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Dynamic observation of the phase transformation in Cu–Al–Ni alloys using an optical reflectivity technique

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The colour change of Cu–13.8 mass% Al–4.0 mass% Ni and Cu–14.2 mass% Al–3.1 mass% Ni alloys was measured after annealing at 500 and 620 °C, and quenching from 900 °C by means of a recording spectrophotometer equipped with an integrating sphere. A large colour change of these alloys occurred on heat treatment, depending on the different phases of γ', β_1, $(\gamma_2 + \beta_1)$ and $(\alpha + \gamma_2)$. The phase transformation between β_1 phase with the DO_3 structure, and γ' martensite with the Cu_3Ti-type structure, occurred in the alloys. The phase transformation was dynamically observed by the change in the spectral reflectivity on the surface of these alloys during heating and cooling. A great hysteresis in the phase transformation was noticed in the spectral reflectivity–temperature curves and the premonitory phenomenon of the martensitic transformation was observed in the curves.

1. Introduction

Thin films of alloys and intermetallics have been developed for use in recording materials on the basis of their magnetic properties and optical–magnetic interaction effect. Optical properties of alloys have been of great interest in the development of a new recording material [1, 2]. The colour of the materials is known to vary depending on three optical properties: interference, scattering and absorption phenomena. The optical interference and scattering phenomenon is not effective in changing the colour of metals and alloys, however, because the intrusive depth of visible light into a metal surface is too short to create interference between the incident and reflective beams. Therefore, the colour of metals and alloys can be changed only by use of selected absorption of a light with a certain wavelength. The absorption is influenced by the band structures, Fermi surface and density of state curves of alloys, which depend on crystal structures and their alloying compositions. Because the crystal structure of Kurnakov-type ordered alloys, which show the order–disorder transition below their melting temperatures, can be easily controlled by heat treatment, the ordered alloys may be beneficial for the industrial application of optical properties to a recording material.

Several investigations to develop recording films using spectral reflectivity change between crystalline and amorphous structures were carried out on In–Se, Sb–Se, Ge–Te systems, etc. [3, 4]. A great difference in optical reflectivity between ordered and disordered structure was found in Cu–Al–Ni and Ag–Zn alloys [5–7].

Cu–Al–Ni alloys are well known to show the shape memory effect based on their martensitic phase transformation. An alloy in the Cu–Al–Ni system crystallizes in the DO_3 ordered structure at room temperature, and several phases, including martensite, can be stabilized by proper selection of annealing temperatures and cooling rates [8].

In this study, the wavelength dependence of optical reflectivity of Cu–Al–Ni alloys with various phases was examined. In addition, the phase transformation between the martensite and the ordered phase in these alloys was dynamically observed using the spectral reflectivity change during the heating and cooling processes.

2. Experimental procedure

Two alloys of Cu–13.8 mass% Al–4.0 mass% Ni (alloy A) and Cu–14.2 mass% Al–3.1 mass% Ni (alloy B) were prepared by vacuum induction melting. The phase transformation temperatures were measured using a differential scanning calorimetric (DSC) method at the heating and cooling rate of 3 °C min^{-1}. Alloy B was annealed at 900 °C for 20 min and then quenched into water at 40 °C to stabilize the β_1 phase with the DO_3 structure. The martensite phase, γ', for alloy A was obtained by quenching into iced water at 0 °C from 900 °C. To stabilize different equilibrium phases, alloy A was annealed at 500 and 620 °C for 24 h, and then rapidly quenched. Crystal structures of these alloys were identified by X-ray diffractometry using CuK_α radiation. After electropolishing in a solution of H_3PO_4 (250 ml), H_2O (100 ml) and Cr_2O_3 (100 g), the microstructure was observed using an optical microscope equipped with Nomarski interference contrast. Specimens with dimensions of 20 mm × 20 mm × 1 mm were prepared for observation of optical properties. Spectral reflectivities were measured in the wavelength range 300–800 nm using a Shimadzu UV-3100 recording spectrophotometer equipped with an integrating sphere. Reflectivities were normalized by the standard reflectance of $BaSO_4$. The phase transformation between the martensite (γ' phase) and the DO_3 structure (β_1 phase) was dynamically observed by measurement of spectral reflectivity change during the heating and cooling processes in 1 °C steps from 16–80 °C.

3. Results and discussion

Fig. 1 shows optical micrographs of alloys A and B quenched after annealing at 900, 620 and 500 °C. The single phase of β_1 is known to be stable at 900 °C in both alloys from an equilibrium phase diagram [9]. The unique morphology with a spear-like form in Fig. 1a shows the γ' martensite which was induced in alloy B during quenching from 900 °C. The crystal structure of γ' martensite was confirmed to be the Cu_3Ti-type structure from X-ray diffraction patterns [10]. In alloy A, the β_1 phase must be stabilized at room temperature after quenching from 900 °C because no significant precipitates, and no surface steps related to the martensitic transformation, were observed as shown in Fig. 1b. X-ray diffraction patterns showed the presence of single phase (β_1) with the DO_3 structure.

After annealing at 620 °C, a mixture of two phases, β_1 and γ_2 (a cubic Cu_9Al_4 intermetallic compound), was obtained as shown in Fig. 1c. Alloy A annealed at 500 °C (Fig.1d) showed two phases composed of α (f c c solid solution) and γ_2. Their crystal structures were confirmed by X-ray analysis.

Colour change of alloys with different phases is expected because the absorption of a visual light occurs at a certain wavelength range, depending on the band structure, Fermi surface and density of state curves, which are all influenced by the crystal structure. Fig. 2 shows the spectral reflectivities of alloys A and B with different heat treatments. Alloy A, quenched from 900 °C, showed a copper-like colour because the reflectivity at the wavelengths around 500 nm sharply decreased. After annealing at 500 or 620 °C, the spectral reflectivity changed; the reflectivity gradually decreased with decreasing wavelength and the colour changed to gold-like. Therefore, the difference in spectral reflectivities between specimens of alloy A quenched from 900 °C and annealed at 500 °C (or 620 °C), is attractive for development of a recording material. By quenching from 900 °C, the β_1 phase with the DO_3 structure and the γ' martensite phase were stabilized in alloys A and B, respectively, at room temperature, because their M_s temperatures

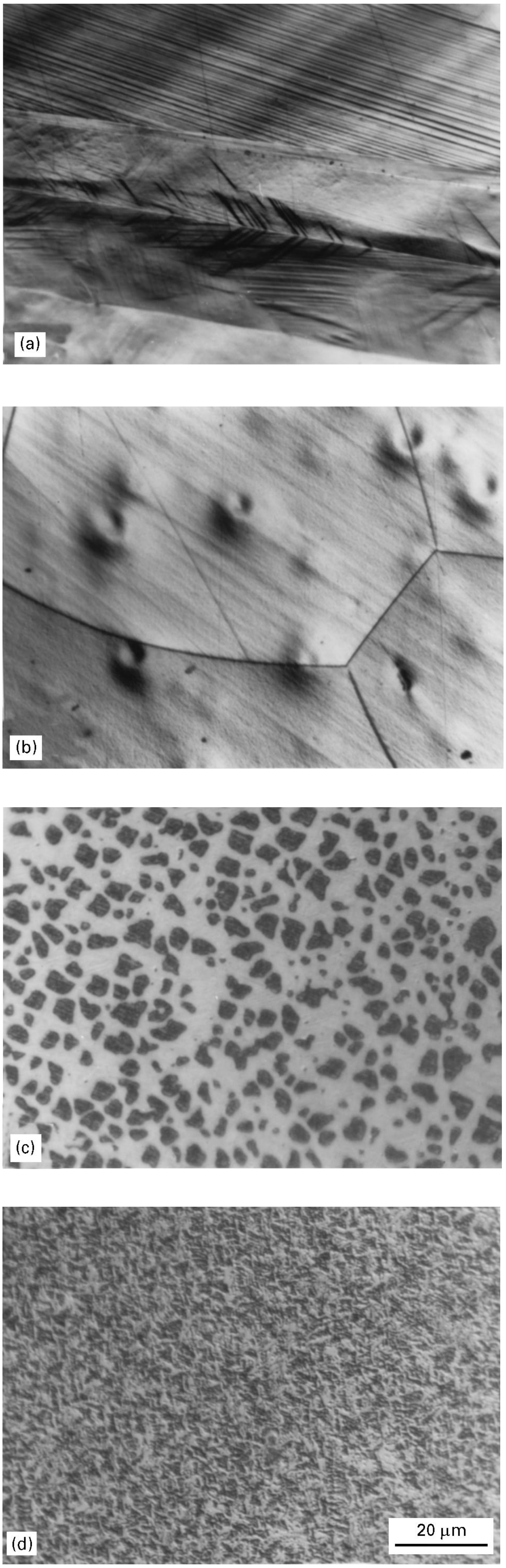

Figure 1 Optical micrographs of Cu–Al–Ni alloys: (a) alloy B quenched from 900 °C, (b) alloy A quenched from 900 °C, (c) alloy A annealed at 620 °C, (d) alloy A annealed at 500 °C.

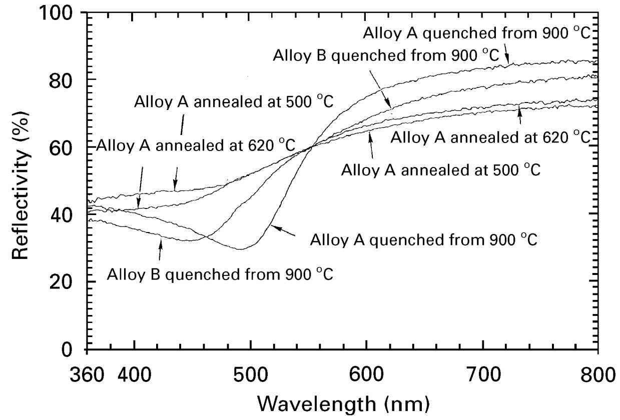

Figure 2 Spectral reflectivities of alloys A and B measured at 16 °C.

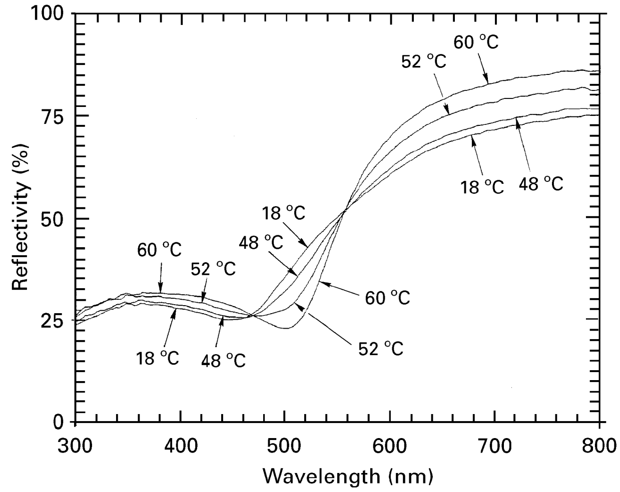

Figure 3 Variation in spectral reflectivities of alloy B quenched from 900 °C with various temperatures during heating.

were above or below room temperature. Spectral reflectivities in Fig. 2 showed the appearance of strong absorption bands around 460 nm for a specimen of alloy B with the γ' phase, while the absorption for the β_1 phase occurred around 500 nm. The results suggest that the electronic structure of the γ' phase differs greatly from that of the β_1 phase. Because a noticeable change of spectral reflectivities was observed between β_1 and γ' phases, dynamic observation of the phase transformation between these two phases in alloy B was made using a spectral reflectivity technique.

Figs 3 and 4 show the spectral reflectivities of alloy B at various test temperatures during heating and cooling, respectively. Strong absorption occurred around 460 nm at 18 °C on the basis of the γ' phase, while a deep valley in the reflectivity–wavelength curves shifted to around 500 nm at 52 °C and higher temperatures. To examine the relationship between the reflectivity and the phase transformation, the reflectivities at three different wavelengths of 400, 500 and 700 nm (where a remarkable change might appear depending on the equilibrium phases) were chosen and plotted as a function of temperature. The reflectivity changes during the heating and cooling processes are given in Figs 5 and 6, respectively.

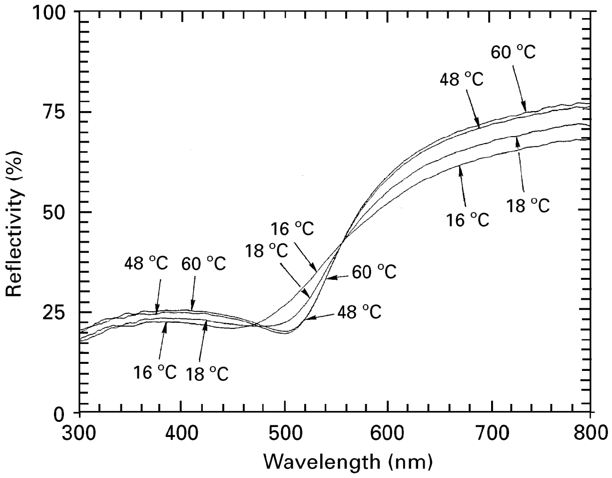

Figure 4 Variation in spectral reflectivities of alloy B quenched from 900 °C with various temperatures during cooling after the measurements in Fig. 3.

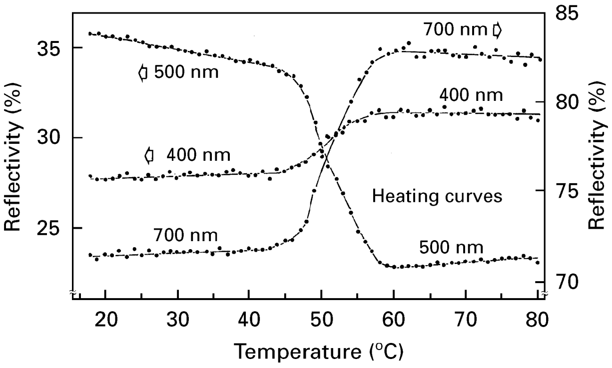

Figure 5 Temperature dependence of reflectivity of alloy B quenched from 900 °C at several wavelengths during heating.

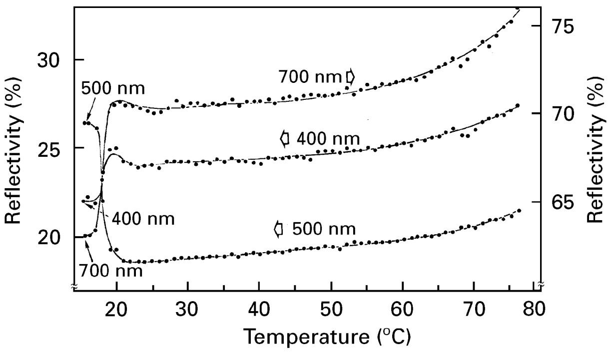

Figure 6 Temperature dependence of reflectivity of alloy B quenched from 900 °C at several wavelengths during cooling after the measurements in Fig. 5.

There is a great hysteresis in the reflectivity–temperature curves during heating and cooling. A large change in reflectivities at the wavelengths of 400, 500 and 700 nm began around 45 °C and the reflectivities were saturated around 58 °C during heating. These changes are probably due to the phase transformation from the γ' to the β_1 phase. In the temperature range before and after the phase transformation, the reflectivities at wavelengths of 400 and 700 nm maintained a constant value, independent of the temperature, while the reflectivity at 500 nm showed a strong temperature dependence. The reflectivity–temperature curves suggest that the phase transformation from the γ' phase to the β_1 began around 45 °C and was completely finished around 58 °C. The transition temperatures were in good agreement with the results obtained by DSC measurement. The reflectivity changed more sharply during cooling than that during heating in the limited temperature range where the $\gamma' \rightleftharpoons \beta_1$ phase transformation occurred. In Fig. 6 the reflectivity–temperature curves at various wavelengths suggest that the β_1 to γ' phase transformation started around 20 °C and finished at 15 °C during cooling. Possibly because the specimen surface might be contaminated in air during testing, the reflectivity of alloy B with the γ' phase before heating was larger than that during the cooling process after heating. The reflectivity decreased with decreasing temperature in the temperature range above 25 °C where the β_1 phase was observed. In contrast, the reflectivity of alloy A with the β_1 phase, which was completely stable above room temperature, exhibited no strong temperature dependence in the temperature range between 16 and 80 °C during heating. Therefore, the temperature dependence of alloy B with the β_1 phase during cooling cannot be simply explained by the effect of the contamination on the specimen surface during heating and cooling, but other effects of the electron structure and density of state related to the phase stability must be considered.

The martensitic transformation of Cu–Al–Ni alloys is known to occur thermo-elastically [11–13] but the reflectivity change in Fig. 6 showed that nucleation and growth of a martensite appeared in the limited temperature range. Anomalous peaks in the reflectivity–temperature curves at the wavelengths of 400 and 700 nm were found just above the transition temperature, while the reflectivity at 500 nm exhibited a smooth change. Shear displacements should be induced for the martensitic transformation on the basis of the lattice softening in an appropriate direction on an appropriate plane. A premonitory phenomenon for the martensitic transformation may be responsible for the anomalous change of reflectivity around 20 °C.

As seen in Fig. 5, the γ' to β_1 phase transformation occurred in a wide temperature range, because thermal activation was necessary for nucleation and growth; this might depend on grain orientations, and polycrystalline specimens containing large grains were used in this work. Anomalous change in the reflectivity as a premonitory phenomenon was not found in this case. A different temperature dependence of reflectivity between γ' and β_1 phases, which might be related to the electron band structure, was noticed at 500 nm after and before the phase transformation in Fig. 5, but the cause is not yet clear.

4. Conclusions

Variation in colour of Cu–13.8 mass % Al–4.0 mass % Ni (alloy A) and Cu–14.2 mass % Al–3.1 mass % Ni (alloy B) with various phases was investigated. Using spectral reflectivities, the phase transformation between the γ' and β_1 phases was dynamically observed and the following conclusions were reached.

1. A large change in colour of alloys A and B with the γ', β_1, $(\gamma_2 + \beta_1)$ and $(\alpha + \gamma_2)$ phases was identified. These alloys could be applicable to recording materials using a reflectivity change depending on the annealing and quenching temperatures.
2. The transformation between the β_1 and γ' phases could be dynamically observed by the spectral reflectivity change during heating and cooling processes. A great hysteresis in the phase transformation was noticed.
3. Anomalous changes in the reflectivity–temperature curves just above the transformation temperature from the β_1 phase to the γ' were found at the wavelengths of 400 and 700 nm during cooling. The premonitory phenomenon of the martensitic transformation may be responsible for the anomalous change in spectral reflectivity.

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