

Research of Mechanical Properties of Random Disordered CuNi Alloys

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Abstract— Preparation technique and structural analysis of random CuNi disordered alloys have been discussed. The arc-melting method is used to prepare different compositions of substitutional random disordered $\text{Cu}_{1-x}\text{Ni}_x$ (0.1, 0.3, 0.5, 0.7, 0.9) alloys. The stoichiometric amounts of highly purity constituents copper and nickel metals 5 N (99.999%) have been melted under argon atmosphere in vacuum chamber of 10–3 torr. The substitutional random disordered alloys free from carbon and oxygen traces are confirmed from XPS data. A lattice strain is produced in CuNi alloys as the environment of Ni atoms change from sites to sites. Lattice parameters, unit cell volume, structure and inter-planar spacing were calculated from XRD analysis. The average crystallite size of different compositions of random disordered CuNi alloys is calibrated by using Scherer's method and Williamson-Hall (W-H) method. The roles of crystallite size and lattice strain on the XRD peak broadening of the random disordered CuNi alloys were analyzed. The strain increases with increase in concentration of Ni and exhibits a maximum of 0.00247 at 50% Ni concentration. The CuNi alloys find very wide applications in oil refining and long corrosion free life.

Index Terms: arc-melting, binary alloys, crystallite size, lattice parameter, & W-H analysis.

I. INTRODUCTION

Formation of substitutionally random disordered A_{1-x}B_x alloys is one of the advance steps in ceramics [1], semiconductor [2] and metallurgy [3] to facilitate new findings in science and technologies. In the alloys, atom B may be localized randomly or in very unique way of periodic distribution. The effect of randomness or periodicity in substitutionally random alloys may be the cause of the presence of various types of carriers [4], bonds [5] and excitons [6-7]. The composition and microstructure are general used to predict mechanical behaviors of a material by scientists and engineers. Complete understanding of mechanical behaviors of materials remains mystery for long time and attracts many researchers. Generally, an alloy is formed by intermixing of two or more elements. The complete burning of two solid metals solution form single phase alloys while two or more phases may found from incomplete solid solutions which depends on the thermal treatment.

The thermal properties of individual constituent elements are different from the alloys [8-13]. Any composition of CuNi alloys can be formed because of strong miscible character of Cu and Ni atoms and thus formed random disordered alloys. Every random disordered alloys show chemical shift because introduction of disorder in alloys forced to change the inhabitant framework from atomic sites to atomic sites which manifests core level shift and core disordered broadening [14-23]. The microscopic properties of substitutionally random disordered alloys display from perfectly ordered alloys. Disorder performs a crucial role in condensed matter because of many challenging and interesting problems have been directly or indirectly connected to disorder. Sometime we observe weak disorder in alloys which may be result of an anxiety of the perfect crystalline ordered alloys. Defects, dislocations and vacancies are the examples of this category in material science. But in case of strong disorder found in random disordered alloys can be indentify from a large deviation from crystalline order. There have been extensive theoretical and experimental studies to determine of the effective lattice parameter in more complex alloy systems [24]. Random disordered CuNi alloys have been subject of substantial study due to their future applications in different areas like electronic industry, fire extinguisher, resistance to biofouling, desalination, resistant to corrosion, acid resistant, commentators, remelted and reused properties and catalysis etc [25-27]. Though the CuNi alloys were subjected to investigations for several decades, the role played by disorder on mechanical properties such as lattice strain and elastic moduli is not well understood.

In this paper, we discuss the method of preparation of substitutionally random $\text{Cu}_{1-x}\text{Ni}_x$ (0.1, 0.3, 0.5, 0.7, 0.9) alloys. The XRD analysis is done to calculate lattice parameters, unit cell volume. Due to arc-melting of binary solid solution of two metals, Ni atoms interact in the vicinity Cu producing lattice strain is calculated using the Williamson-Hall relation.

II. EXPERIMENTS

The arc-melting technique is being used to prepare the substitutionally random $\text{Cu}_{1-x}\text{Ni}_x$ ($x = 0.1, 0.3, 0.5, 0.7, 0.9$) disordered alloys. The stoichiometric amounts of high purity (99.999%) Cu and Ni metals are put in the high temperature resistant copper hearth under argon atmosphere inside the arc furnace. The environment of the arc furnace is maintained the vacuum pressure around 10^{-3} Torr and slowly the argon gases were injected inside the chamber to maintain

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the said pressure. To liberate the presence of oxygen traces from the vacuum chamber, a small titanium ball was melted near the copper hearth. The special character of the titanium is to form various oxide compounds during its melting period and help to release the oxygen from the chamber. It is convenient to put the metal having high melting point on the top over the metal having low melting point inside the copper hearth so that top metal will receive more heat and transfer to the bottom for better mixing. This method is also help to maintain the stoichiometric ratio of the inter-mixing elements by giving differential heating simultaneously. It is advisable to repeat the melting several times to crush the chunk that comes in each time. Some time, though sufficient care has been taken for removal of the oxygen trace from the chamber, it seems difficult to say the samples were completely free from oxygen impurities. Some residual oxygen impurities were still present in the samples and stay preferably in the inter-grain regions. For the removal of such oxygen traces, one has to anneal the prepared samples below the melting points of the used constituent elements. The Mo foil is used to wrap over the each sample so that there is no electrical connection between the samples during the process of annealing. The prepared samples have closed securely in the airtight quartz tube. For removal of impurities like oxygen and carbon traces, samples were annealed at a temperature of 850°C for 48 hours. The other benefit of high temperature annealing helps to form best quality samples because of homogeneous mixture of constituent elements. It has been noticed that annealing also helps in the growth of the grain size of the sample. On the expansion of the grains in the samples, the bulk impurities present in the inter-grain space like oxygen and carbon come out to the surface.

III. RESULTS AND DISCUSSION

The X-ray photoelectron spectrum recorded on Cu_{0.9}Ni_{0.1} alloy using monochromatic AlK_α radiation is demonstrated in figure 1. The different electronic states of Cu and Ni are shown by all the sharp peaks. The features of C 1s and O 1s corresponding to common impurities like carbon and oxygen were found to be below detection limit of the spectrometer i.e.

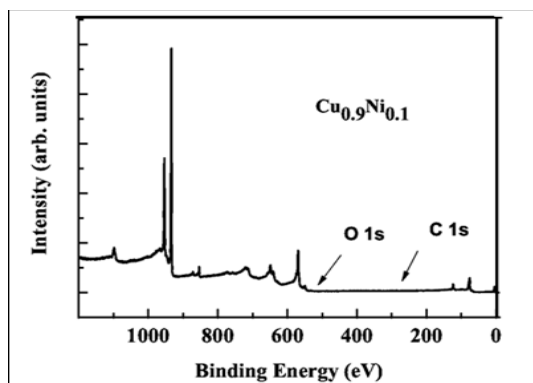


Fig 1. XPS spectrum of Cu_{0.9}Ni_{0.1} alloy

below 0.1% in concentration. Similarly X-ray photoelectron spectra were also observed for other compositions indicating formation of good quality of the alloys. Fig. 2 shows the X-ray diffraction patterns of

substitutionally random disordered Cu_{1-x}Ni_x (x = 0.1, 0.3, 0.5, 0.7, 0.9) alloys. The lattice parameters of the random disordered alloys were refined using POWDERX software [28]. The highest intensity reflection (111) occurs at around 44.3° and exhibits slight variation in position with compositions. All the peaks are indexed assuming FCC structure for CuNi alloys. No impurity phases are observed, which again supports good quality of the preparation of random disordered alloys. The linear dependence of lattice parameters on composition of alloys [29] confirms the preparation of random disordered CuNi alloys as suggested by Vegard's law [30-31]. The lattice parameters and volume of the unit cell of the random disordered CuNi system have been calculated using Unit-Cell-Win software which is presented in Table 1.

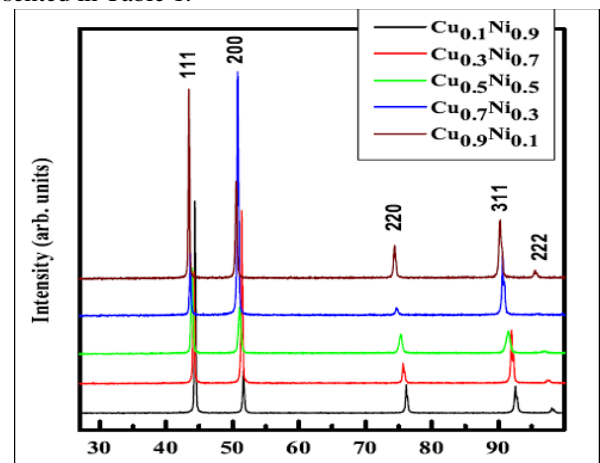


Fig 2. XRD patterns of Cu_{1-x}Ni_x alloys recorded using CuK_α radiation.

Scherrer method:

It is used to calculate crystalline size from the X-ray diffraction pattern of random disordered CuNi alloys. The Scherrer's equation can be written as, $D = \frac{k\lambda}{\beta \cos \theta}$, where D = crystallite size, λ = wavelength of the used X-ray source ($\lambda = 1.54056 \text{ \AA}$), k = anisotropic constant (~ 0.89), θ = peak position and β = full width at half maximum (FWHM) measured in radians [32]. The lattice strain, dislocations and defects of random alloys depend on the peak broadening (β) [33]. On the simplification of Scherrer equation, we can write the expression in form of equation of straight line as,

$$D = \frac{k\lambda}{\beta \cos \theta} \Rightarrow \cos \theta = \left(\frac{k\lambda}{D} \right) \frac{1}{\beta}$$

For a given composition of random alloy, select few reflections and plot $\frac{1}{\beta}$ as a function of $\cos \theta$ and fit a linear regression line. The slope of the linear regression line is equal to $\frac{k\lambda}{D}$. As k and λ are given, crystallite size (D) can

be calculated. $\frac{1}{\beta}$ versus $\cos \theta$ for different compositions of Cu_{1-x}Ni_x alloys are shown in fig. 3. For example in Cu_{0.9}Ni_{0.1} alloy, the equation of the fitted line $y (= \cos \theta) = 0.56726 + 0.00166 x = 1/\beta$ and $k\lambda D = 0.00166$. Therefore, the calculated value of D is 79.59.

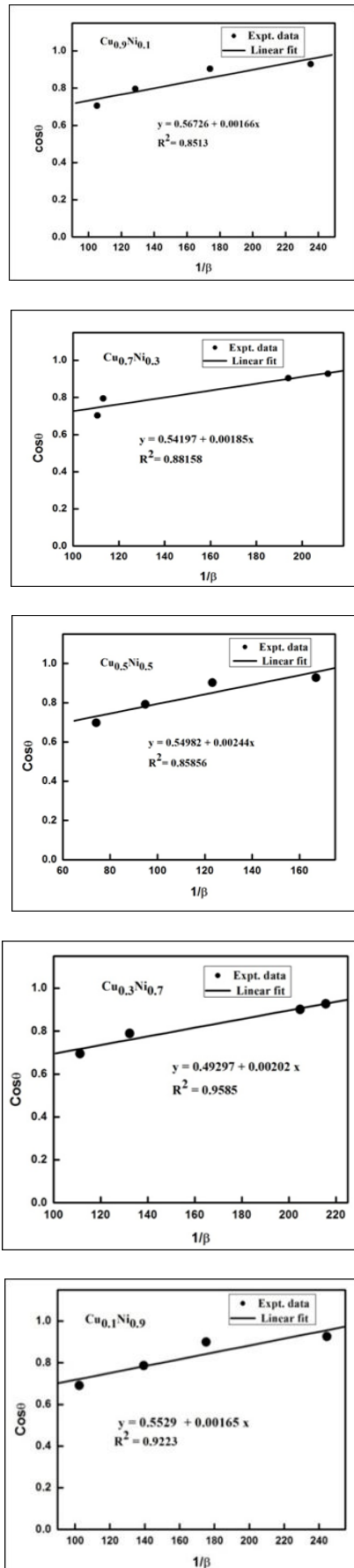


Fig 3. Scherrer plots $\text{Cu}_{1-x}\text{Ni}_x$ ($x=0.1, 0.3, 0.5, 0.7, 0.9$) alloys. Fit to the data, the crystalline size D is extracted from the slope of the fit line.

Williamson-Hall Method:

In this present study, during the preparation of random disordered alloys, the concentration of Ni atoms slowly increases and enters into the Cu vicinity. On account of changing of bond length, binding energy and local environment of Cu and Ni atoms in the random disordered CuNi alloys, the mechanical strain produced. A mathematical model has formulated by Williamson-Hall as $\beta \cos \theta = \frac{k\lambda}{D} + 4\epsilon \sin \theta$, where ϵ is the strain that produced in alloys. Two terms crystallite size and lattice strain are real contributors to the broadening of Bragg's peak observed in XRD analysis and in crystal imperfections and distortions in the material. The induced strain is given by Williamson-Hall (W-H) equation, $\epsilon \approx \beta / \tan \theta$. This implies that the peak width β has another contribution proportional to $\tan \theta$ coming from W-H equation apart from the contribution $\frac{1}{\cos \theta}$ given by the Scherrer equation. The total peak broadening that induced in random disordered alloys is an additive property. In designing the model, Williamson-Hall assumed that total broadening observed in Bragg's peak is equal to broadenings due to the crystallite size plus the broadening due to lattice strain [34]. The dependency of θ on the crystallite size and lattice strain is well defined in the W-H method [35]. The lattice strain is assumed to be uniform in all crystallographic directions is the basic of a mathematical model called Uniform Deformation model (UDM). In this model; a plot has to be drawn in which the term $4\sin \theta$ is taken in x-axis of the coordinate and $\beta \cos \theta$ is taken in y-axis of coordinate. The slope of the fitted linear regression line gives lattice strain whereas y-intercept of the fitted linear regression line gives crystallite size shown in fig. 4. The crystallite size of the random disordered $\text{Cu}_{1-x}\text{Ni}_x$ ($x = 0.1, 0.3, 0.5, 0.7, 0.9$) alloys has been calculated by both Scherrer and Williamson-Hall methods. Table 2 describes the resemblances with the crystallite sizes obtained by above two methods and also shows the strain calculated by W-H method. The average crystallite size estimated through Scherrer method and W-H method are reasonably in good agreement with a maximum deviation of 10 nm for $\text{Cu}_{0.1}\text{Ni}_{0.9}$ alloy. The agreement seems to be better for intermediate compositions ($x = 0.3, 0.5$) as compared to others. The calculated strain increases gradually with Ni composition and becomes maximum for $\text{Cu}_{0.5}\text{Ni}_{0.5}$ alloy and then decreases for higher Ni concentrations. The $\text{Cu}_{0.5}\text{Ni}_{0.5}$ alloys possess maximum chemical disorder suggesting maximum in homogeneity at microscopic level. The strain in the lattice is proportional to the disorder in the alloy [36]. As the disorder increases with Ni concentration and exhibits a maximum at $x = 0.5$, the same behavior is expected for the strain [37]. Interestingly W-H calculation exactly gives the same result as expected for disordered alloys.

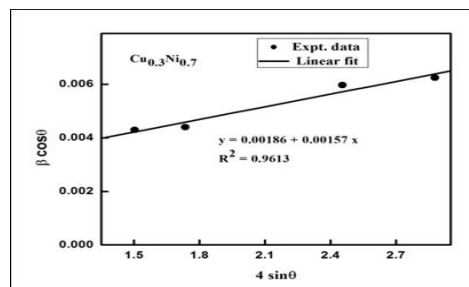
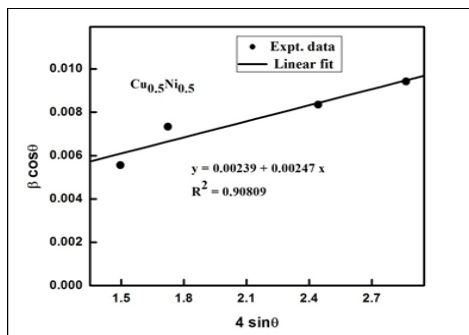
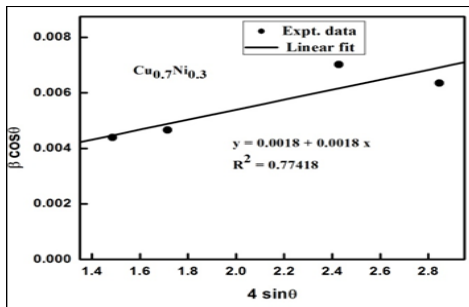
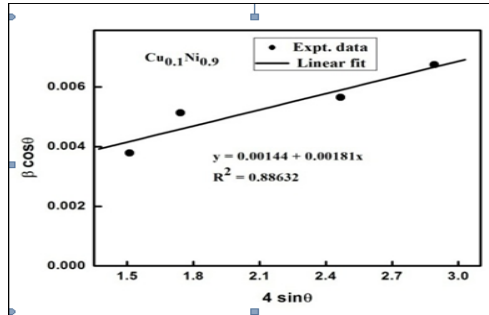
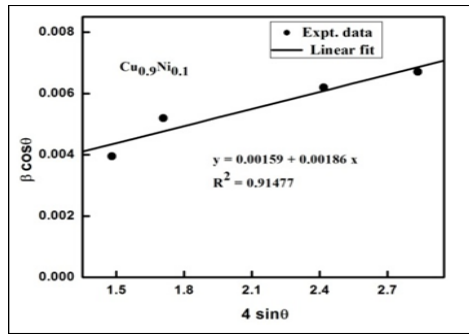


Fig 4. The Williamson-Hall analysis of $\text{Cu}_{1-x}\text{Ni}_x$ ($x = 0.1, 0.3, 0.5, 0.7$ and 0.9) alloys assuming Uniform Deformation Model (UDM). Fit to the data, the strain is extracted from the slope and crystalline size D is extracted from the y-intercept of the fit.

Table: 1 Lattice parameters and volume of $\text{Cu}_{1-x}\text{Ni}_x$ ($x = 0.1, 0.3, 0.5, 0.7, 0.9$) alloys [24]

Sample	Lattice parameter (Å)	Volume (Å) ³
Cu	a = 3.61	47.25
$\text{Cu}_{0.9}\text{Ni}_{0.1}$	a = 3.58	45.88
$\text{Cu}_{0.7}\text{Ni}_{0.3}$	a = 3.57	45.49
$\text{Cu}_{0.5}\text{Ni}_{0.5}$	a = 3.59	46.26
$\text{Cu}_{0.3}\text{Ni}_{0.7}$	a = 3.54	44.36
$\text{Cu}_{0.1}\text{Ni}_{0.9}$	a = 3.51	43.24
Ni	a = 3.52	43.61

Table: 2 Crystallite size and strain by Scherrer and Williamson-Hall methods

Sample	Scherrer method	Williamson-Hall method	
	Crystallite size (D) in nm	Crystallite size (D) in nm	Strain (ε)
$\text{Cu}_{0.9}\text{Ni}_{0.1}$	79.59	73.71	0.00159
$\text{Cu}_{0.7}\text{Ni}_{0.3}$	74.11	76.17	0.00180
$\text{Cu}_{0.5}\text{Ni}_{0.5}$	56.19	57.36	0.00247
$\text{Cu}_{0.3}\text{Ni}_{0.7}$	67.87	73.71	0.00157
$\text{Cu}_{0.1}\text{Ni}_{0.9}$	83.09	95.21	0.00181

IV. CONCLUSION

Different compositions of substitutionally random disordered $\text{Cu}_{1-x}\text{Ni}_x$ (0.1, 0.3, 0.5, 0.7, 0.9) alloys have been prepared by using arc-melting method. The XRD analysis confirms the formation of good quality single phase random disordered CuNi alloys which is well supported from XPS spectrum. The both Scherrer and Williamson-Hall method are employed to evaluate the average crystallite size of random disordered $\text{Cu}_{1-x}\text{Ni}_x$ ($x = 0.1, 0.3, 0.5, 0.7, 0.9$) alloys and the result is well matched. Williamson-Hall method was used to analyze the individual contribution of crystallite sizes and lattice strain on the Bragg's peak broadening of the $\text{Cu}_{1-x}\text{Ni}_x$ ($x = 0.1, 0.3, 0.5, 0.7, 0.9$) alloys. The strain increases with increase in concentration of Ni and exhibits a maximum at 50% Ni concentration.

V. ACKNOWLEDGMENT

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