Journal of Alloys and Compounds 489 (2010) 30–35

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Equilibrium phase of high-entropy FeCoNiCr$Cu_{0.5}$ alloy at elevated temperature

Chun-Ming Lin, Hsien-Lung Tsai*

Department of Mechanical Engineering, National Taiwan University Science and Technology, 43, Keelung Rd., Sec. 4, Taipei 10673, Taiwan

ARTICLE INFO

Article history:
Received 15 July 2009
Received in revised form 31 August 2009
Accepted 1 September 2009
Available online 16 September 2009

Keywords:
High-entropy alloy
FeCoNiCr$Cu_{0.5}$
Heat treatment
Equilibrium phase
Precipitate

ABSTRACT

The phase transformations of FeCoNiCr$Cu_{0.5}$ alloy with the as-cast structure and heat-treated structures were studied. The as-cast alloy specimens were first heated at 1050 °C with a holding time of 1 h. Serial heat-treatment processes at 350 °C, 500 °C, 650 °C, 800 °C, 950 °C, 1100 °C, 1250 °C and 1350 °C with a holding time of 24 h were then carried out to understand the phase evolution and the relationship between the microstructure and the hardness of the specimens. The microstructures were investigated and chemical analyses performed by optical microscopy (OM), scanning elector microscopy (SEM), X-ray diffractometer (XRD) and transmission elector microscopy (TEM). The results show that FCC peaks were observed from the X-ray diffraction of the as-cast specimens and a precipitate phase was present in the specimens that had been heated to 950 °C. The hardness of the FeCoNiCr$Cu_{0.5}$ alloy remained unchanged in the specimens that underwent various heat treatments that were applied in this study.

1. Introduction

In recent years, Yeh et al. developed new high-entropy alloy systems with multiple elements in equi-molar or near equi-molar ratios [1–3]. Alloy systems that are composed of at least five principal elements at 5–35 at% have been reported [4–9]. High-entropy alloy contains no single matrix element. Solid solutions with multiprincipal elements have been found to be more stable intermetallic compounds (IMC) at various temperatures. Since they have large entropies of mixing, IMC nano-precipitates easily form in the as-cast state [3,5–7]. Since they have excellent high-temperature behavior, mechanical behavior, and corrosion resistance, high-entropy alloys are promising materials for industrial applications [8–14]. However, putting FeCoNiCr$Cu_{0.5}$ alloy system in 3.5% sodium chloride (NaCl) solution may have a negative result [15]. The mechanical behavior of a high-entropy alloy, FeCoNiCr$Cu_{0.5}$ as a function of heat-treatment temperature is of interest. This study investigates how the temperature of heat treatment affects the microstructures, mechanical properties and phase transformations of the FeCoNiCr$Cu_{0.5}$ alloy system.

2. Materials and methods

The high-entropy alloy system of FeCoNiCr$Cu_{0.5}$ was remelted in an argon atmosphere in an arc furnace with a mixture of appropriate amounts of high-purity elements (99.99%), listed in Table 1. The specimens with 20 mm × 10 mm × 2 mm were prepared by heating at 1050 °C for 1 h and then heated in an argon atmosphere at various annealing temperatures from 350 °C to 1350 °C with a holding time of 24 h at each temperature. The specimens were polished for observation using an optical microscope and a scanning electron microscope (SEM, JEOL JSM-6500). The chemical compositions of the phases were analyzed by energy dispersive X-ray spectrometry (EDS). X-ray diffraction (XRD, Rigaku D/Max-2500 diffractometer using Cu-Kα radiation) was used to identify the crystalline phases of these alloys at a scan speed of 1°/min and radiation conditions of 30 kV and 50 mA. The precipitate phases were identified by field emission transmission electron microscopy (FE-TEM, Philips Technai G2 Dispersive X-ray Spectrometer) with thin-foil specimens that were prepared by polished thinning and had then undergone electron-polishing and ion milling. Microhardness was measured using a Vickers hardness tester (Matersuzawa, Seiki MV-1) under a load of 300 kgf for 15 s.

3. Results and discussion

3.1. X-ray diffraction of FeCoNiCr$Cu_{0.5}$ alloy analysis

Fig. 1 shows the X-ray diffraction patterns (XRD) of the FeCoNiCr$Cu_{0.5}$ alloy system at various annealing temperatures. As can be seen, there are solid solution phases with a FCC crystal structure. The lattice constant of this phase as calculated from the principal peak was 3.562 Å. The principal peaks of the FCC crystal structure are slightly shifted from those of the matrix substructure, the Cu-rich phase. The minor peaks close to the left of the FCC matrix are identified as Cu-rich FCC. Because they have the same structure and similar lattice parameters, the matrix and the Cr-rich phase show diffraction peaks at the same positions. As a result, different phases can be recognized in backscattered electron images but no distinction can be made in XRD pattern. Fe, Co and Ni elements may promote the formation of the FCC phase. Specifically, the FCC structure remains unchanged for the alloy below 1100 °C. However, increase in annealing temperature has reduced the peaks. The Cu-rich FCC phase dissolves into the FCC matrix at elevated

---

* Corresponding author. Tel.: +886 2 2737 6485; fax: +886 2 2737 6460.
E-mail addresses: D9503503@mail.ntust.edu.tw (C.-M. Lin), johntsai@mail.ntust.edu.tw (H.-L. Tsai).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.09.041

Table 1
Physical properties of elements [6].

Element	Fe	Co	Ni	Cr	Cu
Crystal structure	BCC	HCP	FCC	BCC	FCC
Atomic radius (Å)	1.241	1.251	1.246	1.249	1.278
Lattice constant (Å) a	2.866	2.506	3.524	2.885	3.615
Lattice constant (Å) c	–	4.069	–	–	–

annealing temperature. The lattice distorted by copper is associated with extensive thermal migration under heat treatment and differs in atomic size.

3.2. Microstructure of FeCoNiCrCu$_{0.5}$ alloy analysis

Fig. 2 shows SEM backscattered electron images of the alloy system after various annealing processes. The second phase in this alloy precipitated over a range of annealing temperatures. Table 2 presents the chemical compositions of the alloy under various conditions. The solidification phases were identified as the matrix phase (MP), the Cr-rich phase (SP) and the Cu-rich phase (TP). The morphology formed precipitate phase gradually changes over a range of annealing temperatures [13]. The formation of intragranular phase segregations occurs dramatically at high annealing temperatures. The segregation ratio (SR) represents the degree of element segregation and is defined as

$$\mathrm{SR} = \frac{\text{matrix phase (MP) in zone A}}{\text{second phase (SP) or third phase (TP) in zone B}},$$

where zone A is the zone of matrix phase (MP); zone B is the zone of segregation of the second phase (SP), and the third phase (TP).

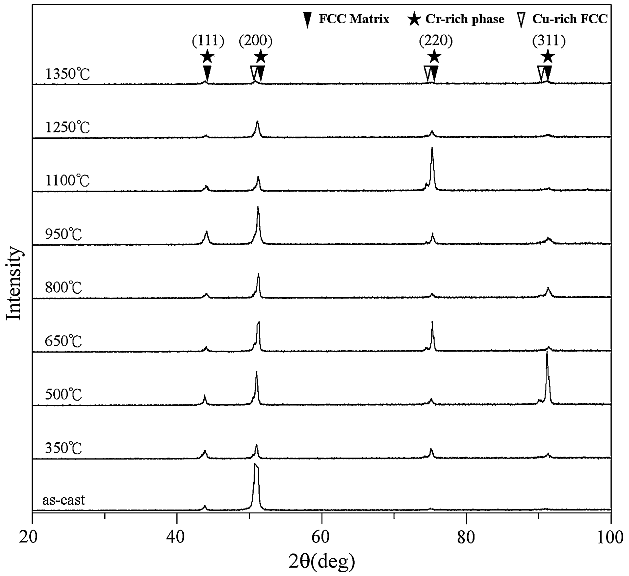

Fig. 1. XRD patterns of FeCoNiCrCu$_{0.5}$ high-entropy alloy.

Table 2
EDX analysis of chemical composition of FeCoNiCrCu$_{0.5}$ alloy under various heat treatments.

Temperature		(unit: at%)				
		Fe	Co	Ni	Cr	Cu
AS-C	MP	24	24	25	22	9
	SP	15	14	14	47	12
	TP	5	5	9	4	77
350 °C	MP	24	24	22	22	8
	SP	15	14	13	47	11
	TP	3	3	7	3	83
500 °C	MP	23	24	22	21	9
	SP	8	8	7	67	11
	TP	4	4	7	3	82
650 °C	MP	23	23	23	22	9
	SP	8	3	9	44	31
	TP	3	3	7	3	84
800 °C	MP	23	23	23	22	9
	SP	8	S	9	44	31
	TP	3	3	6	5	87
950 °C	MP	23	24	23	21	9
	SP	14	13	13	46	14
	TP	4	4	8	3	81
1100 °C	MP	23	23	23	22	9
	SP	2	2	1	92	3
	TP	8	9	11	8	63
1250 °C	MP	23	22	22	22	11
	SP	2	1	2	95	0
	TP	8	9	10	9	65
1350 °C	MP	25	23	25	20	10
	SP	2	1	1	94	2
	TP	–	–	–	–	–

AS-C: as-cast, MP: matrix phase, SP: Cr-rich phase and TP: Cu-rich phase.

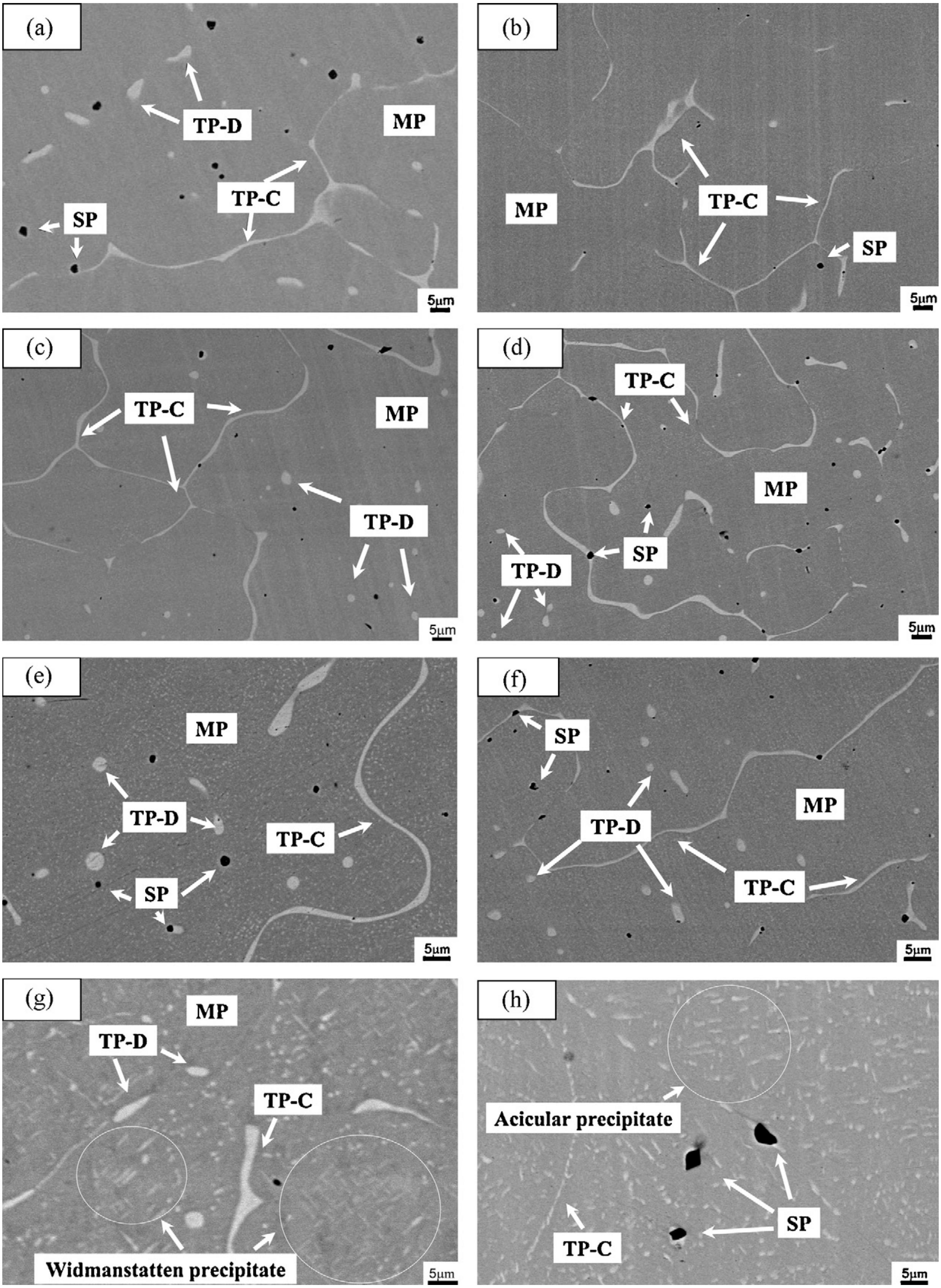

Fig. 2. The SEM micrographs of $FeCoNiCrCu_{0.5}$ alloys: (a) as-cast, (b) 350 °C, (c) 500 °C, (d) 650 °C, (e) 800 °C, (f) 950 °C, (g) 1100 °C, (h) 1250 °C and (i) 1350 °C. (Matrix phase: MP; second phase (SP): Cr-rich phase; third phase-discontinuous (TP-D): discontinuous Cu-rich phase; third phase-continuous (TP-C): continuous Cu-rich phase.)

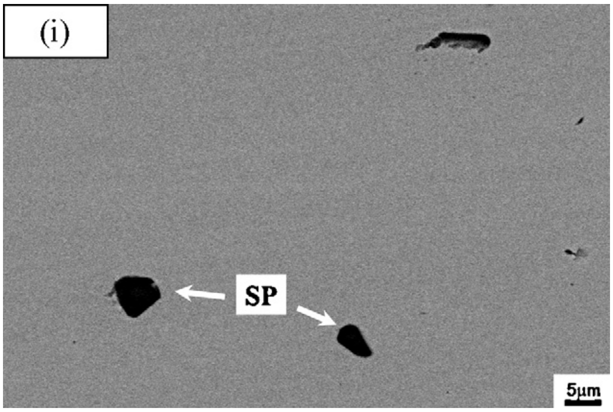

Fig. 2. (*Continued*).

Table 3
Segregation ratio (SR) for both Cr-rich and Cu-rich phases.

		Fe	Co	Ni	Cr	Cu
As-cast	SR_1	2	2	2	0.5	0.8
	SR_2	5	5	3	5	0.1
350 °C	SR_1	2	2	2	0.5	0.8
	SR_2	8	7	3	6	0.1
500 °C	SR_1	3	3	3	0.3	0.8
	SR_2	6	6	3	7	0.1
650 °C	SR_1	3	3	3	0.5	0.3
	SR_2	9	7	3	8	0.1
800 °C	SR_1	3	3	3	0.5	0.3
	SR_2	9	8	4	4	0.1
950 °C	SR_1	2	2	2	0.5	0.7
	SR_2	6	6	3	7	0.1
1100 °C	SR_1	11	11	30	0.2	3
	SR_2	3	3	2	3	0.1
1250 °C	SR_1	15	16	11	0.2	36
	SR_2	3	3	2	3	0.2
1350 °C	SR_1	13	21	16	0.2	7
	SR_2	–	–	–	–	–

SR_1 = matrix phase (MP)/second phase (SP) and SR_2 = matrix phase (MP)/third phase (TP).

Table 3 presents the phase segregation ratios. The matrix phases are the major phases of the as-cast specimens and of those annealed at up to 950 °C. The matrix phase became a Cr-rich phase when the specimen was treated from 1100 °C to 1350 °C.

The morphology of the third phase (Cu-rich phase) varied with the annealing process. When the temperature was less than 350 °C, the third phase morphology was a continuous precipitate. When the specimen was treated from 350 °C to 950 °C, the third phase morphology had coexisting continuous precipitate and discontinuous precipitate. Lastly, the specimens treated from 1100 °C to 1350 °C comprised short precipitate and acicular precipitate phases. The positive mixing enthalpy of the copper element is responsible for the Cu-rich phase segregation in the matrix phase, as shown in Table 4 [15–17]. Preventing the segregation of copper by heat treatment may be difficult. The morphology of the copper rich phase may change from continuous precipitate to discontinuous precipitate upon heat treatment. Heterogeneous segregation in solid solution from short-range order condition at low temperature forms a solid solution of the third phase-continuous precipitate, as shown in Fig. 2(a–d). At high temperature, the copper solute atoms tend to segregate as a solid solution with the third phase-discontinuous precipitate, as shown in Fig. 2(e–i). This fact was confirmed using a TEM bright-field image and the corresponding SAD pattern analysis, as shown in Fig. 3(a–f). The analyses were carried out in $FeCoNiCrCu_{0.5}$ high-entropy alloys at various annealing temperatures of up to 1350 °C. The FCC structure with lattice constants of 3.592 Å was further verified. In particular, at higher temperatures, the phase was produced by phase transformation, as shown in Fig. 3(d–e). Due to the third continuous-phase was partially dissolved into a matrix, as shown in Fig. 2(g). The third continuous-phase was transformed into a matrix in which precipitates were dispersed, as shown in Fig. 3(e). The ordered FCC plate transforms into Widmanstatten precipitates along the $\langle 0\,2\,0 \rangle$ direction. At temperatures of under 1350 °C, disordered Widmanstatten precipitates transform into spherical precipitates

Table 4
Chemical mixing enthalpy of a pair of atoms.

Element	(unit: kJ/mol)				
	Fe	Co	Ni	Cr	Cu
Fe	–	−1	−2	−1	13
Co		–	0	−4	10
Ni			–	−7	4
Cr				–	−1
Cu					–

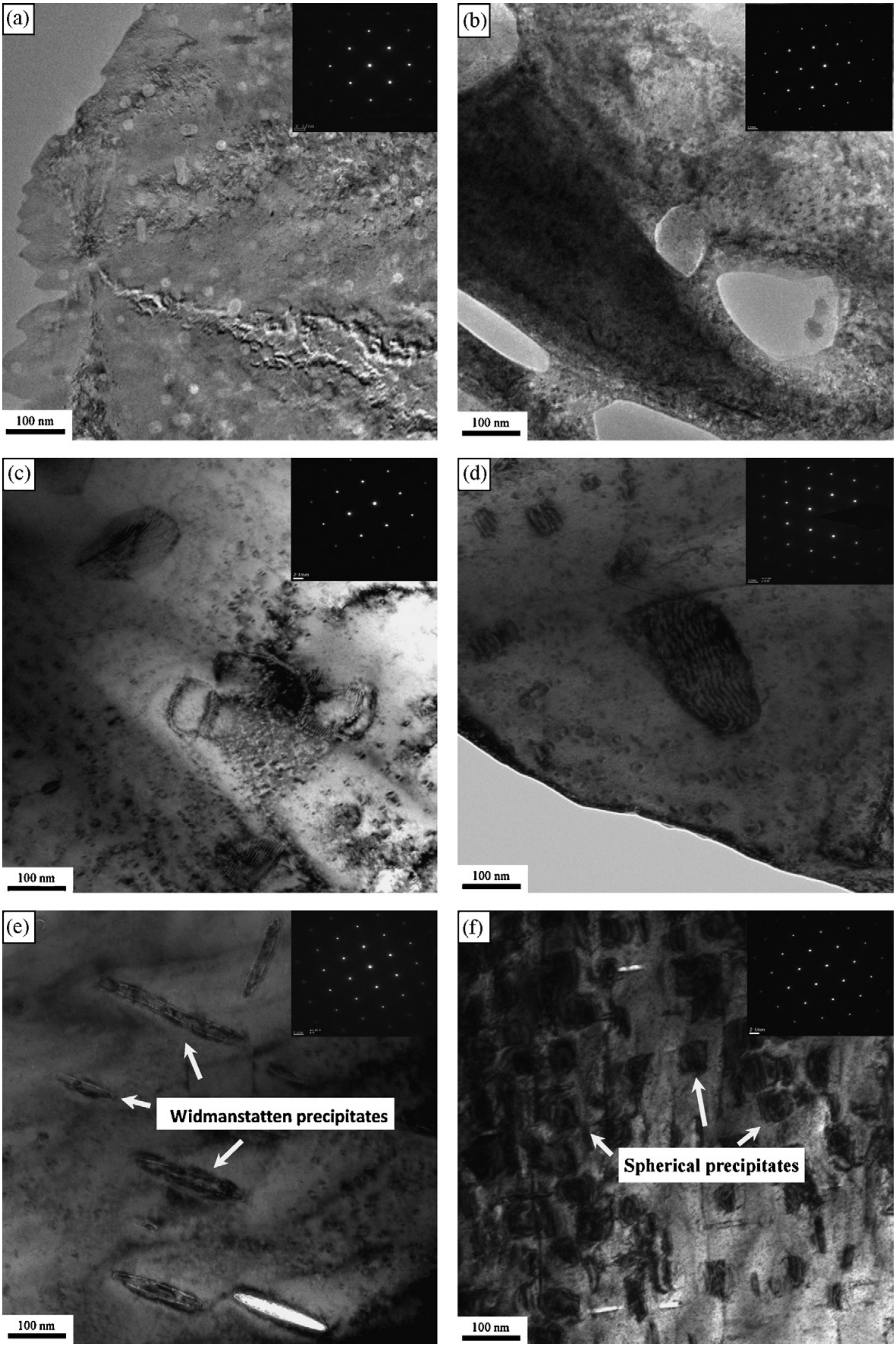

Fig. 3. TEM microstructure of FeCoNiCrCu$_{0.5}$ alloys of bright-field image and corresponding SAD pattern of FCC [0 1 1] zone axis in each insert figure: (a) as-cast, (b) 650 °C, (c) 950 °C, (d) 1100 °C, (e) 1250 °C and (f) 1350 °C annealing temperatures.

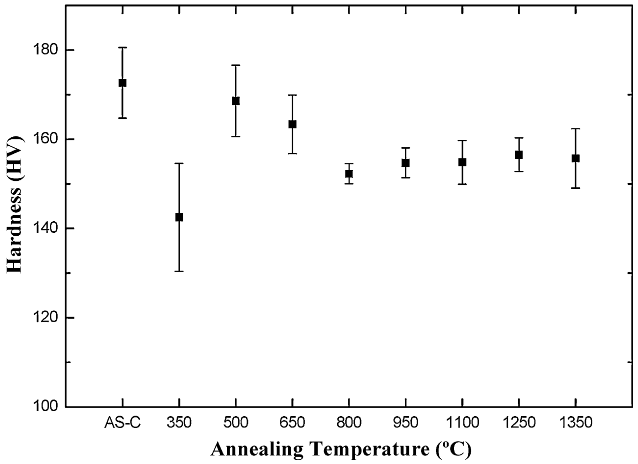

Fig. 4. The hardness values of $FeCoNiCrCu_{0.5}$ high-entropy alloy.

because of the small elastic anisotropy and they disperse in the strongly ordered matrix, as indicated by the arrow in Fig. 3(f).

3.3. Hardness analysis

Fig. 4 shows the hardness values for the $FeCoNiCrCu_{0.5}$ high-entropy alloy system. The alloy system was found to exhibit a hardness of 174 HV under the as-cast condition and a hardness of 152–154 HV following annealing at 350–1350 °C. In this study, the hardness of an alloy system was reduced by a decline in the bonding strength between the element atoms that is caused largely by thermal behavior associated with the positive mixing enthalpies of Cu, Co and Ni.

4. Conclusion

The $FeCoNiCrCu_{0.5}$ alloy system, as-cast or annealed over a range of temperatures up to 1350 °C, exhibits an FCC phase. The FCC phase of the alloy system tends to form a Cu-rich phase (TP) and a Cr-rich phase (SP) during different annealing treatments. In particular, Cu solute atoms tend to segregate as a third phase, potentially favoring the presence of a continuous-third phase because heterogeneous segregation occurs from short–range order in solid solution at the low temperature. Annealing at high temperature may also favor the segregation of Cu solute atoms as a discontinuous-third phase. The hardness declines as the annealing temperature increases because the bonding strength of Cu, Co and Ni is reduced, mostly by the thermal behavior, which is determined by the positive mixing enthalpies and thermal energy.

Acknowledgements

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financially supporting this research under Contract No. NSC 96-2221-E011-072.

References

[1] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Can, T.S. Chin, T.T. Shun, C.H. Tsau, S.Y. Chang, Adv. Eng. Mater. 6 (2004) 299–303.
[2] S. Ranganathan, Curr. Sci. 85 (2003) 1404–1406.
[3] C.J. Tong, Y.L. Chen, S.K. Chen, J.W. Yeh, T.T. Shun, C.H. Tsau, S.J. Lin, S.Y. Chang, Metall. Mater. Trans. A 36 (2005) 881–893.
[4] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent, Mater. Sci. Eng. A 357–377 (2004) 213–218.
[5] Y. Zhang, Y. Zhou, Mater. Sci. Forum 561–565 (Part 2) (2007) 1337–1339.
[6] J.W. Yeh, S.K. Chen, J.Y. Gan, S.J. Lin, T.S. Chin, T.T. Shun, C.H. Tsau, S.Y. Chou, Metall. Mater. Trans. A 35 (2005) 2533–2536.
[7] P.K. Huang, J.W. Yeh, T.T. Shun, S.K. Chen, Adv. Eng. Mater. 6 (2004) 74–78.
[8] C.C. Tung, J.W. Yeh, T.T. Shun, S.K. Chen, Y.S. Huang, H.C. Chen, Mater. Lett. 61 (2007) 1–5.
[9] Y.S. Huang, L. Chen, H.W. Lui, M.H. Cai, J.W. Yeh, Mater. Sci. Eng. A 457 (2007) 77–83.
[10] C.Y. Hsu, J.W. Yeh, S.K. Chen, T.T. Shun, Metall. Mater. Trans. A 35 (2004) 1465–1469.
[11] U.S. Hsu, U.D. Hung, J.W. Yeh, S.K. Chen, Y.S. Huang, C.C. Yang, Mater. Sci. Eng. A 92 (2007) 403–408.
[12] S. Varalakshmi, M. Kamaraj, B.S. Murty, J. Alloys Compd. 460 (2008) 253–257.
[13] Y.P. Wang, B.S. Li, M.X. Ren, C. Yang, H.Z. Fu, Mater. Sci. Eng. A 491 (2008) 154–158.
[14] Y.J. Zhou, Y. Zhang, F.J. Wang, Y.L. Wang, G.L. Chen, J. Alloys Compd. 466 (2008) 201–204.
[15] Y.J. Hsu, W.C. Chiang, J.K. Wu, Mater. Chem. Phys. 92 (2005) 112–117.
[16] A. Takeuchi, A. Inoue, Mater. Trans. JIM 41 (2000) 1372–1378.
[17] A. Takeuchi, A. Inoue, Mater. Trans. JIM 42 (2001) 1435–1444.