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A SOFT X-RAY INVESTIGATION OF THE ELECTRONIC STATES OF METASTABLE PHASES IN Al-Ag ALLOYS

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ABSTRACT.

The electronic structure of Al-Ag alloys in different metastable states was investigated by soft x-ray emission spectroscopy (SXES). A correlation is suggested between the local stability of the different aged states and their electronic structure.

INTRODUCTION.

Many investigations have been carried out into the reasons for the metastability of the different states of age-hardenable aluminium alloys [1]. The formation mechanism of metastable phases is dependent on many factors [2] one of which is the electronic structure of the alloy. In most experimental studies of the electronic structure of alloys only alloy concentration is considered, however the effect of metastable phases on the electronic structure has been shown to have significant effects [3,4].

EXPERIMENTAL.

Aluminium $L_{2,3}$ emission spectra from a series of Al-Ag alloys subjected to various heat treatments were measured using a concave grating soft x-ray emission spectrometer described in detail elsewhere [5]. The specimens were attached to a water-cooled copper anode using a cold setting conducting cement and the spectra were excited by electron bombardment with low input power (2.5kV and 3mA). The electron gun used a nickel filament coated with BaO and SrO to minimise heating by radiation. The vacuum in the spectrometer was 10^{-6} torr during operation. Multiple scanning was used with the sample being scraped clean under vacuum after each scan. The data were summed and processed by computer.

The alloys were prepared from high purity (99.999%) materials which were melted in alumina crucibles and stirred with an alumina rod. The cast samples were cold rolled and given an homogenising anneal at 550°C for 24 hours. The specimens were solution treated at 550°C, water quenched to produce a supersaturated solid solution (SSSS) and given the required ageing treatment just prior to mounting in the spectrometer. The particular stage in the formation of precipitates due to the different heat treatments was determined using differential thermal analysis (DTA) and microhardness measurements.

Some heating of the samples under the electron beam during measurement of the spectra was unavoidable and constitutes an 'in situ' ageing treatment. Use was

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made of this to monitor the effect of the ageing process on the electronic structure by plotting individual scans which took half an hour to complete. The surface temperature of the sample under the electron beam was calculated using the formula of Lang and Baer [6] to be 70°C. Hardness measurements of samples susceptible to ageing at this temperature after study confirmed that this is a reasonable estimate.

In all cases the SXES presented here are the Al $L_{2,3}$ emission bands which relate to the partial density of states of 's' and 'd' symmetry at the aluminium sites. The intensities of the spectra were all normalised at the point of maximum intensity. Emission spectra from silver in the alloys was of too low an intensity for accurate examination.

The alloy compositions investigated were Al-8, 12 and 16at% Ag. The ageing treatments the alloys were subjected to to produce the various metastable states were the following.

1. SSSS
2. SSSS 140°C for 22 hrs and quenched
3. SSSS 200°C for 32 mins and quenched
4. SSSS 300°C for 3 hrs and quenched
5. SSSS 300°C for 3 hrs slowly cooled

RESULTS AND DISCUSSION

The sequence of evolution of metastable states on ageing a SSSS of silver in aluminium is the following [7]:

SSSS \rightarrow spherical GP zones (η) \rightarrow disordered (partially redissolved) GP zones (ϵ) \rightarrow hexagonal intermediate Al_7Ag -type precipitates (γ') \rightarrow equilibrium Al_7Ag precipitates (γ). The initial state of the alloys investigated was the eta phase and by suitable heat treatments the different intermediate metastable phases can be produced and monitored using DTA. Heat treating at 300°C and slowly cooling produces the equilibrium precipitate (γ) with a small amount of γ' phase remaining. Only the alloys subjected to heat treatments 1 and 3 showed any change due to the in-situ heat treatment of the electron beam and in these cases individual

TABLE I

Condition*	Composition at% Ag	State*	Position of $E_F \pm 0.1eV$	Half-band-width* $eV \pm 0.2eV$	Position of MC* $eV \pm 0.1eV$
1	8	η'	72.78	9.73	68.25
1	12	η	73.1	9.9	68.10
1	16	η	73.25	10.3	68.30
2	8	ϵ	72.78	9.82	68.40
2	12	$\eta + \epsilon$	73.45	10.0	68.75
2	16	η	73.5	10.1	68.60
3	8	$\epsilon + \gamma'$	72.78	9.3	68.10
3	12	ϵ	73.4	10.0	69.00
3	16	ϵ	73.4	10.1	69.00
4	8	$\gamma' + \gamma$	72.78	9.85	68.70
4	12	$\gamma' + \gamma$	73.1	9.75	69.00
4	16	$\gamma' + \gamma$	73.4	10.0	69.00
5	8	$\gamma (\gamma')$	73.1	9.7	68.55
5	12	$\gamma (\gamma')$	73.1	9.9	68.70
5	16	$\gamma (\gamma')$	73.5	10.1	68.50

* Values at start of the measuring process.

scans were recorded. For the other heat treatments, the temperature was too low or the time too short during recording compared with the external heat treatments to have much effect and the average of several scans was used. Changes in the electronic structure due to the different metastable states is apparent from the results given in Table I.

The relative stability of a metastable phase depends on the energy difference between that phase and the equilibrium one. One factor contributing to the stability is the electronic structure [8,9]. Assuming that the partial density of 'p' states in the valence band does not counterbalance any energy change, the electronic contribution to the free energy can be monitored by measuring the energy of the mass centre (MC) of the area under the SXES curve. The position of the MC will be independent of the effects of the normalisation of the spectra and of instrumental effects. The energy of the MC's for the alloys studied are plotted against the estimated phases existing in the alloys in Figure 1. The similarity between the alloys of different silver concentrations is apparent. In the early stages of GP zone formation the MC position is low indicating a strong electronic contribution to the metastability, lower than in the γ phase. The important stabilising factor for the coherent GP zones is the electronic structure this is supported by other investigations [3,4,10]. The endothermic processes accompanying the production of the partially disordered phase (ϵ) is accompanied by an increase in the MC energy and the stability of this phase must be controlled by the increase in entropy. In the next stage of precipitation (γ') the MC position again decreases while the hardness increases indicating the formation of another metastable state stabilised by the electronic structure. At higher temperatures the equilibrium precipitate is formed, the dominating stabilising factor is again configurational and the electronic energy (the MC) reverts to a value close to that of pure aluminium since the electronic structure is little disturbed by the small amount of the precipitated grains of the gamma phase.

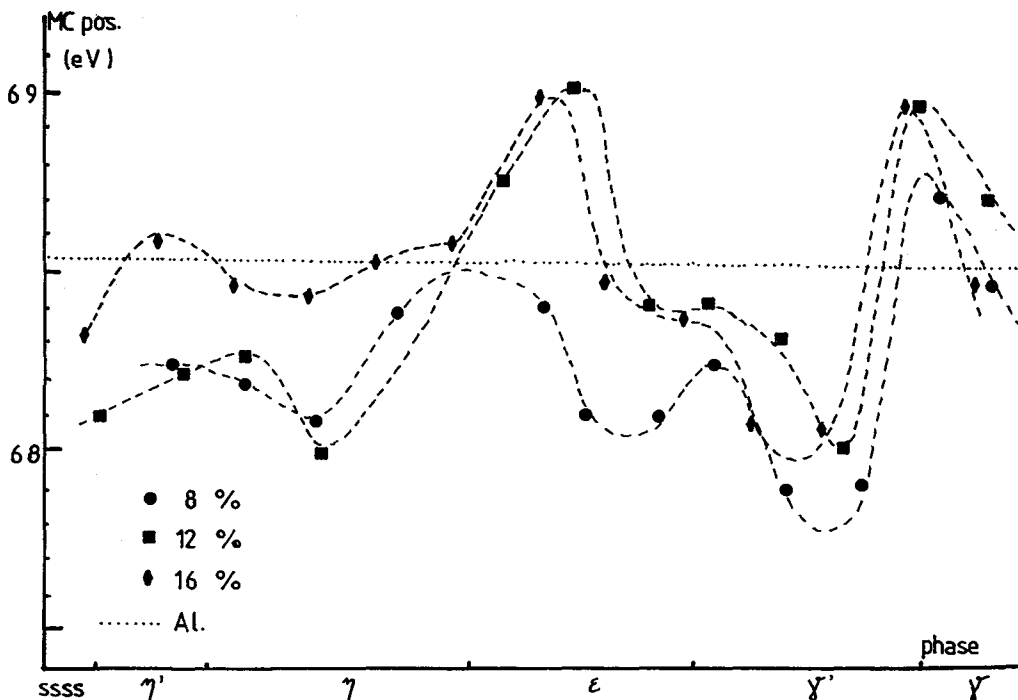


Figure 1

CONCLUSION.

The systematic investigation of the Al-Ag age hardenable alloys provides evidence for the basic role that electronic structure plays in stabilising the precursor states in the formation of equilibrium precipitates and perhaps goes some way to explaining the enigma mentioned in a recent review by Cohen [11] concerning the metastability of these age hardening states.

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