Reprint from
Volume 61 (1985)
No. 7, pp. 515/517

ALUMINIUM

A. Szász, L. Kertész, J. Hajdu and J. Kollar, Budapest

The role of the electronic structure in the solid phase transitions in age-hardenable aluminium alloys

(Communication from Institute for Solid State Physics, Eötvös University, Budapest)

Aluminium-Verlag
Königsallee 30
D-4000 Düsseldorf 1 · Tel. 02 11/32 08 21

A. Szász, L. Kertész, J. Hajdu and J. Kollar, Budapest

The role of the electronic structure in the solid phase transitions in age-hardenable aluminium alloys

(Communication from Institute for Solid State Physics, Eötvös University, Budapest)

During recent years, the special phases formed in alloys have enabled the materials to be utilized widely. From this point of view, the metastable phases represent a special category which can be regarded only in the case of the determined specific parameters and circumstances. The metastable phases may be coherent (G.P. zones), semi- and/or incoherent. The mechanism of their formation, the degree of their stability, their role in the improvement of the utilization features, and similar problems raise a number of questions for research. In the present paper, we will examine the changes in the electronic structure as well as its role in the forming and maintenance of the metastable phases through concrete examples of dilute age-hardenable aluminium alloys (Al-Mg-Si, Al-Cu, Al-Fe).

Experimental

The measuring of electronic structure was performed by soft X-ray emission spectroscopy (SXES), by which the corresponding emission spectra of every component were examined. The Al $L_{2,3}$, the Mg $L_{2,3}$ and the Cu $L_{2,3}$, $M_{2,3}$ lines, respectively, received a special emphasis but, for the sake of completeness, the Al K lines were also examined. The X-ray excitation was performed by means of an electron beam (1 to 6 kV, 0.3 to 3 mA). This enabled us to carry out "in-situ" heat treatment by the power of the exciting electron beam, consequently the controlled temperature of samples is important. During the measurement, the samples were kept at room temperature by intensive heat-exchange with cooling water. About the equipment see, for example, refs.[1][2].

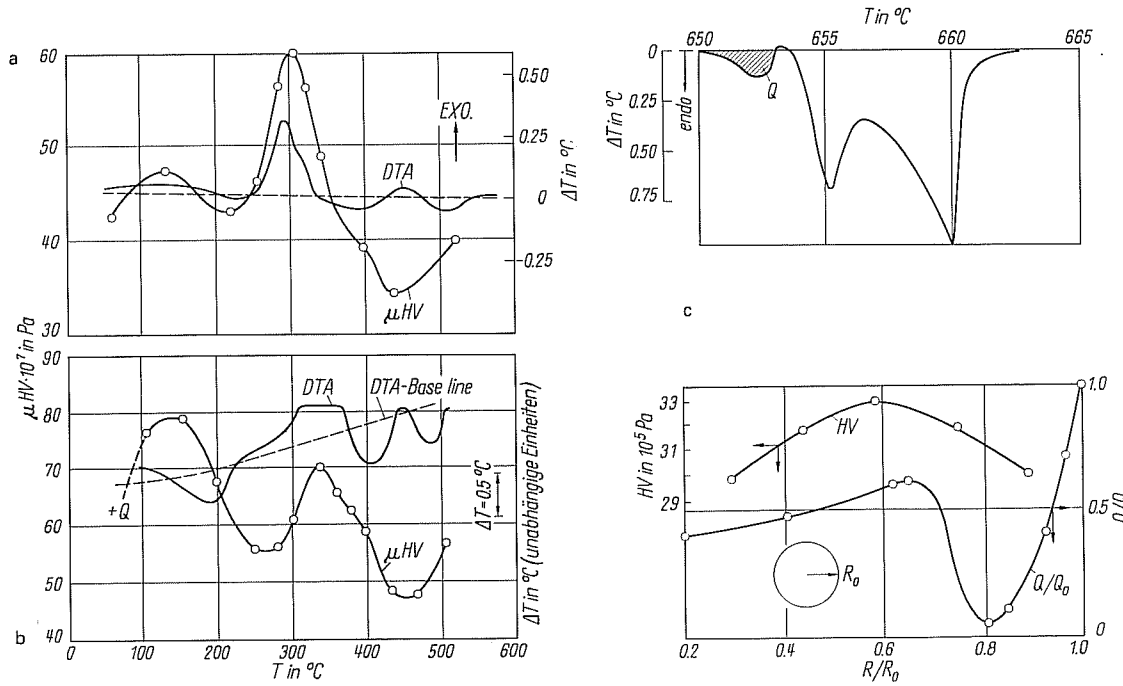
The metastable states of the alloys were indentified by differential thermoanalysis (DTA), by transmission electron microscopy (TEM) and by X-ray diffraction (XRD). To control the mechanical properties we used the microhardness indentation. The composition of the samples examined was as follows: Al-Mg (0.6 mass%)-Si (0.4 mass%), Al-Cu (4 mass%), Al-Cu (8 mass%), Al-Fe (0.68 mass%).

The controlled first stage was a solution heat treatment for each sample: the alloy was treated at 530 °C four 1 hour, and quenched to room temperature in water.

Results

The microhardness and DTA curves of the samples tested (fig. 1) show the good correspondence of the heat effects of the metastable phases (Θ', Θ'', GP-zones)[3][4]. The control structural examinations yielded the expected results at the critical regions[4]. Also examined were the phases formed by different heat treatments by means of the SXES method. The characteristic changes in electronic structure obtained in the case of the Al-Mg-Si alloy[5], (fig. 2a) manifested themselves also in the Al-Cu alloy[6] (fig. 2b), and in the Al-Fe alloy (fig. 2c) also.

The dilute Al-Fe alloy has the same changes between the equilibrium and metastable states. The measured data is



Figs. 1a to c: DTA and microhardness curves; solution heat treated AlMgSi alloy (fig. 1a), solution heat treated Al-Cu (4%) alloy (fig. 1b), continously cast Al-Fe alloy ingot versus the radii of it (fig. 1c).

Figs. 2a to c: Al $L_{2,3}$ SXE-spectra (The pure Al $L_{2,3}$ spectrum is also given for comparison); (fig. 2a) Al-Mg-Si alloys in stable and metastable states; (fig. 2b) Al-Cu alloys in stable and metastable states; (fig. 2c) Al-Fe alloys in stable and metastable states.

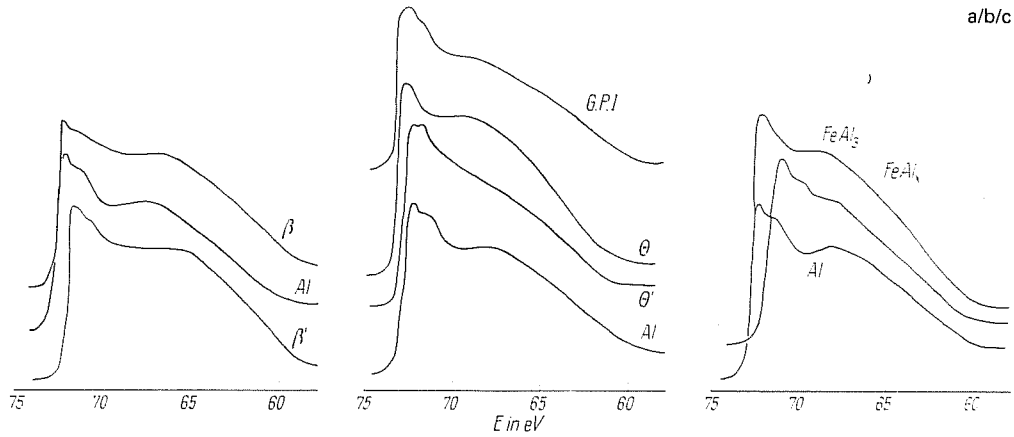


Table 1: Measured data

Alloy	Stability	State	Fermi-edge in eV*)	A/B in %*)
Al (pure)	st	normal	72.8	34
Al-Mg-Si	st		72.85	19
(1% Mg_2Si)	mst		72.0	23
Al-Fe	st	$FeAl_3$	72.4	18
(0.6% Fe)	mst	Fe_xAl_y	71.7	22
Al-Cu	st		72.8	40
(4% Cu)	mst		72.6	52

*) These characteristic parameters of the SXE spectra are shown on fig. 3

given in table 1, and the relevant parameters of the Al $L_{2,3}$ spectrum are shown on fig. 3.

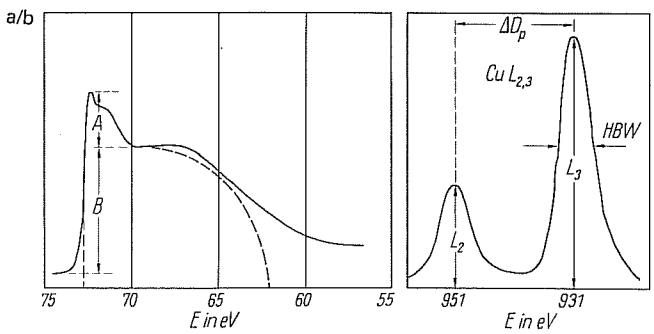
These changes can be followed also in the satellites of the electronic structure spectra of the low-concentration alloying elements. As an example, on the fig. 4 are given some parameters of the SXE-spectra of Cu in the Al-Cu (4%) alloy. The changes in kinetics, provided by "in-situ" heat treatments in SXES – equipment may also be followed. Thus, the mechanism-changes supported by the kinetics of DTA measurements engender characteristic changes also in the Fermi energy but the total density of state changes also (figs. 5a to c).

Discussion

The experiments definitely proved that the changes in the metastable phases results in significant, traceable effects in the electronic structure. In spite of the relatively low alloying concentrations, the mechanical properties of the individual phases at the same concentration are extremely different/see the microhardness measuring/as a result of the long-range ordering caused by the mechanical strains[4)7)]. This effect is well exhibited by the microhardness and by the electrical resistance change, respectively, connected with the long-range order[8)].

The soft X-ray spectroscopy measures essentially the short-range order, discerns the chemical bond states of the given component and the effects of its nearest neighbourhood[9)]. It selects these states in accordance with the quantum mechanical rules of selection (dipole transition), the L-level is sensitive to the s-and d-states, while the K-level to the quantum states of p-type. Accordingly,in the case of the L-lines, we can expect a satellite of the relatively localized d-type wave-functions, which points to a short range order.

The changing of the short-range order is accompanied by an exothermic process. At the same time the changing of the chemical bond-states monitored by the electronic structure leads to endothermic processes for electron



Figs. 3a and b: The relevant parameters of the Al $L_{2,3}$ (fig. 3a) and Cu $L_{2,3}$ (fig. 3b) SXE-spectra

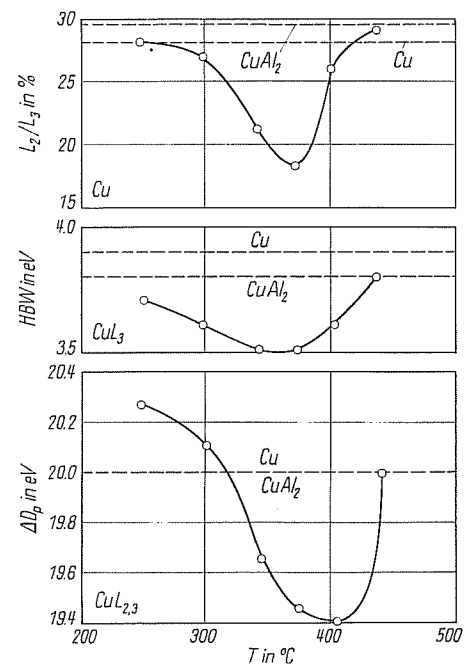


Fig. 4: The changes of the Cu $L_{2,3}$ spectra (heating rate 7.5 °C/min)

states in all the cases driving the samples to the equilibrium, stable states.

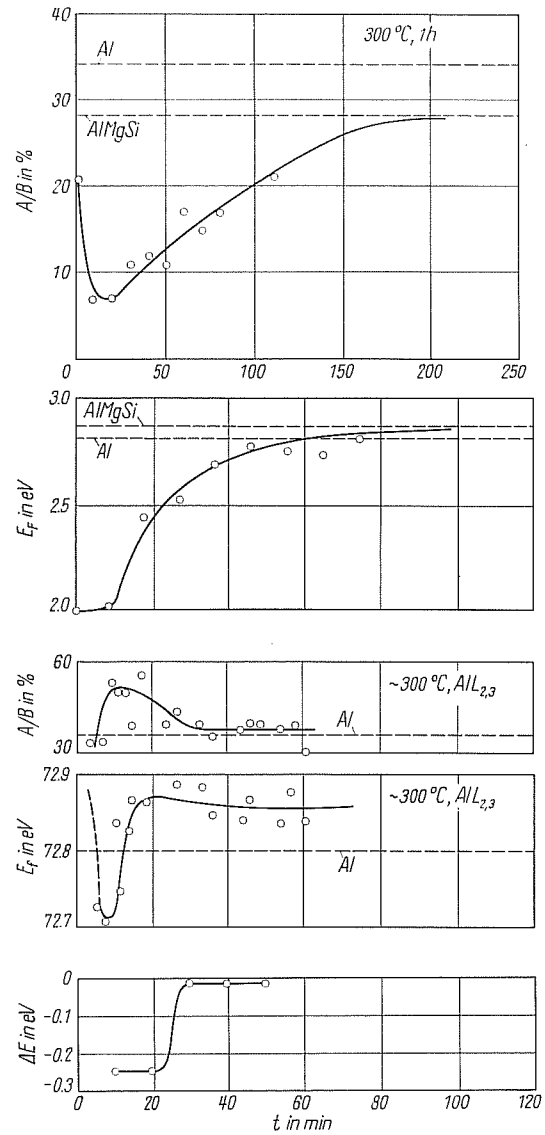
The direction of the changes leads to the conclusion that the electronic structure in the metastable state is definitely more stable than in the equilibrium structure. So, the local minima in the electronic structures are stabilizing factors; that is, the metastable structure is stabilized by the electronic structure, the chemical bond-state changes being responsible for the short range order.

The change of the Fermi-level depending on the concentration of alloys was a well-known consequence of the rigid band model. This model is only valid in the case of some dilute alloys, but it has no general validity. In the ATA and CPA models[10]) for the random alloys no changes are expected in the Fermi energy. The experiments verify in several cases this conclusion. For this reason it was rather unexpected, that some alloys, at the phase transition of their metastable phases, exhibit a considerable change in the Fermi-edge. It was shown earlier, that the changes of concentration may lead to changes in the Fermi-level too, with some amorphous alloys[11]), but no previous experimental evidence of change at the phase transition has been reported prior to our results[12]).

The filling of the second Brillouin-zone (the size of the peak sticking out below the Fermi-edge in Al $L_{2,3}$ spectrum) depends on the density of p-d mixed states, thus the ratio for A and B (denoted on fig. 3) reflects the proportion of the s-type states. A decrease in this means an increase of the s-type free electrons (corresponding to the long range order). This is also reflected in the kinetics of the processes (see figs. 5a to c).

In examining the effect of the alloying components we can realize that the tendencies of the changes in the mechanical and thermal properties and electronic structure have a consequent correspondence (see fig. 1b and fig. 4). The most firmly bonded state (from the point of view of the electronic structure, just the most metastable state) has the least different /the more homogeneous/ chemical bonds but the tendencies of the peak-ratios more interaction between alloying element with the matrix element[13]) and of the peak distances are similarly characteristic, too. All observations confirm the assumption that from the point of view of electronic structure the metastable states of these materials are more stable than their equilibrium states.

Authors thank Dr. J. Kojnok for this careful assistance on SXES measurements. This work was supported by the Ministry of Education under contract 053/81.



Figs 5a to c: Kinetics during in-situ treatment; Al-Mg-Si alloy (fig. 5a), Al-Cu alloy, (fig. 5b) Al-Fe alloy (fig. 5c)

References

[1]) Szász, A; Kertész, L.; Kojnok, J.; Hegedüs, Z.; Tolnai, L.: Vacuum TAIP (Oxford) 33, 1983, p. 107
[2]) Szász, A.; Kertész, L.; Kojnok, J.; Kováts, M.; Csíh, S.Z.: Vacuum TAIP (Oxford) 33, 1983, p. 43
[3]) Hajdu, J.; Kertész, L.; Lénárt, Cs.; Nagy, E.: Crystal Lattice Deffects, 5, 1974, p. 177
[4]) Guy, A.G.: Introduction to Materials Science, McGraw Hill Co, New York, 1975
[5]) Kertész, L.; Kojnok, J.; Szász, A.: Recent Dev. in Cond. Matter Phys. Vol. 2. Metals, Disordered Systems Surf. and Interfaces, Ed.: J.T. Devreeese, L.F. Lemuents, W.E. Van Doren, J. Van Royen, Plenum Press, New York, London, p. 89, 1981
[6]) Kertész, L.; Ahmed, M.A.: J. Phys. F. 13, 1983, p. 2235
[7]) Chan, R.W.: Physical Metallurgy, North Holland, Amsterdam, 1965
[8]) Lendvai, J.: Magyar Fizikai Folyóirat 25, 1978, p. 246
[9]) Fabian, D.J.; Watson L.M.: Band Structure Spectroscopy of Metals and Alloys. Acad. Press. New York, London, 1973
[10]) Ehrenreich, H.; Schwork, L.M.: Solid State Physics, 31, 1976, p. 150
[11]) Kübler, J.; Benneman, K.H.; Lapka, R.; Rösel, F.; Oelhafen, P.; Güntherold, H.J.: Phys. Rew. B.23, 1981, p. 5176
[12]) Kertész, L.; Szász, A.; Kojnok, J.: Vacuum 33, 1983, p.63
[13]) Holliday, J.E.: in ref.[9]), p. 713

Authors

A. Szász, Dr. ac. Prof. (1947)
L. Kertész, Dr., ac. Prof. (1925)
J. Hajdu (1932), Lecturer
J. Kollár (1945), Assistant Lecturer

all: Institute for Solid State Physics, Eötvös University, Budapest (Hungary).