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STUDY OF PHASE CHANGES IN THE ALLOYS OF COPPER WITH TITANIUM BY X-RAY SCATTERING AND PSEUDOPOTENTIALS

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X-ray diffraction and pseudopotential studies have been performed on Cu-Ti alloys. It has been observed that complex phases like Cu_3Ti exist in these alloys at temperatures up to 600 °C. The pseudopotential calculations take into account the experimental observations in alloys with greater concentration of Ti.

1. Introduction

Phase changes in alloys are based on the internal energy of the system at absolute zero temperature[1]. Therefore, in order to discuss such changes, it is desirable to introduce physical quantities of constituent atoms into the expression for total energy. The total energy expressions for binary alloy systems have been developed by many authors[2-4].

There is not much literature available on the Cu rich Cu-Ti system from the point of view of its total energy expression. In the present work the effect of addition of Ti on the structure and consequently the structure dependent energy expression at different temperatures have been studied. It is observed that addition of Ti has significant effect on the structure of Cu. New phases are observed which have structure altogether different from Cu matrix. Particularly the Cu_3Ti phase appears in all the alloys at room temperature, 450 °C and 600 °C.

From the phase diagram given in Ref. 5 it is observed that Cu_3Ti phase exists in equilibrium in Cu-20 at. % Ti alloy. From *X*-ray analysis Pefier et al.[6] have studied the structure of alpha phase in Cu rich Cu-Ti alloys as Cu_4Ti rather than Cu_3Ti reported by Karlsson[7]. It has been shown by *X*-ray energy dispersive analysis[8] that the composition of beta precipitates in dilute Cu-Ti alloys corresponds to Cu_4Ti but the Cu_3Ti structure should be modified if the presence of some forbidden reflection in the selected areas of electron diffraction patterns is to be considered.

Recently[9] some investigations have been made by high resolution electron microscopy and it has been observed that Cu_4Ti phase has also a deformed hexagonal close packed structure like Cu_3Ti reported by Laves and Wallbaum[10]. The Ti atoms in close packed layers are arranged in isolated bands of triangle and running in the *d* direction and the Ti atoms of the layers above and below avoid each other.

These apparently conflicting results, therefore, encourage us to study the structure of equilibrium phases in Cu-Ti system for low concentration of Ti by means of *X*-ray diffraction. The experimental data is then compared with the theoretical calculations based on the pseudopotential technique. The results are discussed in details.

2. *Experimental*

The Cu-Ti alloys were prepared from pure Cu and Ti in an arc furnace in helium atmosphere. The samples were prepared in the form of small pellets which were then cut into two halves and subsequently ground and polished in the form of a mirror surface. The samples were homogenised in an electric furnace at 500 °C up to 15 hours in vacuum. The subsequent heat treatments were also performed in vacuum.

The *X*-ray diffraction experiment was performed on a Shimadzu automatic *X*-ray diffractometer. The diffractograms were taken in atmosphere from 10—90° in 2Θ. Special plastic sample holders were fabricated for polycrystalline metallic samples. The Cu-K_α radiation was used for diffraction.

3. *Calculation of structure dependent energy of the alloy*

Theory of calculation of crystal structures have been discussed in Ref. 11. The total energy of the alloy may be thought of sum of two parts. First of these depends upon the volume and is composed of the kinetic energy of free electrons, exchange and correlation effects of the components and does not depend upon the structure. This part of the total energy is not important from the point of view of the analysis of stability of phases.

The second part depends upon the structure of the alloy and is comprised of the band structure energy and the electrostatic energy.

For calculation of the structure dependent part of the total energy we have used the method proposed in Ref. 12. Animalu's[4)] model pseudopotential has been used for calculation. We have used the virtual crystal model[2)] for calculating the energy-wave-number-characteristic of the Cu-Ti alloy for different concentration of Ti. The atomic bare potentials are proposed to be localised nearly spherically around each nucleus. The atomic volume of the AB alloy is taken to be equal to the weighted average of volume of the constituents with their concentration. The volume change due to alloying gives rise to some modification of the potential and other physical quantities of the constituent atoms. If the volume of the alloy varies with composition obeying the Vegardis law, however, the electronic structure may not be directly affected by this. Thus the form of atomic potential of the components is treated as the same as in pure metal. Density of conduction electrons is assumed to be uniform throughout the crystal. The number of electrons per atom of an alloy system is evaluated to vary linearly with composition. The treatment is just the same as that in the Brillouin zone effect. In order to deal with the electron density, its reduction inside ion cores due to orthogonality hole effect should be taken into account. The dielectric screening resulting from the interaction between conduction electrons is also introduced into the expression for the energy. The energy-wave-number-characteristic is summed up over all reciprocal lattice vectors for respective crystal structure and the value of structure dependent part of total energy is calculated.

4. Results and discussion

The results of the experiment are presented in Table 1. It can be observed from this table that in the alloy Cu-20 at. % Ti at room temperature the most stable

TABLE 1.

Sample	Most probable phases		
	Room temp.	450 °C	600 °C
Cu 80 at. % — Ti	c-$CuTi_2$	o-Cu_3Ti	o-Cu_3Ti + hcp Ti + fcc-Cu
Cu 85 at. % — Ti	o-Cu_3Ti	o-Cu_3Ti + fcc-Cu	o-Cu_3Ti + fcc — Cu
Cu 90 at. % — Ti	o-Cu_3Ti	o-Cu_3Ti	bct-CuTi
Cu 95 at. % — Ti	o-Cu_3Ti	o-Cu_3Ti + fcc — Cu + bct — CuTi	bct — CuTi + o — — Cu_3Ti
Cu 98 at. % — Ti	o-Cu_3Ti + fcc — — Cu	fcc — Cu	fcc — Cu

Table 1. Analysis of the diffractogrammes of the various samples indicating most probable phases at different temperatures.

phase can be indexed as cubic $CuTi_2$ with $a = 1.104$ nm. This phase transforms into orthorhombic Cu_3Ti with $a = 0.515$ nm and $c = 0.452$ nm at 450 °C. Even more heating of the alloy at 600 °C does not appreciably change the situation. Only traces of hep Ti and fcc Cu become some more evident.

In the alloy Cu-15 at. % Ti at room temperature the most stable phase has been observed as Cu_3Ti with the same orthorhombic structure. At 450 °C the phase Cu_3Ti remains stable along with traces of fcc Cu. Further increasing of the temperature up to 600 °C does not affect the diffractograms.

In the alloy Cu-10 at. % Ti the stable phase at room temperature is again Cu_3Ti orthorhombic which remains stable up to 450 °C. At 600 °C strong diffraction reflections of bct CuTi phase with $a = 0.314$ nm and $c = 0.286$ nm start appearing.

In dilute Cu-5 at %Ti and Cu-2 at %Ti alloys the Cu_3Ti phase exists along with the Cu matrix and CuTi tetragonal phase at room temperature, 450 °C and 600 °C, respectively.

The structure dependent part of total energy calculated for different crystal structures yield the values which have been presented in Table 2. We observe from these calculations that the most stable phase for the alloy Cu-20 at. %Ti and Cu-15 at. %Ti corresponds to Cu_3Ti phase which actually exists in these alloys. For other alloys the theoretical calculations do not correctly explain the experimental observations. We can thus propose that the pseudopotential calculations are more suitable for alloys with greater concentration of Ti which may be due to the presence of mean pseudopotentials of the constituents in the expression for energy of the crystal structure and the lower concentration does not appreciably affect the pseudopotential of the alloy.

TABLE 2.

Sample	Total energy		
	fcc-Cu	hcp-Ti	o-Cu_3Ti
Cu 80 at. % − Ti	−0.30	−0.34	−0.28
Cu 85 at. % − Ti	−0.40	−0.42	−0.29
Cu 90 at. % − Ti	−0.64	------	−0.33
Cu 95 at. % − Ti	−0.32	------	−0.31
Cu 98 at. % − Ti	−0.60	------	−0.35

Values are given in at. units.

Table 2. The structure dependent part of the total energy for Cu-Ti alloys for different concentrations.

5. *Conclusions*

1. The alloys of copper with titanium do not make homogeneous solid solutions in the concentration range from 2 to 20 at. %Ti and up to 600 °C.
2. The pseudopotential theory can take into account the correct type of crystal structure appearing in the diffraction patterns of the Cu-Ti aloys at least for greater concentration of Ti.

Appendix

The mean energy $\overline{U}_e$ for an AB alloy can be written as

$$\overline{U}_e = \sum_{g_n} W'(g_n)\, F(g_n)$$

where

$$W(g_n) = \sum_{|Q_n| = g_n} |S(Q_n)|^2$$

and

$$F(q) = |\overline{W}^b(q)|^2 f(q)/\varepsilon(q)$$

$W(g_n)$ is the structural weight of a set of the reciprocal vectors g_n. The function $F(q)$ is the energy wave-number characteristic for the mean energy. $\overline{W}^b(q)$ is the mean atomic bare potential of the alloy and

$$\overline{W}^b(q) = (1 - C)\, W_A^b(q) + C\, W_B^b(q).$$

$W_A^b(q)$ and $W_B^b(q)$, respectively, represent the atomic bare potentials of constituent A and B, while C is the concentration of B type of atoms,

$$f(q) = -\frac{\Omega k_F}{4\pi^2}\left(1 + \frac{4k_F^2 - q^2}{4k_F q}\ln\left|\frac{q + 2k_F}{q - 2k_F}\right|\right)$$

$$\varepsilon(q) = 1 - \frac{8\pi}{\Omega q^2} f(q)$$

$$k_F = \left(\frac{3\pi^2 Z}{\Omega}\right)^{1/3}$$

$$\Omega = (1 - C)\,\Omega_A + C\,\Omega_B$$

$$Z = (1 - C)\, Z_A + C\, Z_B.$$

k_F is the Fermi wave-vector for the alloy, Z_A, Z_B, Ω_A and Ω_B, respectively, represent the atomic number and volume of the constituents of the alloy. The atomic bare potentials have been calculated by the method given in Ref. 4.

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PROUČAVANJE PROMJENA FAZA U TITANOVIM LEGURAMA BAKRA RASPRŠENJEM *X*-ZRAKA I METODOM PSEUDOPOTENCIJALA

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Raspršenje *X*-zraka i metoda pseudopotencijala primjenjeni su na Cu-Ti legure. Opaženo je da kompleksne faze kao Cu_3Ti egzistiraju u tim legurama na temperaturama do 600 °C. Računi metodom pseudopotencijala uzimaju u obzir eksperimentalna opažanja na legurama s većom koncentracijom Ti.