COMMEMORATIVE LECTURE BY THE FORTY-SECOND GOLD MEDALIST OF
THE JAPAN INSTITUTE OF METALS

On the Small Atomic Clusters Dispersed in Solids†

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Small dispersed clusters of foreign atoms or a foreign structure in the mother phase, appearing as a precursor or a remnant of phase transformation, are treated by a statistical thermodynamic calculation. The entropy of mixing of the clusters and uncluttered atoms is formulated and combined with the enthalpy change associated with the cluster formation to find the equilibrium or quasi-equilibrium state of the dispersion of small particles. It is applied to the cases of the medium range order structure in amorphous alloys, the precursory premartensitic structure, the early stage of aging and precipitation in alloys, etc. It is concluded that the entropy of mixing of small atomic clusters in the matrix plays an important role in the appearance of very fine dispersed structure prior to and/or after various types of phase transformations of metals and other solid materials.

Keywords: configurational entropy, entropy of mixing, atom clusters, short and medium range order, statistical thermodynamics, Guinier-Preston zone, amorphous structure, embryo, nucleation, ω-phase transformation, martensite transformation, tweed pattern

I. Introduction

It is the present author’s great honour to be awarded with the forty-second Gold Medal of the Japan Institute of Metals. When he was young, he was very fortunate to be able to study metal physics under the guidance of excellent teachers in different laboratories, and later, he was fortunate again to meet many brilliant younger people in and around his own laboratory. From this experience he believes that good scientific creations and contributions are produced not by an isolated single person but bred in a good atmosphere of people’s group or cluster. Therefore, he wishes to share the present honour with all the persons in the clusters to which he has ever belonged. From other recollections and experiences in his study life, the present author also believes that creations and good contributions always arise not from the quick understanding of complicated things but from the basic understanding of simple and fundamental matters.

In selecting the subject of the present memorial lecture, the author thought about the above mentioned beliefs that scientific creations arise from clusters and at the same time from basic understanding of simple matters, and, accordingly, decided to talk about the clusters in a basic way. The clusters in this presentation are not meant by the human clusters but those of foreign atoms contained in solids and the basic way means that the author will develop his own theory with fundamental description. This would be different from what people expected from him: He could have chosen another popular and exciting subject from his experienced fields of physical metallurgy, such as Mössbauer spectroscopy, electron microscopy, amorphous metals, dislocation theory, radiation damage or martensitic transformation. The author wishes, however, to keep up with his own philosophy mentioned above by confining the subject to a rather narrow and fundamental problem, the atom clusters dispersed in solids, and using rather simple and fundamental descriptions, which might ask the readers’ tolerance and patience.

II. The Basic Idea of the Study

Small atomic clusters of a certain species and/or a certain structure different from those of the mother phase are often observed in the form of dispersed very small particles in the matrix. In some cases, they fluctuate time-wise and space-wise, appearing and disappearing, and in other cases, they are static, showing no fluctuations at all. Such an extremely fine dispersed structure wouldn’t always attract many metallurgists’ attention. However, if one considers any heterogeneous structure appearing in the materials he is dealing with, he may automatically imagine a dispersed state of very small particles, for instance, in age hardening alloys, liquid metals, crystallizing glass, amorphous alloys, β-phase (shape memory) alloys or nano-phase materials. By further extension of the picture, one would imagine similar structures, for

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instance, in quenched and tempered carbon steel, metallic multilayers, various magnetic materials, dispersion hardening alloys and ceramics, etc.

Spontaneous appearance of the fine dispersed structure in a material is undoubtedly due to the reduction of free energy, and the process is carried by the driving force. The probability or the frequency of appearance of nuclei of the fine particles has been treated by the theory of nucleation\(^\text{[1]}\). Another accompanying important factor to control the process is the diffusion rate. Nevertheless, the theory of nucleation treats the problem from the non-equilibrium (or quasi-equilibrium) state, such as the super cooled state, and the process to reach the final configuration of dispersed small particles is treated also kinematically by the theory of growth, both of which cannot always manage the thermal equilibrium state of the cluster distribution actually often observed.

For instance, although it is still controversial whether the GP-zone (Guinier-Preston zone)\(^\text{[2]}\) appearing in the early stage of aging of light alloys is a real first quasi-stable precipitation or not, they are undoubtedly the small foreign atom clusters, generation and distribution of which are difficult to be dealt with by the theory of nucleation; GP-I of the Al–Cu alloy system consists of one or two layer platelets of Cu atoms, to which rigorous application of the volume energy and the surface energy defined in the nucleation theory is difficult. There is no observation of the so called critical size, and their sizes and numbers seem to be determined by the aging temperature or by the thermal equilibrium condition. In addition, they disappear above a certain temperature before a real precipitate phase appears at a higher temperature, which is called the reversion and rather easy to understand as a thermal equilibrium configuration.

Crystalline nuclei or embryos in the solidification process could also be considered as a thermal equilibrium or a quasi-equilibrium existence since they exist continuously from above to below the solidification point. Many experimental evidences show that there are already a large number of small atomic clusters which have a short range or a medium range pseudo-crystalline order. The chemical and medium range order structure found in amorphous alloys obtained by rapid quenching from liquid must be closely related with the crystalline embryos in liquids and super-cooled liquids\(^\text{[3]}\). Instead of combining the ordinary theory of fluctuation and that of nucleation, it is attempted in the present paper to analyze and explain the above problem in terms of the free energy criterion in thermal equilibrium or quasi-equilibrium conditions.

One more clear case of the small clusters in thermal equilibrium in solid is found in the premartensitic phenomenon of the $\beta$-phase alloys. Far above the transformation temperature, $M_s$, a precursory martensite-like structure appears as the static dispersed small particles, which can be observed in the electron microscope due to the clear strain image contrast associated with and named as the tweed structure\(^\text{[4]}\).

To understand the above examples of static small atom clusters dispersed in the mother phase\(^\text{[5]}\), it seems to be necessary not to employ the ordinary theory of nucleation but to develop a new statistical theory in thermal equilibrium condition as a renewed starting point. For that purpose, the configurational entropy and free energy of the system of the small dispersed clusters in a matrix must be considered. The theory to be developed in this paper, however, will not be always applicable to all the systems containing small particles, which frequently appear in natural and useful artificial materials. For instance, in the dispersion-hardening composite materials, there are undoubtedly small particles dispersed in the matrix phase, but they must be excluded from the application of the present statistical thermodynamic theory, because the dispersed particles artificially mixed in the materials are far from thermal equilibrium and their sizes are too large and their numbers are too small.

### III. Configurational Entropy of Clusters

The configurational entropy of mixing of the atoms of two species is given by

$$S = - R \left( c \ln c + (1 - c) \ln (1 - c) \right),$$  

(1)

where $c$ is the concentration of one component and $R$ the gas constant, as is well known. Any configurational change from this random mixture, such as ordering, clustering, separation and others, reduces the entropy. However, when only a single species exists in the beginning (or even when different species with unaltered mixed configuration coexist), sudden appearance of local small clusters of a different phase will produce a new configurational entropy. Simple examples are; formation of small crystallites in liquid before or in the process of solidification and starting of a phase transformation in the form of dispersed small particles in the mother phase.

Consider the number of ways $w$ to make $n$ small clusters with a certain structure and a certain size, consisting of $i$ atoms each, randomly in a condensed matter containing $N$ atoms in total. After making $(p-1)$ clusters, $N-i(p-1)$ ways are possible to assign the position of the first atom of the $p$-th cluster among the unclustered atoms. The possibility to place the neighbouring second atom associating with the first one is $\{1-i(p-1)/N\}$, since $i(p-1)/N$ gives the probability that the considered atomic site is already occupied by another cluster’s atom. By associating successively the third, fourth atoms and so on for $(i-1)$ times more, the $p$-th cluster will be completed. Accordingly, the number of ways to form the $p$-th cluster is

$$w_p = \left\{ \left. N - i(p-1) \right\} \left\{ 1-i(p-1)/N \right\}^{i-1} \right\}^{-1} \xi$$

$$= (i\xi/N^{i-1}) \left\{ N/\left( N-(p-1) \right) \right\}^i$$  

(2)

where $\xi$ is the number of shape diversity of the cluster: If the cluster can take various shapes as a flexible chain polymer does, $\xi$ will be a large number, and, if it has a solid shape like a small spherical precipitate, $\xi$ will be almost unity. By taking account of the flexibility of thin clusters, the equation will lead to Flory’s calculation for
the entropy of mixing of polymer solution\(^{(7)}\). However, in the present case, \(\xi\) will stay at a very small number since any complicated shapes of the clusters are not considered. Any change of the order in the assignment of atoms will not result in a different configuration of the cluster, so that this variety does not come into the number of ways in the calculation as well. Therefore, the configurational entropy arising from the number of ways of  

distribute \(n\) clusters in the matrix is  

\[
k \ln W = k \ln \left\{ \frac{(1/n)}{\prod_{p=1}^{n} w_p} \right\}  
\]

\[
= k \left\{ \left(\frac{n! \xi^n}{(n/N)^n(i-1)} \right) \times \left(\frac{(N/i)!}{(N/i-n)!}\right) \right\}  
\]

\[
= k \left\{ -n \ln \left(\frac{n/N}{N-ni}\right) - (N-ni) \ln \left(\frac{(N-ni)/N}{\xi}\right) \right\}  
\]

\[
+ n \ln \xi - n(i-1) \right\}  
\]

(3)

where \(k\) is the Boltzmann’s constant. Using the concentration of the clustered atoms, \(c=ni/N\), and gas constant \(R\) instead of \(k\), as in eq. (1), the configurational entropy of the dispersed clusters of the size, \(i\), and the total concentration, \(c\), is written as\(^{(6)}\)

\[
S = -R \left[ \frac{c(i)}{i \xi} \ln \left( \frac{c(i)}{i \xi} \right) + (1-c) \ln \left( 1-c \right) + c(1-i^{-1}) \right].  
\]

(4)

This equation has some characteristic features: Firstly, by putting \(i=1\), it reduces to the ordinary entropy of mixing, eq. (1), and by increasing the size \(i\), \(S\) becomes smaller as a whole with gradual shift of the maximum point from \(c=0.5\) to the smaller values of concentration, as Fig. 1 shows. For instance, for \(i=20\), its maximum is found at around \(c=0.25\) and the value is 0.055R, which is about a tenth of the maximum value, 0.693R, of eq. (1). Such a small value of entropy for a large number of \(i\) seems to be useless in actual applications: An entropy one or two order of magnitude smaller than that of eq. (1) would be negligible in the contribution to Gibbs’ energy, \(G=H-TS\), comparing with the enthalpy, \(H\), and usually the phenomenon would be fully controlled by the latter. However, as will be seen later, when the temperature, \(T\), is high enough or the enthalpy \(H\) is comparably small as \(TS\), the entropy of eq. (4) will play an important rôle. Another problem with eq. (4) is that it is asymmetrical, as shown in Fig. 1, \(S\) decreasing from a maximum with increasing \(c\) to overshoot finally to below zero, which is certainly improper. Nevertheless, this arises from somewhat insufficient assumption in the above calculation, and the actual value of \(S\) will gradually reach zero, as a small additional bent to the curve for \(i=20\) shows. The reduction of \(S\) to zero at a certain value of \(c\) can be explained as follows: By putting clusters one by one in possible spaces of the matrix lattice, there will be less and less rooms for accepting them and finally the structure will be densely packed, where no freedom for selection of places for clusters, that is no other than the state of \(S=0\). Formulation of the equation will be further extended to make some more variations for actual applications.

In Figs. 2 are schematically shown different ways of distribution of clusters with various sizes. Figure 2(a) shows a random mixture of atoms of two species, just corresponding to eq. (1), and in Fig. 2(b) are the dispersed clusters with the same simple shape and size, containing \(i\) atoms each, the configurational entropy of which is given by eq. (4) where \(\xi\) is nearly unity. In the case of solidification or transformation of single component materials, the state of Fig. 2(b) can appear as the dispersion of embryos, irrelevant to Fig. 2(a), and the entropy of eq. (4) increases. In each crystalline embryo in solidification, there will be a decrease of another sort of entropy nearly corresponding to the entropy of fusion with the opposite sign, which is competitive with the above mentioned configurational entropy increase. In the case of the transformation of alloys, in which the alloy concentration or the degree of ordering becomes different between the matrix and the clusters, the configuration shown by Fig. 2(a) will be concerned and the calculation will be more complicated. In the present paper, however, such a redundant case will not be considered.

On the other hand, in the case of aging and precipitation of alloys, the situation will not proceed directly from Fig. 2(a) to Fig. 2(b), but pass through or even end up in the configuration of Fig. 2(c), where the solute atoms of concentration \(c\) are not fully clustered but only by the amount \(c_s\), and \((c-c_s)\) still remains in solution as the unclustered. In order to calculate the configurational entropy for that, first the clusters with the size \(i\) and concentration \(c_s\) are distributed in the whole body, and then scattered are the remnant solute atoms of the concentration \((c-c_s)\) in the still available space. The result is\(^{(6)}\):

\[
S = -R \left[ \frac{(c)}{i \xi} \ln \left( \frac{c}{i \xi} \right) + (c-c_s) \ln \left( c-c_s \right) \right]  
\]

\[
+ (1-c) \ln \left( 1-c \right) + c_s(1-i^{-1}) \right\}  
\]

(5)

A further extension of calculation to the case of Fig. 2(d), where isolated solute atoms and clusters of various sizes coexist, can be done by distributing the clusters of different sizes from \(i=1\) to \(q\) in due order as in the above calcu-
Fig. 2. Different modes of distribution of foreign atoms and/or foreign phase clusters. (a) uniform solid solution, (b) clusters of the same size and shape, (c) isolated foreign atoms and their clusters of the same size and shape, (d) clusters of different sizes co-existing.

The result can be written as:

$$
S = -R \left[ \sum_{i=1}^{g} \left( c_i / i \right) \ln \left( c_i / i \xi_i \right) + \sum_{i=1}^{g} c_i (1 - i^{-1}) \right] \\
+ \sum_{i=1}^{g} \left[ c_i (1 - i^{-1}) \ln \left( 1 - \sum_{i=1}^{g} c_i \right) \right] \\
+ \left( 1 - \sum_{i=1}^{g} c_i \right) \ln \left( 1 - \sum_{i=1}^{g} c_i \right)
$$

(6)

The stability of each configuration shown in Figs. 2 will be checked by finding the enthalpy change associated with the cluster formation, $\Delta H$, and making the change of Gibbs’ energy, $\Delta G = \Delta H - T \Delta S$, to obtain the energy minimum condition.

IV. Medium Range Order in the Melt and Amorphous Structure

As the first example of application of the above calculation, let us consider the medium range order in molten metals and amorphous materials obtained by rapid cooling of the melt. The picture that not only the short range order but there also exist the small clusters with crystalline order has been generally considered, supported by some experiments by X-ray diffraction, thermal analysis, etc. and treated theoretically. Especially, from the electron microscopical observations of the medium range order in rapidly quenched amorphous alloys, an outline of the process that, small atomic clusters with the crystalloid order may appear and disappear dynamically in the melt in thermal equilibrium, grow in the size, density and stability during supercooling, and finally remain as the dispersed small crystallite particles in the frozen structure below the glass point, can be figured out. Introduction of the experimental facts and discussion on their compatibility with the dense random packing structure have been given elsewhere, and, in the present paper, whether or not the ordered small clusters can exist as a thermal equilibrium entity in the disordered condensed matter (liquid or solid) will be discussed from the viewpoint of statistical thermodynamics.

When the small clusters of a size, $i$, a concentration, $c_i$, and a pseudo-crystalline structure are formed in the melt, the increase of configurational entropy will be given by eq. (4). If each cluster has a degree of order so high as to be almost regarded as a crystalite, it may have an enthalpy change, $\Delta H'$, comparable to the heat of fusion, $\Delta H_m$, and an entropy change, $\Delta S'$, comparable to the entropy of fusion, $\Delta S_m$. In the real solidification to produce the crystalline materials, the relation,

$$
\Delta H_m - T_m \Delta S_m = 0,
$$

(7)

is given at the solidification temperature, $T_m$, above which the free energy of the melt is lower than that of the crystal and below which it is reversed. For each cluster, the free energy change measured from the mother melt, $-(\Delta H' - T \Delta S')$ will be also reversed when passing through a certain temperature, $T_r$. It must be noted that this characteristic temperature is not as definite as $T_m$. 
since both of $\Delta H'$ and $\Delta S'$ must be size dependent. Taking consideration of the above mentioned, and employing eq. (4), the Gibbs' energy change by the appearance of the crystalline embryos, each consisting of $i$ atoms and having the concentration, $c=n_i/N$, can be expressed as

$$\Delta G = -c(\Delta H' - T\Delta S') + RT\left[\frac{c}{i} \ln \left(\frac{c}{i}i\right)\right] + (1-c)\ln(1-c)+c(1-i^{-1}).$$  (8)

From the free energy minimum conditions, $\partial \Delta G/\partial c = 0$ and $\partial \Delta G/\partial i = 0$, thermal stability of the dispersed pseudo-crystalline particles in the melt can be investigated. The $i$ dependence of $\Delta H'$ and $\Delta S'$ are not easy to define nor to determine, because it includes the problems of the boundary energy, the relaxation time of formation and dissolution and the volume expansion or contraction of the surrounding matrix. From a simple consideration on the change of the bond number with the increasing size of the cluster, $\Delta H'$ is expected to increase with $i$, the rate of the increase, on the other hand, decreasing with the increasing $i$, and finally $\Delta H'$ will gradually reach $\Delta H_m$ when $i$ becomes sufficiently large. Its simplest form, not far from the bond number consideration, is

$$\Delta H' = \Delta H_m\left(1-(i/i_0)^{-\tau}\right),$$  (9)

where the power $\tau$ may be assumed to be about 2 and the smallest significant size, $i_0$, may be taken as 4. $\Delta S'$ arises from the difference of degree of order and/or of the vibrational frequency between the liquid and crystalline state, but at present its $i$ dependence cannot be discussed with enough foundation. Let us tentatively assume $\Delta H_m = 5000 J/mol$ and $\Delta S' = 6.3 J/(mol \cdot K)$, although one could say that the latter's $i$ dependence may be more or less similar to that of the former. According to eq. (7), the melting temperature of this material is given as 800 K. The above values are not determined to represent any real material but employed just to visualize the basic idea of the calculation. Another important enthalpy term, especially indispensable in the theory of nucleation is the boundary energy. When $i$ is very small, however, it will become essentially indistinguishable with the boundary energies and their changes, $\Delta H'$. So that, it is not always reasonable to add a new term to represent the boundary energy when $i$ is small, but, instead, better to take it in the term of $\Delta H'$ and assume that the latter represents all the enthalpy terms and their changes. That the essential part of the surface energy arises from the deficit of the bond numbers of the outermost atoms of a condensed body, and similarly the boundary energy mainly arises from the bonding energy difference at the periphery of the collective atoms. From this point of view, it is doubtful that the surface energy term always exceeds the volume or the bonding energy term when $i$ is small, as the theory of nucleation definitely states.

To describe exactly the energy state of the inside and outside of a small cluster is difficult not only because of the above mentioned necessary considerations but also of other thinkable energies such as the boundary misfit energy and strain energy (except the liquid part). Nevertheless, for the purpose of the present theory to find the thermal stability of the dispersed state of small clusters, eqs. (8) and (9) are simply employed with some numerical assumptions mentioned above and the calculation to find the thermal equilibrium state has been done, the result of which is shown in Fig. 3. The equilibrium is actually obtained as the thick broken line on the curved surface in the three dimensional space with the temperature ($T$), the size ($i$) and the concentration ($c$) axes. With the lowering temperature, or the increasing degree of super-cooling, the equilibrium size $i$ and concentration $c$ gradually grow larger, as expected. The fragmented local order generally observed in amorphous alloys and various glass materials may be built up in this way. Especially, in the former case, cooling from the melt is so rapid that the formation of order clusters will not be able to exactly follow the thermal equilibrium but delayed in growing and finally frozen at the glass point $T_g$, below which $i$ and $c$ will stay fairly smaller than the calculated values. The dotted line on the $T-i$ plane in Fig. 3 shows the delayed growth of $i$ departing from the thermal equilibrium line (dot and dashed), which is a projection of the calculated thick broken line. In the present example of calculation, the local order structure already exists in the liquid state and the expected size $i$ ultimately reached after the delayed growth is around 20, that is the medium range order size in good agreement with observations. In the actual processes of formation, the size and the concentration of the local order will be various, depending upon the cooling rate and material's nature.

The short range order is a structure in which the chemical bonding between the central atom and its first nearest neighbours concretely exists to maintain the molecular unit structures in the otherwise disordered structure. That is the chemical short range order, like the bonding tetrahedron, SiO4 in silicate glass or the triangular prism unit, Fe6C, which is a structural component of

![Fig 3 Thermal equilibrium size (i) and concentration (c) of order clusters in supercooled liquid (and amorphous phase obtained by rapid quenching). Dotted line shows the delayed growth of the clusters.](image-url)
Fe₃C compound in iron and steel. The medium range order has a longer ordered arrangement beyond the first nearest neighbours, but still not producing the characteristic crystalline reflection lines in the X-ray and other diffraction patterns. In the present theory, the short range and medium range order are continuously treated and their thermal stability and the temperature dependence of their structure in liquid and supercooled liquid are calculated. The diffraction methods are not always suitable to determine the size \( i \) and concentration \( c \) to be compared with the theory, but, instead, the high resolution electron microscopy can be used effectively to make the quantitative observation of the local order clusters since the computer aided analysis is available to figure out their expected image contrast and determine \( i \) and \( c \).

Recently, a remarkable improvement of amorphous magnetic materials has been carried out by applying a newly developed technique, in which a heat treatment around the glass point gives rise to a long range order structure with the average grain size of 10–100 nm, that is so called the nanocrystalline structure, and high quality magnetic materials with high magnetic moment and high permeability are obtained\(^{13}\). In this crystallization process, instead of the ordinarily considered nucleus formation from perfectly random structure, the medium range order clusters may potentially work as the pre-existing nuclei to produce the superfine structure. In fact, taking account of the delayed growth of the concentration \( c = n_i / N \) and the size \( i \), the final frozen concentration could be roughly estimated to be as high as 0.1, and then the number of the order clusters would be \( n \sim 10^{20} \) mol. If all the order clusters grew to the nanocrystals, their final average size would be a few nanometer, showing that they are plenty enough to be the source of nanocrystals. It is, therefore, concluded that the nanocrystalline structure obtained by the aging at around \( T_g \) most likely arise from the medium range order structure. Since the thermal equilibrium condition for the medium range order structure has been sought in the above discussion, its change to the micro- or nano-crystalline structure at around \( T_s \) might sound somewhat contradictory. However, the supercooled state is not in real thermal equilibrium but in quasi-equilibrium, and formation of the nano structure must be regarded as a crystallization process toward the final equilibrium state not carried by the normal nucleation reaction but started and modified from the medium range order structure, which can offer an enormous number of crystalline embryos.

V. Precursor Phenomena of Thermoelastic Martensite Transformation

Martensite transformation of steel is a typical first order transformation accompanied by a large diffusionless lattice deformation, a large heat of transformation and other remarkable discontinuous changes. On the other hand, there is another type of martensite transformation in which the lattice parameter changes, the heat of transformation, the temperature hysteresis of transformation and other discontinuous changes are all small. It is called the weak first order transformation, and Ni–50%Ti alloy (CsCl type), many \( \beta \) phase (bcc) alloys, and Fe–30%Pd and other alloys which transform from fcc to bcc belong to this type. Another remarkable feature of the transformation of the latter type is that, from far above the transformation point, \( M_s \), the lattice becomes soft in the shear mode toward the main displace deformation necessary to accomplish the transformation, for instance, \((110)\{\bar{1}10\}\) shear in the case of the bcc structure. In parallel with it, a clear strain contrast similar to the tweed pattern of texture is observed under electron microscope, as is shown by a transmission electron micrograph of Fe–30%Pd alloy in Fig. 4, which is taken at a temperature more than 50 K higher than the \( M_s \) temperature. This characteristic pattern arises from the dispersed martensite embryos more or less aligned due to the strain interactions between them\(^{15}\). The size of the embryo in the centre of each contrast is estimated to be about 3 nm in diameter\(^{14}\).

Since the origin of the tweed contrast is a premartensitic structure consisting of the static martensite embryos and appearing dispersedly in the mother phase, it can be treated by the formulation of eq. (8)\(^{15}\), although it sounds like a contradiction such that the transformation already occurs partially before the transformation. An additional factor to be taken into account in the solid-to-solid transformation is the strain energy, even if the lattice softening would make it very small. Denoting the strain energy accompanying an embryo by \( \chi \) and using the relation, \( n = cN / i \), the total strain energy can be expressed as \( c\chi / i \) per mol. If the lattice softening reduces the modulus of rigidity to 1/10 of the original value and the volume change of the lattice is 1%, a simple calculation will give the value of \( \chi \) to be the order of \( 10^{-14} \) J or \( \sim 50 \) cal/mol. On the other hand, the heat of transformation, \( \epsilon \), will be as small as 100 cal/mol in the thermola-

![Fig. 4 A transmission electron micrograph of tweed structure of Fe-30%Pd alloy 50 K above the martensite transformation temperature.](image-url)
tic case, and if the transformation point is assumed to be 300 K as is the case of Fe-30%Pd, the entropy change, \( \phi \), will be as small as 1.4 J/(mol·K) = 0.33 cal/(mol·K).

Since the above-mentioned quantities typical of the thermoelastic transformation are all one order of magnitude smaller than in the ordinary first order transformation, the configurational entropy of dispersed clusters (embryos) may play a leading role even at low temperatures around 300 K where the transformation takes place in the present case. Summing up all the parameters mentioned above, the Gibbs' energy change associated with the emergence of the tweed structure, which is in reality the dispersed static martensite embryos, can be written as

\[
\Delta G = -c(e - T\phi) + c_i x / i + RT \left[ \ln \left( c_i / i \right) + c(1 - c) \ln (1 - c) - c(1 - c) \right] .
\]

In the strong first order solid to solid transformations, such as the martensite transformation of ordinary steel, the large enthalpy change and strain energy will prevail over the configurational entropy, giving no precursor phenomenon, but in the weak first order transformation as is the present case, the latter becomes influential enough to give rise to the appearance of the tweed structure. An example of calculation employing the above mentioned values of the included parameters is shown in Fig. 5. Since the precise calculation to find the ultimate thermal equilibrium state is not fully developed yet, the trajectory of energy minimum is not shown in the \( T-i-c \) diagram, but, instead, the \( T-c \) diagram with various fixed values of the size \( i \) shows that the tweed structure may already appear at a temperature more than 100 K higher than the transformation temperature, \( M_s \). From the electron microscopical observation, the average size of the clusters is estimated to be \( i \sim 400 \), gradually increasing with the decreasing temperature. The electron microscopy also shows that the growth of the clusters is not isotropic but mainly lateral in parallel directions to form a layered structure of thin platelets with clear twin relations, which largely reduces their own strain energy, including the strain interactions of each other. Further growth of this fine layered structure ends up in the micro twin martensite structure below the \( M_s \) temperature. Therefore, at the temperature range around \( M_s \), the calculation to find the stability of this kind of precursor structure must be a two dimensional one taking account of the strain interactions of the micro twin layers.

The weak first order phase transformation is found not only in alloys but also in other kinds of materials; for instance, in barium titanate (BaTiO₃) and other pervoskite type dielectric materials and Nb₅Sn and other A 15 type superconducting intermetallic compounds. All of them exhibit the lattice softening from far above the transformation temperature, and the precursor tweed structure has been reported although in a few cases. Therefore, in this type of transformation, the appearance of the fine dispersed clusters of the new phase may be generally expected as a precursor. The present theory is not completed yet but already shows that their transformation energy, \( c \) (and entropy, \( \phi \)), is very small, their small lattice deformation of shear type necessary for transformation has a very small strain energy, specially being aided by the lattice softening, and these enthalpy terms ultimately yield to the configurational entropy term, finally allowing the dispersed precursor structure to appear.

Interstitial carbon atoms in the fresh martensite in quenched carbon steel sometimes exhibit uneven distribution already and form clusters in the tempering process. This might be at least partially related with the above theory, but probably not be able to be treated as a thermal equilibrium state.

VI. Stability of GP Zone

As already introduced in Section II, whether or not the GP zone structure, which frequently appears in aluminium based age hardening alloys, can be considered as a thermal equilibrium existence is controversial, but here let us try to apply the present theory to this problem. The mixed state of the alloy after the solution treatment can be expressed by the normal entropy of mixing of eq. (1). When the GP-I clusters are formed, distribution of solute atoms will be the one shown in Fig. 2(c) and their configurational entropy will be given by eq. (5). The entropy change from the original solution state will be then obtained by subtracting eq. (1) from eq. (5), that is,

\[
\Delta S = -R \left[ \ln \left( c_i / i \right) + (c - c_i) \ln (c - c_i) - c \ln c + c_i (1 - i^{-1}) \right] ,
\]

where notation, \( c_i \), in eq. (5) is replaced by \( c \). This is always a decreasing quantity to increase the free energy. On the other hand, the associated enthalpy change is lowering the free energy because of the bond formation of solute atoms to make their clustering, and, from the competition of the two terms, the thermal equilibrium state of the GP-I clusters is expected. By assuming the

![Fig. 5 Temperature and size dependence of the concentration of dispersed martensite embryos.](image)
cohesive energy per one cluster as $B(i)$, the bond energy change per clustered atom is written as $B(i)/i$, which may be approximated by a certain decreasing function. As in the case of eq. (9), taking account of the ratio between the increasing number of the bonds and that of the atoms, the simplest form will be

$$B(i)/i = -q(i - i_0)/i = -q(1 - i_0 i^{-1}),$$  \hspace{1cm} (12)

where $q$ is twice as large as the bond energy. If $i_0$ is taken as 1.5, this equation well approximates the tendency of the change of the bonding per atom in the clusters, which grow two dimensionally.

In the case of platelet clusters, the strain energy arising from the difference of the diameters of solvent and solute atoms and that of their potentials, the boundary energy and the entropy difference of their atomic vibrations must be considered. The last one could be estimated from the difference of mass and bond strength, but it will not be taken into consideration since no usual theories of precipitation have treated it. In analogy with a sessile edge dislocation loop, the strain energy of a disc shaped cluster can be described as

$$E_d = \pi Db r_0 \ln (r_d/r_0),$$  \hspace{1cm} (13)

where $r_0$ is the radius of the cluster, $r_0$ the core radius of the analogized dislocation, $G$ the modulus of rigidity, $b$ the amount of the Burgers vector of the dislocation which corresponds to the difference of atomic radius of the solute and solvent, and $\nu$ the Poisson’s ratio. Denoting the area occupied by an atom on the surface of the disc cluster by $a^2$, a relation, $\pi r_0^2 = a^2 i$, is obtained and $r_d$ in eq. (13) can be replaced by $a$. The core energy of the analogized dislocation can be included in eq. (13) by selecting conventionally a small value of $r_0$. The boundary energy, $E_b$, on the two surfaces of the disc is

$$E_b = 2\pi r_0^2 \gamma = 2a_i i^2 \gamma,$$  \hspace{1cm} (14)

where $\gamma$ is the boundary energy per unit area. It arises from the difference in the bond strength and in the atomic radius and accordingly partially overlaps with the cohesive energy difference, $B$, and the strain energy, $E_d$. Both of eqs. (13) and (14) must be divided by $i$ to represent the energy per atom, as is done on eq. (12). By summing all the energies considered above, the enthalpy change associated with the formation of GP clusters is given by

$$\Delta H = c_i [-q(1 - i_0 i^{-1}) + 2a_i i^2 + Gb^2 \pi a^{-2} \alpha^{1/2} i^{-1/2} / 4 \times \ln (a\pi^{-1/2} i^{1/2} / r_0)].$$  \hspace{1cm} (15)

The Gibbs’ energy change associated with the GP zone formation can be expressed by adding $\Delta H$ of eq. (15) and $\Delta S$ of eq. (11) multiplied by $-T$. Then, from the equilibrium conditions, $\partial \Delta G / \partial c_i = 0$ and $\partial \Delta G / \partial i = 0$, the thermal equilibrium state of the GP zone will be found at every temperature. Instead of describing whole of the intricate calculations, in the following is shown their outline. First, by assuming that the strain energy is negligibly small, the equilibrium concentration and the size are obtained respectively as

$$c_i = c - \exp \left\{-q(2a_i i^{-1}) / RT \right\},$$  \hspace{1cm} (16)

$$i = \frac{c}{\zeta} \exp \left\{1.5 q(2a_i i^{-1}) / RT \right\} - \exp \left\{0.5 q(2a_i i^{-1}) / RT \right\}.$$

In the case of Al–2 at%Cu alloy, by employing the numerical values, $c = 0.02$, $\zeta = 1$, $q = 2.35 \times 10^6 \text{J/mol}$, $a = 0.25 \text{nm}$, and $\gamma = 10^{-1} \text{J/m}^2$, the condition of no clusters, $c_i = 0$ in eq. (16) gives the reversion temperature, $T_R = 486 \text{K}$. When the strain energy term with the modulus of rigidity, $G = 40 \text{GPa}$, is taken into account, $T_R = 475 \text{K}$ is obtained. By changing the alloy concentration, the reversion temperature is drawn with a full line in Fig. 6, which can be compared with the experimental values represented by small circles and the lower dotted line in the same figure. Similarly, from the equilibrium conditions presented by the partial differential equations, the thermal equilibrium values of $c_i$ and $i$ are calculated and shown by the full and broken lines respectively in Fig. 7. The calculation shows that, below $T_R = 475 \text{K},$

![Fig. 6 Comparison between the experimental data (small circles and lower dotted line) of reversion temperature, $T_R$, of GP-1 zone of Al-Cu alloys and its calculated line (full line).](image)

![Fig. 7 Temperature dependent size ($i$) and concentration ($c$) of GP zone of Al-2 at%Cu alloy calculated by the present theory. Dotted line shows the limit of the retarded growth of GP-1 clusters.](image)
the amount of GP zone, $c_0$, and their size, $i$, will increase rapidly with lowering the temperature. Nevertheless, when the aging temperature is too low, diffusion of the solute atoms will be retarded and GP zone will not appear. In the case of Cu solute in Al, the activation energy for GP zone formation is not of the normal value for diffusion, $Q = 1.4$ eV, but as small as $Q = 1.02$ eV ($\approx 1.007 \times 10^5$ J/mol) because of a large degree of excess vacancies produced by quenching from the solid solution state. In the average diffusion distance, 

$$X^* = (Dt)^{1/2} = \left(D_0 \exp \left(-\frac{Q}{RT}\right) \cdot t\right)^{1/2}, \quad (18)$$

take the time of observation as $t = 10^3$ s, the activation energy of diffusion as $Q = 1.02$ eV, and the preexponential factor as $D_0 \sim 1$ cm$^2$/s. Then, $X^*$ can be calculated at different temperatures. By assuming one cluster to be growing in the centre of a spherical region with the radius of $X^*$ by gathering all the solute atoms within this diffusion range, the growth limit of the size $i$ is given as a function of temperature, which is shown by a dotted line in the figure. This is the growth limit or the diffusion limit line. According to the above calculation, the GP zone of Al–2%Cu alloy will be formed above 300 K, grow to the maximum size as large as $i \sim 10^3$ and the maximum amount of $C \sim 0.015$, become smaller by raising the aging temperature, and finally disappear at around 475 K. Quantitative experimental observations corresponding to Fig. 7 are not yet found.

VII. Other Kinds of the Dispersed Clusters in Solids

Another typical example of the dispersed small clusters in solids is the $\omega$ phase$^{20-23}$, which appears with nanometer size, $i = 10^3 - 10^5$, in Ti–Cr, Ti–Mo and other Ti and Zr based alloys. Although it could be understood and analyzed by the present theory, precise thermal data do not exist and concentration change in the clusters is not known so that the calculation is not yet applicable. In the order-disorder alloys with deviation from the definite atomic proportion, the finely dispersed distribution of ordered particles in disordered matrix or vice versa is often observed as a thermal equilibrium state in electron microscopy. The theoretical calculation, however, is not yet carried since the change of local concentrations and that of degree of order must be taken into consideration in addition to what are mentioned above. One easy example of the present calculation is to find the thermal equilibrium concentrations of coexisting vacancies, divacancies and trivacancies in a solid at high temperature. By combining eq. (6) containing three terms of $i = 1, 2$ and $3$ and their binding enthalpies, their concentrations will be exactly found with the well known relations that the dimers’ and trimers’ concentrations, $c_2$ and $c_3$, are proportional to the square and cubic of that of the monomers, $c_1$, respectively. The same equation may be applicable to find the dimer, trimer and other clusters of solute atoms within the solid solubility limit of alloys.

VIII. Conclusion and Acknowledgments

Further possible introductions are, for instance, an approximate formula for the entropy of fine mixture of topologically equivalent and exchangeable two phases, especially at concentrations around $c = 0.5$, and the formulation of entropy of very fine two-dimensional mixtures. However, the discussion will be closed here because no suitable examples are found for these cases. In conclusion in the present paper, the configurational entropy of small particles dispersed in solids or liquids is calculated, and, by utilizing it, various very fine dispersion states found in solid and liquid materials are explained and calculated. As already mentioned in the beginning, the author has joined to various groups or clusters in his study life, and the present theory is one of the products brought about from what he studied in them. Therefore, the author wishes to express his deep acknowledgments to all the members of the clusters he has ever belonged to.

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