Reversible colour change in Ag–Zn alloy ribbon

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The reversibility of a colour change and its relationship to the phase transformation of Ag–50 at % Zn alloy ribbon produced by the twin-roller type melt-quenching method were investigated by spectral reflectivity measurements and X-ray diffractometry. This ribbon turns pink-coloured on quenching from a temperature above 560 K, and turns silver-coloured on ageing between 423 and 553 K. By alternating these heat treatments, either of the two colours can be acquired around room temperature interchangeably. The spectral reflectivity also changes with respect to the colour change. The pink-coloured alloy shows a CsCl structure which is the metastable β_1 phase. The silver-coloured alloy shows a hexagonal structure which is the ζ equilibrium phase. Therefore, the colour change between pink and silver is due to the solid-state phase transformation between β_1 and ζ caused by heat treatment.

1. Introduction

The β-phase alloys, often known as electron compounds [1], are used as decorative materials due to their brilliant colour. Investigations of the optical properties of the β phase have focused on determining their band structure [2–4] rather than developing coloured materials. The colour of a metal or alloy depends on the band structure determined by the crystalline structure [5]. Consequently, if the crystalline structure, that is the phase, is controlled by heat treatment it should be possible to determine the alloy colour. Minemura *et al.* [6] have found that for Cu–14 wt % Al–4 wt % Ni shape-memory alloy ribbon, around room temperature, two colours of copper and gold can be reversibly acquired by selected heat treatments. That colour change is due to the solid-state phase transformation between β_1 and γ_2 + (α and/or γ_1'). Their results suggest that Cu–Al–Ni shape-memory alloy is a new functional material having a reversible colour-change property, and it has been called a "reversible colour-change alloy".

The β_1 phase in that shape-memory alloy has an ordered structure (DO_3). It can be obtained by quenching the β phase having a disordered structure (b c c), which exists at elevated temperatures and is called a 3/2 electron compound [1]. The colour is due to absorption in the visible wavelength range of spectral reflectivity, and it may depend on the band structure of the electron compound. Therefore, it is proposed that a colour change should be acquired in alloy compositions of electron compounds. There are many 3/2 electron compounds in the I b–II b binary systems [1]. The authors have found a reversible colour change in an Ag–Zn alloy which has the β phase of a 3/2 electron compound. This paper describes the reversibility of the colour change in Ag–50 at % Zn alloy, and discusses it in relation to phase transformations caused by heat treatments.

2. Experimental procedure

A mixture of 99.99% Ag and 99.8% Zn was melted in a high-frequency induction furnace under an argon atmosphere to prepare a master alloy with the composition of Ag–50 at % Zn. The melt was sucked up into quartz tubes (inner diameter: 4 mm) and solidified there. The alloys were formed in the shape of a ribbon, which has advantages for rapidly quenching and reflectivity measurements because of its small heat capacity and flat surface, respectively. Ribbon specimens with a thickness of about 80 μm and width 5 mm were produced by a twin-roller type melt-quenching apparatus [7], which is suitable for making ribbons of less formable materials. The chemical compositions of the master alloy and ribbon are given in Table I.

After mechanical polishing to smooth the ribbon surfaces, specimens were aged at temperatures between 373 and 723 K for 600 sec under an argon atmosphere, followed by quenching in water. The colours of the ribbons were determined by spectral reflectivity. They were measured in the wavelength range 200 to 1200 nm using a spectrophotometer with an integrating sphere (diameter: 60 mm) normalized by the reflectance of MgO compound. The phases in the specimens were identified by X-ray diffractometry using Cu$K\alpha$ radiation. The phase transformation behaviour in the ribbons on heating (rate: 1.6×10^{-1} $K\,sec^{-1}$) was investigated by differential scanning calorimetry (DSC).

3. Results

3.1. Reversible changes in spectral reflectivity

A photograph of Ag–50 at % Zn alloy ribbon is shown in Fig. 1. The left-side half was heated with a gas burner and quenched in water. The ribbon has two colours, purplish pink (pink) and metallic silver

TABLE I Chemical compositions (at %) of master alloy and melt-quenched ribbon of Ag–Zn alloy

	Zn	Ag
Master alloy	49.8	Bal.
Melt-quenched ribbon	49.6	Bal.

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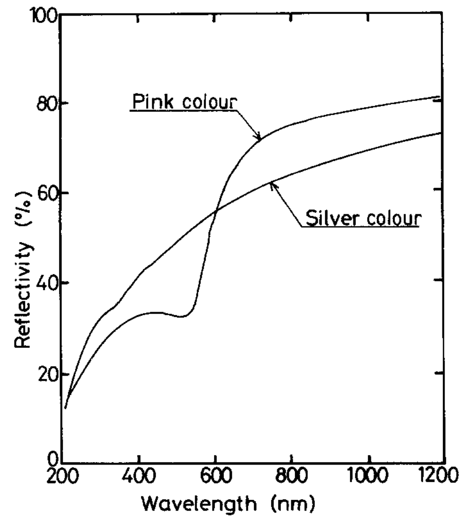

Figure 2 Spectral reflectivities of pink- and silver-coloured ribbons of Ag–50 at % Zn alloy.

(silver) at room temperature, and the boundary between them is very clear. Furthermore, the pink colour can be changed to silver by selecting the heating conditions. From these qualitative observations, it appears possible to change the colour of Ag–50 at % Zn alloy ribbon reversibly between pink and silver by selective heat treatments.

Fig. 2 shows the spectral reflectivities of these two colours. The reflectivity of the pink colour drastically decreases below 600 nm. In other works, the pink-coloured ribbon absorbs high-energy photons above about 2 eV, which should be related to the band structure of the alloy. The reflectivity of the silver increases with increasing wavelength. Consequently, the reflectivities of the two colours clearly differ at wavelength ranges between 400 and 550 nm, and above 700 nm. This suggests that the colours can be distinguished using these wavelength ranges for spectral reflectivity measurements. Then, for the purpose of investigating the reversibility of the colour change in this alloy, the spectral reflectivities of ribbons aged at various temperatures between 373 and 423 K were measured.

Fig. 3 shows the change in the spectral reflectivity of

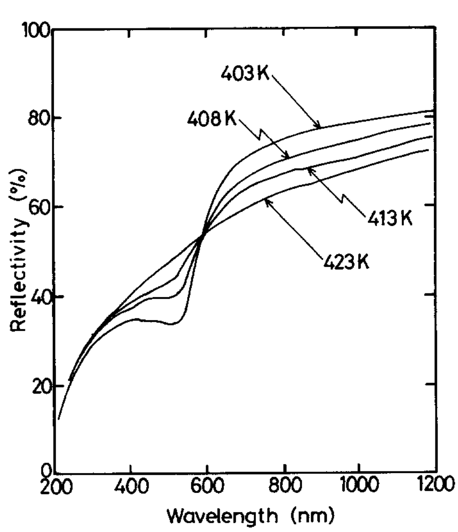

Figure 3 Change in spectral reflectivities of Ag–50 at % Zn alloy ribbons with ageing temperature (403 to 423 K). Ageing time: 600 sec.

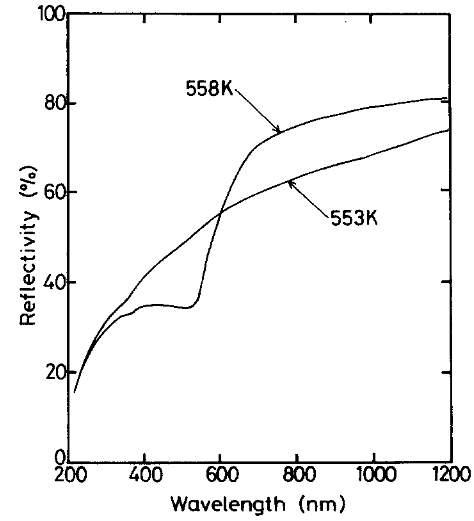

Figure 4 Change in spectral reflectivities of Ag–50 at % Zn alloy ribbons with ageing temperature (553 to 558 K). Ageing time: 600 sec.

Ag–50 at % Zn alloy ribbons quenched from 623 K followed by ageing at temperatures between 403 and 423 K. The colour of the quenched ribbon, which is pink, transitionally turns silver on ageing between 403 and 423 K. The pink remains unchanged by ageing below 403 K, that is, its spectral reflectivity is the same as that of the pink-coloured ribbon of Fig. 2. By ageing at temperatures between 408 and 413 K, the reflectivities increase around 500 nm and decrease above 700 nm. Visual observations show that these aged ribbons turn pale pink. The ribbon aged above 423 K has the same spectral reflectivity as the silver-coloured ribbon of Fig. 2.

The spectral reflectivities of Ag–50 at % Zn alloy ribbons aged at temperatures above 553 K are shown in Fig. 4. The ribbon aged at 553 K has the same reflectivity as that aged at 423 K. This indicates that the ribbon turns to a silver colour by ageing between 423 and 553 K. On increasing the ageing temperature by 5 K, however, the reflectivities change drastically, decreasing around 500 nm and increasing at 700 nm, which represent the colour change from silver to pink. They remain unchanged on ageing above 558 K. These results confirm that the Ag–50 at % Zn alloy ribbon acquires a pink colour on ageing above 558 K and turns a silver colour on ageing between 423 and 553 K. By repeating these heat treatments alternately, either of these two colours can be acquired interchangeably.

3.2. Phase changes accompanied by colour change

Fig. 5 shows the X-ray diffraction patterns of typical pink- and silver-coloured ribbons of Ag–50 at % Zn alloy. The pink-coloured ribbon quenched from 623 K has a CsCl-type ordered structure which is known as the β_1 phase [8]. This is a metastable phase obtained by quenching of β existing above about 550 K in the phase diagram [9]. On the other hand, the silver-coloured ribbon aged at 473 K has a hexagonal structure which is the ζ equilibrium phase existing below 550 K.

Fig. 6 shows the changes in the X-ray diffraction patterns of Ag–50 at % Zn alloy ribbons aged at

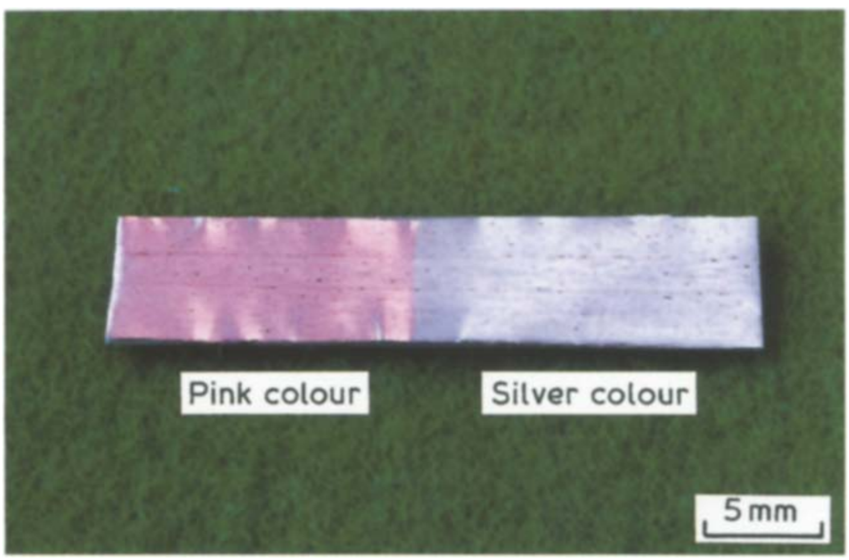

Figure 1. Photograph of Ag-50 at % Zn alloy ribbon with pink and silver colours, respectively.

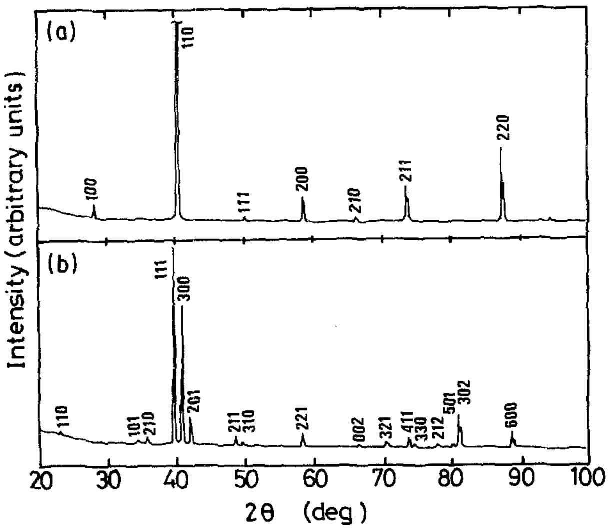

Figure 5 X-ray diffraction patterns of typical (a) pink-coloured and (b) silver-coloured ribbons of Ag–50 at % Zn alloy.

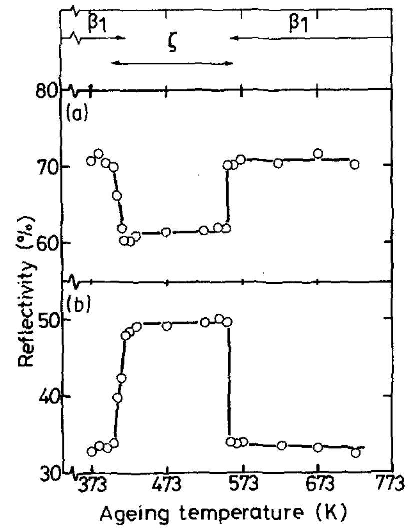

Figure 7 Change in reflectivities at (a) 700 and (b) 500 nm with ageing temperatures together with identified phases in Ag–50 at % Zn alloy ribbons. Ageing time: 600 sec.

various temperatures. The ribbons are quenched from 623 K beforehand. On ageing between 403 and 433 K accompanied by a colour change from pink to silver, some peaks of the ζ phase appear and become stronger on raising the ageing temperature, while those of β_1 become weaker. In particular, these changes in the diffraction peaks with ageing temperature clearly appear in the (1 1 1) and (3 0 0) planes of ζ and the (1 1 0) plane of β_1. The colour of the ribbon aged at 423 K is identified as silver from its spectral reflectivity

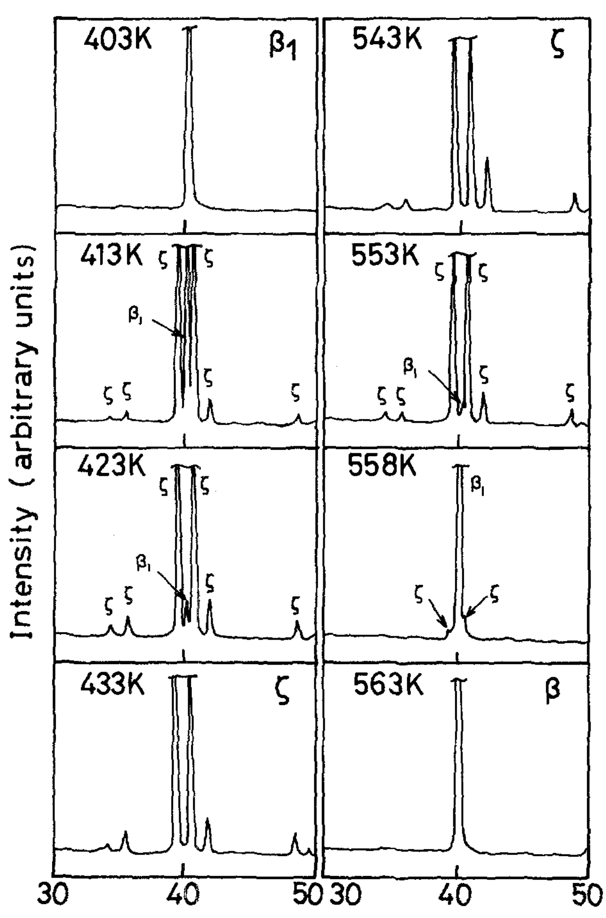

Figure 6 Changes in X-ray diffraction patterns of Ag–50 at % Zn alloy ribbons with ageing temperatures.

(Fig. 3), although the weak (1 1 0) plane of the β_1 phase can be found, which indicates that a small amount of β_1 may be left. This suggests that small amounts of β_1 and ζ in the ribbon have no influence on the colour, but the quantitative amounts are unknown. On ageing above 543 K, the diffraction patterns clearly change in the narrow temperature range between 553 and 558 K accompanied by the colour change from silver to pink. In this case, the silver-coloured ribbon aged at 553 K contains a very small amount of β_1 and the pink-coloured aged at 558 K contains a very small amount of ζ.

4. Discussion

From the above results, it is clear that the colour changes are closely related to phase transformations in Ag–50 at % Zn alloy ribbon. As shown in Figs 2 to 4, the spectral reflectivities of the two colours clearly differ at wavelengths around 500 nm and above 700 nm, and colour changes due to ageing also appear there. Then, for the purpose of discussing the relationship between colours and phases in this alloy, the changes in reflectivities at 500 and 700 nm with ageing temperature are plotted in Fig. 7 together with the phases identified in the ribbons. The reflectivities of pink-coloured alloys transitionally become those of silver-coloured alloys on the appearance of the ζ phase by ageing between 403 and 423 K, where the reflectivities increase at 500 nm and decrease at 700 nm. They are almost unchanged by ageing at temperatures between 423 and 553 K, where β_1 transforms to the ζ phase. But they dramatically become those of the pink-coloured materials again by ageing above 558 K where the β_1 phase is observed.

These changes in the phase transformations of β_1 with ageing temperature can be predicted from the Ag–Zn binary phase diagram [9]. As the temperature is raised, the Ag–50 at % Zn alloy exhibits several phases, ζ (below 550 K), $\zeta + \beta$ (in a very narrow range around 550 K) and β (above 550 K). By quenching from above 550 K, the β phase (b c c structure) which is a 3/2 electron compound with the stoichiometric composition of

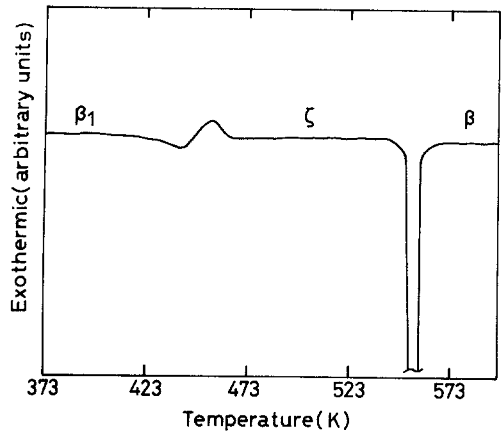

Figure 8 DSC curve of pink-coloured Ag–50 at % Zn alloy ribbon when heated at a rate of 1.67×10^{-1} K sec^{-1}.

Ag–50 at % Zn, transforms to the metastable β_1 phase (CsCl-type ordered structure) with an order–disorder transformation [8]. The β_1 phase in the pink-coloured ribbon quenched from above 558 K is formed by this $\beta \rightarrow \beta_1$ phase transformation. The ζ phase in the silver-coloured alloys aged between 423 and 553 K results from the phase transformation from metastable to equilibrium ($\beta_1 \rightarrow \zeta$), which is known as a massive transformation [10].

Fig. 8 shows the DSC curve of pink-coloured Ag–50 at % Zn alloy ribbon when heated at a rate of 1.67×10^{-1} K sec^{-1}. The ribbon was quenched from 623 K. In the temperature range from 420 to 450 K, a broad endo–exothermic peak appears, while a sharp endothermic peak appears around 550 K. The former should be due to the $\beta_1 \rightarrow \zeta$ transformation and the latter, the $\zeta \rightarrow \beta$ transformation. But the temperature ranges of the peaks due to those transformations, especially that of the $\beta_1 \rightarrow \zeta$ transformation, are slightly different from those of the reflectivities on ageing, because the measurement processes are different. The endo–exothermic transformation is unusual for a metastable to equilibrium change, which suggests that the enthalpy and entropy changes in different temperature ranges are accompanied by the structural change from β_1 to ζ. Noguchi [11] has discussed a mechanism for this transformation based on the results of specific heat measurements. Kitchingman and Buckley [12] have also discussed it from the results of resistivity measurements, but the mechanism has not been clearly defined.

Therefore, the colour change from pink to silver in Ag–50 at % Zn alloy is due to the massive transformation from β_1 to ζ accompanied by an endo–exothermic reaction. Conversely the change from silver to pink is due to the $\zeta \rightarrow \beta \rightarrow \beta_1$ phase transformation, including the order–disorder transformation. Fig. 9 indicates a schematic diagram of the heating process inducing the reversible colour change. If the ribbon is silver-coloured it should be heated above 558 K and rapidly quenched to turn pink. The pink colour can be returned to its original silver by heating between 423 and 553 K.

Fig. 1 shows that this reversible colour change can be induced in only part of a ribbon, if the heating conditions satisfy the above process.

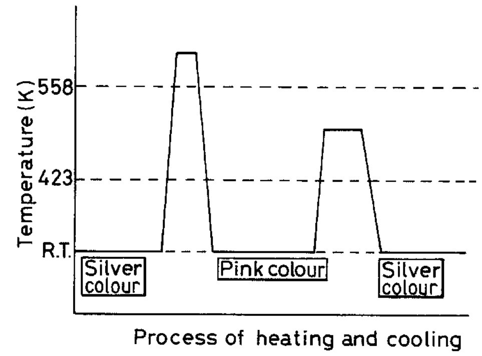

Figure 9 Schematic diagram of heating process inducing reversible colour change. R.T. = room temperature.

5. Conclusions

An Ag–50 at % Zn alloy ribbon turns pink-coloured at room temperature on quenching from temperatures above 553 K, and turns silver-coloured on ageing between 423 and 553 K. By alternating these heat treatments, either of the colours can be acquired interchangeably. The spectral reflectivity also reversibly changes with respect to the colour change. The colour change between pink and silver is due to the solid-state phase transformation between β_2 and ζ. This alloy is a new functional material having a reversible colour change property, which is designated a reversible colour-change alloy.

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