Kovove Mater. 53 2015 313–317
DOI: 10.4149/km_2015_5_313

Phase analysis of Cu-Fe-Pd ternary alloys

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Received 17 April 2014, received in revised form 5 December 2014, accepted 7 January 2015

Abstract

X-ray diffraction (XRD) experiments have been carried out to determine the structure and volume fractions of various phases present in Cu-Fe-Pd alloys. The volume percentage of each phase has been determined from integrated intensity of Bragg's peaks. The results can be divided into two parts on the basis of alloy composition. The alloys with 5 at.% Pd contain disordered face centered cubic (fcc) type as a major phase with traces of body centered cubic (bcc) (α-Fe) phase, whereas the alloys with Pd content ranging from 9–20 at.% contain ordered Cu_3Au-type phase of Cu-Fe-Pd as a major phase with traces of α-Fe phase. The ordering in various alloys persists up to 1173 K. The results have been explained on the basis of binary phase diagram of Cu-Pd system.

Key words: crystal structure, metals and alloys, phase transformations

1. Introduction

Transition metals alloys have been the subject of many investigations in the recent past due to their interesting physical properties and practical applications. They have high resistance to corrosion, strength, electrical conductivity and harden with aging. The applications of these alloys depend on their properties and microstructure. Therefore, the investigation of the structure-property correlation is quite useful in designing new alloys [1]. These alloys having high hydrogen selectivity and permeability along with electrical, magnetic and mechanical properties, may be used in applications such as hydrogen separation membranes as well as membrane reactor applications [2–6].

Recent studies on ternary Cu-M-Pd (M = 3d metals) alloys have shown that they form a single phase with A1-structure at a composition of 1 : 1 : 6 with M = Ti, V, Mn and Fe. This phase exists as equilibrium ground state structure with a phase boundary extending beyond 1273 K [6]. No evidence regarding the formation of ordered structures in ternary Cu-M-Pd alloys has been reported up till now, although, most of the binary M-Pd alloys exhibit ordering. It is, therefore, interesting from the metallurgical point of view to see the effect of addition of metal M to other compositions of Cu-Pd alloys.

The motivation for choosing M = Fe in Cu-M-Pd for current investigation is the possibility that Fe may render enhanced magnetic properties. The main aim of this work is to study the structure of ternary Cu-Fe-Pd alloys and to determine the percentages of different phases present by carrying out a quantitative analysis. X-ray diffraction technique was used because the microstructure in these alloys has a significant effect on the integrated intensities of Bragg reflections for each phase.

2. Experimental details

The composition of seven alloys selected for this work is given in Table 1. The samples (5 g each) of Cu-Fe-Pd alloys were prepared from pure metals by using an arc-melting furnace with water cooled copper hearth and under an argon atmosphere. The alloys were remelted 6 times to ensure the homogeneity of alloy constituents. The ingots were sealed in quartz tubes under a vacuum of 7.9×10^{-4} Pa and annealed for 20 h at 1323 K in order to homogenize. Two slices were cut from each ingot, one of which was annealed

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Table 1. Chemical composition of the investigated Cu-Fe-Pd alloys

Sample No.	Composition (at.%)		
	Cu	Fe	Pd
1	75	05	20
2	86	05	09
3	85	10	05
4	75	15	10
5	80	15	05
6	70	20	10
7	75	20	05

at 723 K for one week and furnace cooled to room temperature, while the other was annealed at 1173 K for 24 h and quenched in ice cold water.

The chemical composition was determined by using electron probe microanalyzer (EPMA; JEOL JXA-8100). The sample preparation for EPMA involved grinding the samples progressively on finer grades of SiC paper followed by polishing with diamond paste to 0.25 micron finish. The composition was measured at ten different spots in each phase and the average composition was taken as the true composition of the alloy. The homogeneity variation of the alloy was found to be less than 1 at.%. The results are given in Table 1.

X-ray diffraction experiments were performed on a two-circle Philips X'Pert Pro diffractometer equipped with a Philips, X'Celerator solid-state detector. The working conditions for voltage and current were 45 kV and 40 mA, respectively, for X-ray tube, with a step scan mode using Cu Kα-radiations in the angle range of 20°–140° under θ-θ geometry. The sample preparation technique for scanning electron microscope (SEM) was similar to that for EPMA as described earlier. The micrographs were taken with SEM (Hitachi S4700) in back scattered mode. In this mode, heavy elements back scatter electron more strongly than light elements and thus appear brighter in the image. It is thus helpful in detecting contrast between areas of phases with different chemical compositions.

3. Determination of volume percentages

The volume percentage of each phase was determined from the integrated intensities of various Bragg reflections employing the direct comparison method [7]. The volume percentage of phase a is related to the integrated intensities as:

$$c_{\mathrm{a}} = \left(1 + \frac{R_{\mathrm{a}} I_{\mathrm{b}}}{R_{\mathrm{b}} I_{\mathrm{a}}}\right)^{-1}, \tag{1}$$

where c_{a} is volume percentage of phase a, I_{a}, I_{b} are integrated intensity of a and b phases, respectively; the integrated intensity of Bragg reflection was determined by using Philps X'Pert High Score software [8]; and R_{a}, R_{b} are theoretical integrated intensities of phases a and b.

These intensities depend on Miller indices (hkl), volume of unit cell (v), structure factor (F), multiplicity factor (p), Bragg angle (θ), Lorentz-polarization factor (L) and Debye-Waller factor (e^{-2M}) and are given by [9]:

$$R = \frac{1}{v^2}[|F^2|pL]\mathrm{e}^{-2M}, \tag{2}$$

where

$$L = \frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta}. \tag{3}$$

The Bragg reflections from samples containing phases a and b were observed at:

– (110), (111), (200), (220) and (311) planes for body centered cubic (bcc) (α-Fe),

– (220), (311) planes for face centered cubic (fcc) phase and

– (111), (200), (220), (311) and (331) planes for $\mathrm{Cu_3Au}$-type (ordered phase) as shown in Fig. 1a,b.

The volume of the unit cell v was determined from the lattice parameters determined from the diffraction patterns.

4. Results and discussion

The qualitative analysis of the XRD patterns of all samples was done using the Hanawalt search method in order to detect different phases in these alloys [7]. The results show the coexistence of two phases in each alloy annealed at 723 K. The results are summarized in Table 2.

The quantitative analysis was done using the direct comparison method because no standard sample is required for the determination of volume percentages of phases. The data of all Bragg reflections was considered in the analysis and intensity averaging [10] was done to avoid the effects of preferred orientation.

The samples have been prepared in the Cu rich end of Cu-Fe-Pd phase diagram. Order-disorder transformation temperature (T_{c}) (ordered $\mathrm{Cu_3Au}$ to disordered fcc) of Cu-Pd alloys at high contents of Cu lies near 781 K [6]. The results of quantitative analysis given in Table 2 are for two different temperatures, i.e. 723 K and 1173 K. The main purpose of these heat treatments is to determine the structure in the samples above and below T_{c}. As observed in the present study, the samples are single phase at 1173 K (above T_{c}) and ordered at 723 K (below T_{c}).

Table 2. Details of phases along with the volume percentages and lattice parameters in various alloys determined from experiments

Sample No.	Temperature (K)	Phases	Volume (%)			Lattice parameter a (Å)		
			α-Fe	fcc	Cu$_3$Au	α-Fe	fcc	Cu$_3$Au
1	723	α-Fe + Cu$_3$Au*	0.04 ± 0.03	0.0	99.96 ± 0.03	–	–	3.684 ± 0.004
	1173	fcc**	0.0	100.0	0.0	–	3.685 ± 0.003	–
2	723	α-Fe + Cu$_3$Au	0.22 ± 0.12	0.0	99.78 ± 0.12	2.864 ± 0.005	–	3.655 ± 0.006
	1173	fcc	0.0	100.0	0.0	–	3.649 ± 0.002	–
3	723	α-Fe + fcc	0.03 ± 0.02	99.97 ± 0.02	0.0	2.861 ± 0.004	3.634 ± 0.005	–
	1173	α-Fe + fcc	0.02 ± 0.01	99.98 ± 0.01	0.0	2.882 ± 0.005	3.637 ± 0.002	–
4	723	α-Fe + Cu$_3$Au	0.09 ± 0.06	0.0	99.91 ± 0.06	2.869 ± 0.005	–	3.655 ± 0.003
	1173	α-Fe + fcc	0.47 ± 0.06	99.53 ± 0.09	0.0	2.867 ± 0.002	3.654 ± 0.002	–
5	723	α-Fe + fcc	0.29 ± 0.13	99.71 ± 0.13	0.0	2.869 ± 0.002	3.632 ± 0.004	–
	1173	α-Fe + fcc	0.87 ± 0.19	99.13 ± 0.19	0.0	2.871 ± 0.003	3.637 ± 0.004	–
6	723	α-Fe + Cu$_3$Au	0.21 ± 0.09	0.0	99.79 ± 0.09	2.866 ± 0.004	–	3.652 ± 0.003
	1173	α-Fe + fcc	0.52 ± 0.09	99.48 ± 0.07	0.0	2.876 ± 0.003	3.657 ± 0.003	–
7	723	α-Fe + fcc	0.20 ± 0.04	99.80 ± 0.04	0.0	2.848 ± 0.003	3.622 ± 0.002	–
	1173	α-Fe + fcc	1.64 ± 0.35	98.36 ± 0.35	0.0	2.871 ± 0.004	3.637 ± 0.003	–

*Ordered Cu-Fe-Pd phase of Cu$_3$Au-type

**Face centered cubic Cu-Fe-Pd solid solution

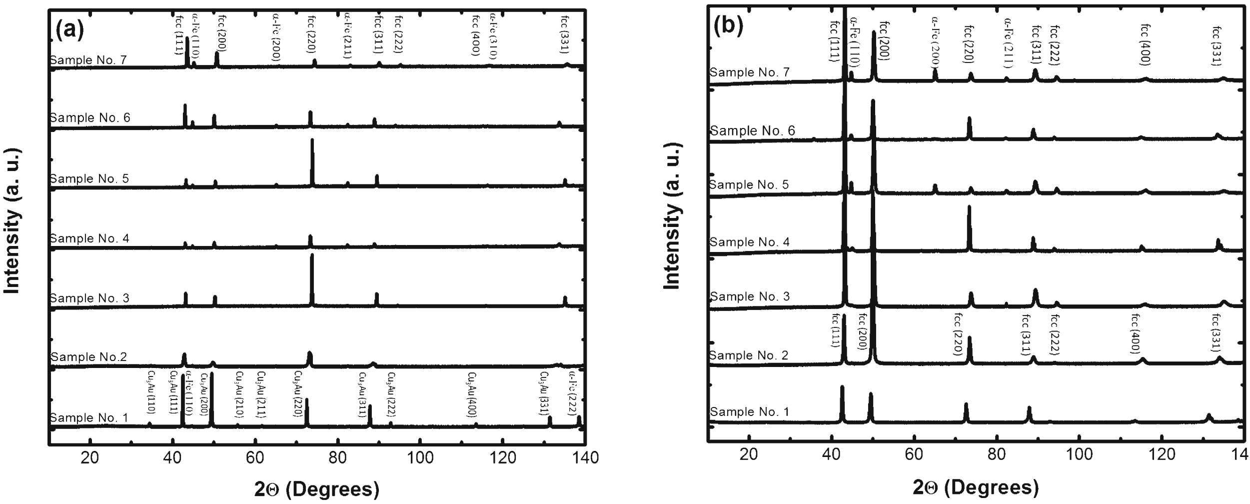

Fig. 1. X-ray diffraction patterns of Cu-Fe-Pd alloys (a) annealed at 723 K (b) quenched from 1173 K.

At 723 K, the alloys with 5 at.% Pd contain mainly disordered face centered cubic (fcc) phase with a trace of bcc (α-Fe) phase, whereas, the alloys with higher Pd (9–20 at.%) contain mainly the ordered Cu$_3$Au-type phase and traces of bcc (α-Fe). At 1173 K, the ordered Cu$_3$Au-type phase disappears. That is why the major phase at this temperature is disordered fcc in all samples. The bcc (α-Fe) phase, however, exists in traces in all samples except sample numbers 1 & 2. It is worth mentioning that sample numbers 1 & 2 become single phase (fcc) at high temperatures showing the limited solubility of Fe in Cu-Pd alloys at 1173 K.

The phases found in the case of Cu-Fe-Pd ternary alloys can be explained on the basis of phase diagram of binary Cu-Pd alloy. In fact, the phases present in binary Cu-Pd alloys are nearly inherited to the ternary alloys; at least for alloys containing Pd up to 20 at.%.

The formation of phases in Cu-Fe-Pd alloys is according to the Hume-Rothery's rules [11]. Solubility of Fe in Cu-Pd satisfies three parameters, i.e. atomic size, valency & electronegativity. But its crystal structure is, however, different (Fe has bcc structure, while

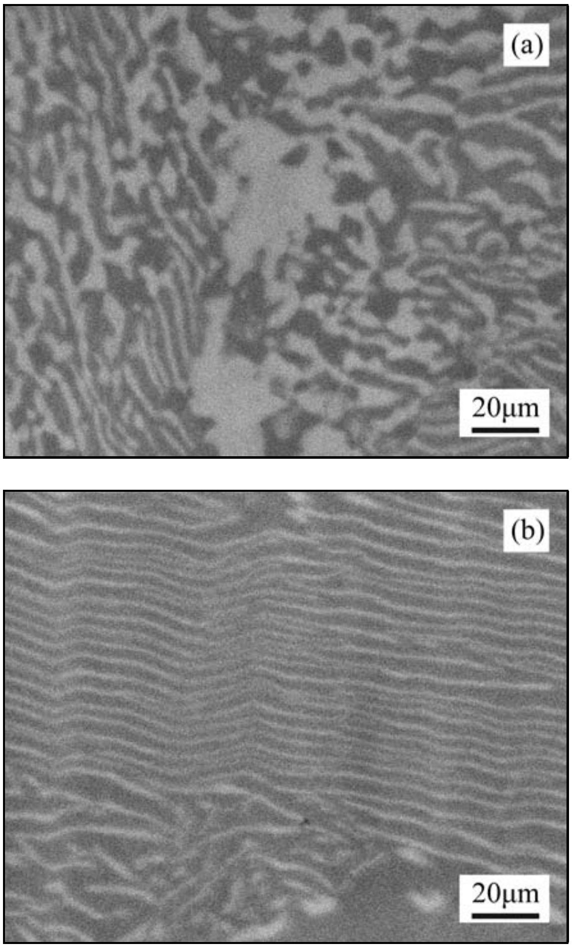

Fig. 2. Micrographs of sample no. 3 taken by a scanning electron microscope showing two phases (bright (α-Fe), dark (fcc)) in (a) annealed state, (b) quenched state.

Cu and Pd have fcc structure) [12]. This may be the primary reason for partial solubility or miscibility gap of Fe in Cu-Pd.

The insolubility of Fe in Cu-Pd can also be explained on the basis of lattice parameter of Fe and Cu-Pd. For samples number 3, 5 and 7 (with fcc + α-Fe phases) in annealed and quenched state, the lattice constant is about 3.63 Å for fcc phase. The lattice constant for the ternary Cu-Fe-Pd alloys is the same as for binary alloys having similar Cu-Pd ratio. Addition of Fe has no effect on the lattice constant of ternary alloys. The Cu-Pd alloys with this ratio are nearly single phase and have fcc structure at all temperatures.

The lattice constant for Cu$_3$Au phase in samples number 1, 2, 4 and 6 (annealed at 723 K) and fcc phase in samples number 4 & 6 (quenched from 1173 K) is about 3.65 Å. The ratio of Cu and Pd in the ternary alloys mentioned above is 88:12 and their lattice parameter is the same as that for binary Cu-Pd alloy of the same composition. The alloys with ratio 88 : 12 in the binary Cu-Pd alloy phase diagram have ordered Cu$_3$Au-type structure at low temperatures and fcc structure at high temperatures. It is thus inferred that Fe does not form solid solution with Cu-Pd alloy and precipitates as α-Fe. The presence of phases in these alloys can also be seen in SEM micrographs in Fig. 2.

5. Conclusions

Volume percentages of various phases appearing in different samples of Cu-Fe-Pd have been determined from XRD measurements. The samples were either annealed at 723 K or quenched from 1173 K. Most of the samples have two phases except sample no. 1 and 2 which are single phase at 1173 K. It is found that Fe when added in binary Cu-Pd alloy (up to 5 at.%) dissolves in Cu-Pd solid solution without formation of any new phase. However, when the concentration approaches 10 at.%, a new phase, namely α-Fe, is formed establishing the fact that Fe has a limited solid solubility in Cu-Pd.

Acknowledgements

One of the authors, Naseeb Ahmad wishes to acknowledge the Higher Education Commission, Government of Pakistan, Islamabad, for financial support under Indigenous Ph.D. program, Batch III.

References

[1] Wang, C. P., Liu, X. J., Ohnuma, I., Kainuma, R., Ishida, K.: Basic and Appl. Research, JPEDAV, *25*, 2004, p. 320. doi:10.1361/15477030420098
[2] Hu, R., Gao, M. C., Dogan, O. N.: Accelerated Materials Design for Hydrogen Separation Membranes. ACS Symposium Series, Chapter 3, *1078*, 2011, p. 27. doi:10.1021/bk-2011-1078.ch003
[3] Gruner, M. E., Hamann, S., Brunken, H., Ludwig, A., Entel, P.: J. of Alloys and Compounds, *577*, 2013, p. S333. doi:10.1016/j.jallcom.2012.02.033
[4] Kauffmann-Weiss, S., Hamann, S., Gruner, M. E., Schultz, L., Ludwig, A., Fahler, S.: Acta Mat., *60*, 2012, p. 6920. doi:10.1016/j.actamat.2012.08.001
[5] Kourov, N. I., Marchenkov, V. V., Pushin, V. G., Buinova, L. N., Weber, H. W.: The Physics of Metals and Metallography, *104*, 2007, p. 232. doi:10.1134/S0031918X07090049
[6] Subramanian, P. R., Laughlin, D. E.: Fluid Phase Equilibria, *12*, 1991, p. 231.
[7] Cullity, B. D., Stock, S. R.: Elements of X-Ray Diffraction. 3rd Edition. New Jersey, Prentice Hall Inc. 2001.
[8] http://philips-x-pert-highscore.software.informer.com/
[9] Cullity, B. D., Stock, S. R.: Elements of X-Ray Diffraction. 3rd Edition. New Jersey, Prentice Hall Inc. 2001.

[10] Ali, A., Ahmad, M., Hashmi, F. H., Khan, A. Q.: J. of Materials Science & Technology, *10*, 1994, p. 97. doi:10.1179/026708394790163799

[11] Axon, H. J., Hume-Rothery, W.: Proc. Roy. Soc. A, *193*, 1948, p. 1.

[12] Howard, B. H., Killmeyer, R. P., Rothenberger, K. S., Cugini, A. V., Morreale, B. D., Enick, R. M., Bustamante, F.: J. of Membrane Science, *241*, 2004, p. 207. doi:10.1016/j.memsci.2004.04.031