the literature<sup>20,21</sup> and will not be discussed in the current study.

## RESULTS

Lu et al.<sup>22</sup> studied the molar volume and thermal expansion of many metallic elements with the Bcc, Fcc and Hcp structures. Their results are adopted in the current study for the pure elements in the solid states. The molar volumes for the pure elements in the liquid state were obtained based on the studies of Iida and Guthrie,<sup>23</sup> Fang et al.,<sup>24</sup> and Paradis et al.<sup>25</sup> For the intermetallic compounds with limited solubility, their molar volumes at room temperature were obtained by computing the unit cell volume using their lattice parameters. Zinelis et al.<sup>26</sup> examined eight Ti-based alloys and obtained the coefficients of thermal expansion (CTE) varying from  $10.1 \times 10^{-6}/K$  to  $13.1 \times 10^{-6}/K$  in the temperature range from 298 K to  $\sim 773$  K. An average value of  $\sim 11.6 \times 10^{-6}/K$  was used for the intermetallic compounds without any experimental data. In the current study, experimental data were not sufficient to assess the molar volume interaction parameters and they were treated as zero. Table I lists the lattice parameter data that have been used to construct the molar volume database. With the new contour line feature of Pandat software,<sup>27</sup> the user can easily compute the density contour curves using the molar volume database.

The thermodynamic descriptions of these two ternaries were adopted from the PanTi database.<sup>28</sup> The constituent binaries were selected from widely accepted binaries<sup>29-32</sup> and the Ti-Al binary was



Table I. Molar volume data for pure elements and compounds at room temperature

Compound/element name	Space group	Prototype	Lattice parameter (Å)				Molar volume ( $\times 10^{-6}$ m <sup>3</sup> /mol)
			<i>a</i>	<i>b</i>	<i>c</i>	<i>c/a</i> ratio	
Al	Fm $\bar{3}$ m	Cu	4.019				9.774
Mo	Fm $\bar{3}$ m	Cu	4.014				9.737
Nb	Fm $\bar{3}$ m	Cu	4.230				11.395
Ti	Fm $\bar{3}$ m	Cu	4.099				10.369
Al	Im $\bar{3}$ m	W	3.244				10.279
Mo	Im $\bar{3}$ m	W	3.143				9.346
Nb	Im $\bar{3}$ m	W	3.293				10.752
Ti	Im $\bar{3}$ m	W	3.241				10.251
Al	P6 <sub>3</sub> /mmc	Mg	2.870		4.707	1.640	10.110
Mo	P6 <sub>3</sub> /mmc	Mg	2.767		4.892	1.768	9.767
Nb	P6 <sub>3</sub> /mmc	Mg	2.880		5.244	1.821	11.343
Ti	P6 <sub>3</sub> /mmc	Mg	2.929		4.628	1.580	10.353
Al <sub>2</sub> Ti <sup>33</sup>	I4 <sub>1</sub> /amd	Ga <sub>2</sub> Hf	3.971		24.313	6.123	9.621
Al <sub>11</sub> Ti <sub>5</sub> <sup>34</sup>	I4/mmm	Al <sub>11</sub> Ti <sub>5</sub>	3.917		16.524	4.219	9.542
Al <sub>5</sub> Ti <sub>2</sub> <sup>34</sup>	P4/mmm	Al <sub>5</sub> Ti <sub>2</sub>	3.905		29.196	7.476	9.577
Al <sub>3</sub> Ti <sub>2</sub> <sup>34</sup>	I4/mmm	Al <sub>3</sub> Ti	3.846		8.594	2.235	9.569
AlTi <sub>3</sub> <sup>34</sup>	P6 <sub>3</sub> /mmc	Ni <sub>3</sub> Sn	5.780		4.647	0.804	10.121
AlTi <sup>34</sup>	P4/mmm	AuCu	4.001		4.071	1.017	9.811
Al <sub>12</sub> Mo <sup>35</sup>	Im $\bar{3}$	Al <sub>12</sub> W	7.573				10.060
Al <sub>5</sub> Mo <sup>35</sup>	P6 <sub>3</sub>	Al <sub>5</sub> W	4.912		8.842	1.800	9.271
Al <sub>4</sub> Mo <sup>35</sup>	Cm	Al <sub>4</sub> W	5.260	17.785	5.226		11.146
Al <sub>3</sub> Mo <sup>35</sup>	Cm	Al <sub>3</sub> Mo	16.396	3.594	8.386		9.101
Al <sub>3</sub> Mo <sup>35</sup>	Pm $\bar{3}$ n	WO <sub>3</sub>	4.945				9.102
Al <sub>8</sub> Mo <sub>3</sub> <sup>35</sup>	Cm	Al <sub>8</sub> Mo <sub>3</sub>	9.207	3.641	10.060		9.068
Al <sub>3</sub> Nb <sup>36</sup>	I4/mmm	Al <sub>3</sub> Ti	3.844		8.605	2.239	9.571
AlNb <sub>2</sub> <sup>36</sup>	P4 <sub>2</sub> /mnm	$\alpha$ -CrFe	9.945		5.171	0.520	10.266
AlNb <sub>3</sub> <sup>36</sup>	Pm $\bar{3}$ n	Cr <sub>3</sub> Si	5.186				10.499
Ti <sub>2</sub> AlNb <sup>37</sup>	Cmcm	NaHg	6.090	9.570	4.547		9.974
Ti <sub>4</sub> Al <sub>3</sub> Nb <sup>38</sup>	P6 <sub>3</sub> /mmc	Ni <sub>2</sub> In	4.580		5.520	1.205	10.065

modified to include the B2/Bcc transformation. The ternary parameters were adopted from Witusiewicz et al.<sup>14</sup> and Cupid et al.<sup>19</sup> with minor modifications due to different binaries used.

Figure 1a shows the calculated liquidus projection of the Ti-Al-Nb ternary system with experimental data.<sup>39–46</sup> The primary  $\beta$  phase occupies most of the areas with Al content lower than 50 at.% and the primary  $\eta$  phase occupies the area with Al content higher than 60 at.%. The primary  $\gamma$  and  $\sigma$  phase regions connect with each other inbetween the  $\beta$  phase and  $\eta$  phase. The primary  $\alpha$  and  $\delta$  phase extend from the relevant binary into the ternary field with about 10 at.% of the third element. The calculated liquidus projection is in accord with most of the experimental data, which indicates the accuracy of the thermodynamic database. Figure 1b and c shows the calculated density contour curves superimposed on the isothermal section at 1273 K and isopleth with fixed Al content at 45 at.%, respectively. The density contour curves in Fig. 1b are almost equidistant with small fluctuations when the  $\delta$  phase is involved. The density contour curves in Fig. 1c show a general trend that the density

decreases with increasing temperature and decreasing Nb content.

Figure 2a is the calculated liquidus projection of the Ti-Al-Mo ternary system. The primary  $\beta$  phase occupies the majority of the ternary phase field. Figure 2b and c shows the calculated density contour curves superimposed on the isothermal section at 1273 K and isopleth with fixed Al content at 50 at.%, respectively. The density contour curves in Fig. 2b are similar to those in the Ti-Al-Nb ternary, as shown in Fig. 1b. In Fig. 2c, since the high density  $\delta$  phase is stable in wide composition range at low temperature, the density tends to be high at low temperature. The density goes higher with higher fraction of  $\delta$  phase near Mo-rich side. With such phase diagrams combined with the specific property, alloy developers may immediately obtain the density of an alloy given an alloy chemistry and temperature.

## CONCLUSION

Molar volume modeling is performed for the Ti-Al-Mo and Ti-Al-Nb ternaries. The density contour curves can be calculated using the molar volume

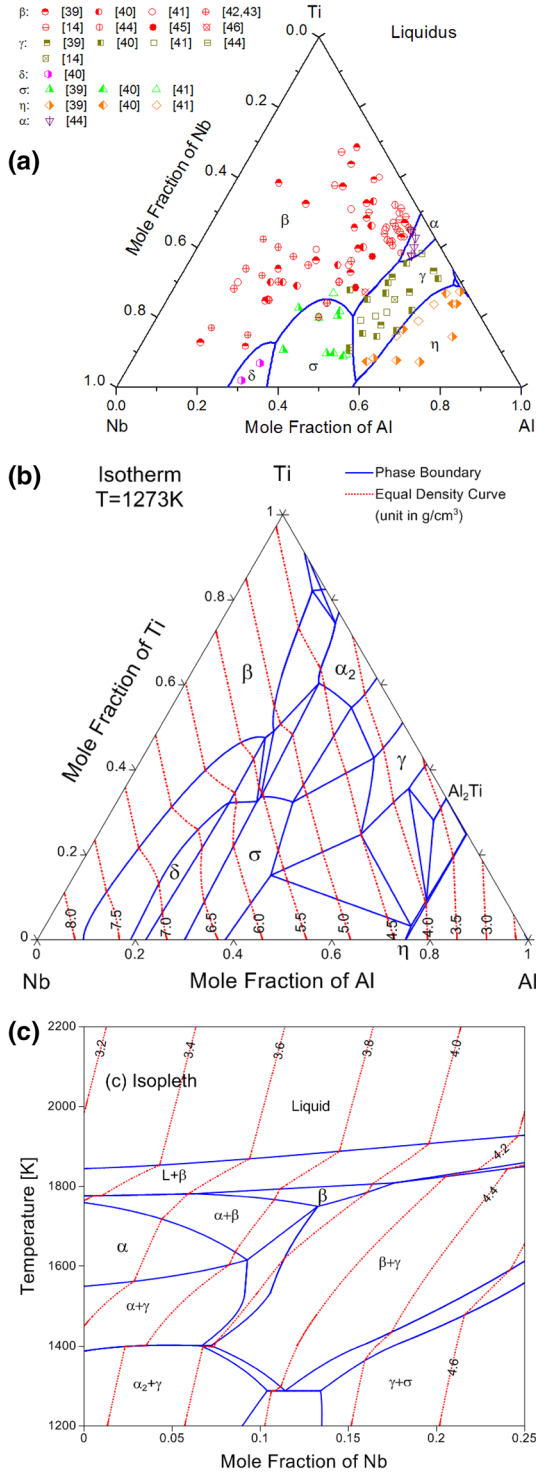


Fig. 1. (a) Calculated Ti-Al-Nb ternary liquidus projection with experimental data [39–46] (b) Calculated density contour curves (red line) superimposed on the isothermal section at 1273 K for the Ti-Al-Nb ternary system. (c) Calculated density contour curves (red line) superimposed on the isopleth with fixed Al content at 45 at.% for the Ti-Al-Nb ternary system.

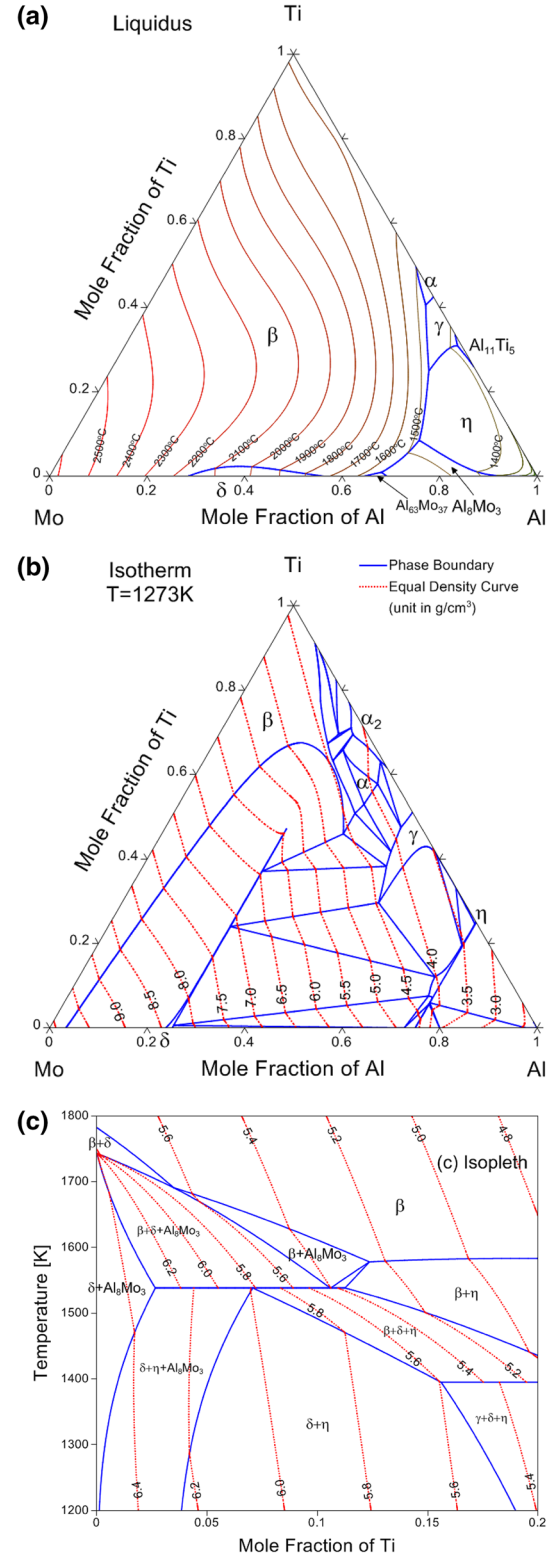


Fig. 2. (a) Calculated Ti-Al-Mo liquidus projection. (b) Calculated density contour curves (red line) superimposed on the isothermal section at 1273 K for the Ti-Al-Mo ternary system. (c) Calculated density contour curves (red line) superimposed on the isopleth with fixed Al content at 50 at.% for the Ti-Al-Mo ternary system.

databases and superimposed on the equilibrium phase diagrams. The combined diagrams allow alloy developers to quickly identify the promising alloy compositions that satisfy both the phase stability and density requirements and rule out those that fail to meet the requirements.

### ACKNOWLEDGEMENT

Professors J.S. Park and S. Yi would like to thank the Agency of Defense Development, Republic of Korea, for financial support.

### REFERENCES

1. S.R. Singh and J.M. Howe, *Philos. Mag. Lett.* 65, 233 (1992).
2. Y. Gao and J. Zhu, *Scripta Metall.* 28, 651 (1993).
3. Y.G. Zhang and M.C. Chaturvedi, *Mater. Sci. Eng. A* 174, 45 (1994).
4. C.T. Liu, J.H. Schneibel, P.J. Maziasz, J.L. Wright, and D.S. Easton, *Intermetallics* 4, 429 (1996).
5. C.M. Austin, *Curr. Opin. Solid State Mater. Sci.* 4, 239 (1999).
6. F. Ebrahimi, D.T. Hoelzer, and J.R. Castillo-Gomez, *Mater. Sci. Eng. A* 171, 35 (1993).
7. W.J. Zhang, E. Evangelista, L. Francesconi, and G.L. Chen, *Mater. Sci. Eng. A* 207, 202 (1996).
8. Z.C. Liu, J.P. Lin, S.J. Li, and G.L. Chen, *Intermetallics* 10, 653 (2002).
9. O. Rios, S. Goyel, M.S. Kesler, D.M. Cupid, H.J. Seifert, and F. Ebrahimi, *Scripta Mater.* 60, 156 (2009).
10. H. Erschbaumer, R. Podlucky, G. Temnitschka, and R. Wagner, *Intermetallics* 1, 99 (1993).
11. C. Woodward and S. Kajihara, *Phys. Rev. B* 57, 13459 (1998).
12. Y. Song, D.S. Xu, R. Yang, D. Li, and Z.Q. Hu, *Intermetallics* 6, 157 (1998).
13. Y. Liu, H. Li, S. Wang, and H. Ye, *J. Mater. Res.* 24, 3165 (2009).
14. V.T. Witusiewicz, A.A. Bondar, U. Hecht, and T. Ya, Velikanova, *J. Alloys Compd.* 472, 133 (2009).
15. D.M. Cupid, O. Fabrichnaya, O. Rios, F. Ebrahimi, and H.J. Seifert, *Int. J. Mater. Res.* 100, 218 (2009).
16. T. Maeda, M. Okada, and Y. Shida, *MRS Proc.* 213, 555 (1990).
17. M. Kimura and K. Hashimoto, *J. Phase Equilib.* 20, 224 (1999).
18. S. Kabra, K. Yan, S. Mayer, T. Schmoelzer, M. Reid, R. Dippenaar, H. Clemens, and K.D. Liss, *J. Mater. Res.* 102, 697 (2011).
19. D.M. Cupid, O. Fabrichnaya, F. Ebrahimi, and H.J. Seifert, *Intermetallics* 18, 1185 (2010).
20. L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams* (New York: Academic Press, 1970).
21. Calphad website: [http://www.calphad.com/calphad\\_method.html](http://www.calphad.com/calphad_method.html).
22. X.G. Lu, M. Selleby, and B. Sundman, *Calphad* 29, 68 (2005).
23. T. Iida and R.I.L. Guthrie, *The Physical Properties of Liquid Metals* (Oxford: Clarendon Press, 1988), p. 105.
24. H.P. Wang, S.J. Yang, and B.B. Wei, *Condens. Matter. Phys.* 57, 719 (2012).
25. P.F. Paradis, T. Ishikawa, and S. Yoda, *J. Mater. Sci.* 36, 5125 (2001).
26. S. Zinelis, A. Tsetsekou, and T. Papadopoulos, *J. Prosthet. Dent.* 90, 332 (2003).
27. Pandat™ software, for Multicomponent Phase Diagram Calculation is available from CompuTherm LLC, Madison.
28. PanTi database, a thermodynamic database for multi-component titanium alloys, is available from CompuTherm LLC, Madison.
29. B.J. Lee and N. Saunders, *Z. Metallkd.* 88, 152 (1997).
30. I. Ansara, A.T. Dinsdale, and M.H. Rand editors. COST 507-Thermochemical database for light metal alloys. European Commission EUR 18499 EN, Luxembourg, 1998, p. 69.
31. Z. Du, C. Guo, C. Li, and W. Zhang, *J. Phase Equilib.* 30, 487 (2009).
32. K. Santhy and K.C. Hari, Kumar, *Intermetallics* 18, 1713 (2010).
33. J. Braun and M. Ellner, *J. Alloys Compd.* 309, 118 (2000).
34. D. Batalu, G. Coşmeleată, and A. Aloman, *U.P.B. Sci. Bull. Series B* 68, 77 (2006).
35. J.C. Schuster and H. Ipser, *Metall. Trans.* 22A, 1729 (1991).
36. P. Villars and L.D. Calvert, eds., *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd ed. (Materials Park, OH: ASM International, 1991).
37. B. Mozer, L.A. Bendersky, W.J. Boettinger, and R. Grant Rowe, *Scripta Metall.* 24, 2363 (1990).
38. L.A. Bendersky, W.J. Boettinger, B.P. Burton, F.S. Biancaniello, and C.B. Shoemaker, *Acta Metall. Mater.* 38, 931 (1990).
39. K. Kaltenbach, S. Gama, D.G. Pinatti, K. Schulze, and E.-T. Henig, *Z. Metallkd.* 80, 535 (1989).
40. J.H. Perepezko, Y.A. Chang, L.E. Seitzman, J.C. Lin, N.R. Bonda, and T.J. Jewett, *High Temperature Aluminides and Intermetallics*, ed. S.H. Wang, C.T. Liu, D.P. Pope, and J.O. Stiegler (Warrendale: The Minerals, Metals and Materials Society, 1990), pp. 19–47.
41. A. Zdziobek, M. Durand-Charre, J. Driole, and F. Durand, *Z. Metallkd.* 86, 334 (1995).
42. K.J. Leonard, J.C. Mishurda, and V.K. Vasudevan, *Metall. Mater. Trans.* 31B, 1305 (2000).
43. K.J. Leonard and V.K. Vasudevan, *Intermetallics* 8, 1257 (2000).
44. O. Shuleshova, T.G. Woodcock, H.-G. Lindenkreuz, R. Hermann, W. Löser, and B. Büchner, *Acta Mater.* 55, 681 (2007).
45. D.M. Cupid, Thermodynamic assessment of the Ti-Al-Nb, Ti-Al-Cr, and Ti-Al-Mo systems, Ph.D. Thesis, University of Florida (2009).
46. C.R. Feng and D.J. Michel, *Mater. Sci. Eng. A* 152, 202 (1992).