THE LATTICE SPACINGS OF EQUILIBRIUM SOLID SOLUTIONS OF SILVER IN ALUMINIUM

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This paper describes the measured dependence of the lattice spacings of equilibrium Al-Ag solid solutions on temperature and composition. The form of the lattice spacing composition curve is found to differ considerably from that for the supersaturated Al-Ag solid solutions. The differences between the spacings of equilibrium and quenched Al-Ag solid solutions plotted against the electron concentration yield a curve similar to that constructed from the analogous measurements on Al-Zn given by Ellwood. The differences can be attributed to the influence of changes accompanying the increased solute clustering introduced by quenching the solid solutions into the supersaturated state.

ПОСТОЯННЫЕ РЕШЕТКИ РАВНОВЕСНЫХ ТВЕРДЫХ РАСТВОРОВ СЕРЕБРА В АЛЮМИНИИ

Эта работа описывает измерение зависимости постоянных решетки равновесных твердых растворов Al-Ag от температуры и состава. Было обнаружено, что форма зависимости постоянной решетки от состава у равновесных твердых растворов Al-Ag отличается от формы той же зависимости у пересыщенных твердых растворов. Разность постоянных решетки равновесных и закаленных твердых растворов Al-Ag, представленная как функция электронной концентрации (т. е. числа валентных электронов, приходящихся на один атом в твердом растворе), имеет аналогичную форму как у системы Al-Zn, для которой эта зависимость была построена по измерениям, проведенным Эллвудом. Возникшие разницы в постоянных решетки у равновесных и пересыщенных твердых растворов можно объяснить влиянием изменений, обусловленных повышенным образованием групп атомов легирующего элемента при закалке твердого раствора до пересыщенного состояния.

INTRODUCTION

The lattice spacings of quenched solid solutions of silver in aluminium are practically independent of the solute concentration according to the reported experimental data [1], [2] and [3]. These measurements give the spacings of the supersaturated solid solutions. It therefore seemed useful to measure the lattice spacing/composition curve of the Al-Ag solid solutions at temperature of equilibrium. The comparison of this curve with that for the quenched alloys may reveal the influence of the pre-precipitation phenomena on the lattice spacing of a supersaturated solid solution. These measurements also show to what extent the linear expansion coefficients of Al-Ag alloys differ from that of pure aluminium, sometimes used for the aluminium-rich solid solutions Al-Ag.

EXPERIMENTAL PROCEDURE

The alloys used for the present investigation were prepared by melting pure 99·9% silver supplied by Safina Co. and high-purity 99·99% aluminium imported from Hungary. The aluminium contained as major impurities 0·005% Fe, 0·003% Si, 0·001% Cu and 0·002% Mg indicated by spectral analysis. The silver content in the alloys varied from 1·22 to 14·55 at. % Ag. The determination of the exact composition of the alloys and their homogeneity control were carried out by chemical analysis and density measurements. The filings prepared from the alloys were separated in a laminar stream of dry air to contain particles with linear dimensions less than 30 μ. The filings of each alloy were then compressed into flat briquettes. The nickel chosen as an external calibration standard for the temperature measurements was of 99·9%-purity containing 0·01% Fe, 0·02% Si, 0·01% Cu, 0·03% Al, 0·002% Co and 0·001% Mg as determined by spectral analysis. Two narrow parallel strips of solid nickel were pressed onto the surface of flat samples of alloys. Each alloy specimen was annealed for 1 hour in vacuo below the solidus before each exposure.

The high-temperature vacuum X-ray camera "Unicam" of 190 mm diameter was used for recording all diffraction photographs with Cu $K\alpha$ radiation. The back-reflection technique with a flat sample in the centre of a cylindrical camera was employed. The ratio method described by Černohorský [4] was used for simultaneous lattice parameter measurements of the Al-Ag solid solutions and of nickel. This method is advantageous in eliminating the systematic error in lattice spacings which may be introduced by different effective diameters of the camera when recording simultaneously the patterns of two samples with different absorption. The lattice parameter a of a cubic polycrystalline sample is determined by means of the ratio method from the relation

$$(1) \qquad \frac{s_i}{s_j} = \frac{\arccos(v_i/a)}{\arccos(v_j/a)}$$

where $v_i = \frac{1}{2}\lambda\sqrt{(h_i^2 + k_i^2 + l_i^2)}$ and $2s_i$ is the distance of the segments of the diffraction line h_i, k_i, l_i measured in the back-reflection region along the equator of the photograph. The measurements of $2s_i$ were carried out on a Zeiss comparator. The solution of equation (1) for a was obtained graphically. The plot of the right-hand side of equation (1) against a covered the whole interval of expected a-values in all measurements.

Different combinations of diffraction lines 333, 224, 024, 133 were used for determining the lattice spacings of Al-Ag solid solutions from (1), and 024, 133, 004, 113 lines for nickel. Each photograph recorded at a certain temperature t of the sample gave the a-value of the solid solution investigated and simultaneously the a-value of nickel. The exact value of the temperature was obtained using the dependence $a(t)$ of nickel given in [5]. The same kind of measurement with pure aluminium was carried out for the elimination of a possible systematic error in a of the Al-Ag solid solutions. The resulting values were in good agreement with those given for Al by Wilson [6] and Ellwood and Silcock [7].

EXPERIMENTAL RESULTS

The results of the measured temperature dependence of the lattice parameter *a* in the interval of the existence of the equilibrium solid solution are summarized in Fig. 1 for alloys having a composition from 0·00 to 14·55 at. % Ag. The maximum variation of the temperature of the sample during each exposure was ± 2°C so that any particular measurement of *a* cannot be claimed to be better than ± 0·0003 kX units. It can be seen from Fig. 1 that all curves of $a(t)$ for the solid solutions investigated practically follow parallel straight lines. The lines are shifted to higher values of *a* with increasing solute concentration. It follows that within the accuracy of the measurements, the linear expansion coefficients are the same for all aluminium-rich solid solutions of Ag in Al and equal to the value of α of pure aluminium.

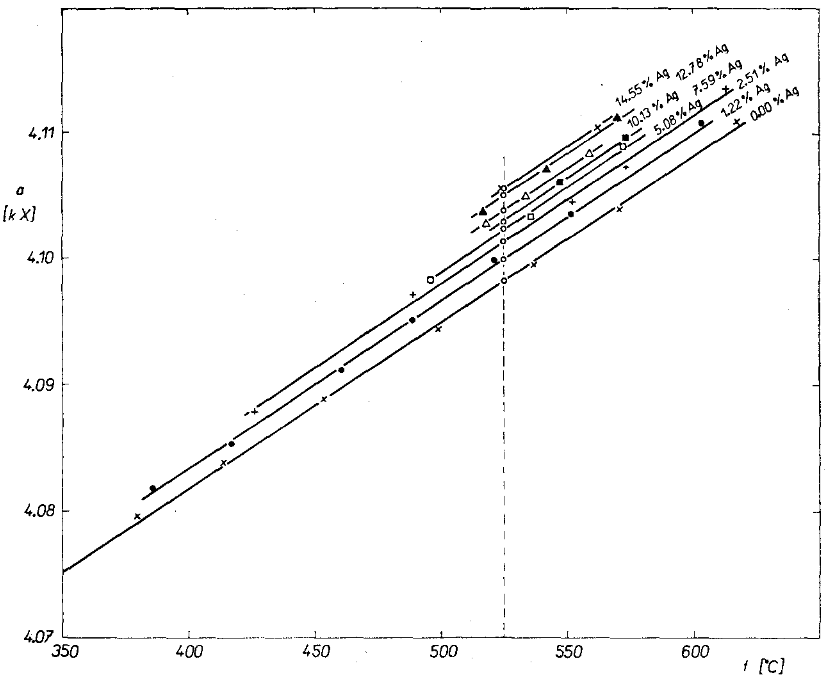

Fig. 1. Lattice spacing/temperature curves of equilibrium Al-Ag solid solutions.

The lattice spacing/composition curves are therefore analogous in the whole temperature range of the equilibrium solid solution. Curve (*1*) in Fig. 2 represents one of these curves and corresponds to the temperature 525°C. The positive deviation was found for the equilibrium solid solutions of Ag in Al from Vegard's law which at this temperature is represented by the straight line (*2*) in the same figure.

DISCUSSION OF RESULTS

In Fig. 3 the curves denoted by (*1*), (*2*), and (*3*) show the room-temperature lattice spacings of quenched Al-Ag solid solutions plotted against the atomic concentration of silver. These curves follow from the measurements of Axon and Hume-Rothery [1], Ellwood [2], and Hill and Axon [3]. Practically no obvious increase of lattice spacing with increasing solute concentration is revealed by the measurements on quenched alloys, whilst the similar curve resulting from our measurements on equilibrium solid solutions shows the clear increase with silver content [curve (*4*) representing the *a*-values reduced to room-temperature]. The lattice spacing/composition curve, which would correspond to Vegard's law, is included in the same figure [line (*5*)]. The quenched solid solutions Al-Ag thus show a negative deviation from Vegard's law.

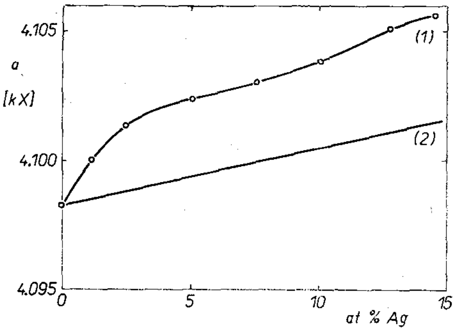

Fig. 2. Lattice spacing/composition curve of Al-Ag solid solutions at 525°C: curve (*1*) represents our measurements, curve (*2*) Vegard's law.

It seems that the most probable interpretation of the different form of the lattice spacing/composition curve for the equilibrium and quenched alloys can be seen in the different local arrangement of the constituent atoms in equilibrium and supersaturated solid solutions respectively. The spherical silver-rich clusters are formed even during a rapid quenching of the equilibrium Al-Ag solid-solutions to room-temperature as found by Guinier in small-angle scattering studies [8]. The silver atoms have a tendency to form clusters also in the equilibrium solid solutions Al-Ag [9] but the resulting silver-rich nuclei are of much smaller size than in the quenched alloys.

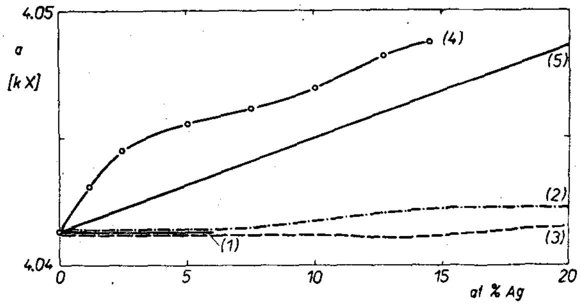

Fig. 3. Lattice spacing/composition curves of quenched Al-Ag solid solutions measured by Axon and Hume-Rothery (*1*), Ellwood (*2*), Hill and Axon (*3*); curve (*4*) represents our *a*-values reduced to 25°C, curve (*5*) Vegard's law at 25°C.

The weaker bonds between unlike atoms has been recently found by the present author in an as yet unpublished X-ray investigation of lattice vibrations in equilibrium Al-Ag solid solutions. The average number of weaker bonds in the equilibrium solid solutions of Ag in Al is thus greater due to the more random substitutional disorder than is the case in the same alloy after quenching. This indicates that the lattice spacings of Al-Ag solid solutions in equilibrium and supersaturated states will show a positive difference Δa after reducing to the same temperature. This was also confirmed by the present measurements.

It is clear that for the same reason the positive Δa derived in an analogous way should also occur in other aluminium-rich alloys showing similar pre-precipitation phenomena in quenching. A close similarity with Al-Ag in the local arrangement of atoms has been found for both the quenched [10] and equilibrium [11] Al-Zn alloys. The small difference in atomic diameters between the atomic constituents in both these binary systems is a further favourable factor indicating the values Δa to be of the same order. This comparison can be carried out because the necessary data can be taken from the lattice spacing measurements by Ellwood [12] on equilibrium and supersaturated Al-Zn solid solutions. The different forms of the lattice spacing/composition curves illustrated in Fig. 4 of [12] has been noted already by Ellwood. He points out that while the structure of the alloy may be preserved by water quenching, the anomalies in lattice spacing cannot.

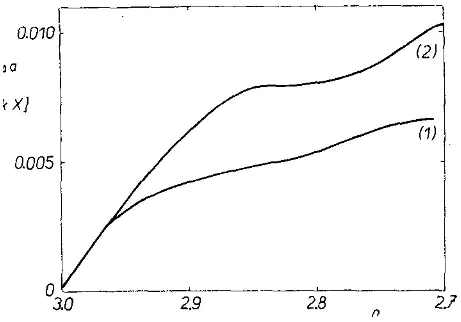

Fig. 4. The variation of Δa with n, the number of valency electrons per atom, for Al-Ag [curve (*1*)] and Al-Zn [curve (2)] solid solutions.

The difference Δa between the lattice spacing of the equilibrium and quenched solid solutions reduced to the same temperatures are plotted against the electron: atom ratio for both Al-Ag and Al-Zn in Fig. 4. [The electron: atom ratio n defined as the number of valency electrons per atom of the solid solution is given by $n = c_A n_A + c_B n_B$, where c_A and c_B are the fractional concentrations of atomic constituents A and B, and n_A and n_B denote the numbers of their valency electrons.] The curve (*1*) of Δa for Al-Ag was constructed using our measurements of lattice spacings at 525°C [curve (*1*) in Fig. 2] and the room-temperature values of a taken from Fig. 1 in [2] reduced to the temperature of 525°C by applying the corrections for expansion with temperature. The analogous curve (*2*) for Al-Zn was computed in the same way from the data of Fig. 4 in [12], the lattice spacings of quenched alloys being fitted to the temperature 360°C.

The close similarity both in the order of magnitude of Δa and in the general form of the curves for Al-Ag and Al-Zn solid solutions can be seen in Fig. 4. The increase of Δa with solute concentration is in agreement with the fact that the small size of solute-rich clusters in equilibrium solid solutions favours the more rapid increase of the number of weaker bonds between unlike atoms with increasing solute content than is the case in quenched alloys.

The main result following from the present work is that the anomalies found in the lattice spacing/composition curves are due to the different local arrangement of atoms in equilibrium and supersaturated solid solutions. The conclusions from lattice spacing measurements on quenched alloys should be drawn very carefully, especially for alloy systems with a large miscibility gap at lower temperatures.

The author wishes to express her thanks to Ing. J. Lašek for his care in carrying out the chemical analysis of the aluminium-silver alloys. The careful density measurements of these alloys made by J. Bednář are greatly appreciated.

Received 6. 5. 1961.

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