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Optical Properties of Copper-Rich Cu-Ni-Zn Alloys with 20 at. % Zinc and up to 25 at. % Nickel at Room Temperature[*]

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Normal-incidence reflectance measurements on mechanically polished specimens of copper-rich copper nickel zinc alloys with up to 25 at. % nickel and about 20 at. % zinc were obtained in the photon energy range 1.55–5.18 eV. These measurements were taken at room temperature under vacuum (lower than 10^{-7} Torr). The absorption edge associated with interband transitions which is observed between 2 and 3.2 eV is, within experimental accuracy, independent of nickel concentration. This indicates that nickel and zinc atoms do not interact directly. At nickel concentrations above 5 at. %, a reflectance minimum appears near 4 eV. The position of this minimum shifts with increasing nickel concentration to higher energies. The width and the depth of the minimum increases as the concentration of nickel is increased. It is similar to the reflectance minimum which pure nickel exhibits near 4 eV.

INTRODUCTION

COPPER shows an optical absorption edge at photon energies of about 2.2 eV, and a reflectance minimum near 4 eV.[1,2] Mott and Jones[3] suggested that the absorption edge is associated with electron transitions from the *d* band to the Fermi surface, whereas the reflectance minimum near 4 eV is associated with transitions from the Fermi level to higher states. This interpretation can qualitatively explain shifts of the absorption edge to shorter wavelengths in binary Cu-Zn alloys with increasing zinc concentration[4,5] since the addition of zinc increases the electron-per-atom ratio. One can calculate the shift of the Fermi level ΔE with alloying as a function of the electron-to-atom ratio $\mathfrak{z}$ assuming a rigid-band model. Biondi and Rayne[4] showed that such a rigid-band model cannot explain quantitatively the experimental results. The assumption that part of the extra electrons form screening electron clouds round Zn impurities gives better agreement between theory and experiments. The experiments show that the shift of the Fermi level for the onset of interband transitions for an alloy with 20 at. % zinc in copper is about 0.18 eV. However, the position of the first absorption maximum seems to shift by nearly 1 eV for the same concentration change. Therefore, one may say that the experimental data can be explained only qualitatively with a rigid-band model. It is neither possible to calculate exactly the screening radius of the electron cloud around zinc ions, nor the shift of different energy subbands in respect to the Fermi energy. On the other hand, it seems to be equally difficult to explain the experimental results of measurements on *Cu*Zn and *Cu*Ge[6] alloys with the assumption that both the absorption maximum near 4 eV and the absorption edge near 2.2 eV are associated with electron transitions from states below the Fermi level. This concept was, e.g., proposed by Cooper, Ehrenreich, and Philipp,[1,7] who suggested that the 4-eV absorption peak of pure copper is associated with transitions between the symmetry points X_5 and X_4' in k space and the 2.2-eV absorption edge with transitions between L_3 and the Fermi level. However, it is not possible to exclude other possibilities as discussed in detail by Seib and Spicer,[8] especially if one takes experimental uncertainties in all these measurements into account.[9]

A rigid-band model of Cu-Ni alloys[10,11] and alloys with similar electronic structures has been used to analyze the low-temperature electronic specific-heat coefficient γ_0 and the susceptibility χ. χ of Cu-Pd, Ag-Pd, and Au-Pd alloys is nearly composition-independent and negative for $10.5 > \mathfrak{z} < 11$ and then increases rapidly with decreasing $\mathfrak{z}$ ratios.[12] Nickel alloys are ferromagnetic for lower $\mathfrak{z}$ values, whereas nonferromagnetic palladium and platinum have a high positive susceptibility. This is interpreted with the concept of open *d* and *s* bands for transition elements with $\mathfrak{z} = 10$. Increasing $\mathfrak{z}$ values above 10 lift the Fermi level and decreases the density of states of the *d* band, $N_d(E)$, which would be filled at $\mathfrak{z}$ close to 10.5. This interpretation agrees qualitatively with optical, electron emission, x-ray and other experiments and theoretical

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calculation on the band structure of noble elements.[13] One always obtains a low density-of-states value close to $\mathfrak{z}=11$ and a rapid increase of $N(E)$ below a specified energy level. However, the detailed shapes of the $N(E)$ curve for the d band obtained from such measurements disagree with each other and with most theories in their details.[13]

Optical-reflectance[14] and photoemission studies[8] on copper-rich copper-nickel alloys show no marked shift of the main absorption edge with increasing nickel concentration. Therefore, alloy data have been interpreted with the concept of "virtual energy states," [15–18] which are formed by nickel atoms in solid solution. These energy states may exist both below and above the Fermi level. Alloying Ni to Cu will not necessarily change the energy gaps between different electron states in the Cu matrix.

A combination of the rigid-band model and the concept of virtual energy states has been used to interpret optical-absorption data of $Cu_{1-x-y}Ni_yZn_x$ alloys with about 8–10 at. % nickel.[19] In these alloys the absorption near 4 eV separates into two peaks, one nearly independent of zinc concentration, the other moving to longer wavelength. The latter one is found at approximately the same position as the peak in $Cu_{1-x}Zn_x$ alloys.

We decided to investigate a series of ternary $Cu_{1-x-y}Zn_xNi_y$ with concentrations of up to 25 at. % nickel to obtain a more detailed picture of the absorption peak near 4 eV then obtained before. We selected alloys with about 20 at. % Zn. The absorption curve of $Cu_{0.8}Zn_{0.2}$ has only one peak at about 3 eV.[4] It is quite smooth near 4 eV. Therefore, these alloys with 20 at. % zinc should give a relatively clear picture of changes in the reflectance between 3 to 5 eV as a function of nickel concentration.

We were further interested to find out if nickel atoms in larger concentrations would interact directly with zinc atoms. The study on alloys with 10 at. % Ni shows that, within experimental error, the Fermi level is the same as that of the copper-zinc alloy with the same zinc concentration. In the present series of alloys the zinc concentration is twice as large as before. One should therefore expect that any interaction between zinc and nickel atoms should be more pronounced and could lead to a noticeable shift of the onset of interband transitions. Further, the absorption peak and the high-energy end of the absorption edge coincide at the same photon energy for the alloys with 20 at. % zinc concentration. An interaction of nickel atoms with zinc atoms, where the extra electron of zinc with respect to copper would compensate the deficit of one electron of nickel with respect to copper, would lead to a separation of the absorption peak and the high-energy end of the absorption edge with high nickel concentrations. This should be more easily detected than the much smaller shift of the onset of interband transitions determined by extrapolating the slope of $R(E)$ to unity at the absorption edge.

EXPERIMENTAL PROCEDURE

Absorptivities of solid opaque samples were measured calorimetrically by determining the ratio of the heating rate of the sample when illuminated with light of a certain wavelength to that of a blackened absorber, similarly illuminated. Details of the experimental system have been given elsewhere.[14,19] Only the recording of the heating rate was changed. The thermocouple voltage was amplified with a Keithley millimicrovolt meter. Its voltage output was electronically differentiated. The differentiator design was similar to that given by Chapman.[20] The reflectance R of the sample is given by $R=1-A$, where A is the absorptivity.

Copper-nickel ingots were prepared under argon in alumina crucibles in an induction furnace. These ingots were then melted together with appropriate amounts of zinc in Vycor tubing under argon. Samples were kept in the molten state for about 2 min. Each sample was sealed in a Vycor tube filled with argon, annealed at 800°C for 24 h and quenched in water. Specimens were machined from the annealed ingots to a size of about $8\times6\times0.5$ mm and mechanically polished using a final polish powder size of 0.05 μ. After rinsing with absolute alcohol, acetone, and distilled cold water, the specimens were studied under the microscope and found to be appropriate for study. Composition given herein are nominal. Actual compositions are well within 1% of those given.

RESULTS AND DISCUSSION

Figure 1 gives the measured reflectance R curves of our Cu-Zn-Ni alloys and R of $Cu_{0.8}Zn_{0.2}$ as obtained from data by Biondi and Rayne.[4] Alloys with higher nickel concentration show two minima in the reflectance curve. The minimum at 3.2 eV degenerates into a horizontal line for the alloy with 25 at. % nickel concentration. The general shape of these curves below photon energies of 3.2 eV is nearly independent of composition. Only the reflectance values R at the minimum increase and the R values near 1.5 eV decrease with increasing nickel concentration.

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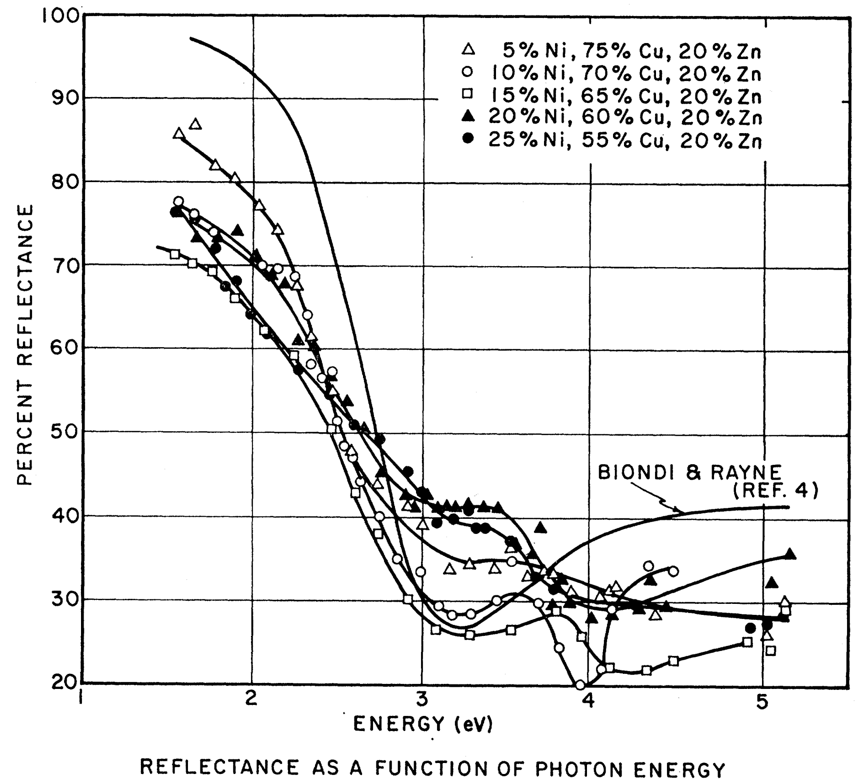

FIG. 1. Room-temperature values of the optical reflectance of Cu-Ni-Zn alloys as a function of photon energy. Composition given in at. %.

The binary $Cu_{0.8}Zn_{0.2}$ alloy has one reflectance minimum at 3.2 eV. The $Cu_{0.8-x}Zn_{0.2}Ni_x$ alloys have a minimum at the same energy. This reflectance minimum should therefore be associated with electron transitions in the Cu-Zn matrix. Nickel produces a relatively sharp minimum at 4 eV for the alloy with 10 at. % Ni. Such a sharp minimum in R is also found for a series of Cu-Ni-Zn alloys with up to 25 at. % Ni.[19] This minimum seems therefore typical for the absorption structure of 10 at. % Ni alloys. The minimum broadens and extends to higher photon energies with larger Ni concentrations. It is not possible within the experimental accuracy (light intensities are rather low for some of the photon energies above 4 eV) to state that this peak is shifted to higher photon energies by 0.18 eV with respect to that of pure nickel (0.18 eV is the shift of the Fermi level due to 20 at. % Zn in Cu-Zn alloys[4]).

The detailed features of the reflectance curves are not of interest for our discussion. We only desire to find out how $R(E)$ changes with nickel concentration, and how this can be related to the energy-band structure of the alloys. The position of the reflectance minimum at 3.2 eV is within experimental accuracy independent of nickel concentration and the same as that of the $Cu_{0.8}Zn_{0.2}$ alloy. This minimum has been associated with the superposition of the high-energy end of the absorption edge and the absorption minimum. The edge has been associated with electron transitions from the top of the d band to the Fermi energy level, the reflectance minimum with transitions from the Fermi level to higher states, respectively.[4] The independence of the position of the reflectance minimum on nickel concentration should therefore be interpreted with the model that nickel in Cu-Zn-Ni alloys does not shift the Fermi energy level, even with 25 at. % nickel. This model could also explain qualitative the rather high values of R at 3.2 eV for alloys with 20 and 25 at. % nickel. The decrease of the number of Cu and Zn atoms per volume should lead to a decrease in the number of electron excitations per volume and with it the absorptivity $A=1-R$, if these transitions occur only in the Cu-Zn matrix.

One may wonder if it is possible to have small volume elements in nickel alloys with properties of pure nickel which are responsible for the reflectance minimum near 4 eV. One should keep in mind that each lattice point for the alloy with 25 at. % nickel has on the average three nickel atoms as nearest neighbor if the alloy is disordered. Short-range order could produce volume elements even richer in nickel than the average composition. Susceptibility data showed that clusters of nickel atoms should be expected before the onset of ferromagnetic ordering.[21] The same conclusions were drawn

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from specific-heat measurements[22–24] and from diffuse magnetic neutron experiments by Hicks *et al.*[25] which indicate both polarization effects and chemical clustering. Neutron scattering measurements by Mozer, Keating, and Moss[26] show only a slight increase of nickel nearest-neighbor concentration. It has been pointed out by Kidron[10] that these results represent average values for the nearest-neighbors concentration. One cannot conclude from a small excess of one type of atoms that there are no clusters. Another example of clustering in an alloy with only 10 at. % Ag in aluminum has been given by Rudman and Averbach[27] where the short-range ordering parameter α is 0.15 and where it is well known that clusters of nearly pure silver exist.[28]

On the other hand, the total number of nickel-rich clusters in alloys with up to 25 at. % nickel should be quite small. Even if they exist in our Cu-Ni-Zn alloys, it is unlikely that they would influence the total reflectance markedly unless they should be concentrated at the surface. This seems unlikely in our mechanically polished samples. It is more likely that the absorption structure at and above 4 eV should be associated with energy states of nickel atoms, but not necessarily with "metallic" nickel.

It has been proposed that impurity atoms create new energy states, which are called "virtual energy states." [15–18] The atomic *d* states of an impurity atom mix with those wave functions of the conduction band which have *d* character. The energy level of the impurity electron will shift due to this interaction and will than have a resonance energy E_r. The impurity atom will scatter markedly conduction electrons with this energy E_r. Virtual energy states will lead to an extra term in the specific heat proportional to T, and will be responsible also for large residual resistivities $\Delta\rho$ if $E_r \approx E_F$. This concept of virtual energy states will therefore easily explain the observed increase in $\Delta\rho$ values.[18] These impurity states are close to and at the Fermi level and may be responsible for additional electron transitions which lead to the decrease in R near 1.5 eV (see Fig. 1). Similarly, infrared studies on Cu-Ni alloys by Feinleib *et al.*[29] indicated virtual bound states at 1 eV below the Fermi level. The minimum in R between 4 and 5 eV should again be attributed to virtual energy states of nickel impurities. These minima are found at a similar position as the minimum in R of pure nickel. It seems likely, therefore, that the impurity energy states responsible for this minimum change gradually with increasing nickel concentration to states of pure nickel which are located below the Fermi energy level E_F. They should not be due to copper, because the $Cu_{0.8}Zn_{0.2}$ matrix has no minimum in this energy interval.

SUMMARY AND CONCLUSION

Optical-reflectance measurements in the photon energy range 0.5–5 eV on *Cu*ZnNi alloys with about 20% zinc and up to 25 at. % nickel show a minimum at 3.2 eV. Alloys with nickel concentrations at and above 10 at. % have a second minimum near 4 eV. This second minimum increases in breadth with increasing nickel concentration and extends to higher photon energies. The reflectance values below 3.2 eV decrease slightly with nickel concentration. These results cannot be reconciled with a simple rigid-band model. It is proposed that the band model of *Cu*NiZn alloys consist of a band associated with the *Cu*Zn matrix. Virtual energy states associated with nickel atoms are superimposed on this band and are responsible for the reflectance minimum at 4 eV and the decrease in R for low photon energies.

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