A study of structure of ternary Cu-Ni-Pd alloys

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Abstract

X-ray diffraction (XRD) and differential scanning calorimetry (DSC) have been used to study the structure and phase transformations in Cu-Ni-Pd alloys at various compositions. XRD experiments have been performed at two different temperatures 723 and 1173 K. The structure of all samples was found to be face centered cubic (fcc). The lattice parameters were found to depend strongly on concentration of Ni and Pd and are in good agreement with those calculated by Vegard's rule. Results of experiments show that Ni is completely soluble in Cu-Pd because its atomic size matches with Cu and Pd atoms.

K e y   w o r d s: X-ray diffraction, structure, Cu-Ni-Pd ternary alloys

1. Introduction

The production of new materials having high strength and ductility at high temperature is increasing. Stable materials responding to these requirements have structural properties which differ greatly from constituent metals [1]. Pd-based membranes have been the focus of many studies because of their high selectivity of hydrogen gas as compared to other gases due to the high solubility, mobility and high corrosion resistance in oxidation environments. However, Pd-based membranes demand considerable thickness of Pd, as much as several tens of microns, for high selectivity of hydrogen. This leads to a decrease of permeability of hydrogen and an increase of Pd material--cost. In addition, pure Pd also has tendency to undergo hydrogen embrittlement. However, hydrogen embrittlememt can be effectively decreased by alloying with Cu and Ni. Ni plays an important role in preventing hydrogen embrittlement and Cu is a good alloying element for the prevention of hydrogen embrittlement and hydrogen separation caused by phase transition of Pd lattice as well as for its low cost [2–9].

The Cu-Pd system has recently received a lot of attention because of hydrogen permeation properties of thin membranes of binary Cu-Pd and the existence of particular superstructures in this binary alloy. This alloy in ordered phase exhibits excellent hydrogen permeability and resistance against degradation mechanisms comparable to those of pure Pd [10–12].

The filler metal used for welding of corrosion resistant alloys such as stainless steel is often over-alloyed to compensate the loss of alloying elements in the welding fume and segregation in the weld metal. However, Ni-Cu and Ni-Cu-Pd alloys are more resistant to corrosion than stainless steel welds. The addition of a small amount of Pd has been found to improve the corrosion resistance relative to Ni-Cu welds. Other corrosion studies suggest that Ni-Cu-Pd filler metal can be a potential replacement for the conventional grades of stainless steel filler [13]. Spinodal decomposition for Cu-Ni-Pd alloys is of particular interest because one of the decomposition products is a ferromagnetic phase rich in Ni, while the other is a paramagnetic phase rich in Cu and Pd [14].

In the present study, structure and phase transformations have been investigated in Cu-Ni-Pd system using X-ray diffraction (XRD) and differential scanning calorimetry (DSC) in order to understand the role of Ni on the structure of Cu-Ni-Pd alloys.

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Table 1. Chemical composition and lattice parameter a (Å) for annealed and quenched samples along with melting temperature T_{m} (K) determined from DSC experiments

| Sample No. | Composition | Lattice parameter a (Å) | | Vegard's rule | Melting temperature T_{m} (K) | Grain size (Å) |
| | | Experiment | | | | |
		Annealed	Quenched			
1	$Cu_{75}Ni_5Pd_{20}$	3.672 ± 0.002	3.673 ± 0.003	3.665	1396	177.7
2	$Cu_{86}Ni_5Pd_9$	3.639 ± 0.004	3.639 ± 0.005	3.635	1351	170.8
3	$Cu_{85}Ni_{10}Pd_5$	3.622 ± 0.002	3.622 ± 0.002	3.619	1354	166.3
4	$Cu_{75}Ni_{15}Pd_{10}$	3.632 ± 0.003	3.633 ± 0.002	3.628	1391	170.9
5	$Cu_{80}Ni_{15}Pd_5$	3.615 ± 0.005	3.617 ± 0.003	3.615	1367	166.0
6	$Cu_{70}Ni_{20}Pd_{10}$	3.628 ± 0.002	3.628 ± 0.004	3.624	1407	171.1
7	$Cu_{75}Ni_{20}Pd_5$	3.611 ± 0.003	3.612 ± 0.004	3.610	1382	165.7

2. Experimental details

The samples (5 g each) of Cu-Ni-Pd alloys were prepared from 4N-grade pure metals by using an arc--melting furnace with water cooled copper hearth and under an argon atmosphere of 450 Torr. The alloys were remelted several times to ensure the homogeneity of alloy constituents. The chemical composition was determined by using electron probe microanalyzer (EPMA, JEOL JXA-8100). 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.

The ingots were sealed in quartz tubes under a vacuum of 2.0×10^{-5} Torr and annealed for 20 h at 1323 K in order to homogenize them. Two slices were cut from each ingot, one of which was annealed at 723 K for one week and furnace cooled to room temperature, while the other was annealed at 1173 K for 24 h and subsequently quenched in ice cool water. The samples were polished using standard techniques involving grinding and polishing progressively on finer grades of diamond paste up to 0.25 μ. Samples were then etched in equal part nitric acid and acetic acid solution for 10 s. Samples were then observed on a LECO LX-31 optical microscope equipped with image analyzer.

XRD experiments were performed on a two-circle X-ray diffractometer (Philips X'Pert Pro) equipped with a solid-state detector (Philips X'Celerator). The working conditions for voltage and current were 45 kV and 40 mA, respectively, for X-ray tube, with a step scan mode using Ni-filtered Cu Kα-radiations in the angle range of 20–140° under $\theta - \theta$ geometry with divergence and receiving slits of 0.5°.

The thermal analysis of the sample was performed using a differential scanning calorimeter (model SBT--Q600) under nitrogen atmosphere at a heating rate of 20 K min^{-1} up to the maximum temperature of 1450 K.

3. Results and discussion

The composition of alloys selected for this work lies in the Cu rich end of the phase diagram of ternary Cu-Ni-Pd alloy. The data presented in this paper is a part of more detailed study revealing phase relationships in Cu-Ni-Pd system, found in Cu-rich end of the ternary phase diagram. The phase diagram data would be further correlated to the properties of phases in this system. The samples were heated at two different temperatures in order to check the ordering in the samples above and below T_{c}. It is worthwhile to note that order-disorder transformation temperature (T_{c}) of binary Cu-Pd alloys at Cu rich end lies near 781 K [15].

The XRD data of the samples has been used for phase identification. It is found that all the samples have single phase fcc structure. Figure 1a,b shows the diffraction patterns of samples annealed at 723 K and those quenched from 1173 K, respectively. All fundamental reflections for fcc structure ($h + k = 2n$; $k + l = 2n$ & $h + l = 2n$ (n is an integer)) can be clearly seen. The space group of these alloys was determined using the computer program indxJPL [16] and was found to be Fm3m. No evidence of the formation of superstructures was found in all annealed and quenched samples. Therefore, it can be concluded that ordering tendency existing in the binary Cu-Pd alloys is no more active in the case of ternary Cu-Ni-Pd alloys.

The reflections in XRD patterns of all alloys under study are essentially the same, leading to the fact that no crystallographic change is affected in any alloy either by annealing or quenching. However, the relative intensity of (200) and (220) reflections is greater for quenched samples. This phenomenon can be attributed to the longer time given to the samples to
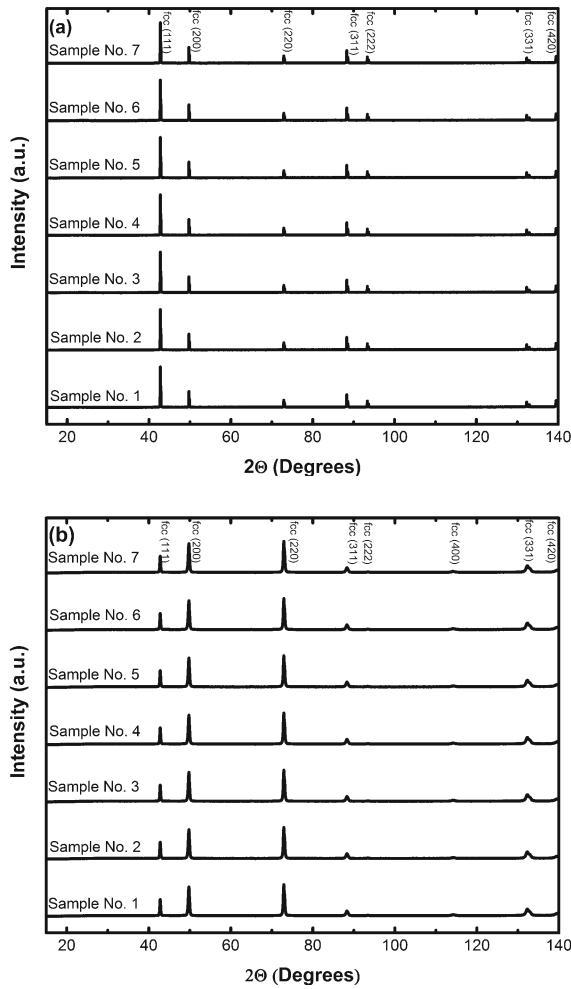
Fig. 1. X-ray diffraction patterns of Cu-Ni-Pd alloys: annealed at 723 K (a) and quenched from 1173 K (b).

cool during annealing which tends to promote (111) and (311) planes.

The grain size was determined from the diffraction data using the Scherrer formula [19]:

$$D_V = \frac{0.9\lambda}{\beta\cos\theta},\qquad(1)$$

where λ is the wavelength of incident radiation, β is the integral width of the Bragg reflection in radians and θ is the diffraction angle.

It is seen that the addition of Pd in Cu-Ni alloys tends to act as a grain coarsener. As the Pd content increases from 5 to 20 wt.%, an increase in grain size is observed (Table 1). However, the Pd content has no significant effect on the morphology of the grains as can be seen in the selected optical micrographs shown in Fig 2. Microstructures in all the samples appear to be single phase with random grain size. Figure 3 shows the DSC thermograms of Cu-Ni-Pd alloys. The change in heat flow beyond 1273 K reflects the on-set
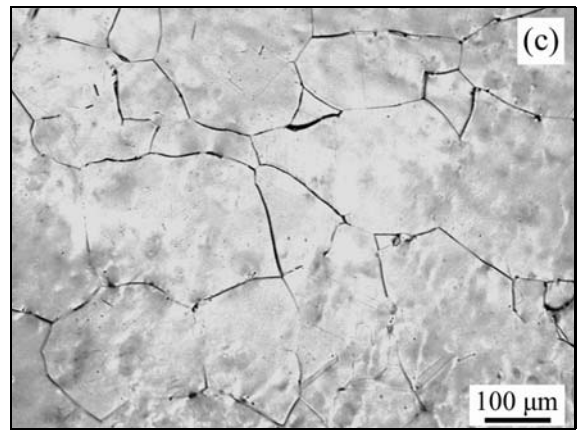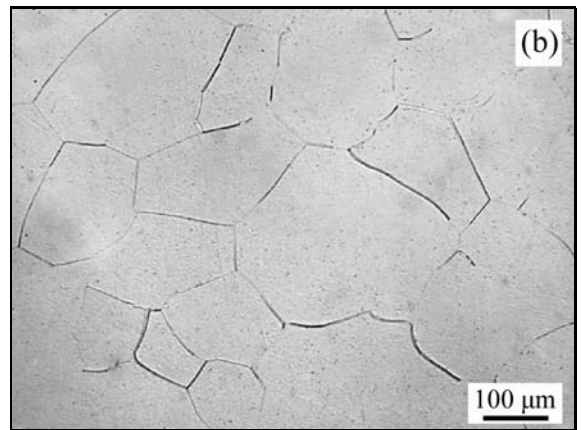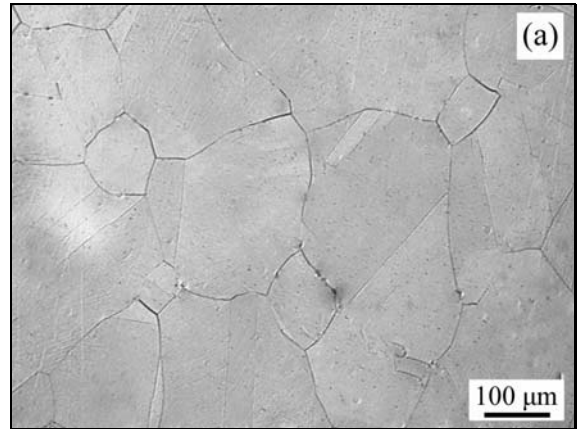

Fig. 2. Optical micrographs at 100x of $Cu_{86}Ni_5Pd_9$ (a), $Cu_{75}Ni_{15}Pd_{10}$ (b) and $Cu_{75}Ni_{20}Pd_5$ (c) alloys.

of melting of the alloys. No exothermic or endothermic peak was observed before melting point, which shows that no phase change occurs in the investigated temperature range. These results are consistent with those obtained from XRD. Hence, all the samples have a disordered fcc structure at both temperatures. This was expected for quenched samples because the structure of Cu-Pd alloy is fcc at 1173 K. However, the single fcc phase was not expected for annealed samples because
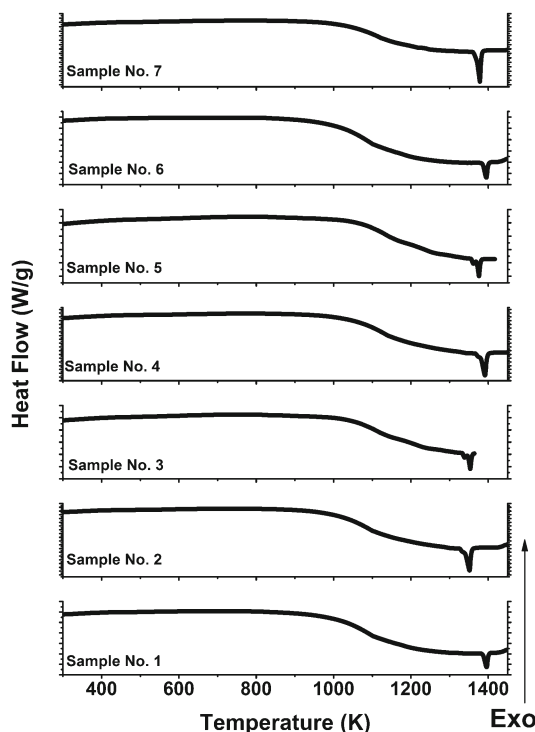
Fig. 3. Differential scanning calorimetry curves of annealed Cu-Ni-Pd alloys obtained at the heating rate of 20 K min^{-1}.

Fig. 4. Dependence of lattice constant a (Å) of Cu-Ni-Pd alloys on concentration of Ni and Pd: annealed alloys (a) and quenched alloys (b).

Cu-Pd alloy forms ordered L1$_2$ structure at 723 K. This may be due to the fact that Ni-Pd and Cu-Ni binary alloys form single fcc phase at 723 K. This may be due to the fact that free energy of Ni-Pd and Cu-Ni alloys is greater than ordering energy [17, 18].

The true values of lattice parameters were determined from the plot of lattice parameter of each Bragg reflection against Nelson-Riley function [19]. The results are consistent with the previous investigations for other compositions of these alloys [20]. The values of lattice parameters of these alloys show a positive deviation from Vegard's rule. This observation is in accordance with the expectations as the atomic radius of Ni is comparable to the radii of Cu and Pd. It has been reported that addition of Ni to Cu-Pd changes the lattice parameter [21].

Figures 4a,b show the dependence of the lattice parameter a (Å) on the Ni and Pd concentration for annealed and quenched samples. The relationship between the concentration of Ni and Pd and the value of the lattice parameter is linear (as evident from Fig. 3). The value of lattice parameter increases as the concentration of Ni decreases or Pd increases. Ni has atomic radius slightly greater than Cu. On the other hand, Pd has atomic radius greater than both Ni and Cu [22]. The lattice parameter must increase by increasing Ni or Pd contents. This is true for the case of Pd. The decrease in lattice parameter with the
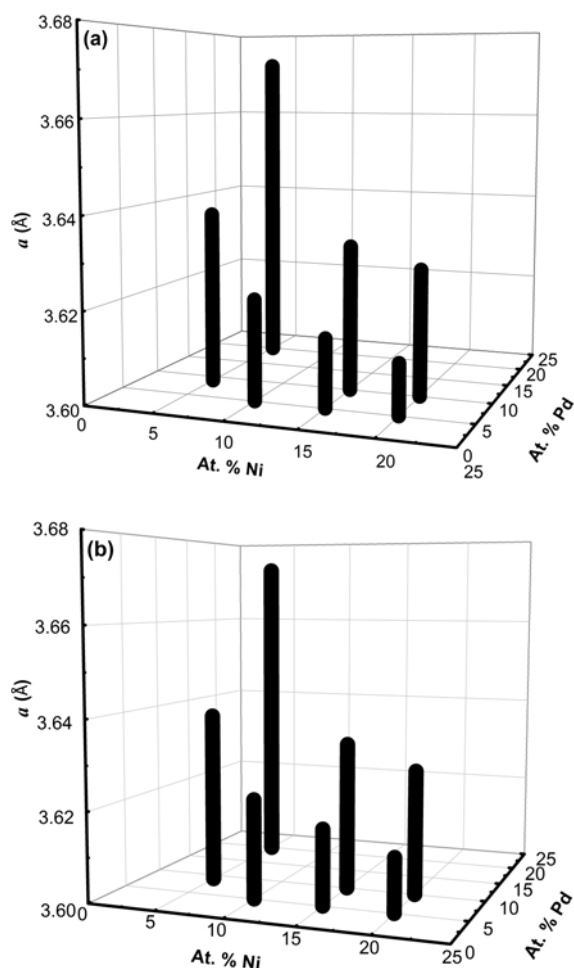
increase in concentration of Ni is in accordance with the Hume-Rothery rules [23]. The atomic radius of Ni is smaller than the average radius of Cu and Pd, so the addition of Ni in Cu-Pd alloys is expected to reduce the value of lattice parameter [24].

A comparison of lattice parameters of annealed, quenched and those calculated by Vegard's rule shows that the lattice parameter of annealed samples is slightly smaller than that of quenched samples (Table 1). This increase in lattice parameter occurs because the samples were quenched from a higher temperature [25].

The solubility of Ni in Cu-Pd can also be explained on the basis of lattice parameter of ternary Cu-Ni-Pd and binary Cu-Pd alloys. The lattice parameters of ternary alloys have nearly the same values as those of Cu-Pd alloys having the same ratio of Cu and Pd (in annealed and quenched samples). Therefore, it is suggested that Ni makes solid solution with Cu-Pd.

The melting points T_{m} (K) of Cu-Ni-Pd alloys ob-

tained from DSC curves are given in the Table 1. Melting points of alloys depend on concentration of Pd. Pd is responsible for the expansion of the lattice due to its greater atomic size as compared to Cu and Ni. According to Lindemann's melting rule, more energy is required for fluctuation in atomic positions above the equilibrium lattice positions [26].

4. Conclusions

The structural properties of Cu-Ni-Pd alloys have been studied by differential scanning calorimetry and X-ray diffraction. The structure and lattice parameter of Cu-Ni-Pd alloys have been determined. The results show that all the investigated alloys form a single phase and have fcc structure. Solubility of Ni in Cu-Pd alloys is also attributed to nearly the same values of lattice parameter of ternary alloys to their corresponding binary alloys.

Lattice parameters of Cu-Ni-Pd alloys strongly depend on Pd concentration because of larger atomic radius of Pd than Ni and Cu. Lattice parameter of quenched sample is larger than that of annealed sample due to high quenching temperature. Change in melting points of Cu-Ni-Pd alloys is mainly attributed to the concentration of Pd.

Acknowledgement

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