

Thermodynamic Assessment of the Al-Ba System

Xiaoheng Bao, Libin Liu, Yurong Jiang, Yun Jiang, Cun Mao, Xian Li, and Ligang Zhang

(Submitted December 2, 2015; in revised form March 10, 2016; published online May 2, 2016)

The Al-Ba was thermodynamically optimized with the help of CALPHAD method. The solution phases such as liquid, fcc and bcc phases were modeled as substitutional solution phases. The excess Gibbs energies of these phases were treated with Redlich-Kister polynomial functions. A set of self-consistent thermodynamic parameters for describing various phases in the Al-Ba system was obtained, which can well reproduce the corresponding experimental data. The Al-Ba-Ni ternary system were also extrapolated based on the present binary system.

Keywords Al-Ba, Al-Ba-Ni, CALPHAD, phase diagram, thermodynamic

1. Introduction

Aluminum amorphous alloys caused tremendous research interest due to their high specific strength, high toughness and high corrosion resistance.^[1–4] However, small size of Al based amorphous alloy limits its application in the industry area. Improving the glass formation ability (GFA) of aluminum alloy is an important subject to obtain the large size amorphous alloys for our material researchers. It was proved that the addition of large atoms (such as rare earth elements) in the alloys can increase the glass formation ability (GFA).^[5–7] The GFA of alloys were also improved when the addition of Ca, Sr, and Ba elements in the Al-Y-Ni-Co alloys.^[8] Phase diagram of Al-Y-Ni-Co-(Ca, Sr, Ba) systems will be a fundamental information for us to understand the experimental phenomenon.^[9,10]

The aim of this work is to establish a thermodynamic database of Al-Ba system based on the CALculation of PHase Diagram (CALPHAD) technique, which is a sub-system of Al-Y-Ni-Co-(Ca, Sr, Ba) systems. With the help of this database, the phase diagram information can be obtained to investigate the glass formation ability (GFA) of Al alloys.^[11]

Xiaoheng Bao and **Ligang Zhang**, School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, People's Republic of China; and State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, People's Republic of China; **Libin Liu**, **Yurong Jiang**, **Cun Mao**, and **Xian Li**, School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, People's Republic of China; and **Yun Jiang**, College of Automotive and Mechanical Engineering, Changsha University of Science and Technology, Changsha 410114, People's Republic of China. Contact e-mail: ligangzhang@csu.edu.cn.

2. Experiments Information

2.1 The Binary Systems

The thermodynamic describe for the Al-Ni and Ba-Ni systems are from literatures,^[12,13] as shown in Fig. 1 and 2. The phase diagram information of Al-rich region (0 to 10 at.% Al) in the Al-Ba system were reported by Alberti^[14] with the help of thermal and microscopic studies. And a eutectic reaction between liquid, Fcc_Al and Al₄Ba at 934 K was indicated in this work.

Based on the thermal and x-ray analysis, the phase relations of Ba-rich region (44 to 100 at.%) were investigated by Flanigen.^[15] The Ba-rich region compound was determined as Al₂Ba, which formed from peritectic reaction at 1118 K. And the eutectic reaction between liquid, Al₂Ba and Ba at 811 K was confirmed in his work.

With the above phase information, Iida^[16] used thermal analysis and microscopic analysis of 13 alloys to set up the whole phase diagram of the Al-Ba system. However, only Al₄Ba phase was reported in his work.

The Al-Ba binary system was assessed by Elliott and Shunk,^[17] three intermediate phases: Al₄Ba, Al₂Ba, AlBa had been reported in their work.^[17] Structure analysis Al₂Ba compound was not completed, but the formula Al₂Ba was assigned to it based only on the DTA data. It was also reported that about 5.4 at.% Al dissolved in Bcc_Ba and No appreciable solid solubility of Ba in terminal phase Al was observed.

Bruzzone and Merlo^[18] published a phase diagram of this system similar with that of Elliott and Shunk.^[17] After their results, a reexamination was conducted by Fornasini,^[19] this new experiments show that the formula of Al₂Ba and AlBa compounds are more appropriate as Al₁₃Ba₇ and Al₅Ba₄. No solid solubility of Al and Ba in terminal phase was found in this work.

The enthalpy of mixing of Al-Ba alloys at 1215 K from 0 to 47 at.% Ba was determined by drop calorimetry.^[20] Unfortunately, due to the temperature at 1215 K, only in the region of $0.0129 < X_{Ba} < 0.0450$ and $0.3439 < X_{Ba} < 0.4664$, their alloys were pure liquid. So only the enthalpies of mixing of the alloy compositions in these areas were accepted in our optimization. The activities of Ba in liquid Al-Ba alloys at 1373 K were determined with a

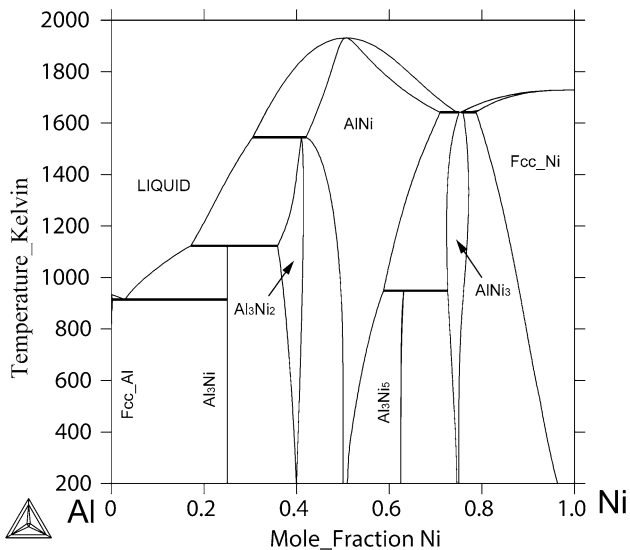


Fig. 1 The calculated phase diagram of the Al-Ni system^[12]

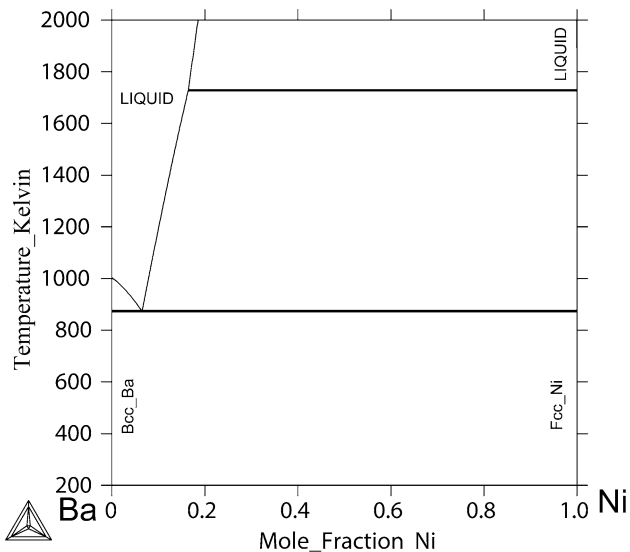


Fig. 2 The calculated phase diagram of the Ba-Ni system^[13]

combination of Knudsen effusion-mass and pseudo-isopiestic measurements.^[21]

2.2 The Ternary System

The Al_9BaNi_2 ternary compound with hexagonal structure was reported by Turban and Schafer.^[22] With the help of metallography, X-ray diffraction analysis and microhardness measurements, the isothermal section at 773 K of Al-Ba-Ni system was determined by Ainutdinov et al.^[23] as shown in Fig. 3, and the Al_9BaNi_2 was also confirmed in their work. The solubility of Ba in the Al-Ni intermetallic compounds and of Ni in the Al-Ba intermetallic compounds

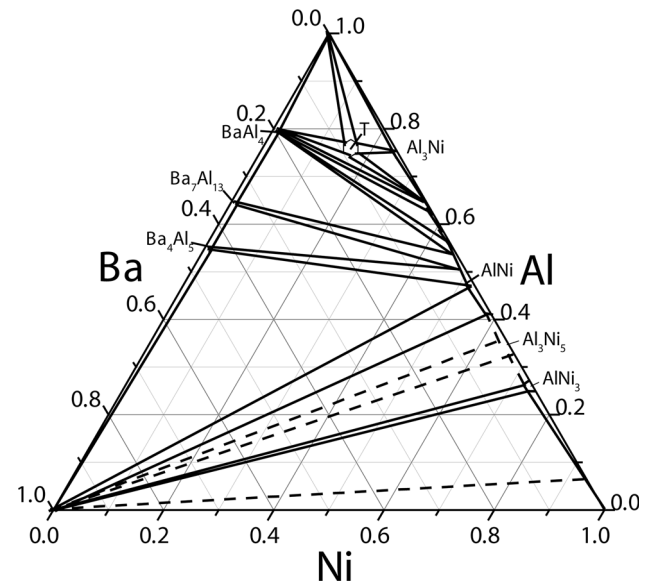


Fig. 3 The experimental isothermal section of Al-Ba-Ni system at 773 K^[23]

is less than 3 at.%. In the present work, the solubility was ignored.

Up to now, there is no experimental or calculated thermochemistry of the Al-Ba-Ni system available in the literature. Therefore, the Al-Ba-Ni system has been extrapolated on basis of the above ternary phase diagram information.

3. Thermodynamic Models

The CALPHAD approach^[24] was applied in the Al-Ba-Ni system, each phase in this system has a Gibbs energy function. For solution phase (φ) such as liquid, fcc, bcc and hcp, the Gibbs energy was described as followed:

$$G^\varphi = \sum_{i=\text{Al,Ba,Ni}} x_i {}^0G_i^\varphi + RT \sum_{i=\text{Al,Ba,Ni}} x_i \ln(x_i) + {}^{ex}G^\varphi$$

where

$$\begin{aligned} {}^{ex}G^\varphi = & x_{\text{Al}}x_{\text{Ba}} \sum_{j=0,1,\dots}^N (x_{\text{Al}} - x_{\text{Ba}})^{j(j)} L_{\text{Al,Ba}}^\varphi \\ & + x_{\text{Al}}x_{\text{Ni}} \sum_{j=0,1,\dots}^N (x_{\text{Al}} - x_{\text{Ni}})^{j(j)} L_{\text{Al,Ni}}^\varphi \\ & + x_{\text{Ba}}x_{\text{Ni}} \sum_{j=0,1,\dots}^N (x_{\text{Ba}} - x_{\text{Ni}})^{j(j)} L_{\text{Ba,Ni}}^\varphi + x_{\text{Al}}x_{\text{E}}x_{\text{E}} L_{\text{Al,Ba,Ni}}^\varphi \end{aligned}$$

where φ denotes the solution phases, x_i ($i = \text{Al, Ba and Ni}$) denotes mole fraction of component i , and ${}^0G_i^\varphi$ is the molar Gibbs energy of pure element i in the structural state of φ .

(j) $L_{Al,Ni}^\varphi$ and $L_{Ba,Ni}^\varphi$ are taken from Ref 12 and 13 is describing as,

$$L_{Al,Ba}^\varphi = A_j + B_j T + C_j T * \ln(T)$$

A_j , B_j and C_j are the adjusted parameters being optimized in the present work. $L_{Al,Ba,Ni}^\varphi$ is ternary interaction parameters. Due to lack of experiment data, it is set to be zero.

For the intermetallic compounds (Al_4Ba , $Al_{13}Ba_7$ and Al_5Ba_4), the Gibbs energy function is :

$$G_{Al_xBa_y} = \frac{x}{x+y} {}^0G_{Al}^{Fcc} + \frac{y}{x+y} {}^0G_{Ba}^{Bcc} + A + BT$$

The parameters A and B need to be optimized in this work.

For the ternary compound Al_9BaNi_2 , it is modeled as stoichiometric phase $Al_xBa_yNi_z$. The Gibbs energy expression for each of these stoichiometric compounds is written as

$$G_{Al_xBa_yNi_z} = \frac{x}{x+y+z} {}^0G_{Al}^{Fcc} + \frac{y}{x+y+z} {}^0G_{Ba}^{Bcc} + \frac{z}{x+y+z} {}^0G_{Ni}^{Fcc} + A + BT$$

where x , y and z are the stoichiometry ratios of the sublattices. A and B are the adjusted parameters to be optimized in the present work.

4. Results and Discussion

On the basis of lattice stabilities cited from Dinsdale,^[25] the optimization of the Al-Ba system is carried out using the Parrot module in the Thermo-Calc program.^[26] The parameters of liquid phase were first optimized from the enthalpies of mixing and activity data of the liquid alloys. Then, phase diagram information was introduced to obtain the parameters of solid phases. Finally, all parameters were evaluated together to make sure self-consistent. All the evaluated parameters are listed in Table 1.

Figure 4 shows the calculated phase diagram of Al-Ba system compared with experimental data,^[14,16,18] while Table 2 lists the invariant reactions in the Al-Ba system. An

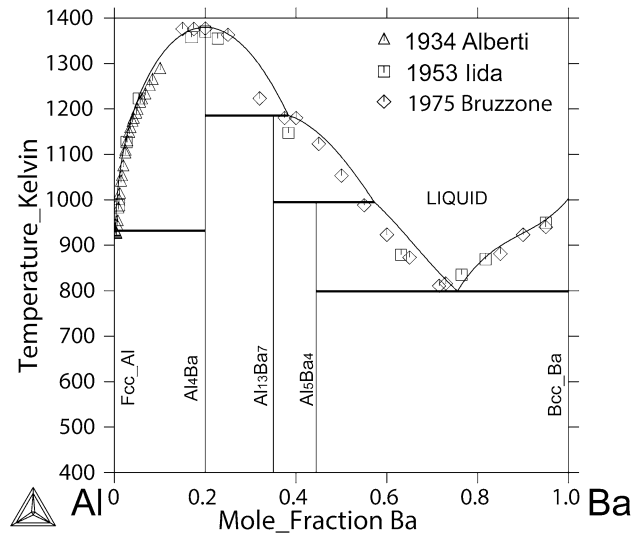


Fig. 4 The calculated phase diagram of the Al-Ba system with experimental data^[14,16,18]

Table 2 Invariant reactions in the Al-Ba system

Reaction	T (K)	Phase composition			Ref
		X_{Ba} (at.3%)			
Liquid \leftrightarrow (Al)+Al ₄ Ba	932	0.2	0	20.0	This work
	933	0.2	0	20.0	18
	933	0.2	0	20.0	21
Liquid \leftrightarrow Al ₄ Ba	1379		20.0		This work
	1377		20.0		18
	1377		20.0		21
Liquid + Al ₄ Ba \leftrightarrow Al ₁₃ Ba ₇	1186	38.3	20.0	35.0	This work
	1187	34.7	20.0	34.5	18
	1187	37.0	20.0	35.0	21
Liquid + Al ₁₃ Ba ₇ \leftrightarrow Al ₅ Ba ₄	995	57.2	35.0	44.4	This work
	1003	52.3	34.5	44.4	18
	1003	52.3	35.0	44.4	21
Liquid + Al ₅ Ba ₄ \leftrightarrow (Ba)	799	75.5	44.4	100	This work
	801	71.5	44.4	100	18
	801	71.5	44.4	94.6	21

Table 1 Thermodynamic parameters of the Al-Ba-Ni system

Phase	Thermodynamic parameters
Liquid: (Al,Ba)	${}^0L_{Al,Ba}^{Liq} = -121395 + 42.28T - 0.08T \ln T$ ${}^1L_{Al,Ba}^{Liq} = -58814 + 20.5T + 0.2T \ln T$ ${}^2L_{Al,Ba}^{Liq} = 14329 - 5T$ ${}^3L_{Al,Ba}^{Liq} = 6309$
Al ₄ Ba:	$G_{Al_4Ba}^{Al_4Ba} = -46649 + 17.46T + 0.8 {}^0G_{Al}^{Fcc} + 0.2 {}^0G_{Ba}^{Bcc}$
Al ₁₃ Ba ₇ :	$G_{Al_{13}Ba_7}^{Al_{13}Ba_7} = -53874 + 22.49T + 0.65 {}^0G_{Al}^{Fcc} + 0.35 {}^0G_{Ba}^{Bcc}$
Al ₅ Ba ₄ :	$G_{Al_5Ba_4}^{Al_5Ba_4} = -48160 + 19.88T + 0.556 {}^0G_{Al}^{Fcc} + 0.444 {}^0G_{Ba}^{Bcc}$
Al ₉ BaNi ₂	$G_{Al_9BaNi_2}^{Al_9BaNi_2} = -41862.3 + 1.88T + 0.75 {}^0G_{Al}^{Fcc} + 0.083 {}^0G_{Ba}^{Bcc} + 0.167 {}^0G_{Ni}^{Fcc}$

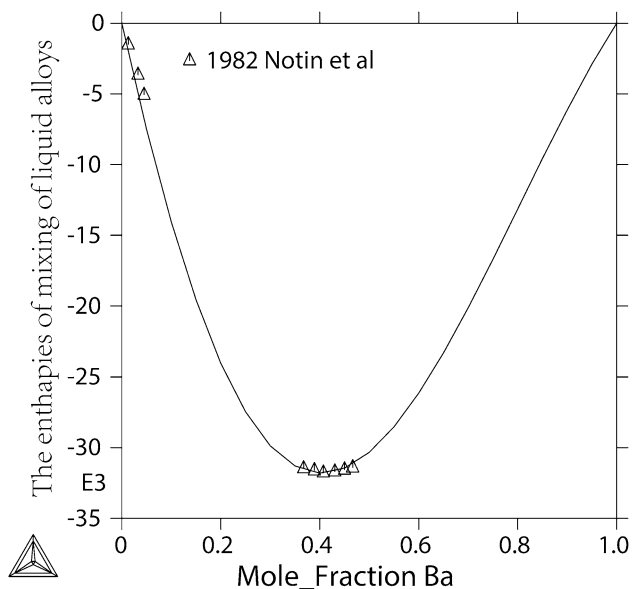


Fig. 5 The calculated enthalpy of mixing of liquid at 1215 K in Al-Ba system with the experimental data.^[20] Reference states: liquid Al and liquid Ba

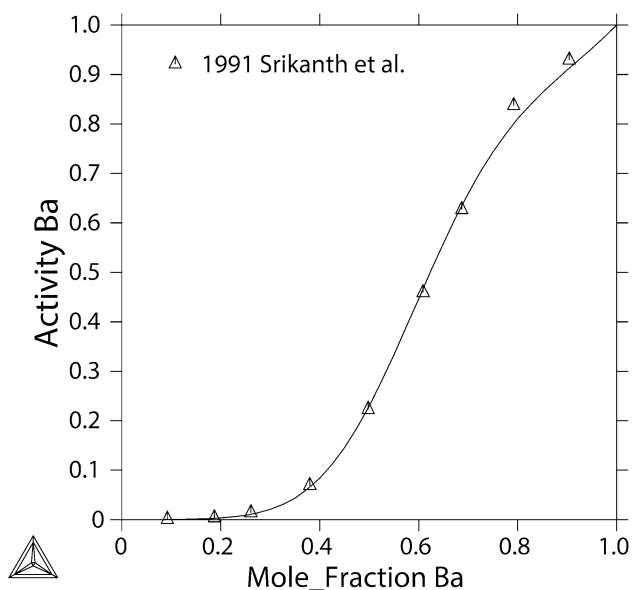


Fig. 6 The calculated activity of Ba in liquid alloy at 1373 K in Al-Ba system with experimental data.^[21] Reference states: liquid Ba

agreement within 10 K between the calculated and experimentally determined temperature are achieved.

As shown in Fig. 5, the calculated mixing enthalpy is reasonably agreement with the experiment data.^[20] The comparison of the experimental activity^[21] and the calculated one are presented in Fig. 6. It is demonstrated that the experimental data of thermodynamically properties can be

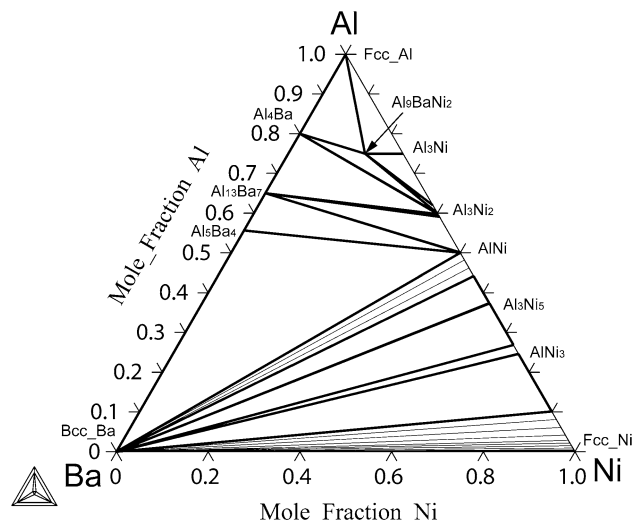


Fig. 7 The calculated isothermal section of Al-Ba-Ni system at 773 K

well described by the present calculation within the experimental errors.

The calculated Al-Ba-Ni isothermal section at 773 K is shown in Fig. 7. The calculated isothermal section results have well reproduced the experimental data^[23] except the phase between Al_4Ba and $AlNi$. From the results of Ainutdinov et al.,^[23] the two phase region of $Al_4Ba+AlNi$ existed. However, in our calculated results, the two phase region in this area is $Al_{13}Ba_7+Al_3Ni_2$. we found that it was very difficult to fit the result of Ainutdinov et al.^[23] in our optimization, such two-phase region were not available even after introducing the solubilities of Ba in $AlNi$ phase. Moreover, comparing with the other isothermal of Al-Ni-Ca and Al-Ni-Si systems^[27,28] at 773 K, we found there are no such two phase regions ($Al_4Ca+AlNi$ and $Al_4Sr+AlNi$), therefore we think our calculation is reasonable. Further experimental verification is still needed.

5. Conclusions

The Al-Ba system has been assessed thermodynamically based on reported experimental phase diagram and thermodynamic properties. Reasonable agreement between calculated and experimental data has been obtained and thermodynamic parameters for various phases in this system have been obtained.

Acknowledgments

The authors would like to express gratitude to the financially support by the National Natural Science Foundation of China (Grant Nos. 51371200 and 51501229), National Basic Research Program of China (2014CB644000), Fundamental Research Funds for the Central

Universities, Central South University (502044009). This work is also sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

References

1. A. Inoue, B. Shen, H. Koshiba, H. Kato, and A.R. Yavari, Cobalt-Based Bulk Glassy Alloy with Ultrahigh Strength and Soft Magnetic Properties, *Nat. Mater.*, 2003, **2**, p 661-663
2. J. Schroers and W.L. Johnson, Ductile Bulk Metallic Glass, *Phys. Rev. Lett.*, 2004, **93**, p 255506
3. B. Zhang, M.X. Pan, D.Q. Zhao, and W.H. Wang, "Soft" Bulk Metallic Glasses Based on Cerium, *Appl. Phys. Lett.*, 2004, **85**, p 61-63
4. Y.H. Liu, G. Wang, R.J. Wang, D.Q. Zhao, M.X. Pan, and W.H. Wang, Super Plastic Bulk Metallic Glasses at Room Temperature, *Science*, 2007, **315**, p 1385-1388
5. Z.P. Lu and C.T. Liu, Role of Minor Alloying Additions in Formation of Bulk Metallic Glasses: A Review, *J. Mater. Sci.*, 2004, **39**(12), p 3965-3974
6. C.T. Liu and Z.P. Lu, Effect of Minor Alloying Additions on Glass Formation in Bulk Metallic Glasses, *Intermetallics*, 2005, **13**, p 415-418
7. W.H. Wang, Roles of Minor Additions in Formation and Properties of Bulk Metallic Glasses, *Prog. Mater. Sci.*, 2007, **52**, p 540-596
8. J.Q. Wang, Y.H. Liu, S. Imhoff, N. Chen, D.V. Louzguine-Luzgin, A. Takeuchi, M.W. Chen, H. Kato, J.H. Perepezko, and A. Inoue, Enhance the Thermal Stability and Glass Forming Ability of Al-based Metallic Glass by Ca Minor-Alloying, *Intermetallics*, 2012, **19**, p 35-40
9. L.G. Zhang, P.J. Masset, X.M. Tao, G.X. Huang, H.T. Luo, L.B. Liu, and Z.P. Jin, Thermodynamic Description of the Al-Cu-Y Ternary System, *CALPHAD*, 2011, **35**, p 574-579
10. J.P. Huang, B. Yang, H.M. Chen, and H. Wang, Computational Study of Mobilities and Diffusion in Ti-Sn Alloy, *J. Phase Equilib. Diffus.*, 2015, doi:10.1007/s11669-015-0390-6
11. L.G. Zhang, H.Q. Dong, J.F. Nie, F.G. Meng, J. Shan, L.B. Liu, and Z.P. Jin, Thermodynamic Analysis of the La-Mg-Ni Bulk Metallic Glass System, *J. Alloy Compd.*, 2010, **491**, p 123-130
12. N. Dupin, I. Ansara, and B. Sundman, Thermodynamic Re-assessment of the Ternary System Al-Cr-Ni, *CALPHAD*, 2001, **25**, p 279-298
13. S.L. Shang, Z.J. Liu, and Z.K. Liu, Thermodynamic MODELING Of The Ba-Ni-Ti System, *J. Alloy Compd.*, 2007, **430**, p 188-193
14. E. Alberti, Investigation of the Aluminum-Barium System, *Z. Metallkd.*, 1934, **26**, p 6-9
15. E.M. Flanigen, Unpublished thesis, Syracuse University, Syacuse, NY (1952)
16. M. Iida, *Nippon Kinzoku Gakkaishi*, 1953, **17**, p 632-634
17. R.P. Elliott and F.A. Shunk, The Al-Ba (Aluminum-Barium) System, *Bull. Alloy Phase Diagr.*, 1981, **2**, p 351-353
18. G. Bruzzone and F. Merlo, The Strontium-Aluminum and Barium-Aluminum Systems, *J. Less Common Met.*, 1975, **39**, p 1-6
19. M.L. Fornasini, Ba3Al5, A Simple Atomic Arrangement Also Present in More Complex Structures, *Acta Crystallogr. C*, 1988, **44**, p 1355-1357
20. M. Notin, B. Djamshidi, and J.C. Gachon, Calorimetric Measurement of the Enthalpy of Formation of Some Al-Ba Alloys, *Thermochim. Acta*, 1982, **57**, p 57-66
21. S. Srikanth and K.T. Jacob, Thermodynamics of Aluminum-Barium Alloys, *Metall. Trans. B*, 1991, **22**, p 607-616
22. K. Turban and H. Schafer, Zur kenntnis des BaFe2Al9-strukturtyps: Ternäre aluminide at2Al9 MIT A = Ba, Sr und T = Fe, Co, Ni, *J. Less-Common Met.*, 1975, **40**, p 91-96
23. F.A. Ainutdinov, S.K.H. Khairidinov, and A.V. Vakhobov, The Phase Diagram of the Al-Ba-Ni System, *Dokl. Akad. Nauk Tadzh. SSR*, 1987, **30**, p 169-172
24. X. Wang, L.B. Liu, M.F. Wang, X. Shi, G.X. Huang, and L.G. Zhang, Computational Modeling of Elastic Constants as a Function of Temperature and Composition in Zr-Nb Alloys, *CALPHAD*, 2015, **48**, p 89-94
25. A.T. Dinsdale, SGTE Data for Pure Elements, *CALPHAD*, 1991, **15**, p 317-425
26. B. Sundman, B. Jansson, J.O. Andersson, The Thermo-Calc Databank System. *CALPHAD* (1985) 153-190
27. A. Prince, *Aluminium-Calcium-Nickel. Ternary Alloys*, Vol 3, VCH Verlagsgesellschaft, Weinheim, 1990, p 618-619
28. A. Prince, *Aluminium-Nickel-Strontium. Ternary Alloys*, Vol 7, VCH Verlagsgesellschaft, Weinheim, 1993, p 481-482