Physical properties of solid solutions containing spherical Guinier-Preston zones

Volkmar Gerold

To cite this version:

HAL Id: jpa-00236684
https://hal.archives-ouvertes.fr/jpa-00236684
Submitted on 1 Jan 1962

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
PHYSICAL PROPERTIES
OF SOLID SOLUTIONS CONTAINING SPHERICAL GUINIER-PRESTON ZONES

By Volkmar GEROLD,
Max-Planck-Institut für Metallforschung, Stuttgart, Germany.

Résumé. — En combinant les mesures de diffraction de rayons X aux petits angles avec les mesures des propriétés physiques, il est possible d'obtenir une explication quantitative des variations des propriétés en fonction des variations de structure. Dans le cas des alliages Al-Ag et Al-Zn, une formule est donnée qui relie la variation de résistivité électrique avec la variation de la concentration du soluté et la taille des zones G.-P. Les expériences sont en très bon accord avec cette formule, en valeur relative. En valeur absolue, les valeurs expérimentales sont supérieures aux valeurs théoriques d'un facteur 10 à 15. Les écarts, pour les alliages Al-Ag, la zone de température de vieillissement allant de 100 à 175 °C, sont dus au passage désordre-ordre à l'intérieur des zones.

Dans le cas des alliages Al-Zn, le dégagement de chaleur dû à la croissance de la zone a été calculé théoriquement. L'accord avec l'expérience est suffisamment bon.

Abstract. — In combining the measurements of X-ray small angle scattering with those of physical properties, it is possible to get a quantitative explanation of property changes as a function of structural changes. In the case of Al-Ag and Al-Zn alloys, a formula is given which correlates the change in electrical resistivity with the change in solute concentration and in the size of G.-P. zones. The experiments agree well with this formula on a relative scale. On an absolute scale, the experimental values exceed the theoretical values by a factor of 10 to 15. Deviations for Al-Ag alloys in the ageing temperature range from 100 to 175 °C are due to the change from disorder to order inside the zones.

In case of Al-Zn alloys, the evolution of heat due to zone growth has been calculated theoretically. The agreement with experiments is reasonably good.

Introduction. — In the field of metallurgical research, changes in physical properties are commonly used to detect changes in the atomic configurations in solid solutions. The dependence of properties on experimental parameters, such as ageing temperature and ageing time, solute concentration, etc., is used to deduce the type of structure changes. However, as the parameters affected by structure changes are numerous, it is nearly impossible to get all information about structure changes from the study of property changes alone.

In using X-ray scattering or electron microscopy, one has the advantage of obtaining direct information on the change of several structure parameters, e.g., the size or the number of G.-P. zones, which have been formed during heat treatments. In combining these methods with the measurement of physical properties, one can understand the property changes in a more quantitative way. Furthermore, one can get more information about structure changes, e.g., the amount of order inside the G.-P. zones. This method has been used for Al-Ag alloys, where X-ray methods have been combined with the measurement of electrical resistivity. Also some preliminary experiments have been done with Al-Zn alloys.

In the case, where the property change is only a function of structure changes already known from X-ray experiments, one is able to predict the amount of property changes. This will be shown for the evolution of heat due to zone growth in Al-Zn alloys.

Structure parameters describing the zone stage. — The formation and growth of G.-P. zones have been observed to occur in two separate steps after quenching. The fast reaction at the beginning of the process is due to the quenched-in vacancies. In the case of Al-Ag alloys, it is complete at room temperature several minutes after quenching from 550 °C. Thereafter, G.-P. zones are present in the alloy, having radii of the order of 10 Å. At ageing temperatures above ca. 80 °C, a slow reaction becomes appreciable. This latter is the subject of the present investigations. As has been shown [1] the following structure parameters have been evaluated by X-ray methods:

1. The formation of zones is governed by a metastable miscibility gap (fig. 1). The atomic fraction of solute atoms inside the zones is called $m_1$ the fraction of solute atoms in the remaining matrix is $m_2$. The concentrations $m_1$ and $m_2$ have been evaluated as functions of the ageing temperature. Two different stages must be distinguished. Below 175 °C, the miscibility gap is broadened producing the $\gamma$ stage, whereas at higher temperatures a small gap is observed which yields the $\varepsilon$ stage.
2. The whole solid solution has been segregated into zones, at least after the completion of the fast reaction. The observed zone growth during the slow reaction is due to a coarsening process, the volume fraction of zones, \( v_z \), remaining constant during isothermal treatments. Is \( m_A \) the solute concentration in the supersaturated solid solution, and \( R \) is the radius of the growing zones, the number of zones per unit volume, \( n_z \), is then related to the other quantities by the equation

\[
v_z = \frac{n_z}{(\pi^3/3)} R^3 = \left(m_A - m_2\right) / (m_1 - m_2).
\]

The volume fraction of the zones, \( v_z \), is a function only of \( m_A \), \( m_1 \), and \( m_2 \). In case of changing the ageing temperature eq. (1) holds only after the new equilibrium concentrations \( m_1 \) and \( m_2 \) have been reached. For Al-Zn alloys, the existence of a metastable miscibility gap has also been established \([2, 3]\). At room temperature the zinc atomic fractions are \( m_1 = 0.79 \) and \( m_2 = 0.18 \) (*).

**The resistivity of alloys containing G.-P. zones.** — Assuming the validity of the free electron theory to the problem, one can try to calculate the resistivity by setting

\[
\rho = \rho_{oo}(m_1, S) + \Delta \rho(m_1, R)
\]

where \( m_1 \) represents all of the concentrations \( m_A \), \( m_1 \), and \( m_2 \). The term \( \rho_{oo} \) is the resistivity which would be reached if the zones have grown to infinite size. It is a function of the resistivities both from zones and depleted matrix. Besides the influence of the concentrations \( m_1 \) the influence on \( \rho_{oo} \) of an ordered arrangement inside the zones may be characterized by the long-range ordering parameter \( S \). It should be noted that \( \rho_{oo} \) is independent of the zone size, whereas the second term in eq. (2), \( \Delta \rho \), is due to the scattering of electrons by the zones and therewith a function of the zone size. It is proportional to the number of zones \( n_z \) times the scattering cross section \( \sigma \) of a single zone:

\[
\Delta \rho = \left(\frac{\hbar}{m_e e^2}\right) n_z \sigma.
\]

In this equation, \( \hbar \) is Planck's constant, \( k \) the wave number at the Fermi level, \( n_e \) the number of electrons per unit volume and \( e \) the electronic charge. The cross section of a single zone can be calculated assuming a square well potential of height \( w \) for each zone and using Born's approximation:

\[
\sigma = \int (1 - \cos \xi) I(\xi) d\omega
\]

with

\[
I(\xi) = \left(\frac{m_e}{2\pi \hbar^2 \omega}\right)^{3/2} \left(\frac{k}{3}\frac{R^3}{\omega}\right)^{3/2} \varphi^4(\xi)
\]

\[
\varphi(\xi) = \frac{3}{\omega^3} \left(\sin x - x \cos x\right)
\]

\[
x = 2kR \sin (\xi/2)
\]

\[
\xi = \text{scattering angle}
\]

\[
m_e = \text{effective electronic mass}
\]

\[
d\omega = 2\pi \sin \xi d\xi = \text{space angle}.
\]

eq. (4) can be solved and becomes, for \( kR \gg 1 \):

\[
\sigma = 2\pi \left(\frac{m_e \omega}{\hbar^2 k}\right)^{3/2} R^3 \ln (\omega R)
\]

with \( \alpha = 2.62 \) being an integration constant. As Born's approximation may not be valid, the method of partial waves has also been applied in calculating \( \sigma \) (4). The results show that for the region of zone sizes of interest the \( \sigma \)-values have nearly the same dependence with \( R \) as shown by eq. (5), however the slope is smaller by a factor of 0.8. In both cases, Friedel's condition for charge neutrality leads to potential values of \( \omega \) in the order of 3 to 4 eV for Al-Ag alloys. For Al-Zn, this value is reduced by a factor of two.

Using eq. (1), (3) and (5), the term \( \Delta \rho \) is calculated to be

\[
\Delta \rho = \frac{3}{2} \left(\frac{m_e}{e^3}\right)^{2/3} \frac{m_A - m_2}{m_1 - m_2} \ln (\omega R)
\]

for \( kR \gg 1 \).

In this equation, the height of the potential well, \( \omega \), is a function of the concentrations \( m_A \) and \( m_1 \).

**Experimental results on resistivity.** — Using three alloys of the system Al-Ag, the resistivity at 20 °C has been measured for different ageing
temperatures and times. The same foils have been used to determine the zone radius $R$ by X-ray small angle techniques. The measured resistivities have been plotted versus the zone radius, using a $(R^{-1} \ln (a k R))$-scale in the inverse direction. Thus during zone growing, the measured points go through the diagrams from left to right. The silver concentrations of the alloys were 6, 9 and 12 at. % silver. Some measurements have been made also with a 4 at. % alloy. Figure 2 shows the result for all four alloys with a 175 °C treatment. In figure 3 the curves for the 6 at. % alloy have been drawn for different ageing temperatures between 100 and 300 °C. The other alloys show similar curves with different slopes. Nearly all curves show straight lines except the 154 °C curve. All further investigation of the 6 and 9 at. % alloy below the 175 °C isotherm exhibited this same remarkable deviation from a straight line, as shown for the 9 at. % alloy in figure 4. For all subsequent samples employed in this investigation, we failed to reproduce the straight lines for the 100 °C — and the 140 °C isotherm shown in figure 3. As it seems highly unlikely, that the first measurements were wrong, the two curves in figure 3 (and the similar curves for the 9 and 12 % alloys) must be due to special pretreatments of the foils which are at present unknown. For zone radii $R \approx 40 \, \text{Å}$ the curved lines approach the straight lines measured in the former experiments.

**Discussion on the resistivity experiments.** — In this section the experimental results are compared with the theory. According to eqs. (2) and (6), straight lines should be observed in figures 2 to 4 for the following conditions:

1. The concentrations $m_i$ are constant.
2. The long-range order parameter $S$ does not change.
3. The zone radii are sufficiently large.

These conditions have been fulfilled in all cases where straight lines have been observed, that is for ageing temperatures of 175 °C and above ($\epsilon$ stage, fig. 1). In these cases, no long-range order has been observed inside the zones by X-ray techniques [5], [6]. Below 175 °C ($\gamma$-stage) the deviation from straight lines can be explained assuming a change in the long range ordering parameter $S$ during heating. For small zone sizes, there is a disordered arrangement ($S \approx 0$) of atoms inside
the zones. Therefore the term $\rho_\infty$ in eq. (2) has a relatively high value, similar to the value for the 175°C isotherm. With increasing zone size more and more ordering occurs inside the zones ($S$ is increased), thus reducing the $\rho_\infty$-value as shown schematically in figure 4. Ordering is complete after zones radii of 30 to 40 Å are obtained in accord with X-ray measurements [6].

Besides these qualitative results, the following quantitative results have been found:

**The slope of the curve.** — Since the concentrations $m_1$ and $m_2$ and also the potential high $\omega$ are functions of the temperature only, the slopes for different alloys at the same ageing temperature must be proportional to $(m_1 - m_2)$, as follows from eq. (6). This has proved true for all ageing temperatures and all solute concentrations $m_1$ where straight lines have been observed. The concentrations $m_2$ used for these calculations, are given in figure 5.

With the aid of eq. (6), the value of the potential well height, $\omega$, can be evaluated from experimental curves. These values are of the order of 10 eV and are too high by a factor of 3 to 4 compared with the theoretical values. The reason for this will not be discussed here. The following empirical relation have also been found:

$$\omega = a + b(m_1 - m_2)$$

with $a = 5.8$ eV and $b = 11$ eV. (7)

The values of $m_1$ have been taken from the limits of the miscibility gap (fig. 1). The change from the ordered $\eta$-stage to the disordered $\varepsilon$-stage has no special influence on the value of $\omega$.

**The term $\rho_\infty$ as function of the solute concentration and of the ageing temperature.** — In figures 2 and 3, the term $\rho_\infty$ is given by the intersection of the extrapolated straight curves with the right hand ordinate axes. For each ageing temperature, the term $\rho_\infty$ can be written empirically as a function of solute concentration [4].

$$\rho_\infty = A + Bv_2^2$$

where $v_2$ is the volume fraction of the zones, given by eq. (1). The parameters $A$ and $B$ are functions of the ageing temperature, or more specifically, the concentrations $m_1$ and $m_2$. The parameter $A$ is the resistivity when the volume fraction $v_2$ of the zones becomes zero. Therefore, $A$ is the resistivity of the depleted matrix having a solute concentration $m_2$. The resistivity of aluminium alloys containing small amounts of silver has been measured by D. Turnbull and al. [7]. Using these values, it is possible to deduce from the resistivity $A$ the silver concentration $m_2$ as a function of temperature. Figure 5 gives the result, which is in good agreement with the former determination of $m_2$ from X-ray small angle scattering (fig. 1).

The parameter $B$ in eq. (8) is a measure for the resistivity of the silver-rich zones, therefore it must be a function of the silver concentration $m_2$ inside the zones and the long range ordering parameter $S$. Figure 6 shows the parameter $B$ as proportional to the solute concentration inside the zones, $m_2$, so long as the long range ordering parameter $S$ has not changed. The change from disorder to order reduces the value of $B$, as shown in the figure. For the 140°C isotherm, two values of $B$ have been calculated. The first value is determined from the term $\rho_\infty$ at the beginning of the growth process (disorder), whereas the second value corresponds to the end of ageing (order). The two $B$-values differ by nearly a factor of two.

**The resistivity of Al-Zn alloys.** — In the case of Al-Zn alloys, curves similar to those of figure 2 have been observed for ageing treatments at room temperature. The potential well height, $\omega$, has been
found to be roughly half of that obtained for Al-Ag alloys. This is in agreement with the theory which predicts a reduction of $w$ by a factor of 2. Therefore the discrepancy between theory and experiment for Al-Zn alloys is of the same order as has been found for Al-Ag alloys.

**The evolution of heat in Al-Yn alloys.** — After quenching to room temperature, the fast reaction in Al-Zn alloys continues for longer times than in Al-Ag alloys, especially when low quenching temperatures have been used. Furthermore, during this reaction, a coarsening of G.-P. zones has been observed, all concentration values remaining constant [2], [3]. The main change of thermodynamic properties during this process is the change of the integral interface energy $U_B$. This takes place because the total amount of interface surface between zones and depleted matrix is reduced during ageing. The interface energy is given by

$$u_B = N_B u_B$$

where $N_B$ is the number of boundary atoms per g-atom and $u_B$ is the boundary energy per atom.

In using the zero approximation of the theory of regular solutions, the boundary energy per atom, $u_B$, is given by [7].

$$u_B = \beta z V (m_1 - m_2)^2$$

with $\beta \approx 1/3$; $z$ = coordination number; $V$ = interaction energy; $m_1$, $m_2$ = solute concentrations on both sides of the boundary.

The number of boundary atoms is given by

$$N_B = n_B \gamma a R^2 v_M$$

with $n_B$ = number of zones per unit volume, given by eq. (1); $R$ = zone radius; $v_M = Na^3/4 =$ mole volume; $N = \text{Loschmidt number}$; $a = \text{lattice constant}$; $\gamma \approx a^2/2$.

The constants $\beta$ and $\gamma$ depend on the particular boundary model, but their product, i.e., the value of $N_B z$ gives the right value for the total number of nearest neighbor bonds crossing the boundary, as long as $R \gg a$.

In using eqs. (1) and (9) to (11) the boundary energy is given by

$$u_B = \frac{1}{2} (m_A - m_d) (m_1 - m_2) N a V a f R.$$  

The change of the internal energy during an isothermal ageing treatment can be observed experimentally in measuring the evolution of heat, $\dot{Q}$, which is related to the energy term $U_B$ by

$$\dot{Q} = - \frac{dU_B}{dt} = - (\frac{dU_B}{dR}) (dR/dt).$$  

The last equation can be written because all other parameters remain constant after the initial ageing time $t_0$, i.e., after about one minute. Following eq. (13), the evolution of heat has been calculated using X-ray values for the zone radius $R(t)$ and thermodynamic values by J. E. Hilliard and al. [9] for the evolution of $N_z V$, which is about 3.5 kcal/g-atom. The details will be given elsewhere. The calculated curve has been compared with measured points as shown in figure 7. As the calculations are only crude approximations, the agreement is tolerably good.

**Acknowledgements.** — The author is indebted very much to Mr. W. Merz who has carried out all experimental work described in the first part of this paper. He is also obliged to thank Dr. O. Kriese and Dr. F. Bell, both of the Max-Plack Institut für Eisenforschung, Düsseldorf, who have made available the measured values of the evolution of heat used for comparison in the second part of this paper. The X-ray measurements referred to in the same part have been made by Mr. W. Zürn. The greatest part of these investigations has been supported by the Deutsche Forschungsgemeinschaft.

The author thanks Dr. J. A. Hren for reading the English manuscript.

**REFERENCES**