JPEDAV (2008) 29:493–499
DOI: 10.1007/s11669-008-9388-7
1547-7037 ©ASM International

The 450 °C Isothermal Section of the Zn-Bi-Ni System

Yongxiong Liu, Fucheng Yin, Hao Tu, Zhi Li, Jianhua Wang, and Xuping Su

(Submitted December 11, 2007; in revised form May 14, 2008)

The isothermal section of the Zn-Bi-Ni ternary system at 450 °C was determined experimentally using the equilibrated alloys approach. The specimens were investigated by means of optical microscopy, scanning electron microscopic/energy-dispersive spectrometric analysis and x-ray diffraction. Six three-phase regions exist in this isothermal section. The L-Bi phase is in equilibrium with all phases of Ni-Zn binary system except the α-Ni phase. Experimental results indicate that the third element, Zn or Bi, is almost insoluble in the Bi-Ni or Ni-Zn intermetallic compounds.

Keywords phase diagram, scanning electron microscope, Zn based alloy, Zn-Bi-Ni

1. Introduction

The hot-dip zinc coatings have been used for protection of steel and iron substrates from corrosion for almost a century.[1-3] However, galvanizing Si-containing steels is still a technical challenge. Silicon is introduced into steels either as a deoxidant or as an alloying element. In general galvanizing, silicon in steel gives rise to dull gray coatings with excessive thickness. The coatings adhere poorly to the steel. This phenomenon is referred to as Si reactivity or Sandelin effect has been studied extensively.[4-6] A practical solution to this problem is galvanizing the steels in alloyed baths. The primary alloying elements used in the galvanizing industry are Al[7] and Ni.[8]

In addition, Pb is added traditionally in the galvanizing bath. Pb has a beneficial effect on zinc drainage when the substrate is withdrawn from the melt, because it lowers the surface tension of the liquid zinc. Hence, zinc consumption is reduced and the galvanizing process becomes more economical. But Pb is unfriendly to the environment.[9] It has been reported[10,11] that Bi has the same beneficial effect. So Bi is considered as an excellent alternative of Pb to improve bath fluidity.

The synergistic effect of Ni and Bi on the Fe-Zn reactivity was studied.[12,13] The information of phase equilibria in the Zn-Bi-Fe-Ni quaternary system, especially in the Zn rich corner, at the temperature relevant to hot-dip galvanizing is very important to the galvanizing industry. The purpose of the present study is to experimentally determine the Zn-Bi-Ni isothermal section at 450 °C and prepare for studying the Zn-Bi-Fe-Ni quaternary system.

The Zn-Bi-Ni ternary system has three well studied binary systems. Researchers have studied the Bi-Zn system through different methods.[14-20] The phase diagram is uncommon because the miscibility gap is flat and asymmetric. The experiential data concerning the miscibility gap show large variation.

The Ni-Zn binary system has been experimentally determined and thermodynamically assessed by different researchers.[21-23] There are five phases in this system at 450 °C, namely α-Ni (0 to 32.1 at.% Zn), β_1 (44.8 to 52.1 at.% Zn), γ (72.6 to 84.3 at.% Zn), δ (88.2 at.% Zn) and L (99.1 to 100 at.% Zn). The composition ranges are evaluated values.

The Bi-Ni binary system has two intermetallic compounds, $NiBi_3$ and NiBi, at 450 °C. All researchers agree that $NiBi_3$ is stoichiometric while NiBi exhibits a small homogeneity region. Researchers suggested different homogeneity ranges as 46.3-44.3 Bi at.%,[24] 48.8-45.2 Bi at.%,[25] 50.9-51.2 Bi at.%.[26] Vassilev et al.[27] experimentally determined and assessed this system recently. Their EPMA results showed the composition range was 50.5 to 51.5 Bi at.%.

Crystallographic data of the binary compounds in the Zn-Bi-Ni ternary system are listed in Table 1.[24,28-31]. There is no information about phase equilibria of the Zn-Bi-Ni ternary system in the literature. In the present work, the isothermal section of the Zn-Bi-Ni system at 450 °C was determined experimentally. The boundaries of the phase diagram were based on the information of the Ref 16,22,27.

2. Experimental Procedure

The design compositions of the alloys are listed in Table 2 (Column 2). The purity of the starting materials is all 99.99%. Samples were prepared by carefully weighing the Ni powders, Zn blocks and Bi pellets, 5 g in total for each sample. All masses were weighed to an accuracy of 0.0001 g.

Yongxiong Liu, Fucheng Yin, Hao Tu, Zhi Li, Jianhua Wang, and **Xuping Su,** Key Laboratory of Materials Design and Preparation Technology of Hunan Province, School of Mechanical Engineering, Xiangtan University, Hunan, P.R. China. Contact e-mail: sxping@xtu.edu.cn.

Table 1 Crystallographic data of the binary compounds in the Zn-Bi-Ni ternary system

Compound	Structure type	Space group	Lattice parameters, Å			Reference
			a	*b*	*c*	
NiBi	NiAs	*P*63/*mmc*	4.080		5.365	[24]
$NiBi_3$	$CaLiSi_2$	*Pnma*	8.884	4.101	11.485	[28]
NiZn (β_1)	AuCu	*P*4/*mmm*	3.898		3.1927	[29]
$NiZn_3$ (γ)	$NiZn_3$	*Ab*2*m*	33.32	8.869	12.49	[30]
$NiZn_8$ (δ)	$NiZn_8$	*C*2/*m*	13.37	7.47, β = 111.3°	7.65	[31]

Table 2 The designed alloys and corresponding phase composition (all in at.%)

No.	Designed composition	Phase	Zn	Ni	Bi
A1	92Zn-2Ni-6Bi	L-Zn	98.0	0.4	1.6
		L-Bi	23.6	0	76.4
		δ	87.3	12.7	0
A2	92Zn-4Ni-4Bi	L-Zn	97.1	0.9	2.0
		L-Bi	25.5	0	74.5
		δ	87.2	12.8	0
A3	92Zn-6Ni-2Bi	L-Zn	96.7	1.4	1.9
		L-Bi	26.5	0	73.5
		δ	87.3	12.7	0
A4	85Zn-13Ni-2Bi	L-Bi	15.0	0.4	84.6
		γ	81.7	18.3	0
		δ	85.4	14.6	0
A5	85Zn-11Ni-4Bi	L-Bi	14.9	0.3	84.8
		γ	84.8	15.2	0
		δ	86.2	13.8	0
A6	85Zn-8Ni-7Bi	L-Zn	96.5	2.0	1.5
		L-Bi	25.8	0	74.2
		δ	86.8	13.2	0
A7	85Zn-5Ni-10Bi	L-Zn	97.1	1.2	1.7
		L-Bi	25.7	0	74.3
		δ	87.5	12.5	0
A8	85Zn-2Ni-13Bi	L-Zn	97.5	0.5	2.0
		L-Bi	24.7	0	75.3
		δ	87.4	12.6	0
A9	70Zn-20Ni-10Bi	L-Bi	4.8	1.9	93.3
		γ	72.4	27.6	0
A10	58Zn-32Ni-10Bi	L-Bi	3.5	2.3	94.2
		β_1	51.2	48.8	0
		γ	69.7	30.3	0
A11	42Zn-48Ni-10Bi	β_1	47.3	52.7	0
		$NiBi_3$	0	25.1	74.9
A12	10Zn-54Ni-36Bi	α-Ni	31.2	68.8	0
		β_1	44.5	55.5	0
		NiBi	0	47.6	52.4
A13	10Zn-42Ni-48Bi	NiBi	0	47.1	52.9
		β_1	47.2	52.8	0
		$NiBi_3$	0	24.8	75.2
A14	5Zn-10Ni-85Bi	L-Bi	0.2	8.5	91.3
		β_1	49.9	50.1	0
		$NiBi_3$	0	24.9	75.1

Each alloy mixture was put in quartz tube, rinsed three times with pure argon, and sealed under vacuum of 0.01 Pa. Then it was heated to 1100 °C and kept at this temperature for 30 h, followed by quenching in water using a bottom-quenching technique[32] to minimize Zn loss and reduce sample porosity. The quenched samples were sealed again

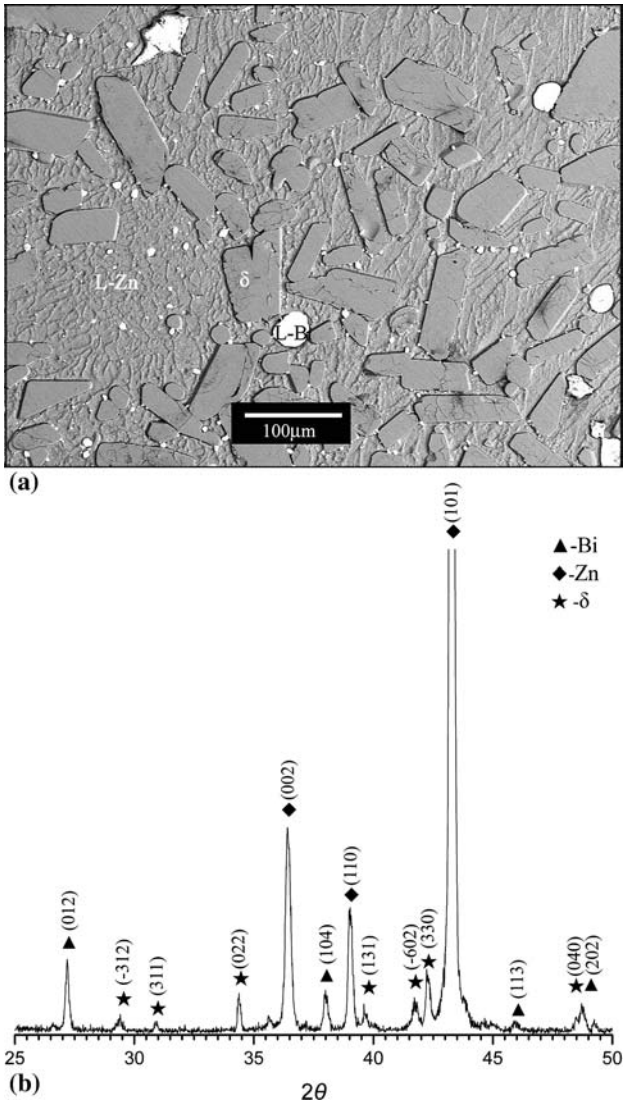


Fig. 1 The microstructure (a) and the x-ray diffraction pattern (b) of A2. Three phases, the L-Zn, L-Bi and δ co-exist in this alloy

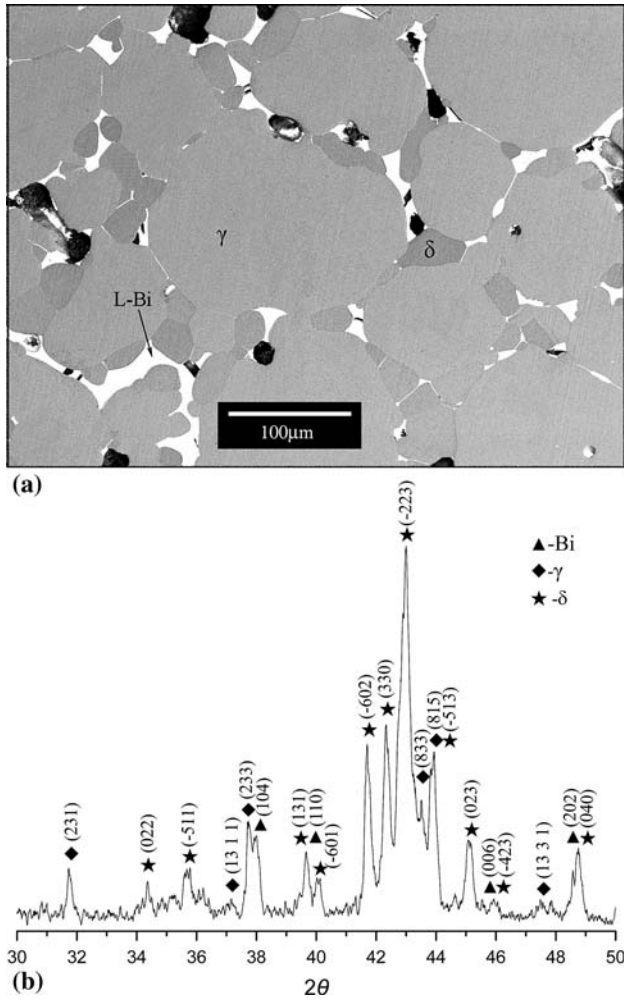


Fig. 2 The microstructure (a) and the x-ray diffraction pattern (b) of A4. They indicate the L-Bi, γ and δ phases co-exist in this alloy

individually in evacuated quartz tubes, and annealed at 450 °C for 30 days to ensure the establishment of equilibrium state. The treatment was completed with rapid water quenching to preserve the equilibrium state at 450 °C.

The specimens were prepared in the conventional way for microstructure examination using both optical and scanning electron microscopes (SEM). A nital solution was used for revealing the microstructures of the samples. A JSM-6360LV scanning electron microscope (SEM) equipped with an OXFORD INCA energy dispersive x-ray spectroscope (EDS) was utilized in studying the morphology and chemical compositions of various phases in the samples. The phase makeup of the alloys was further determined by analyzing x-ray diffraction patterns generated by a D/max-rA x-ray diffractometer, operating at 50 kV and 100 mA with Cu Kα radiation.

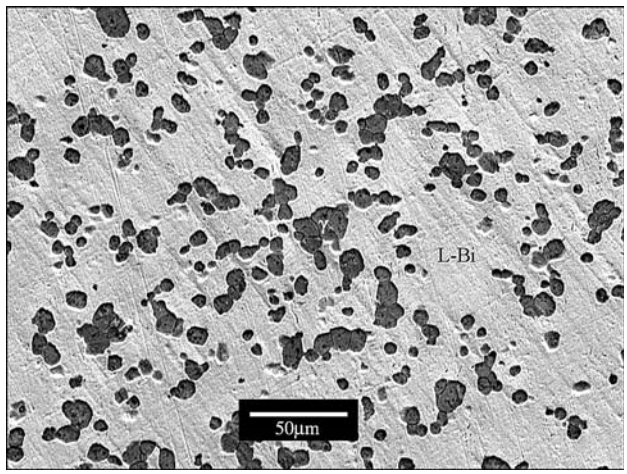


Fig. 3 The microstructures of A9. L-Bi + γ two-phase equilibrated state

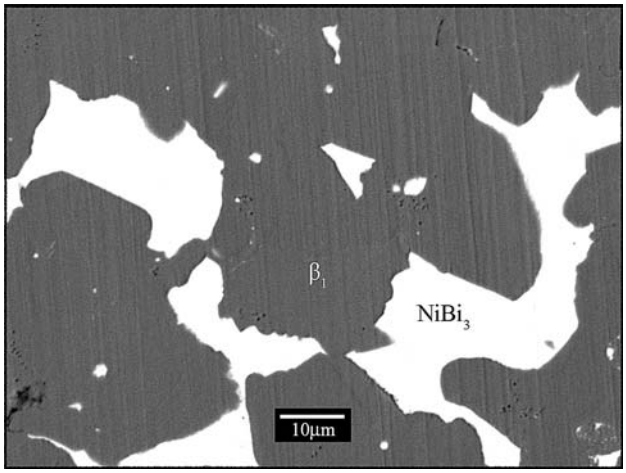


Fig. 4 The microstructures of A11. It consists of β_1 and $NiBi_3$ phases

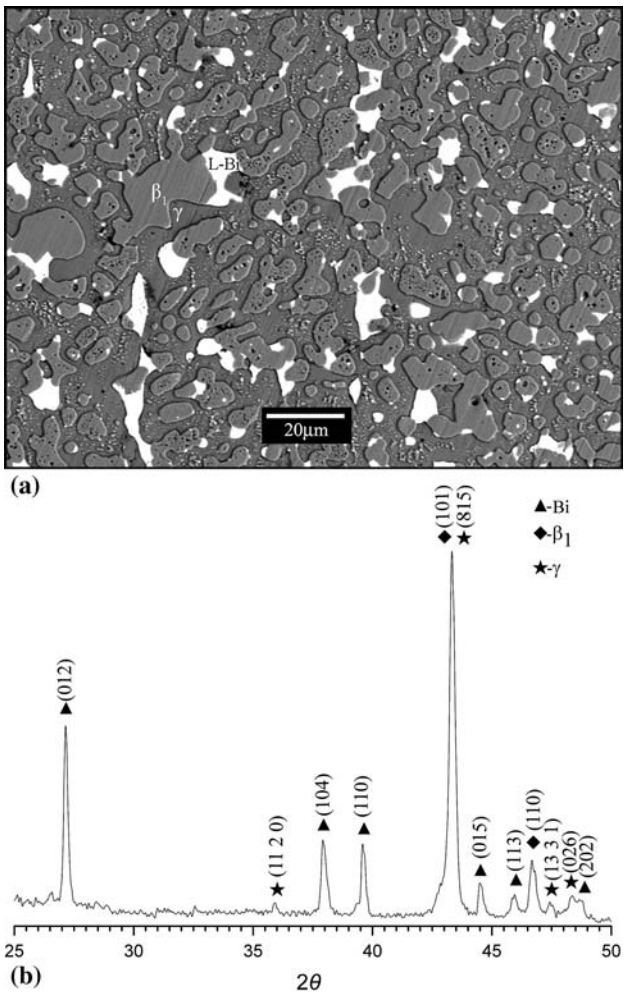
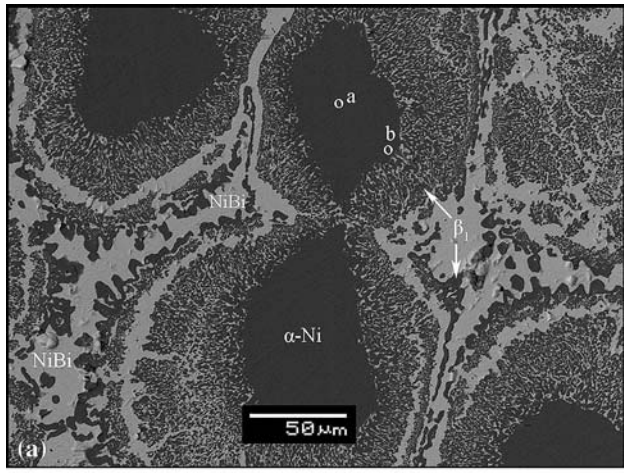
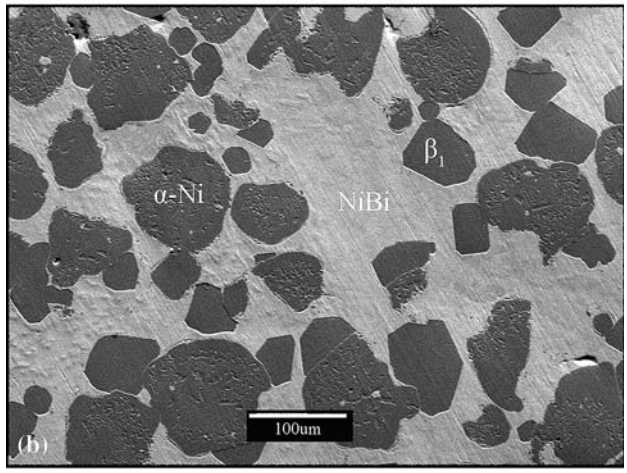


Fig. 5 The microstructures (a) and the x-ray diffraction pattern of A10. It consists of the β_1, γ and L-Bi phases





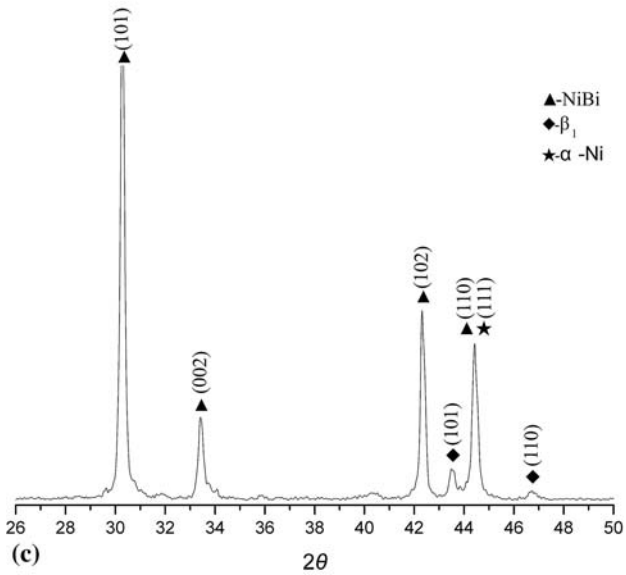


Fig. 6 The microstructures (a, annealed for 30 days and b, annealed for 60 days) and the x-ray diffraction pattern (c) of A12. The β_1, NiBi and α-Ni three phases co-exist in this alloy. In (a), the composition of the α-Ni phase at the center (a) and boundary (b) are Zn18.1Ni81.9 and Zn31.5Ni68.5, respectively

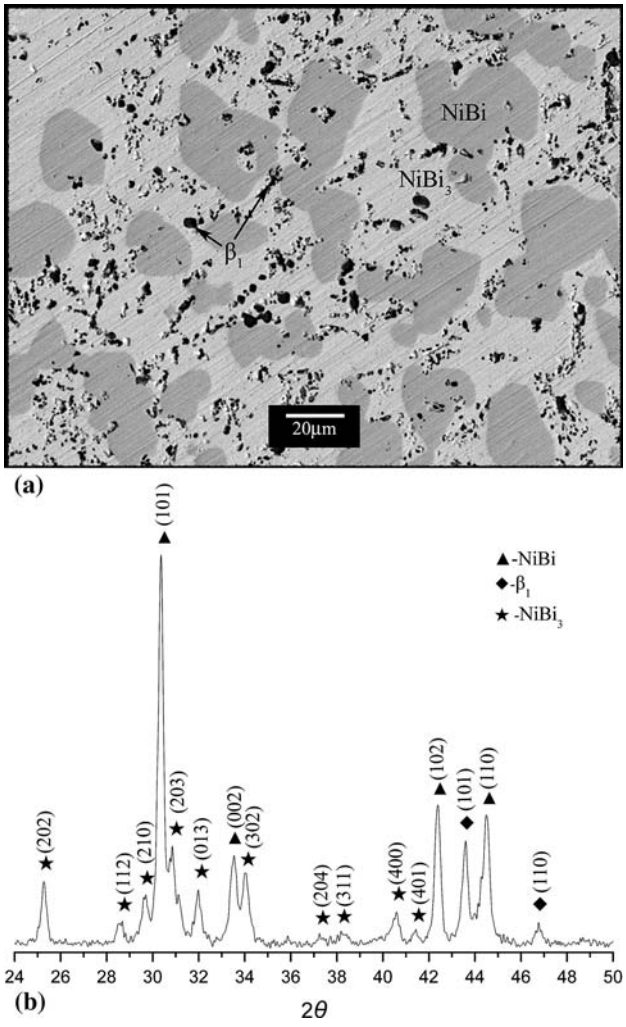


Fig. 7 The microstructures (a) and the x-ray diffraction pattern (b) of A13. It is three-phase equilibrated state of the β_1, NiBi and $NiBi_3$ phases

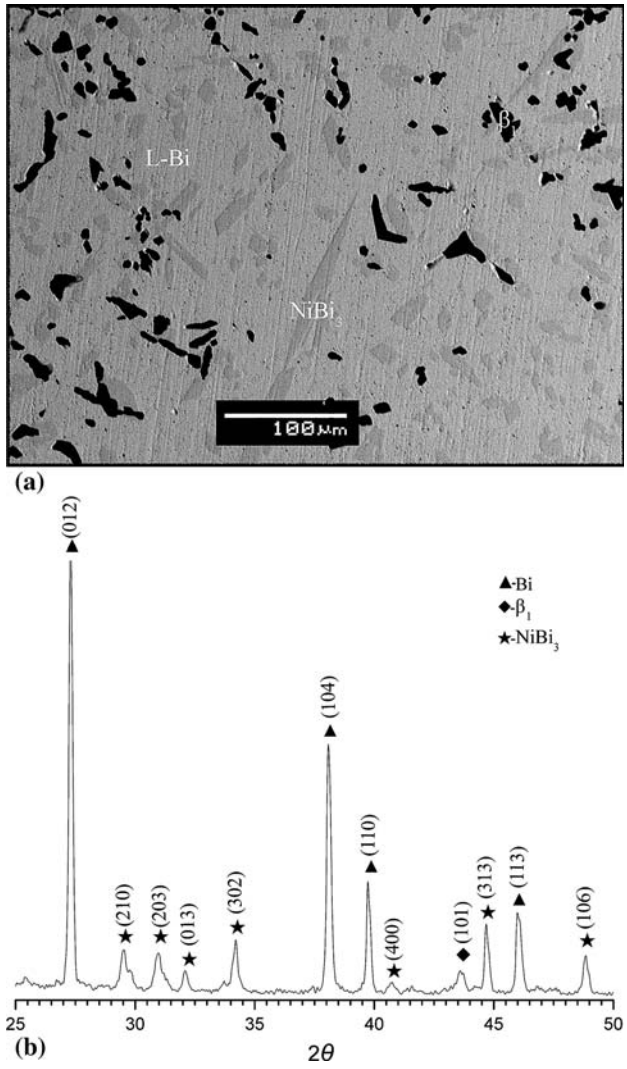


Fig. 8 The microstructures (a) and the x-ray diffraction pattern (b) of A14. The β_1, L-Bi and $NiBi_3$ three phases co-exist in this alloy

3. Results and Discussion

The phases that appeared in an alloy could be easily differentiated based on the morphology, color, and chemical composition. In most case, the results obtained from SEM-EDS analysis are sufficient for phase identification; however, the true identities of the phases were confirmed by analyzing the relevant x-ray diffraction patterns. All phases found in the alloys are listed in the Table 2 (Column 3) together with the chemical compositions determined by the SEM-EDS in BSE model (Column 4, 5, and 6). The compositions reported are the averages of at least 5 measurements. The phases of the alloys are confirmed by analyzing the relevant XRD patterns.

SEM-EDS analyses indicate that the microstructure of alloys A1-A3 and A6-A8 corresponded to the (L-Zn + L-Bi + δ) three-phase equilibrium state. The η-Zn and Bi are marked in this paper as L-Zn and L-Bi, respectively, because they are in the liquid state at 450 °C. The L-Bi phase contains 23.6 to 26.5 at.% Zn and no Ni. According to the information of the Bi-Zn system,[16] the L-Bi phase contains 45.0 at.% Zn at 450 °C. As the samples are cooled down from 450 °C to the room temperature, Zn-rich phases precipitate from L-Bi phase. The same phenomenon appeared in the study of Zn-Fe-Bi ternary system.[33] The L-Zn phase contains 1.8 at.% Bi and 1.1 at.% Ni. Bi is not detected in the δ phase. The microstructure of A2 is shown in Fig. 1(a). The white L-Bi particles and the gray δ block coexist with the matrix of the L-Zn phase. There are some small white L-Bi particles which forms during the quenching process. The x-ray diffraction pattern of A2 is shown in Fig. 1(b) which confirmed the alloy corresponding to (L-Zn + L-Bi + δ) three-phase equilibrated state.

SEM-EDS analyses indicate that A4 and A5 consists of three phases, L-Bi, γ and δ. Figure 2(a) is the microstructure of A4 in which the L-Bi coexists with the light gray γ phase and the dark gray δ phase. The relief and compositions of

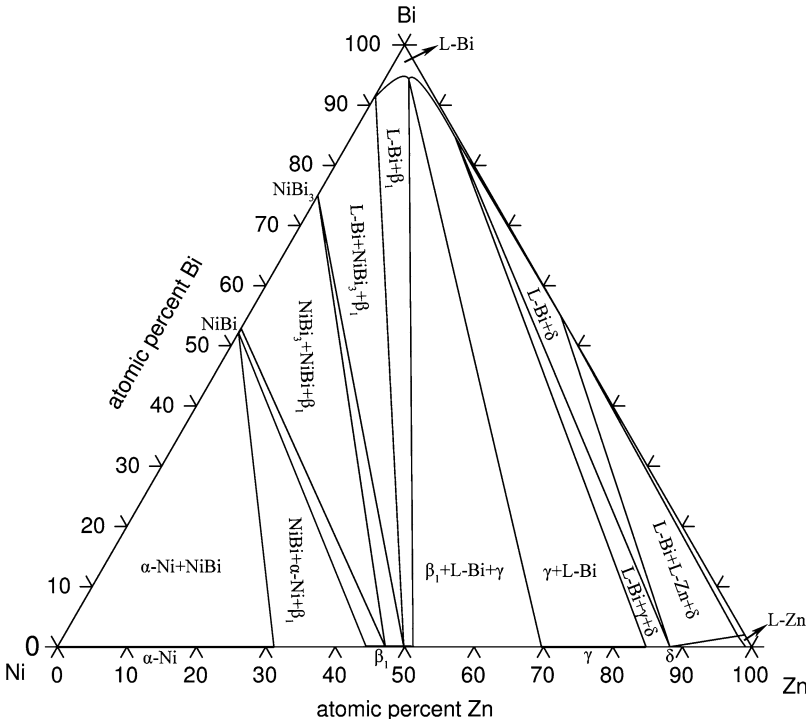


Fig. 9 The isothermal section of the Zn-Bi-Ni ternary system at 450 °C

the L-Bi phase, the γ phase and the δ phase are significantly different. Figure 2(b) is the x-ray diffraction pattern of A4 which indicted that A4 alloy corresponds to three-phase equilibrated state.

Figure 3 and 4 are microstructures of A9 and A11 which indicate the (L-Bi + γ) and (β_1 + $NiBi_3$) two-phase equilibrated states, respectively. Bi is not detected in the Ni-Zn binary intermetallic compounds, the γ phase and the β_1 phase. The L-Bi phase contains 4.8 at.% Zn and 1.9 at.% Ni.

The microstructure and x-ray diffraction pattern of specimen A10 are shown in Fig. 5, which indicates β_1, γ, and L-Bi co-existing. The gray block β_1 phase appears buried in the γ phase matrix. The white L-Bi phase contains 3.5 at.% Zn and 2.3 at.% Ni.

The microstructure of A12 consists of the β_1 phase, the NiBi phase and the α-Ni phase. The β_1 phase contains 44.1 at.% Zn. In present work, the NiBi phase contains more Bi than the result of Nash,[25] but agrees well with Vassilev et al.[27] Zn is not detected in the NiBi phase. And Bi is not detected in the β_1 phase. The microstructure and x-ray diffraction pattern of specimen A12 are shown in Fig. 6, in which β_1 and NiBi coexist with the α-Ni phases. The EDS results showed the composition of the α-Ni phase is not uniform. The composition changed from Zn18.1Ni81.9 at the center to Zn31.5Ni68.5 at the boundary of the α-Ni phase. So it is difficult to determine the equilibrium composition, especially that of α-Ni. The sample A12 is annealed at 450 °C for another 30 days to ensure the establishment of the equilibrium state. The microstructure is shown in Fig. 6(b), in which β_1 phases grow to dark gray blocks and contain 44.5 at.% Zn. The EDS results showed the composition of the α-Ni phase is Zn31.2Ni68.8. The results are quite consistent with the Ni-Zn system.[22] These compositions are adopted as the equilibrium composition of the tie-triangle.

The microstructure and x-ray diffraction pattern of specimen A13 are shown in Fig. 7, in which β_1, NiBi and $NiBi_3$ phases coexist. Black β_1 grains and gray block NiBi phases are buried in light gray $NiBi_3$ phases.

SEM-EDS analyses indicate that the microstructure of alloy A14 corresponded to the (β_1 + L-Bi + $NiBi_3$) three-phase equilibrium state. The microstructure and x-ray diffraction pattern of specimen A14 are shown in Fig. 8. Black block β_1 phases and gray $NiBi_3$ phases buried in light gray L-Bi matrix.

Based on the SEM-EDS analyses and the x-ray diffraction pattern of the above-mentioned alloys combined with the equilibria composition of three binary systems,[16,22,27] the phase diagram of the Zn-Bi-Ni ternary system at 450 °C is determined as shown in Fig. 9. It shows that there are six three-phase regions in this section. The L-Bi phase is in equilibrium with all phases of Ni-Zn binary system except the α-Ni phase. The third element cannot be dissolved in any of the phases except the liquid-phase. As mentioned above, it is very difficulty to avoid the precipitation of the Zn-rich phases from the L-Bi phase, the accurate composition of the L-Bi phase needs further work.

4. Conclusions

The isothermal section of the Zn-Bi-Ni ternary system at 450 °C was determined in the present work. The main results are listed below:

1. At 450 °C, there are six three-phase regions in the Zn-Bi-Ni ternary system;
2. The L-Bi phase is in equilibrium with all phases of Ni-Zn system except the α-Ni phase;
3. Bi is almost insoluble in the three Ni-Zn intermetallic compounds and α-Ni phase, and Zn is almost insoluble in NiBi and $NiBi_3$.

Acknowledgment

This investigation is supported by the National Science Foundation of China (No. 50671088), the Ph.D. Programs Foundation of Ministry of Education of China (No. 20070530006) and Scientific Research Fund of Hunan Provincial Education Department (No. 07A069).

References

1. A.R. Marder, The Metallurgy of Zinc-Coated Steel, *Prog. Mater. Sci.*, 2000, **45**, p 191-271
2. J.W. Cambel, *Hot-Dip Coatings*, Vol. Corrosion, ASTM, 2000, p 436-445
3. D. Horstmann, *Faults in Hot Dip Galvanizing*, Stahleisen M.b.H., Max-Planck Institut, Düsseldorf, 1975, p 6-7/32-33
4. T.W. Sandelin, Galvanizing Characteristics of Different Types of Steel, *Wire Wire Prod.*, 1940, **11**, p 655-676
5. J. Foct, P. Perrot, and G. Reumont, Interpretation of the Role of Silicon on the Galvanizing Reaction Based on Kinetics, Morphology and Thermodynamics, *Scripta Metall. Mater.*, 1993, **28**(5), p 1195-1200
6. H. Guttman and P. Niessen, Reactivity of Silicon Steels in Hot-Dip Galvanizing, *Can. Metall. Q.*, 1972, **11**, p 609
7. A.R.P. Ghuman and J.L. Goldstein, Reaction Mechanisms for the Coatings Formed During the Hot Dipping of Iron in 0 to 10 pct Al-Zn Baths at 450 to 700 °C, *Met. Trans.*, 1971, **2**, p 2903-2914
8. A.F. Skenazi and D. Rollez, Hot Dip Galvanizing of Semi-Killed Steels with the Zinc-Nickel Bath, *Proceedings of the 15th International Galvanizing Conference*, GE2/1-5(1988)
9. N. Irving Sax, *Dangerous Properties of Industrial Materials*, VNR, New York, 1979
10. N. Pistofidis, G. Vourlias, S. Konidaris, El. Pavlidou, and G. Stergioudis, The Effect of Bismuth on the Structure of Zinc Hot-Dip Galvanized Coatings, *Mater. Lett.*, 2007, **61**, p 994-997
11. M. Gagne, *Bull. Bismuth Inst.*, 1998, **72**, p 1
12. R. Fratesi, N. Ruffini, M. Malavolta, and T. Bellezze, Contemporary Use of Ni, Bi in Hot-Dip Galvanizing, *Surf. Coat. Technol.*, 2002, **157**, p 34-39
13. N. Pistofidis, G. Vourlias, S. Konidaris, El. Pavlidou, and G. Stergioudis, The Combined Effect of Nickel and Bismuth on the Structure of Hot-Dip Zinc Coatings, *Mater. Lett.*, 2007, **61**, p 2007-2010
14. W. Seith, H. Johnen, and J. Waagner, Miscibility Gaps in Molten Binary and Ternary Metallic Systems, *Z. Metallkd.*, 1995, **46**, p 773-779
15. K. Okajima and H. Sakao, Equilibria Between the Two Immiscible Liquid Phases in the Zinc-Bismuth System, *Trans. Jpn. Inst. Met.*, 1980, **21**(4), p 226-236
16. T.B. Massalski, Bi-Zn Phase Diagram, *Binary Alloy Phase Diagrams*, 1990, **1**, p 815-816
17. F. Bouharkat, J.J. Counioux, J.R. Vignalou, and J. Said, Miscibility Study in the Bismuth-Zinc System Extension to the Isotherms 425, 500 °C of the Ternary System Bi-Sb-Zn, *J. Alloys Compd.*, 1996, **238**, p 149-154
18. H. Okamoto, Bi-Zn (Bismuth-Zinc), *J. Phase Equilib.*, 2000, **21**(6), p 571-571
19. D.M. Malakhov, Thermodynamic Assessment of the Bi-Zn System, *Calphad*, 2000, **24**(1), p 1-14
20. Y. Djaballah, L. Bennour, F. Bouharkat, and A Belgacem-Bouzida, Thermodynamic Assessment of the Binary System (Bi-Zn), *Modell. Simul. Mater. Sci. Eng.*, 2005, **13**, p 361-369
21. G.P. Vassilev, T. Gomez-Acebo, and J.C. Tedenac, Thermodynamic Optimization of the Ni-Zn System, *J. Phase Equilib.*, 2000, **21**(3), p 287-301
22. X.P. Su, N.Y. Tang, and J.M. Toguri, Thermodynamic Assessment of the Ni-Zn System, *J. Phase Equilib.*, 2002, **23**(2), p 140-148
23. G.P. Vassilev, Comments on the Thermodynamic Reassessments of the Ni-Zn System, *J. Phase Equilib.*, 2005, **26**(4), p 309-310
24. G. Hagg and G. Funke, X-ray Analysis of the System Ni-Bi, *Z. Phys. Chem. B*, 1930, **6**, p 272-283, in German
25. P. Nash, Bi-Ni Phase Diagram, *Binary Alloy Phase Diagrams*, 2nd, T.B. Massalski, Ed., ASM, 1990, p 768-769
26. P. Feschotte and J.M. Rosset, Phase Equilibria in the Binary Nickel-Bismuth System, *J. Less-Common Met.*, 1988, **143**, p 31-37, in French
27. G.P. Vassilev, X.J. Liu, and K. Ishida, Experimental Studies and Thermodynamic Optimization of the Ni-Bi System, *J. Phase Equilib.*, 2005, **26**(2), p 161-168
28. H. Fjellvag and S. Furuseth, Structural Properties of $Ni_{1-x}Rh_xBi_3$, *J. Less-Common Met.*, 1987, **128**, p 177-183
29. R.P. Anantamula and D. Mason Bruce, Thermodynamic Properties of Solid Ni-Zn Alloys by Atomic Absorption, *Metall. Trans.*, 1974, **5**, p 605
30. G. Nover and K. Schubert, The Crystal Structure of $NiZn_3$, *J. Less-Common Met.*, 1980, **75**, p 51
31. J.K. Critchley and S. Denton, The Crystal Structure of Delta-Ni-Zn, *J. Inst. Met.*, 1971, **99**, p 26-27
32. X.P. Su, N.Y. Tang, and J.M. Toguri, 450 °C Isothermal Section of the Fe-Zn-Si Ternary Phase Diagram, *Can. Metall. Q.*, 2001, **40**(3), p 377-384
33. Z. Li, X.P. Su, and Y.H. He, 450 °C Isothermal Section of the Zn-Fe-Bi Ternary Phase Diagram, *J. Alloys Compd.* (2007). doi:10.1016/j.jallcom.2007.08.029