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Influence of the Short Range Order on the Parting Limits of Certain alloys

By

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Abstract.

The object of this study is to make sure of the reason why the parting limits phenomenon appears in the disordered solid solution alloy. From the experimental results of the anodic polarization of Cu-Pd system alloys in sulphuric acid solution, the parting limits phenomenon is observed at the composition in which the superstructure will be formed, without regard to the degree of ordering. To illustrate this phenomenon, the potential of the alloy which is corroded by corrosive solution is estimated by means of statical thermodynamics. Thus, one comes to the conclusion that the parting limits is a phenomenon which is due to the short range ordering tendency of the alloy. Subsequently, this conclusion is proved to be applicable on the other "parting limits alloys".

§ 1. Introduction.

It has been well known that the corrosion-resisting property of Cu-Au system alloys suddenly increases from about 25 atomic pct. Au. This "parting limits phenomenon" has been discovered subsequently in many other alloys and utilized in some particular industry. The first detailed theory of parting limits was developed by Tammann¹⁻³⁾. He explained by use of a schema that the phenomenon appeared when the two species of atoms arranged in a definite arrangement. Thereafter the superstructure was practically confirmed to exist in Cu-Au system alloys⁴⁾. Therefore this explanation by Tammann of the parting limits has been considered as the origin of the recent order-disorder theory.

As an explanation of the parting limits phenomenon, however, Tammann's theory is very imperfect. Tammann's theory was based

on wrongly-interpreted experiments. Namely, as the disordered samples, he used the work-hardened specimens, and for the ordering heat treatment, he applied the higher temperature than the curie point of the samples. Therefore "disordered sample" must be in a strained state and "ordered sample" may be almost in a disordered state. According to Tammann's explanation, parting limits should not be observed in these samples. Nevertheless, these samples showed clear parting limits.

Thereafter, many examples of the "corrosion chain theory⁵⁻⁸⁾" were published to explain these inconsistencies. By the probability theory, these proved the causes for the appearance of the parting limits also in disorder solid solution. However, these theories maintain that the parting limits must appear at 25 and 50 atomic pct. in the whole solid solution alloys. Therefore, these theories are likewise imperfect.

In the writer's previous report¹¹⁾, it was demonstrated that when the solid solution alloys have a long range order, these solid solution alloys show parting limits on the composition, at which the super-structure is formed. However, if the super-structure exists, the parting limit does not always appear; it appears only under the following conditions and circumstances.

1. One component of the binary solid solution is more preferentially soluble than the other.
2. The natural electrode potential in the corrosive reagent is almost equal or propotional to the thermodynamic equilibrium potential of the alloy.
3. The surface of the alloy is not covered with an oxide film or any other protective film.

But one have the many examples^{6), 10)} where the parting limits are found in the alloy, in which the long range ordering does not exist or is not formed. These examples are classified into the following three types.

1. The phase transformation exists but a worker has not observed carefully and has thought that the alloy was a simple solid solution. Another case is when an inter-metallic compound exists in the alloy. The former examples are 2/8 atomic Si of Fe-Si, 2/8 atomic Ag of Mg-Ag, 2/8, 4/8 atomic Au of Zn-Au, 4/8 atomic Mn of Mn-Cu. In these alloys, sudden change of the potential and also sudden change of corrosion in that composition is due to the phase transformation. It is not strange that these properties are suddenly changed, when a

phase change has occurred. Examples of the latter are 4/8 atomic Ni of Mn-Ni, 4/8 atomic Mn of Au-Mn. These changes can be explained similarly in the case of high ordered solid solution alloys.

2. Parting limits due to the formation of the protective film. An excellent example of this is 13 pct. chrome steel. Cu-Ni alloys and many other examples have been found. These alloys are very important in industrial use, so they will be considered in the next report.

3. The alloys have complete solid solubility in equilibrium diagram and also do not form the protective film but do show the parting limits.

To make sure of the behavior of the alloys belonging the last 3 is the purpose of this study. They are once more separated into the following two types.

A. The alloys are known to form the long range order after a suitable annealing treatment, but without such suitable annealing, the alloys show the parting limits.

B. Super-structure has not been discovered, nevertheless parting limits appear.

Accordingly, studies on the Cu₃Pd super-structure of the Cu-Pd system alloys are reported in this paper, to make sure of the influence of the ordered distribution upon the parting limits. It has been known¹²⁻¹⁴⁾ that the voluntary stages—almost perfect long range ordering state, short range ordering state without long range ordering, perfect disorder state, etc.—are easily gained by the suitable heat treatment in this system alloys. Accordingly this alloy system is selected for the present study because they are convenient for comparison between the different stages and for studies on the relation between ordering and parting limits.

§ 2. Experiment on the parting limits phenomenon of Cu-Pd system alloys.

1. Sample.

Metallic palladium and pure copper are melted together in vacuum melt high frequency furnace, and then platelet samples are made by rolling. Then, these samples are annealed in vacuum furnace at 800 °C × 5 hrs. and cooled in the furnace. Results of analyses of these samples are the following.

These samples are heat treated as shown in Table 2.

TABLE 1. Composition of Cu-Pd alloy.

No.	1	2	3	4	5
Pd. mol %	14.98	20.11	24.58	29.94	34.96

TABLE 2. Heat treatment of the sample.

heat treatment	state
A 800°C×1 hr.→ice water quench	perfect disorder
B 500°C×1 hr.→ice water quench	short range order
C 400°C×100 hrs.→furnace cool	long range order

2. Measurement of the anodic polarization curve in 10% sulphuric acid.

The sample is polished with abrasive paper until 0/5 and the surface of the sample is bared 0.5 cm² wide and remaining part is covered with max. This bared surface of the electrode is pickled by an etching solution during 30 sec. for removal of the polished layer and then the electrode is set in the measuring cell which is shown in Fig. 1.

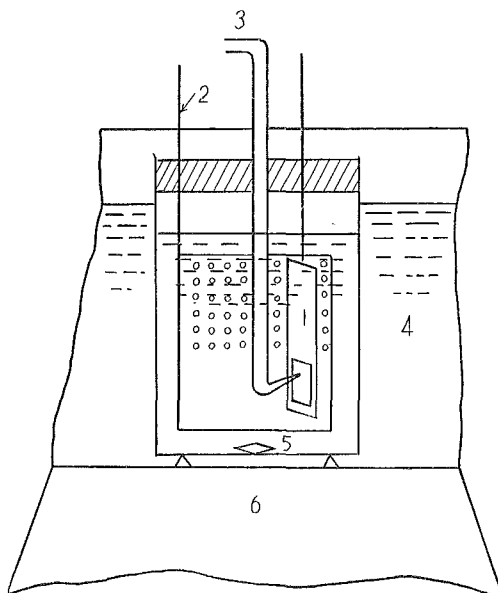


Fig. 1. Sketch of polarization cell.

1. Sample 2. Pt. cathode 3. Calomel electrode
4. Water bath 5. Stirrer 6. Magnetic stirrer

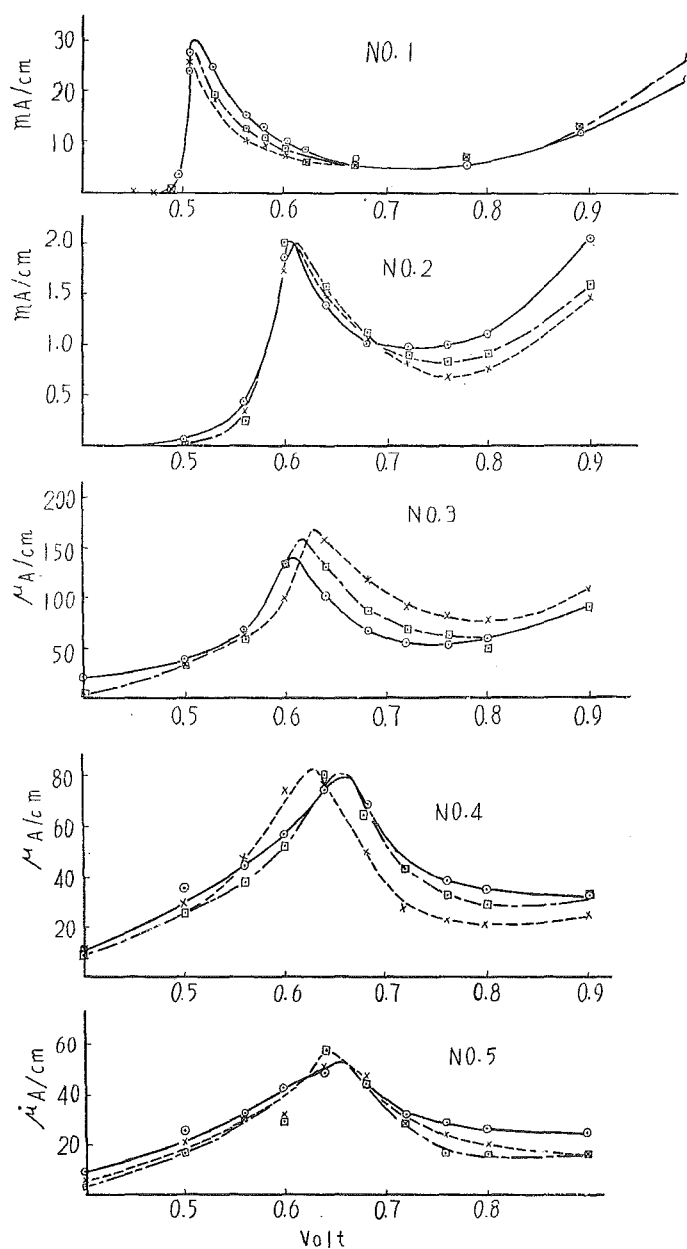


Fig. 2. Anodic polarization of Cu-Pd alloys in 10% H_2SO_4 ; potential vs. saturate calomel electrode, 20°C.

A $\odot$ —, B $\square$ ---, C $\times$,

Electrolyte is 10% sulphuric acid and is stirred by the magnetic stirrer. The temperature is maintained at 20°C during the measurement. The electrode is held in a constant potential during one min., then the current density is measured and the next potential is used. The constant potential is regulated by use of the vacuum tube potentiometer and high current circuits. Experimental results are shown in Fig. 2 and Fig. 3.

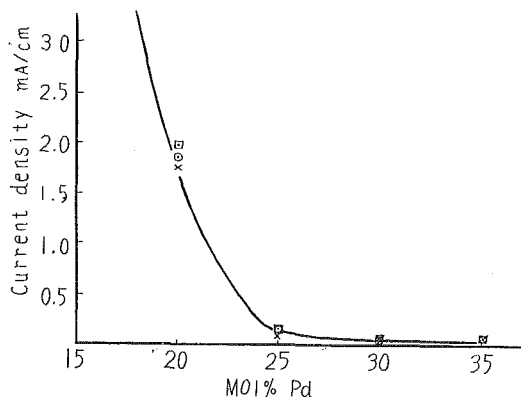


Fig. 3. Current density for a potential of 0.60 V. as a function of electrode composition, deduced from Fig. 2.

It is observed from Fig. 2 that the passivation potential is raised by increase of the palladium content of the sample. The current density of each sample, when the potential reaches to 0.6 volt (reference to the saturated calomel electrode) is shown in Fig. 3. In spite of the variation of its heat treatment, a slight difference is found in the polarization curve of the same sample. Moreover, anodic dissolution suddenly decreases when the palladium content of the sample increases to more than 25 atomic pct. That is to say, if the atomic arrangement in the alloy is either order or disorder, the reaction velocity at the constant potential suddenly increases at the composition in which the super-structure is formed.

§ 3. Relation between the short range ordering tendency and the parting limits.

Müller et al.⁽¹⁵⁾ found that when the constant anodic current is applied on the Cu-Au system alloy, the potential of the alloy suddenly rises from approximately more than 25 atomic pct. Au. Backish and

Robertson¹⁶⁾ have reported that the order-disorder change of Cu-Au system alloy has no influence upon the corrosion of the alloy in FeCl₃ solution. From these two reports and the experimental results reported in this paper, the following fact is concluded: In the case of Cu-Au system and Cu-Pd system alloys which are typical examples of the parting-limits-alloys, the parting limits phenomenon does not always appear only as the result of the ordering of the alloy. Let it now be considered in general, therefore, why the parting limits phenomenon appear even in the solid solution alloy which is quenched from the high temperature and is in perfect disordered state.

1. In the case of the solid solution alloys which have short range ordering tendency of AB type.

Supposing a binary solid solution alloy is made up of two kinds of atoms A and B . At high temperature, the two species of atoms must arrange sporadically in the crystal. Therefore, this state is represented as follows.

$$\left. \begin{aligned} \left[\frac{AA}{I II} \right] &= \frac{Z}{2} N \theta^2 \\ \left[\frac{AB}{I II} \right] &= \frac{Z}{2} N \theta (1-\theta) \\ \left[\frac{BA}{I II} \right] &= \frac{Z}{2} N \theta (1-\theta) \\ \left[\frac{BB}{I II} \right] &= \frac{Z}{2} N (1-\theta)^2 \end{aligned} \right\} \quad (1)$$

In these equation;

$\left[\frac{AA}{I II} \right], \left[\frac{AB}{I II} \right]$ etc.: number of pairs in which A atom exists in sublattice I whilst A and B atoms exist in sublattice II, respectively.

Z : number of nearest neighbour atoms.

θ : mole fraction of A atoms.

N : total number of atoms.

Therefore, free energy of this alloy is;

$$\begin{aligned} F_{AB} = & \frac{ZN}{2} (1-2\theta) V_{BB} - ZN\theta V_{AB} + \frac{ZN}{2} \theta^2 (V_{AA} + V_{BB} - 2V_{AB}) \\ & + kTZN \{ \theta \log \theta + (1-\theta) \log (1-\theta) \} \end{aligned} \quad (2)$$

In this equation ;

- F_{AB} : free energy of the alloy.
 V_{AA}, V_{BB}, V_{AB} : mutual potential between AA, BB and AB respectively.
 k : Boltzmann's constant.
 T : absolute temperature.

Now, when the alloy is quenched, if the stable state of this alloy in high temperature is brought to the low temperature perfectly just as it is, the partial molar free energy of A of this alloy is,

$$\Delta F_A = -RT \log \theta \quad (3)$$

ΔF_A is partial molar free energy.

If B is more electro-negative than A , the potential of this alloy is calculated by the following equation.

$$E_M = \Delta F_A / nF_c = -RT / nF_c \log \theta \quad (4)$$

Obviously, potential of this alloy changes logarithmically, according to the composition, and the parting limits phenomenon is not expected from the above equation.

Consider case when the alloy is dipped in a corrosive solution. The surface of this alloy will be corroded and as the result of this, the number of each pair in the surface layer will change as follows.

$$\left. \begin{aligned} \left[\frac{AA}{I \ II} \right] &= \frac{Z}{2} N a \theta^2 = \frac{Z}{2} N x \\ \left[\frac{AB}{I \ II} \right] &= \frac{Z}{2} N \beta \theta (1-\theta) = \frac{Z}{2} N (\theta-x) \\ \left[\frac{BA}{I \ II} \right] &= \frac{Z}{2} N \beta \theta (1-\theta) = \frac{Z}{2} N (\theta-x) \\ \left[\frac{BB}{I \ II} \right] &= \frac{Z}{2} N r (1-\theta)^2 = \frac{Z}{2} N (1-2\theta+x) \end{aligned} \right\} \quad (5)$$

Now, the parameter x is brought in and put as the third term of this equation. Then the free energy of the alloy is ;

$$\begin{aligned} F_{AB} &= \frac{ZN}{2} (1-2\theta) V_{BB} + ZN\theta V_{AB} + \frac{ZN}{2} x (V_{AA} + V_{BB} - 2V_{AB}) \\ &\quad + kT \frac{NZ}{2} \left[x \log x + 2(\theta-x) \log(\theta-x) + (1-2\theta+x) \log(1-2\theta+x) \right] \\ &\quad - kT(Z-1)N \{ \theta \log \theta + (1-\theta) \log(1-\theta) \} \end{aligned} \quad (6)$$

The corrosion reaction of the alloy proceeds in the direction to decrease the free energy. That is, it must proceed in the more stable direction. From equation (6), equation (7) is obtained for the equilibrium condition of the alloy.

$$\frac{V_{AA} + V_{BB} - 2V_{AB}}{kT} = \log \frac{(\theta - x)^2}{x(1 - 2\theta + x)} = \log \frac{\beta^2}{\alpha\gamma} \quad (7)$$

When the alloy sufficiently approaches to the equilibrium state, the partial molar free energy of this alloy is calculated by the following equation.

$$\begin{aligned} \Delta F_A = & \frac{ZN}{2}(V_{AA} + V_{BB} - 2V_{AB}) - \frac{ZN}{2}x(V_{AA} + V_{BB} - 2V_{AB}) \\ & - \frac{Z}{2}NkT \{x \log x + 2(1-x) \log(\theta - x) + (x-1) \log(1 - 2\theta + x)\} \\ & + kT(Z-1)N \log \theta \end{aligned} \quad (8)$$

When the nature and temperature of the alloy are given, the left hand term of equation (7) is decided. Therefore it is put as follows.

$$\frac{V_{AA} + V_{BB} - 2V_{AB}}{kT} = -\log K \quad (9)$$

When the nature, composition and temperature are given, θ and K are decided. To substitute these values of θ and K in equation (7) and (9), x which satisfies equation (5), is obtained. By substituting these values of θ , K and x in equation (8), ΔF_A is obtained, and from equation (4), the potential of the alloy is obtained. For example, the relationship between the composition and the potential is calculated in the case of $n=2$, $T=298^\circ K$, $\text{Log}_{10}K = -2.0, -2.5, -3.0, -3.5, -4.0, -4.5, -5.0$ are selected. These results are shown in Table 3 and Fig. 4.

Obviously, from this figure only in the case of $\text{Log } K < 0$, namely,

$$\frac{V_{AA} + V_{BB} - 2V_{AB}}{kT} > 0 \quad (10)$$

does the parting limits phenomenon appear in the alloy system.

Namely, the one and only illustration here employed shows that if the solid solution alloy has a short range ordering tendency, even the atoms arrange sporadically in its crystal as a result of the quenching and parting limits phenomenon may be observed at 50 atomic pct. in the case of alloy which has ordering tendency of AB type.

TABLE 3. Electromotive force of *AB* type short range ordered solid solution alloys ($T=298^\circ\text{K}$, $n=2$) in volt.

$\log_{10}K$ θ	-2.0	-2.5	-3.0	-3.5	-4.0	-4.5	-5.0
0.40	0.1696	0.2288	0.2844	0.3460	0.4034	0.4642	0.5206
0.42	0.1591	0.2173	0.2725	0.3339	0.3903	0.4521	0.5085
0.44	0.1470	0.2031	0.2576	0.3187	0.3750	0.4367	0.4931
0.46	0.1325	0.1847	0.2373	0.2977	0.3537	0.4154	0.4718
0.48	0.1127	0.1565	0.2035	0.2606	0.3155	0.3768	0.4330
0.49	0.1060	0.1431	0.1825	0.2330	0.2845	0.3443	0.4001
0.495	0.1013	0.1341	0.1681	0.2106	0.2556	0.3111	0.3653
0.50	0.0965	0.1253	0.1524	0.1826	0.2104	0.2441	0.2694
0.505	0.0918	0.1164	0.1368	0.1549	0.1658	0.1718	0.1740
0.51	0.0872	0.1079	0.1228	0.1331	0.1377	0.1396	0.1402
0.52	0.0784	0.0947	0.1005	0.1045	0.1059	0.1064	0.1065
0.54	0.0632	0.0700	0.0728	0.0739	0.0742	0.0743	0.0744
0.56	0.0513	0.0549	0.0561	0.0564	0.0567	0.0568	0.0568
0.58	0.0419	0.0442	0.0448	0.0451	0.0451	0.0452	0.0452
0.60	0.0349	0.0362	0.0366	0.0367	0.0368	0.0368	0.0368

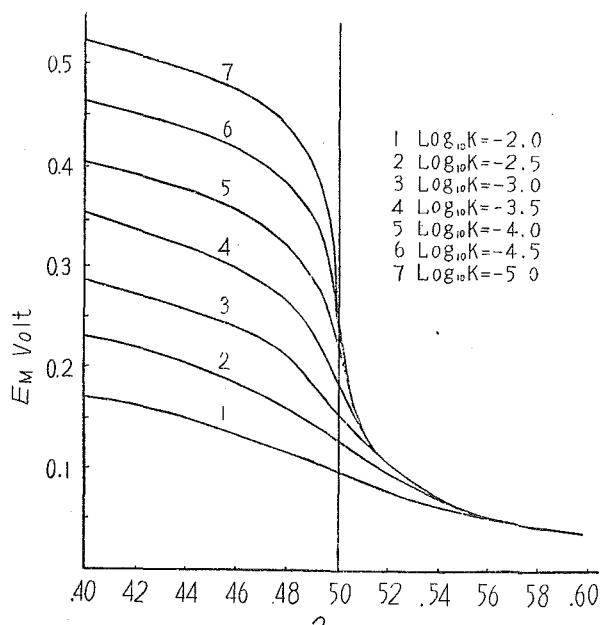


Fig. 4. E. M. F. of *AB* type short range ordered alloys $n=2$ $T=298^\circ\text{K}$.

2. In the case of the solid solution alloy which has short range ordering tendency of A_3B (A_2B_2 , AB_3) type.

Supposing a binary solid solution alloy which is made up of two kinds of atoms A and B . At high temperature, the two species of atoms must arrange sporadically in the crystal. Therefore this state is represented as follows.

$$\left. \begin{aligned} [AAAA] &= \frac{1}{12} ZN\theta^4 \\ [AAAB] &= \frac{1}{12} ZN \cdot 4\theta^3(1-\theta) \\ [AABB] &= \frac{1}{12} ZN \cdot 6\theta^2(1-\theta)^2 \\ [ABBB] &= \frac{1}{12} ZN \cdot 4\theta(1-\theta)^3 \\ [BBBB] &= \frac{1}{12} ZN \cdot (1-\theta)^4 \end{aligned} \right\} \quad (11)$$

In these equations θ is the mole fraction of A atoms, Z is the number of nearest neighbour atoms and N is the total number of atoms. When V_{AA} , V_{BB} and V_{AB} represent the mutual potential between AA , BB and AB , respectively, the free energy of this alloy is calculated by the following equation.

$$\begin{aligned} F_{AB} &= \frac{ZN}{2} \theta V_{AA} + \frac{ZN}{2} (1-\theta) V_{BB} - \frac{ZN}{2} \theta (1-\theta) (V_{AA} + V_{BB} - 2V_{AB}) \\ &\quad + ZNkT \{ \theta \log \theta + (1-\theta) \log (1-\theta) \} \end{aligned} \quad (12)$$

k is Boltzmann's constant and T is the absolute temperature. When the alloy is quenched, if the stable state of this alloy in high temperature, is brought to the low temperature perfectly just as it is, the partial molar free energy is:

$$\Delta F_A = -NkT \log \theta \quad (13)$$

When B is more electro-negative than A , logarithmic relation is expected to exist between the potential and the composition of this alloy, and parting limits phenomenon is not expected.

When the alloy is dipped in a corrosive solution, the surface of the alloy is corroded. Accordingly, number of each pair in the surface layer changes as follows.

$$\left. \begin{aligned} [AAAA] &= \frac{1}{12} ZN \alpha \theta^4 \\ [AAAB] &= \frac{1}{12} ZN \cdot 4\beta \theta^3 (1-\theta) \\ [AABB] &= \frac{1}{12} ZN \cdot 6\gamma \theta^2 (1-\theta)^2 \\ [ABBB] &= \frac{1}{12} ZN \cdot 4\delta \theta (1-\theta)^3 \\ [BBBB] &= \frac{1}{12} ZN \cdot \varepsilon (1-\theta)^4 \end{aligned} \right\} \quad (14)$$

Now, the parameters x, y and w are brought in and one writes

$$\left. \begin{aligned} \frac{1}{12} ZN \cdot \alpha \theta^4 &= \frac{1}{12} ZN \cdot (\theta - 3x - 3y - w) \\ \frac{1}{12} ZN \cdot 4\beta \theta^3 (1-\theta) &= \frac{1}{12} ZN \cdot 4x \\ \frac{1}{12} ZN \cdot 6\gamma \theta^2 (1-\theta)^2 &= \frac{1}{12} ZN \cdot 6y \\ \frac{1}{12} ZN \cdot 4\delta \theta (1-\theta)^3 &= \frac{1}{12} ZN \cdot 4w \\ \frac{1}{12} ZN \cdot \varepsilon (1-\theta)^4 &= \frac{1}{12} ZN (1-\theta-x-3y-3w) \end{aligned} \right\} \quad (15)$$

In this case, the energy of the pairs is:

$$\left. \begin{aligned} \text{energy of } [AAAA] \text{ pairs} &= \frac{ZN}{2} (\theta - 3x - 3y - w) V_{AA} \\ " \quad [AAAB] &= ZN x (V_{AA} + V_{AB}) \\ " \quad [AABB] &= \frac{ZN}{2} y (V_{AA} + V_{BB} + 4V_{AB}) \\ " \quad [ABBB] &= ZN w (V_{BB} + V_{AB}) \\ " \quad [BBBB] &= \frac{ZN}{2} (1-\theta-x-3y-3w) V_{BB} \\ \hline \text{total energy} &= \frac{ZN}{2} \{ \theta V_{AA} + (1-\theta) V_{BB} - (x+2y+w) (V_{AA} + V_{BB} - 2V_{AB}) \} \end{aligned} \right\} \quad (16)$$

Therefore the free energy of the alloy is represented as:

$$\begin{aligned}
 F_{AB} = & \frac{ZN}{2} \{ \theta V_{AA} + (1-\theta) V_{BB} - (x+2y+w)(V_{AA} + V_{BB} - 2V_{AB}) \} \\
 & + NkT \{ \theta \log \theta + (1-\theta) \log (1-\theta) \} - NkT \{ \theta^4 \log \theta^4 - (\theta - 3x - 3y - w) \log \\
 & (\theta - 3x - 3y - w) + 4\theta^3(1-\theta) \log \theta^3(1-\theta) - 4x \log x + 6\theta^2(1-\theta)^2 \log \theta^2(1-\theta)^2 \\
 & - 6y \log y + 4\theta(1-\theta)^3 \log \theta(1-\theta)^3 - 4w \log w + (1-\theta)^4 \log (1-\theta)^4 \\
 & - (1-\theta - x - 3y - 3w) \log (1-\theta - x - 3y - 3w) \} \quad (17)
 \end{aligned}$$

The corrosion reaction of the alloy must proceed to the direction of decrease in the free energy, namely to the more stable direction.

$$\begin{aligned}
 & - \frac{Z}{2kT} (V_{AA} + V_{BB} - 2V_{AB}) \\
 & = \log \frac{(\theta - 3x - 3y - w)^3 (1 - \theta - x - 3y - 3w)}{x^4} = \log \frac{\alpha^3 \varepsilon}{\beta^4} \\
 & - \frac{Z}{2kT} (V_{AA} + V_{BB} - 2V_{AB}) \\
 & = \log \frac{(\theta - 3x - 3y - w)^3 (1 - \theta - x - 3y - 3w)^3}{y^6} = \log \frac{\alpha^3 \varepsilon^3}{\gamma^6} \\
 & - \frac{Z}{2kT} (V_{AA} + V_{BB} - 2V_{AB}) \\
 & = \log \frac{(\theta - 3x - 3y - w)(1 - \theta - x - 3y - 3w)^3}{w^4} = \log \frac{\alpha \varepsilon^3}{\delta^4} \quad (18)
 \end{aligned}$$

From equation (17), equation (18) is obtained for equilibrium condition of the alloy. At last, the surface layer of the alloy approaches sufficiently to its equilibrium state. In this case, the partial molar free energy of this alloy is calculated by the following equation.

$$\begin{aligned}
 \Delta F_A = & \frac{ZN}{2} (x+2y+w)(V_{AA} + V_{BB} - 2V_{AB}) + 3NkT \log \theta \\
 & - NkT \left[(1-3x-3y-w) \log (\theta - 3x - 3y - w) + 4x \log x + 6y \log y \right. \\
 & \left. + 4w \log w + (-x-3y-w) \log (1-\theta - x - 3y - w) \right] \\
 & = 3N(x+2y+w)(V_{AA} + V_{BB} - 2V_{AB}) + 3NkT \log \theta \\
 & - NkT \log (\theta - 3x - 3y - w) \quad (19)
 \end{aligned}$$

When the nature and temperature of this alloy are given, left hand term of equation (18) is decided. Therefore it is put as follows.

$$\frac{V_{AA} + V_{BB} - 2V_{AB}}{2kT} = -\log K \quad (20)$$

When the nature, composition and temperature are given, θ and K are decided. By substituting these values of θ and K in equation (20) and (18), x, y and w which satisfy equation (15), are obtained. By substituting these θ, K, x, y and w in equation (19), the partial molar free energy ΔF_A is obtained. Therefore the potential of the alloy is easily gained by equation (4). For example, the relation between the composition and the potential is calculated in the case of $n=2$, $T=298^\circ K$. $\log_{10} K = -1.0, -1.5, -2.0, -2.5$ are selected. The results are shown in Table 4 and Fig. 5.

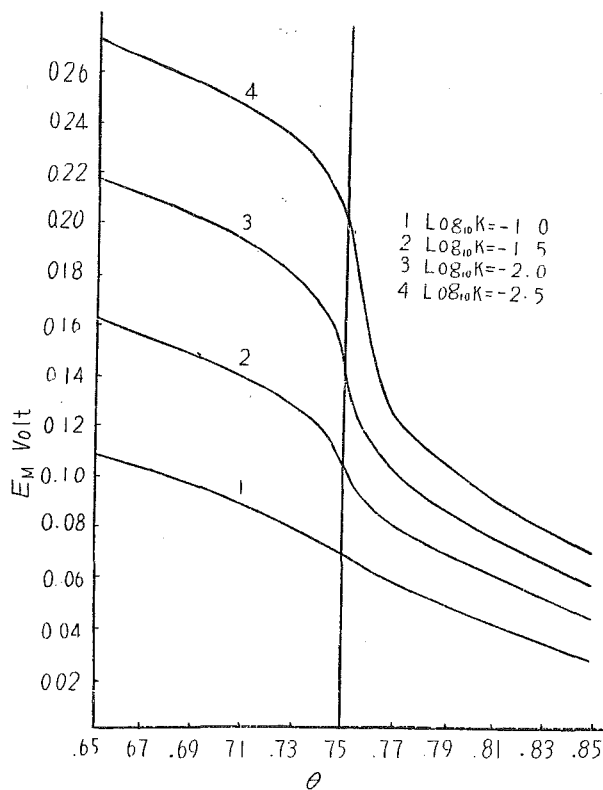


Fig. 5. E.M.F. of A_3B type short range ordered alloys $n=2$ $T=298^\circ K$.

TABLE 4. Electromotive force of A_3B type short range ordered solid solution alloys ($T=298^\circ\text{K}$, $n=2$) in volt.

$\log_{10} K$	0.65	0.70	0.73	0.75	0.77	0.80	0.85
-1.0	0.1081	0.0923	0.0804	0.0702	0.0597	0.0471	0.0294
-1.5	0.1617	0.1442	0.1280	0.1061	0.0880	0.0682	0.0454
-2.0	0.2169	0.1967	0.1797	0.1429	0.1010	0.0860	0.0587
-2.5	0.2710	0.2499	0.2320	$\theta=0.745$ 0.2114	0.1244	0.1008	0.0721

Obviously from this figure, only in the case of $\text{Log}K < 0$, namely,

$$V_{AA} + V_{BB} - 2V_{AB} > 0$$

does the parting limits phenomenon appear in the alloy system. Conclusively, the theoretical illustration shows that on the solid solution alloy which has the short range ordering tendency, even the atoms arrange sporadically in its crystal as a result of quenching; the parting limits phenomenon may be observed at 25 (50 and 75) atomic pct. of A in the case of alloy which has ordering tendency of A_3B (A_2B_2 and AB_3) type.

§ 4. Discussion.

Consider the solid solution alloy in general, which does not show passivity but in which the parting limits phenomenon has been found. The alloys in this category are separated into two types. The first include alloys which have been found to form the superstructure by suitable heat treatment. The second include alloys in which the super-structure has not been found.

The former is a so-called "Super-structure type alloy". In such an alloy ($2V_{AB} - V_{AA} - V_{BB}$) is expected to be negative because the attraction between unlike atoms is greater than that between like atoms. Therefore, as is shown in § 3, it can be explained that the parting limits phenomenon may be observed, even if the heat treatment resulting in formation of the super-structure, has not been applied.

In the latter type alloys, it comes into question whether ($2V_{AB} - V_{AA} - V_{BB}$) is also negative or not. The examples of this type alloys are Ag-Au system alloys (50 atomic pct. and 25 atomic pct. Au), Mg-Ag system alloys (87.5 atomic pct. Ag), Mn-Ag system alloys (75 atomic pct. Ag), Au-Pd system alloys (50 atomic pct. Au), and Ag-Pd system

alloys (50 atomic pct. Ag). To make sure of the conclusion in §3, the short range ordering tendency is discussed in the cases of these alloys.

1. Ag-Au system alloys.

The enthalpy of Ag-Au system alloys, has been measured by many workers. In general, the mixing enthalpy is represented as follows.

$$\Delta H = [AB] \times \left(V_{AB} - \frac{V_{AA} + V_{BB}}{2} \right)^{17)} \quad (23)$$

In this equation ΔH is mixing enthalpy and $[AB]$ is number of AB pairs in the crystal. It has been known that ΔH is almost independent of the temperature.

From a recent paper of Oriani¹⁸⁾,

$$\Delta H = -1000 \text{ cal/g atoms at 50 atomic pct. Au.}$$

$$\Delta H = -750 \text{ cal/g atoms at 25 atomic pct. Au.}$$

are obtained. thus, ΔH is negative, $[AB]$ is positive, hence $(2V_{AB} - V_{AA} - V_{BB})$ is negative. Namely this alloy system has short range ordering tendency at that composition. Therefore, it must be expected from the theory that the alloy shows the parting limits phenomenon.

2. Mg-Ag system alloys, Mn-Ag system alloys.

Mixing enthalpy of Mn-Ag system alloys is measured by the Weibke and Kubaschewski¹⁹⁾. It is -11 Kcal. Thus, ΔH is negative. Therefore $2V_{AB} - V_{AA} - V_{BB} < 0$ and short range ordering tendency are expected. Mixing enthalpy of Mn-Ag system alloys has not been found.

Consider the properties of these alloys according to the Friedel theory²⁰⁾. Let Z be the point charge which is led into the metal. In the case of substitutional impurity, Z is the difference of the valency between solute and solvent. Friedel has shown that $\partial^2 H / \partial \theta^2$ has the same sign as Z , when the polarization or size effect is not so important as the difference of the valency. Therefore, in the case of $Z > 0$, H has positive curvature and the alloy is expected to have the short range ordering tendency. At the silver-rich parts of the Mg-Ag system and Mn-Ag system alloys, Mg and Mn are considered to be the solute, respectively. Therefore $Z > 0$. Accordingly, these alloys have the short range ordering tendency and it must be expected from the theory that both alloys have the parting limits.

3. Pd-Ag system alloys, Pd-Au system alloys.

The enthalpies of these system alloys have not been measured and

Freidel's theory can not apply to 50 atomic pct. of these alloys. Accordingly, it cannot be decided whether these alloys have clustering tendency or short range ordering tendency.

§ 5. Conclusion.

When the super-structure is formed in any solid solution alloy, the parting limits phenomenon appears under the suitable conditions. But parting limits phenomenon has been found in the alloy in which the super-structure does not exist, or in which also the protective film is not formed. The main object of the present investigation is to make sure of this mechanism. For this purpose, Cu-Pd system alloys are used as the specimens, because the voluntary stage of the ordering are easily gained by the suitable heat treatment of the alloys.

Anodic polarization of these alloys, in 10% sulphuric acid are measured by constant potential method. Experimental results are as follows.

(1) A slight difference is found in the polarization curve of the same sample, in spite of the variation of its heat treatment.

(2) Even if the atomic arrangement in the alloy is either in order or in disorder, the anodic dissolution suddenly decreases when the palladium content of the sample increases over 25 atomic pct.

To illustrate these results, the free energy of a binary solid solution alloy is determined by means of statical thermodynamics under the condition that the surface of the alloy is corroded in the corrosive reagent. The conclusion is reached that only in the solid solution alloy which has the short range ordering tendency, even the atoms arrange sporadically in its crystal as a result of the quenching, and then the parting limits phenomenon must be observed at 50, 25, 50 and 75 atomic pct. of A in the cases of AB , A_3B , A_2B_2 , and AB_3 type ordering alloys, respectively.

Subsequently, to confirm whether this theory is adaptable or not, to all alloys which have been found to have the parting limits, the short range ordering tendency is discussed. Excepting a few alloys which can not be discussed for lack of experimental data, this theory is considered to be adaptable to all alloys, from the consideration of the mutual potential, the mixing enthalpy and the differences of the valency.

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