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A lattice parameter method for the investigation of solid state precipitation

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Over strictly limited composition ranges, the relationship between lattice parameter and solid solution composition can often be taken as linear even in multicomponent solid solution systems. The constants in the assumed linear equations relating the lattice parameter to the atomic percentage of each component may be calculated from lattice parameters measured for solution heat-treated alloys of known compositions. The subsequent changes in lattice parameters which occur during ageing of these alloys are shown to yield useful information about composition changes and the precipitate phases which occur during ageing. In particular, if the composition of the precipitate is known, then the linear equations may be used to calculate the composition of the remaining solid solution alloys. Even if both the composition of the precipitate phase and the remaining solid solution are unknown, changes in lattice parameter, combined with known lattice parameter versus composition functions, may be used to determine what average precipitate compositions are not allowed. These methods are illustrated in the case of Al-Cu, Cu-Ni-Al and Cu-Zn-Ni-Al alloys.

1. Introduction

Considerable work has been carried out concerning the variations in lattice parameters which occur when one element (or compound) is dissolved into another. Vegard's law, which was originally stated with respect to isostructural, pseudobinary, mixed-salt solid solutions [1], assumes a characteristic volume associated with each ion. This implies a linear change in lattice parameter between pure solvent and pure solute, usually for solute concentrations given in mol %. Vegard's law is valid for such solid solution systems because the degree of ionization is not altered by ion substitution [2]. Most binary metallic systems, however, show substantial positive or negative deviations from this law [2, 3]. This is so because in dilute solutions the electronic state of the solute atoms is changed while in higher concentration solutions the electronic states of both solvent and solute atoms are altered [2]. A concise review of the efforts which have been made to predict such deviations from Vegard's law is available [4].

Since the lattice parameter is in most cases a slowly varying function of solid solution composition, however, it is still possible in many between solid solution composition and lattice parameter if this linear relation is restricted to a limited composition range. If the first derivative of the relation between lattice parameter and composition is everywhere defined over the composition range of interest, then by making the composition range sufficiently small, the approach to linearity can be made arbitrarily close. That is, over a composition range x_i^k to x_j^k, where the superscript denotes the element whose atom fraction varies from x_i to x_j, the lattice parameter LP can be assumed to be of the form:

$$\mathrm{LP} = \sum V^k(x^k - x_0^k) \qquad (1)$$

where $x_i^k < x_0^k < x_j^k$ and the V^k terms are constants. In general, for systems where Vegard's law is not obeyed, these V^k terms will vary depending on the composition ranges $x^1, x^2, \ldots, x^n$ about which the V^k terms are calculated.

As discussed in the Appendix, this expression is equivalent to a two-term Taylor series expansion for the lattice parameter versus composition function. With the V^k constants known it is possible in a binary system to calculate the solid solution concentration which would give rise to a measured lattice parameter, and conversely. In a alloy systems to assume a linear relationship ternary system, there will in general be a line (in the composition diagram) along which a series of alloys will possess a given lattice parameter. Thus it is in general not possible to determine solid solution alloy compositions for ternary, quaternary, or higher order systems from lattice parameter measurements alone. However, if the composition of the precipitating phase is known, then in the case of systems of any order the composition of the remaining matrix solid solution is uniquely determined by the measured lattice parameter if the starting composition and the constants V^k are known. This information is very often useful, e.g. in corrosion and oxidation studies, and may be difficult to obtain by other means, e.g. microprobe methods, if the precipitate particle spacing is small. In cases where the composition of the precipitate phase is unknown measurements of the constants V^k together with measurements of the changes which occur in lattice parameter during precipitation may be used to show that certain precipitate compositions are not allowed.

The following sections discuss the application and use of linear lattice parameter versus composition functions in studying solid state precipitation in Al-Cu, Cu-Ni-Al, and Cu-Zn-Ni-Al alloys.

2. Discussion

2.1. Al-Cu alloys

Early measurements of the lattice parameter changes which occurred during ageing of Al-Cu alloys revealed that, for many conditions of heat-treatment, changes in hardness substantially preceded any observed change in lattice constant [5, 6]. These observations were suggested to indicate pre-precipitation hardening effects [5]. However, it is now accepted that the greater rapidity of ageing in highly localized areas, e.g. slip bands, when compared with the bulk matrix, accounts for the observed delay in lattice parameter change [6]. If the kinetics of ageing of the bulk matrix are of particular interest, therefore, measurement of changes in lattice parameter may provide a more reliable index to the extent and kinetics of precipitation than mechanical property measurements.

In many cases, precipitation reactions do not involve great changes in composition. Thus, to assume the lattice parameter versus composition relationship to be linear over the expected range of composition change due to precipitation will in general be a good approximation. In the case of Al-Cu alloys, for example, the usual compositions of age-hardenable alloys extend to about 2 at. % Cu. Letting Al and Cu be the atomic percentages of aluminium and copper, respectively, and with A and B as constants, it is convenient to write the linear relationship of lattice parameter and composition first as:

$$\mathrm{LP} = A\mathrm{Al} + B\mathrm{Cu}\,. \tag{2}$$

Since

$$\mathrm{Al} + \mathrm{Cu} = 100\,, \tag{3}$$

one has

$$\mathrm{LP} = 100A + (B - A)\mathrm{Cu}\,. \tag{4}$$

Combining lattice parameter data from Ellwood and Silcock [7], Axon and Hume-Rothery [8], and Dorn, *et al* [9], gives eighteen data points covering the range from 0 to 2.17 at. % Cu. Using Equation 4 and a least-squares analysis of these values gives $A = +0.040494$ and $B = +0.035657$ Å/at. % (at 25°C).

From measurements of the lattice parameter taken after different ageing treatments, it is thus possible from Equation 2, with A and B known, to calculate the atomic fractions of Cu and Al remaining in solid solution, and hence, the fraction of these elements which have gone to $\mathrm{CuAl_2}$. This calculation is illustrated using the data of Phillips and Brick [10, 11], from which one may calculate the percentage of Cu precipitated as a function of ageing time and show this together with the hardness data.* This is given in Fig. 1. In this case, there is close agreement between the point of maximum hardness and the completion of precipitation as evidenced by the point at which additional Cu is not removed from solid solution with continued ageing. For the ageing of similar alloys at lower temperatures, however, the lattice parameter does not begin to change significantly until after the maximum in hardness has been passed, because of localized acceleration of ageing, e.g. at slip bands [6]. Such localized effects may greatly affect mechanical properties, but have only a negligible effect on the lattice parameter. Thus, the use of both lattice parameter and strength data together would allow the separation of heat-treatments which caused bulk precipitation from those which caused only localized precipitation.

The measurement of lattice parameter changes during ageing also permits the determination of the solubility limit at a given temperature, using

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*The data reported by Phillips and Brick [10] were given incorrectly as Å units, but are actually kX units.

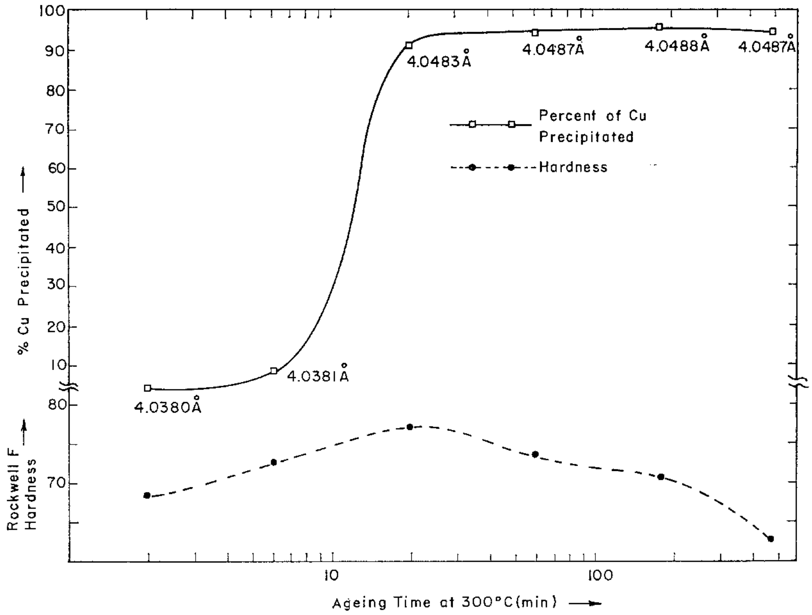

Figure 1 Hardness versus ageing time for an Al-2.37 at. % Cu alloy, after Phillips and Brick [10], giving also the percentage of Cu precipitated calculated from the lattice parameter values shown.

a single alloy, provided the composition of the second phase is known. In the present case, use of the data of Phillips and Brick [10, 11], together with the values calculated for *A* and *B* in Equation 2 shows that after ageing for 9 h at 300°C only 0.15 at. % copper remains in solid solution. This value is to be compared with the same value, 0.15 at. %, determined at 300°C by Stenzel and Weerts using the more usual parametric method [12], as well as to the higher value (approximately 0.32) determined by Dix and Richardson [13] by metallographic means.

It is relevant to compare the present lattice parameter analysis with the quantitative size-factors for binary solutions calculated by King [2, 4, 14]. Both analyses are based on the general observation that lattice parameter changes are linear if taken over sufficiently small regions of composition. King, however, is concerned with the effect of misfit strain on the physical properties of the solvent and hence defines his size-factors in terms of the initial slope of the parameter versus composition relationship. The present interest is in precipitation from solution and hence the concern is with the linearity of the lattice parameter versus composition relationship near the saturation solute concentration. If, however, the solution is very dilute, and the initial slope is maintained till saturation, the two analyses then become identical so that the constant *A* in Equation 2 can be identified with the lattice parameter of the solvent, while B refers to the effective lattice parameter of the solute under the co-ordination and electron concentration conditions of the solution. This situation is approximated to some extent by the relatively limited solution of Cu in Al and hence the term 100 *A* in Equation 4 lies within 0.0002Å of the lattice parameter of Al [15]. In a more extensive solid solution, it is found [2] that the initial slope of the lattice parameter versus composition relationship is not maintained up to the solute saturation limit, so that in general an effective lattice parameter must be determined for both solvent and solute, which is the basis of Equation 2. The size-factors defined by King are thus not generally applicable to the analysis of precipitation from such saturated solid solutions.

The general tendency of a solid solution to deviate from the initial linear lattice parameter versus composition trend is related indirectly to the degree of deviation from a Vegard linear relationship between the sizes of the two component atoms. To eliminate co-ordination effects due to different structures, King [2, 4, 14] defines this deviation in terms of the percentage difference between the atomic volume of the solute and its effective atomic volume in a dilute solid solution. The sign and magnitude of these Vegard Law Factors can thus be used as qualitative indicators of the change in size of a solute atom in a concentrated solution by providing a check on the magnitude of the constant B in Equation 4. Hence, the constant 100 B for Cu in Al-Cu is found to be substantially less than the lattice parameter for pure copper, which is consistent with the relevant Vegard Law Factor of $-$ 12.5% for this solution [2]. The Vegard Law Factors cannot be used to derive B with precision, however, because they are based on lattice parameter versus composition slopes for solvent-rich solutions rather than composition ranges near solute saturation. There is thus no simple alternative to deriving the constants A and B in Equation 2 by the process described above, using the best lattice parameter data available.

2.2. Ternary Cu-Ni-Al alloys

The use of limited composition range linear lattice parameter versus composition relationships for determining the progress of precipitation reactions is not limited to the case of binary alloys. Consider for example, the case of the ternary Cu-Ni-Al system, for which an extensive set of lattice parameter data is available [16, 17]. In this case, one may rewrite Equation 1 as

$$\mathrm{LP} = C\mathrm{Cu} + D\mathrm{Ni} + E\mathrm{Al} \qquad (5)$$

where Cu, Ni, and Al represent the atomic percentages of these elements, respectively, and C, D, and E, are constants. As before

$$\mathrm{Cu} + \mathrm{Ni} + \mathrm{Al} = 100\,, \qquad (6)$$

and thus Equation 5 can be rewritten as

$$\mathrm{LP} = 100\,C + (D - C)\,\mathrm{Ni} + (E - C)\,\mathrm{Al}\,. \quad (7)$$

Since all of the experimental data points will not lie on exactly the same plane in lattice parameter-composition space, it is necessary to use some method of calculating the constants C, D, and E, in Equation 5 so as to determine those which give the best fit to the observed lattice parameter and alloy composition data. This best fit (in the least squares sense) may be calculated by letting

$$\textstyle\sum_i\, [\overline{\mathrm{LP}}_i\,(\mathrm{Cu}_i, \mathrm{Ni}_i, \mathrm{Al}_i, C, D, E) - \mathrm{LP}_i)]^2 \equiv S\,, \quad \ldots\ldots (8)$$

where $\overline{\mathrm{LP}}_i$ represents the value calculated for the lattice parameter at the composition Cu_i, Ni_i, Al_i, using the constants C, D, and E. LP_i is the measured value of the lattice parameter at this composition. S is then the sum of the squares of the differences between the calculated and measured lattice parameter values at each composition. Requiring that the value of S be an extremal with respect to C, D, and E, gives

$$\frac{\partial S}{\partial C} = 0;\ \frac{\partial S}{\partial D} = 0;\ \frac{\partial S}{\partial E} = 0\,. \qquad (9)$$

By applying these relations to Equation 8 and noting that:

$$\frac{\partial \overline{\mathrm{LP}}_i}{\partial C} = \mathrm{Cu}_i;\ \frac{\partial \overline{\mathrm{LP}}_i}{\partial D} = \mathrm{Ni}_i;\ \frac{\partial \overline{\mathrm{LP}}_i}{\partial E} = \mathrm{Al}_i \quad (10)$$

one obtains the following

$$\begin{aligned} \textstyle\sum_i 2(\overline{\mathrm{LP}}_i - \mathrm{LP}_i)\,\mathrm{Cu}_i &= 0 \\ \textstyle\sum_i 2(\overline{\mathrm{LP}}_i - \mathrm{LP}_i)\,\mathrm{Ni}_i &= 0 \\ \textstyle\sum_i 2(\overline{\mathrm{LP}}_i - \mathrm{LP}_i)\,\mathrm{Al}_i &= 0\,. \end{aligned} \qquad (11)$$

This set of three simultaneous linear equations can be solved by Gauss-Jordan reduction or other methods [18] to yield the best (in the least squares sense) values for C, D, and E.

Combining the data of Gridnev [16] and Cocks and Radzinski [17] for the ternary Cu-Ni-Al system with data of Owen and Pickup [19] and Coles [20] for the Cu-Ni system and with data of Obinata and Wasserman [21] for the Cu-Al system gives sixteen points covering the ternary Cu-Ni-Al system from pure Cu up to 14.9 at. % Al and up to 13.70 at. % Ni. Using these data this calculation yields the values 0.036147, 0.035156, and 0.038637Å/at. % for the constants C, D, and E, respectively. The maximum deviation of any of the experimental points from the plane defined by these constants is 0.0022Å and the standard deviation of all points from this plane is 0.00097Å. It will be noted that the constants for Cu and Al are larger and smaller respectively, than those determined previously for Al alloys containing up to 2.17 at. % Cu. This difference in the values of the linear equation constants is, however, what is to be expected from the fact that in the ternary case Cu-rich alloys are being considered while in the binary case Al-rich alloys are examined, remembering negative deviations from Vegard's law which occur in the Al-Cu system.

These values, together with Equations 5 or 6 may be used to calculate the amount of Ni and Al remaining in solid solution as a function of ageing treatment. This information would be of use in, for example, evaluating corrosion resistance as a function of ageing, and would be difficult to obtain by microprobe methods if the

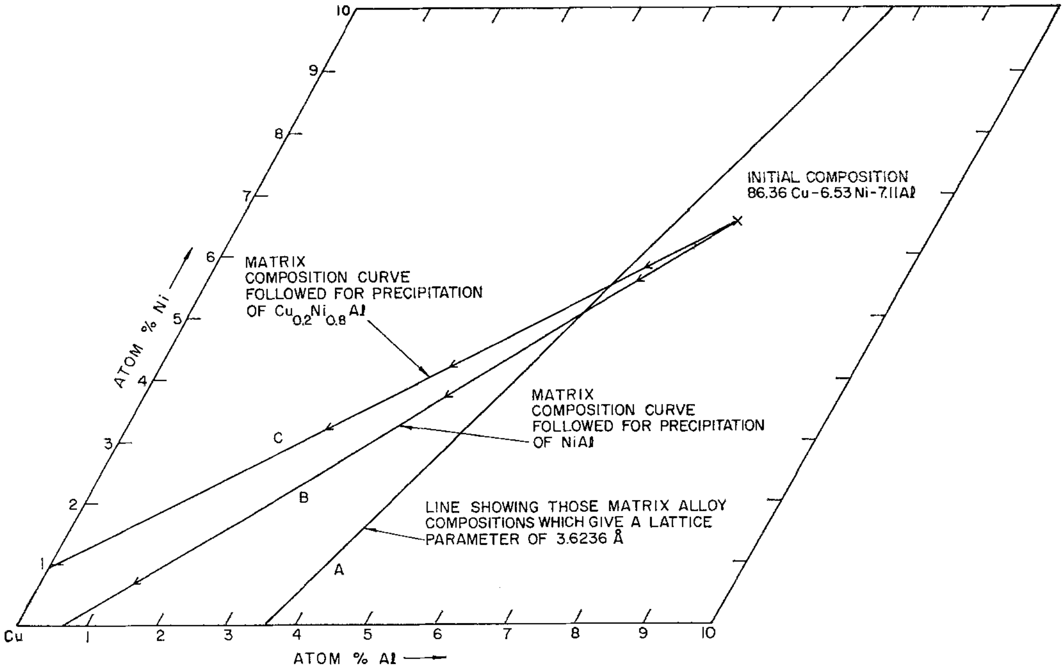

Figure 2 Section of the Cu-Ni-Al composition triangle showing (curve A) those compositions having the lattice parameter shown together with (curves C and B) the average solid solution compositions formed during the precipitation of $Cu_{0.2}Ni_{0.8}Al$ and NiAl.

interparticle spacing is small, as it is in this system for alloys aged at 500°C [22].

Consider the observation that, after ageing at 500°C for 1160 min, the lattice parameter of 6.53 at. % Ni – 7.11 at. % Al-balance Cu alloy decreased from its value of 3.6259Å in the solution heat-treated condition (850°C for 1 h followed by water quenching) to a value of 3.6236 Å [17]. Substitution of these composition values into Equation 5 together with the values of C, D, and E just given, yields a lattice parameter value of 3.62593; hence indicating that, as expected, the lattice parameter for the case of the solution heat-treated condition is in agreement with that predicted from Equation 5. On the other hand, the value of 3.6236Å for the aged alloy, in conjunction with Equation 5 defines an isoparameter line in composition space of possible matrix solid solution alloys which could remain after precipitation. This is shown as curve A in Fig. 2. Some of these compositions are, of course, not allowed since they include alloys which contain more Cu, or Ni, than were contained in the original alloy. With this restriction, it can be seen that all possible remaining compositions are substantially depleted in Al with respect to the original alloy.

It is also possible to trace out the paths which would be followed if the precipitate formed was that indicated by possible phase relations in this system. Examination of the ternary Cu-Ni-Al phase diagram data of Bradley and Lipson, [23] together with that of Alexander [24], indicates that the expected precipitate is NiAl containing dissolved Cu to give a phase of the form $Cu_xNi_{1-x}Al$. For each precipitate composition (assumed to remain constant during precipitation), it is possible to calculate the path in the composition triangle which would be followed by the matrix as the removal of material from solid solution altered the remaining matrix composition. These paths have been calculated for two precipitate compositions, $Cu_{0.2}Ni_{0.8}Al$ and NiAl and are shown in Fig. 2 as curves C and B, respectively. The intersections of these curves with curve A define the compositions which the matrix alloy would have in each case at the point in the precipitation reaction at which the lattice parameter was measured. By comparison with the starting composition, the fraction of Ni and

Al removed from solid solution may also be calculated. Because the line defined by the value of the lattice parameter of the aged alloy covers only a relatively small range of aluminium compositions, it makes relatively little difference to the final Al composition of the matrix alloy whether or not NiAl or $Cu_{0.2}Ni_{0.8}Al$ is considered to be the precipitate phase. If NiAl is formed, the matrix of the aged alloy will retain about 5.6 at. % Al, whereas if $Cu_{0.2}Ni_{0.8}Al$ forms, about 5.8 at. % Al will be retained. On the other hand, the residual Ni content can vary from about 5 to about 5.5 at. %. If the composition of the precipitate were determined, for example, by extraction and chemical analysis, then the residual composition of the matrix could be precisely determined. This could also be found, of course, if the precipitate could be completely extracted and weighed, but it would be difficult to be sure in such a case that none of the precipitate had been lost during the extraction process. In conjunction with the present method, however, it would only be necessary for such extraction to be qualitative in order to determine closely the residual composition of the matrix.

2.3 Quaternary Cu-Zn-Ni-Al alloys

In the cases just considered, we have utilized available phase diagram information in conjunction with lattice parameter data to determine the composition of the matrix alloy after ageing to the point of maximum hardness. We now consider the case of a quaternary alloy of the form Cu-Zn-Ni-Al, where definitive phase diagram information is not available. In this case, we will show how it is possible by means of lattice parameter measurements made as a function of ageing time, as well as measurements made on a series of solution heat-treated alloys, to develop information on the composition of the precipitate phase without the necessity of invoking any phase-equilibrium information.

As before, let the lattice parameter of the alloys in their solution heat-treated condition be represented as a function of composition by:

$$\mathrm{LP} = C\mathrm{Cu} + D\mathrm{Ni} + E\mathrm{Al} + F\mathrm{Zn} \qquad (12)$$

where Cu, Ni, Al, and Zn represent the atomic percentages of these elements and *C*, *D*, *E*, and *F* are constants. Using the data of Cocks and Radzinski [17] and the method described for the ternary case, the constants *C*, *D*, *E*, and *F* may be calculated to be 0.036579, 0.034026, 0.038984, and 0.037026 Å/at. %, respectively. The maximum deviation of any experimentally determined value from that calculated using these constants and Equation 12 is only 0.0007 Å, as shown in Table I. These alloys covered the composition range from 68 to 78 Cu, 19 to 23 Zn, 1 to 7 Ni, and 2 to 5 Al. All of the alloys within this range were strongly age-hardenable, and it was found in every case that the room-temperature lattice parameter decreased by ageing at 500°C [17]. Solution heat-treatments were carried out above 800°C, followed by water quenching. The aim then is to apply Equation 12, with the constants *C*, *D*, *E*, and *F* known, to these observed lattice parameter decreases during ageing in order to determine what information can be deduced concerning the average composition of the precipitate(s) which occur in this system.

Since this is a quaternary system, it is possible to calculate the change in lattice parameter to be expected from the removal of any of the four components from solid solution under the condition that the atomic percentages of any two of the other components remain constant. These expected changes may be readily computed from the twelve partial derivatives which are similar to:

$$\left.\frac{\partial \mathrm{LP}}{\partial \mathrm{Cu}}\right)_{\mathrm{Zn,\,Al}} = -\left.\frac{\partial \mathrm{LP}}{\partial \mathrm{Ni}}\right)_{\mathrm{Zn,\,Al}} = C - D$$
$$= +\,0.00255\,\text{Å/at.}\,\%\,. \qquad (13)$$

It must be remembered that it is the negative of each such partial derivative which shows the expected initial change in lattice parameter per atomic percentage of the element removed by precipitation. Since the precipitate can be expected to be composed of more than one element, it is more informative to compute the change in lattice parameter to be expected from the precipitation of a given compound. Since both Cu-Zn-Ni, and Cu-Zn-Al alloys of the approximate compositions being considered here for Cu-Zn-Ni-Al alloys are not significantly age-hardenable, it is reasonable to expect that the precipitate will contain both Ni and Al. Four possible precipitates are Ni_3Al, NiAl, Ni_2Al_3, and $NiAl_3$. The changes in lattice parameter to be expected from the removal of these compounds from solid solution (at constant Zn concentration) are given by (in Å/at. %):

$$-\left.\frac{\partial \mathrm{LP}}{\partial \mathrm{Ni_3Al}}\right)_{\mathrm{Zn}} =$$
$$-\,3D - E + 4C = +\,0.00525 \qquad (14a)$$

$$-\left.\frac{\partial \mathrm{LP}}{\partial \mathrm{NiAl}}\right)_{\mathrm{Zn}} = -D - E + 2C = +0.00015 \qquad (14b)$$

$$-\left.\frac{\partial \mathrm{LP}}{\partial \mathrm{Ni_2Al_3}}\right)_{\mathrm{Zn}} = -2D - 3E + 5C = -0.00211 \qquad (14c)$$

$$-\left.\frac{\partial \mathrm{LP}}{\partial \mathrm{NiAl_3}}\right)_{\mathrm{Zn}} = -D - 3E + 4C = -0.00466 \qquad (14d)$$

Furthermore, by allowing the zinc to vary, the initial rate of change in lattice parameter with respect to the precipitation of ternary compounds can be calculated similarly. Examination of the ternary Cu-Ni-Al system data of Bradley and Lipson [23] shows that Ni_3Al, NiAl and Ni_2Al_3 can each dissolve sufficient Cu to become $CuNi_2Al$, $Cu_{0.5}Ni_{0.5}Al$, and $CuNiAl_3$. $NiAl_3$ dissolves only relatively small amounts of Cu. There also exists a ternary phase at the composition Cu_3NiAl_6 in the Cu-Ni-Al system. The expected initial change in lattice parameter on precipitation would be in these cases:

$$-\frac{\partial \mathrm{LP}}{\partial(\mathrm{CuNi_2Al})} = -C - 2D - E + 4F = +0.00449$$

$$-\frac{\partial \mathrm{LP}}{\partial(\mathrm{Cu_{0.5}Ni_{0.5}Al})} = -0.5C - 0.5D - E + 2F = -0.00023$$

$$-\frac{\partial \mathrm{LP}}{\partial(\mathrm{CuNiAl_3})} = -C - D - 3E + 4F = -0.03945$$

$$-\frac{\partial \mathrm{LP}}{\partial(\mathrm{Cu_3NiAl_6})} = -3C - D - 6E + 10F = -0.00741$$

These calculations show that initially, the precipitation of both Ni_3Al and NiAl would lead to an increase, not a decrease, in lattice parameter. Furthermore, even if sufficient copper were dissolved into the Ni_3Al to form $CuNi_2Al$, the precipitation of this compound would still lead to an increase in the lattice parameter of the remaining matrix solid solution. In the case of NiAl, however, the inclusion of sufficient copper to form $Cu_{0.5}Ni_{0.5}Al$ would mean that precipitation of this compound would led to a decrease in matrix lattice parameter.

This calculation can still be carried one step further. As in the Cu-Ni-Al case, assume in turn that each of the compounds whose formation is thought to be possible precipitated to the extent that one or more of the elements required for its formation is entirely consumed. Then, using Equation 12 and the calculated composition of the remaining solid solution, the lattice parameter of this solid solution can readily be calculated. If this lattice parameter is greater than that actually measured for the aged alloy, then the average composition of any precipitate phases which might have formed cannot be equal to the assumed precipitate composition. On the other hand, if the composition calculated for the given residual matrix via the use of Equation 12 gives a lattice parameter that is lower than the value measured for the aged alloy, then the assumed precipitate composition is possible. This consideration does not prove, of course, that the assumed precipitate did in fact form, only that its formation is or is not inconsistent with the observed lattice parameter changes.

These considerations are illustrated in the case of the Cu-Zn-Ni-Al system by the data in Tables I and II. Table I shows the alloy compositions and lattice parameters measured in the solution-heat treated state [17], as well as lattice parameter values calculated using Equation 12 and the values for C, D, E, and F just given.

Table II shows the lattice parameter values which were calculated for each alloy, assuming that in each case the precipitate indicated formed to the maximum extent possible. These calculations were made taking into account not only the loss of material from solid solution due to precipitation, but also the increase in atomic percentage of the remaining elements due to the fact that the total quantity of elements present in solid solution had decreased. If the lattice parameter which is calculated assuming total precipitation of a particular precipitate composition is, in this case, higher than that actually observed, then it is clear that precipitate composition which was assumed could not account for the observed lattice parameter change. Thus, referring to Table II, it may be seen that for all alloys the precipitation of Ni_3Al, $CuNi_2Al$, and NiAl cannot give rise to the observed lattice parameter changes. In the case of alloys 1, 2, and 3, the precipitation of Ni_2Al_3 could not give rise to the observed lattice parameter changes, while for alloys 3 and 4 the observed lattice parameter changes are less than that which would be expected from the complete precipitation of Ni_2Al_3 Hence, in the case of these latter two alloys, this precipitate composition may or may not have occurred. Similarly, in the case of the other

TABLE I Quaternary alloy compositions and lattice parameter (LP) data [17]

Alloy no.	Cu	Zn	Ni	Al	Measured LP of solution heat-treated alloy	LP calculated from (Equation 12)
1	Balance	19.31	0.95	1.97	3.6688	3.6688
2	Balance	20.48	3.68	2.32	3.6634	3.6632
3	Balance	22.19	2.82	6.31	3.6752	3.6758
4	Balance	21.33	4.43	6.59	3.6727	3.6720
5	Balance	19.45	7.15	5.03	3.6601	3.6604

TABLE II Lattice parameters (LP) for residual matrix compositions of the Cu-Zn-Ni-Al alloys of Table I calculated on the assumption that for each alloy the compounds indicated formed to the greatest extent possible. (Also shown are the lattice parameters measured for the alloys in the aged condition.)

Alloy no.	Measured LP for the aged alloys [17]	Calculated LP assuming complete precipitation of the indicated compounds							
		Ni_3Al	$CuNi_2Al$	$NiAl$	$Cu_{0.5}Ni_{0.5}Al$	Ni_2Al_3	$CuNiAl_3$	Cu_3NiAl_6	$NiAl_3$
1	3.6661	(3.6707)	(3.6704)	(3.6684)	(3.6670)	(3.6681)	3.6654	3.6668	3.6658
2	3.6613	(3.6683)	(3.6675)	(3.6618)	3.6608	(3.6618)	3.6596	3.6583	3.6597
3	3.6734	(3.6816)	(3.6809)	(3.6773)	3.6713	(3.6740)	3.6667	3.6639	3.6671
4	3.6701	(3.6811)	(3.6799)	(3.6741)	3.6657	3.6682	3.6622	3.6591	3.6621
5	3.6574	(3.6746)	(3.6718)	(3.6615)	3.6544	3.6586	3.6522	3.6498	3.6523

precipitate compositions shown in Table II, it may be seen that in each case the lattice parameter changes which would be expected from the maximum possible precipitate formation would give rise to a lattice parameter change greater than that which is observed. Therefore, the formation of a smaller fraction of any of these precipitates could account exactly for the observed changes in lattice parameter. These data do not provide, of course, any means for deciding which of the possible precipitates did, in fact, form.

This method of precipitate identification by elimination clearly will be most applicable to those systems where a large change in lattice parameter results from a small change in solid solution composition. An extensive collection of data exists on the lattice parameters of binary and higher systems [15], along with tabulations of size-factors based on the initial slopes of lattice parameter versus composition relationships, for both substitutional and interstitial solid solutions [2, 4, 14]. Thus, an assessment may possibly be made in advance as to whether or not significant lattice parameter changes are to be expected during the course of precipitation in particular systems.

3. Summary

Over limited ranges of composition, many solid solutions can be assumed to have lattice parameters which vary approximately linearly with composition. The constants which relate these lattice parameters to each component element of the solid solution may be calculated from lattice parameter values measured using alloys of known composition in the solution heat-treated condition. If precipitation of a second phase occurs during subsequent ageing of these alloys, the composition of the remaining solid solution will change. In the case of binary alloys, the lattice parameter measured for such an aged alloy gives directly both the composition of the remaining solid solution, as well as, by difference the average composition of the phase or phases which precipitate. In the case of ternary alloys, the allowed composition is a multivalued function of the lattice parameter. If, however, only a single phase precipitates and the composition of this phase is known, then the measurement of the lattice parameter after ageing will give uniquely the composition of the remaining solid solution alloy. This information may be difficult to obtain by other means if the precipitate spacing is small, yet is of value in many applications, e.g. corrosion and oxidation studies. If more than one phase precipitates and the ratio in which they form is not known, then the composition of the remaining solid solution can only be stated to lie within certain limits. In the case of quaternary alloys, it is shown that the determination of linear lattice parameter versus composition functions, together with the measurement of the lattice parameter changes which occur during ageing, may be used to show that certain average precipitate compositions are not possible. Thus, this method provides a necessary but not sufficient condition which may be used to make tentative identification of precipitate phases by inference.

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Appendix

As written, Equation 1 is equivalent to the zeroth and first order terms of the Taylor series expansion of the lattice parameter versus composition function about an arbitrary initial composition $x_0^1, x_0^2, \ldots x_0^k$, where each superscript denotes one of the component elements and $\sum x_0^k = 1$. For a binary system the complete Taylor series expansion can be written as

$$\mathrm{LP}_n(x) = \mathrm{LP}(x_0) + \frac{\mathrm{d}(\mathrm{LP}(x_0))}{\mathrm{d}x}\frac{(x - x_0)}{1!} + \frac{\mathrm{d}^2(\mathrm{LP}(x_0))}{\mathrm{d}x^2}\frac{(x - x_0)^2}{2!} + \cdots + \frac{\mathrm{d}^n(\mathrm{LP}(x_0))}{\mathrm{d}x^n}\frac{(x - x_0)^n}{n!} + \; + R_n(x, x_0)$$

Comparing this expression with Equation 4 shows that

$$\mathrm{LP}(x_0) = 100A\,, \tag{3A}$$

$$\frac{\mathrm{d}(\mathrm{LP}(x_0))}{\mathrm{d}x} = B - A\,, \tag{4A}$$

and thus that in Equation 4 x is the atomic percentage of Cu and $x_0 = 0$ (pure aluminium). Equivalent expressions can be derived for the case of Cu-Ni-Al or Cu-Zn-Ni-Al alloys by considering similar Taylor series expansions for two and three independent variables, respectively [25]. In the binary case, the remainder $R(x, x_0)$ introduced by terminating the Taylor series expansion for the lattice parameter versus composition function after the second term is given by

$$R(x, x_0) = \frac{\mathrm{d}^2[\mathrm{LP}(x_\mathrm{c})]}{\mathrm{d}x^2}\frac{(x - x_0)^2}{2!}$$

where, by the Cauchy mean value theorem, x_c lies between x_0 and x. Thus, the error in the linear lattice parameter versus composition approximation, Equation 4, is seen to be proportional both to the square of the composition range $x - x_0$, and to the second derivative of the true lattice parameter versus composition function. Therefore, in alloy systems such as Cu-Mn in which the true lattice parameter versus composition function can have a large second derivative, the range over which the linear lattice parameter versus composition approximation is valid will be reduced In addition, the matrix composition range over which this approximation is applied should not bracket any phase boundaries since the derivative of the true lattice parameter versus composition function changes discontinuously at such boundaries.

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