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INVESTIGATION OF THE APPLICATION OF SPINODAL THEORY TO THE PALLADIUM-IRIDIUM SYSTEM

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INVESTIGATION OF THE APPLICATION OF SPINODAL THEORY TO THE PALLADIUM-IRIDIUM SYSTEM

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ABSTRACT

Hardness, microstructural and x-ray observations of a 56 at.% palladium - 44 at.% iridium alloy were made to investigate the applicability of existing "spinodal" theory. Specimens of the palladium-iridium alloy were aged at temperatures well below the critical temperature predicted by existing theory.

Classic spinodal decomposition was not found to occur in any of the studies even though specimens were aged long times. A theoretical justification is offered for this phenomenon. The modification of existing spinodal theory is based upon effects of differing elastic moduli of the alloy components. Palladium and iridium are excellent metals for such a study because the elastic modulus of iridium is nearly five times that of palladium.

I. THEORY

The main objective of this investigation was to check the applicability of existing theories with regard to the "spinodal" decomposition of alloys of the palladium-iridium system. First it would be appropriate to review briefly the background of the existing spinodal theory. Spinodal is the name given to the inflection point of the Gibbs free energy curve for a metastable solid solution alloy system. The locus of such points comprises the dotted curve in Fig. 1 for the gold-platinum system as shown by Borelius[1] and Carpenter.[2]

Consider an alloy system with a miscibility gap as in Fig. 1. It was reasoned that a supersaturated solid solution alloy of this system, with a composition within the spinodal curve on the phase diagram, could experience spontaneous "demixing" at temperatures within the miscibility gap in order to lower its free energy. (A) in Fig. 1 is an alloy of such a composition. This demixing could be accomplished without overcoming any nucleation barrier.

The composition fluctuations resulting from the free energy lowering are assumed to be sinusoidal in nature. Such composition fluctuations explain the x-ray diffraction effect called "side bands" which are observed in spinodally decomposed alloys. The "side band" effect will be considered again because it has proven to be useful in experimentally identifying spinodally decomposed alloys.

Because no nucleation is necessary for "spinodal decomposition", the rate of spinodal decomposition is controlled by the atomic diffusion rate alone. Thus, the decomposition can occur in a short time compared to a nucleation and growth type reaction for the above reason and also because the diffusion distances are relatively small in the spinodal case.

In studies of the Cu-Ni-Fe-system, Hillert[3] followed the kinetics of the formation of composition modulations by the use of x-rays. Debye x-ray patterns of metals with compositions inside a miscibility gap were previously found by Daniel and Lipson[4,5] to show what are termed "side bands" near the main Bragg reflections. This effect is due to the structure of the modulations themselves and an example of side bands, observed by Carpenter in his study of gold-platinum, is shown in Fig. 2. This x-ray effect is similar to the satellite spots observed by Ogawa et al,[6] in their study of domain structures in ordered Cu-Au using the electron microscope. Daniel and Lipson related the wavelength of the composition modulations to the angular deviation of the x-ray side bands, ($\delta\Theta$) from the parent Bragg angle (Θ) by the equation:

$$L = h \tan \Theta / [h^2 + k^2 + \ell^2) \cdot \delta\Theta] \qquad (1)$$

where L is the wavelength of the modulation and h, k, and ℓ are the Miller indices of the parent Bragg reflection.

For the pseudo binary system of copper and nickle-iron (Cu and $No_{.7}Fe_{.3}$) Hillert et al.[3] confirmed this formula and earlier general findings that the modulation wavelength increased with alloy aging time. That is to say, the side band separations decreased with alloy aging time.

Two explanations of physical states of the alloy that could result in the side band effect have been advanced in the literature. Daniel and Lipson[4,5] explained that the side bands were the result of one dimensional sinusoidal variations in composition in the matrix. In effect, the picture is one of lamella of extremely different concentrations separated by a concentration gradient. These lamella then can lie

in randomly oriented zones. The zones, of course, can have any of three orientations in a single crystal so the x-ray effect is three dimensional. Cahn[8] described the composition fluctuations by a three dimensional Fourier function.

Regardless of the physical model, Carpenter[2] reasoned that spinodal decomposition would affect the physical properties of the alloy. In his study he showed that the reaction could be followed by hardness measurements as well as with x-rays and that spinodal decomposition in gold-platinum was an effective hardening mechanism.

Cahn and Hilliard provided a rigorous application of thermodynamics to precipitation and spinodal reactions in a series of papers.[7,8,9] In those treatments, the free energy per unit volume function was shown to be a significant term. The nucleation and growth phenomena was compared to the spinodal and it was shown that these two phenomena become quite similar as the temperature approaches the critical temperature. The critical temperature is shown as T_c in Fig. 1. It is the highest temperature at which the alloy system will experience thermodynamic equilibrium between the single solid solution state and the two phase state. Another way of saying this is that all possible compositions in the alloy system will be in thermodynamic equilibrium in the solid solution state above the critical temperature.

Cahn and Hilliard also introduced and treated the "interfacial free energy" contribution to the total free energy of a regular solution. The total free energy was defined as:

$$f = \int_V [f'(c) + K(\nabla c)^2]\, dv \qquad (2)$$

where $f'(c)$ is the Helmholz free energy per unit volume of composition, c, and $K(\nabla c)^2$ is the interfacial free energy term. The latter can also be considered the composition gradient energy term when no definite interface or area of compositional discontinuity is present. Thus compositional fluctuations will occur, according to this theory, at such a temperature that the Helmholz free energy term decreases faster than the gradient energy term increases with compositional change. This corresponds to the spinodal. Note that the interfacial energy or composition gradient energy term would have the effect of lowering the T_c at which such coherent compositional fluctuation would occur. That is, the effect of the composition gradient energy term would be to lower the miscibility gap in Fig. 1.

To continue the development of the free energy relationships affecting the formation of the compositional fluctuations associated with the spinodal, it is noted that Eq. (2) is inappropriate for cases where there is a strain energy contribution to the total free energy. Cahn[10] pointed out that such strain energy contributions can be large and significant in solids.

He assumed that the surface energy term would be much less significant than the strain energy term. He thus predicted that the critical temperature depression due to coherency strains would be approximately:

$$T_c - T = \frac{\eta^2 E}{2(1-\nu)kN_v} \qquad (3)$$

where

η = the expansion of the lattice per unit composition change

E = Young's modulus

ν = Poisson's ratio

k = Boltzman's constant

N_v = number of atoms per unit volume (cm^{-3})

The number of degrees centigrade that the coherent miscibility gap is predicted to fall below the standard or incoherent miscibility gap is given by T_c-T. It should be emphasized at this point that Cahn's treatment is derived to apply to initial decomposition. The simplifying assumption inherent in this application is that compositional fluctuations would not be great enough to preclude using an average elastic modulus for the alloy. This assumption yields useful results for the gold-platinum system. Gold and platinum have elastic moduli of 21.3 and 11.6 million psi, respectively. However, palladium and iridium have moduli of 16.3 and 76 million psi, respectively. It would seem that successful application of the above spinodal theory to the palladium-iridium system would probably be fortuitous.

It was thought by the author that the effect of widely differing moduli could greatly alter the strain energy criterion in Cahn's theory. Thus an alloy such as palladium-iridium is ideally suited in investigating this point. The atomic size difference, η, in palladium-iridium alloys is about 0.13 whereas in gold-platinum alloy systems it is about 0.3.

II. EXPERIMENTAL PROCEDURE

Alloys of 55.9 at.% palladium and 44.1 at.% iridium were vacuum cast in a zirconia crucible using a tungsten filament furnace. The metals were then solution-treated at 1575°C for 18 hours in air and water quenched. Finally they were solution-treated at 1600°C for two hours in an inert atmosphere and water-helium quenched to assure retention of the single phase. A delay triggering device allowed the sample to be quenched at the instant the electrical heating power was interrupted.

Microhardness and x-ray diffraction specimens of convenient size were cut from polycrystalline samples with a spark cutter to minimize coldwork. Specimens were vacuum incapsulated in quartz tubing before the aging treatments were performed. The aging treatments were carried out with temperature control of approximately ±5°C at 709°C and 600°C and aging times ranged from 1 to 250 hours.

Debye-Scherrer x-ray photographs were taken of all specimens using Cu K α radiation and a 114.59 mm diameter camera. Microhardness measurements were made on the bakelite mounted specimens using Kentron and Leitz microhardness testers. The loads used in the two cases were 500 and 300 grams, respectively.

Several specimens were studied with the electron microprobe analyzer to determine if there were composition variations in the matrix or near grain boundaries and inclusions. Inclusions observed at 400 metallographically were also identified with the probe. Aqua regia in glycerol was found to be a good grain boundary etchant.

III. EXPERIMENTAL RESULTS

The Debye-Scherrer photographs of samples aged for various times at 709°C and 600°C are shown in Figs. 3 and 4, respectively. The Debye photographs were obtained using Cu K α radiation with 3-hour exposures. The 709°C series reveals that noticeable decomposition had occurred in the fine grained palladium-iridium after aging for four hours. No evidence of the accepted "side band" diffraction effect from a periodically modulated structure is seen in any of these diffraction patterns.

The diffraction lines of the precipitating phase are seen to intensify for the 8 and 16 hour aging treatments. The angle of diffraction of the second phase is larger than that of the parent phase. This indicates the smaller lattice parameter phase (iridium rich) has precipitated. The final observed lattice parameters observed for the two phases were calculated to be 3.834Å and 3.864Å. Such lattice parameters indicate relative phase concentrations of 94% Ir and 34% Ir respectively if Vagard's law is assumed to apply.

The Debye-Scherrer photographs of the samples aged at 600°C also show no sign of "side bands". No evidence of precipitation of a second phase was observed at 600°C for any of the aging times. There is evidence of lattice strains in the specimens which were aged 16, 32, 64 and 128 hours. The diffraction lines become broadened. This effect is easily seen for the 422 line, in which the previously easily resolved K α doublet has become one wide band.

Microhardness data for the two aging temperatures comprises Table I and is shown in Figs. 5 and 6. Again, it is seen that the two treatments yield different results. The 709°C samples show an initial decrease in hardness into the aging time range where second phase is ob-

served by x-rays. Then the hardness increases briefly before falling off again. The alloy never gets much harder than the value of the unaged sample.

On the other hand, the alloy aged at 600°C shows an initial hardening at two hours aging time. The hardness then decreases somewhat before increasing for longer aging times. The second stage hardening is observed to be nearly linear (vs. square root to time) up to 250 hours aging time. The hardness attained at this temperature is substantially greater than the hardness of the unaged specimen.

It was observed metallographically that grains would move with respect to one another when hardness indentations were made on the sample aged at 600°C for 128 hours. That is to say, a given grain would slip in the sample by movement at the grain boundaries. This effect was not observed in the samples aged less than 128 hours at 600°C.

The electron microprobe analyzer was used to check the homogeneity of the alloy. A result of these investigations was identification of inclusions that were observed via the microscope at 400×. The inclusions were identified as zirconium-oxide. There was no evidence of dissolved zirconium in the matrix. Also, there was no evidence of large scale inhomogeneities in the samples due to precipitation at grain boundaries or inclusions. Unaged samples were found to be quite homogeneous everywhere except very near the surfaces that were in contact with the crucible. Thus samples for study were taken from the center of the alloy castings.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

The results of the investigation of the palladium-iridium system have provided much information. The major objective of this investigation, as stated previously, was to check the applicability of existing spinodal theories with respect to the palladium-iridium system, but spinodal decompositions did not occur as predicted by theory. Before going into a complete discussion of this central issue, it is necessary to discuss some observations from the experimental results.

First the lattice calculations made for the two equilibrium phases compare favorably with the results of Raub and Plate[11] which were obtained during their determination of the palladium-iridium phase diagram (see Fig. 7). The iridium rich phase with 94% iridium has a composition very close to that given by the phase diagram at 709°C. The palladium rich phase with 34% iridium is of a different composition than the 2% iridium phase predicted by the phase diagram. This is quite an acceptable result because the palladium rich phase is not in a state of equilibrium. The fact that equilibrium has not been attained in the parent matrix helps to explain the scatter in spot locations observed in the diffraction rings. That is, some of the grains have been depleted more than others. This results in different areas of the parent matrix having different lattice parameters. The differing lattice parameters thus result in scatter in diffraction angles thus scatter in the points makes up the diffraction ring.

The second observation was the rather unexpected hardness versus time curve. A similar effect was observed by Raub and Plate in some of their experiments. This phenomenon will be discussed later in context with the decomposition reaction.

The third noteworthy experimental observation is the movement of grains with respect to one another during hardness testing. This happened in the samples aged for very long times. It indicates grain boundary precipitation of a soft ductile phase. In this way these results agree with the conclusions of Carpenter[2] in his investigation of gold-platinum. The gold-platinum that had been hardened spinodally was found to have nearly no plasticity and appeared to fracture in a brittle manner. Carpenter attributed the apparent brittle fracture to grain boundary precipitation. The grain boundary precipitation competes with the demixing of the alloy. Thus a significant amount of grain boundary precipitation can occur during the hardening process. Deformation then may occur at the grain boundaries after sufficient aging.

Before beginning the experimental investigation of the palladium-iridium alloy system, calculations using Cahn's criterion [Eq. (3)] were made to predict the spinodal; that is, Eq. (3) was used to predict the amount that the miscibility gap (thus the critical temperature) would be lowered due to strain energy contributions to the free energy. The palladium-iridium system has a wider miscibility gap and a smaller size difference than does the gold-platinum system. The system, however, has a larger average Young's modulus and difference in Young's modulus than does the gold-platinum system. All factors considered, one would expect that palladium-iridium alloys would decompose spinodally. Calculations of the coherency strain energy contribution to the free energy indicated the coherent miscibility gap would be lowered by about 300°C. Exaggeration of the factors involved would allow one to rationalize a lowering of the miscibility gap by 600°C. Thus, the expected temperature at which the alloy would undergo spinodal decomposition would be about 900°C to 1200°C.

The latter is most likely according to present theory and the former is somewhat of a lower limit.

Even with such promising theoretical predictions, no "side band" effect was observed in this study at either 709°C or 600°C. The only x-ray diffraction effect observed other than evidence of precipitation was broadening of the diffraction lines. Diffraction theory explains how strains in metal lattices can result in the former effect.[12] A similar effect can result from surface deformation but because of the care in specimen treatment this was not considered likely. The presence of coherency strains in the structure is further indicated by the large increase in hardness that occurred after aging at 600°C for a sufficient time.

Thus, the evidence seems clear that palladium-iridium does not undergo classic spinodal decomposition at 709°C or 600°C. It also seems clear that existing spinodal theory is not applicable to this alloy. A test of the theory could be made at still lower temperatures but the reactions become so slow that such experiments are impractical. Because the atomic size differences in the palladium-iridium system are smaller than in the gold-platinum system, the most plausible factor to consider for the failure of the theory is the Young's modulus. As was noted before, iridium has nearly five times the modulus of palladium.

Let us consider what happens physically in spinodal decomposition. As was mentioned earlier, composition fluctuations which occur during spinodal decomposition are felt to be either in the form of a three-dimensional Fourier function or a one-dimensional sinusoidal variation. It is plausible that the extremely high modulus (low elastic compliance) of the iridium results in the inability of iridium rich "clusters" of atoms to fit coherently in either of the above physical configurations.

In the one dimensionally varying or lamellar model, this could be viewed as resulting in a reduction in lamella length and width. The reduction being to the degree that the iridium-rich clusters would be more like GP zones than real lamella. Such a configuration would not have periodic composition variations and thus would not be expected to yield x-ray diffraction "side bands".

The modification of the Fourier model which would explain the results would be similar. The Fourier configuration would be expected to be replaced by a number of iridium-rich cubes, spheres, or platelets in the matrix. All the iridium-rich metal is surrounded by palladium-rich alloy. Such a structure does not have periodic composition fluctuations. Thus, there would be no x-ray side band effect expected.

Therefore, instead of classical spinodal decomposition occurring in palladium-iridium at the predicted temperature, a decomposition of a different nature evidently occurs. It is emphasized at this point that the effects of the coherency strains observed in the x-ray patterns for samples aged at 600°C strongly indicate that 600°C is below the critical temperature of the coherent miscibility gap for this alloy. Thus, decomposition of some nature has occurred at 600°C but it is not of the classic spinodal type. (The same was not indicated for 709°C case.)

Additional information about the nature of the decomposition reaction is provided by the hardness data. First consider Fig. 8, the hardness versus composition curve for palladium-iridium solid solutions obtained by Raub and Plate.[11] To consider the first stage of hardening shown in Fig. 6, disregard other hardness contributions for the moment and consider the following three states in the demixing process. The first state, (1) in Fig. 8, is the homogeneous alloy of 56-44 at.%

composition. The second state, (2) in Fig. 8, is the state where compositional fluctuations have occurred to the degree that the iridium-rich alloy is of about 50% iridium. The third state, (3) in Fig. 8, is later in the decomposition when the iridium-rich metal has a higher iridium concentration. In the third state, the iridium-rich solid solution has a lower hardness than the iridium-rich clusters of the second state.

Because of the added hardness of the iridium-rich metal in state 2 of Fig. 8, one would expect the total alloy hardness to increase to a maximum when the iridium-rich clusters are near that state. This should be true even though the palladium-rich metal has a lower hardness than the original 56-44 alloy. After state 2, the total hardness would then be expected to fall off rapidly as the hardness of the iridium-rich metal begins to fall off.

Figure 9 shows a sketch of hardness versus composition change of iridium-rich volumes expected from such a demixing phenomenon. No attempt is made to consider size or shape of the various component clusters. Again it is emphasized that the stress necessary to move the dislocation through the harder portions of the alloy is assumed to be the limiting factor for dislocation motion. Thus this factor controls the hardness for the entire alloy. This statement is made because the small distances between iridium-rich clusters expected in the decomposed alloy would not allow dislocations to "bow out". Wavelengths of the composition modulations of the spinodally decomposed Cu-Ni-Fe and AuPt systems average about 150Å. Thus for the Pd-Ir system, composition fluctuations of this order are reasonable. Further justification of the above conclusion is not possible in this study.

The second stage hardening of Fig. 6 could be thought of as the

result of a modulus effect or a strain energy effect.

The line energy of a dislocation is

$$E = \frac{Gb^2}{2} \tag{4}$$

where G is the shear modulus and b is the dislocation Burgers vector. The critical force to move a dislocation is

$$F = \frac{b^2}{2}\frac{\partial G}{\partial x} . \tag{5}$$

Thus one could determine the increase in hardness (difficulty in moving dislocations) by its dependence upon the variation in modulus between palladium-rich alloy volumes and iridium-rich volumes as a function of (x). Unfortunately, no valid shear modulus data is available for palladium-iridium as a function of composition, thus (x).

Equation (5) does point out, however, that an increase in solid solution hardness of the total alloy would be expected to accompany an increase in shear modulus difference between various clusters in the alloy. If the alloy decomposition resulted in a sinusoidal variation of the shear modulus, the maximum increase in shear modulus between clusters would be:

$$\left(\frac{\partial G}{\partial x}\right)_{max} = \frac{2\pi B}{\lambda} \tag{6}$$

where λ is the spacing of the iridium-rich clusters and B is the amplitude of the modulus change from the palladium-rich to the iridium-rich material. Because the magnitude of the variation of shear modulus is indeterminable, one can only estimate the extent to which the iridium-rich clusters

contribute to the proposed hardening.

To consider coherency strain contributions we will neglect the relative hardness contribution of alloy clusters of differing compositions. The stress that can act on dislocations due to coherency strains between adjacent volumes of metal has been treated by Dahlgren.[13] It was shown for the Cu-Ni-Fe spinodal that the yield stress was directly proportional to the difference in cubic lattice parameters of the two extreme compositions present in the aged alloys.

The physical situation of the Pd-Ir system is somewhat different from that of the Cu-Ni-Fe system. Nonetheless, the retarding stress for dislocations due to coherency strains should be much the same. Thus, one would expect an approximately linear increase in yield stress with changing composition within the segregated region. Note that at this point of the discussion no real second phase has precipitated; only a "demixing" has occurred. It is known that hardness increases as yield stress increases for a given alloy. A possible hardness versus cluster composition difference sketch is shown in Fig. 10. It has been drawn linearly implying its proportionality to yield stress. This proportionality need not be the case but was assumed since no better relationship is known. It is a worthwhile assumption to the degree that hardness does increase when yield stress increases.

Combination of the component hardness effect of Fig. 9 and the strain energy effect of Fig. 10 with iridium cluster yields Fig. 11. The hardness versus composition separation of clusters plot of Fig. 11 compares well with the experimental plots of hardness versus square root of time in Fig. 6. One would expect that the controlling factor for this demixing would be the diffusion of atoms. The diffusion rate would be approximately

proportional to the square root of time at early stages in demixing. Later in the demixing process the diffusion rate would be diminished by the strain energy factor. For spinodal decomposition, the interdiffusion coefficient was derived by Cahn[10] to be

$$M \frac{\partial^2 f'}{\partial c^2} + \left(2\eta^2/1-\nu\right) \qquad (7)$$

where the $\left(2\eta^2/1-\nu\right)$ is the strain energy contribution and M is a constant. Taking this into account, one can conclude that relative component hardening and coherency strain hardening satisfactorily explain the two stage hardening curve observed in aged palladium-iridium alloys.

The x-ray results constitute final evidence that coherency strains are significant in the second stage of the hardening and not in the first. Figure 4 shows noticeable x-ray evidence of lattice strains in specimens aged for 16 hours. This would correspond approximately to the onset of the second stage hardening of Fig. 6.

The hardness curve for the specimens aged at 709°C shows an initial decrease in hardness. It is concluded that the 709°C samples do not experience coherency hardening because coherency hardening should increase continuously. Thus, one also concludes that coherent demixing did not occur in the 709°C samples. This then means that 750°C is above the critical temperature, T_c, of the coherent phase diagram. 750°C is chosen as the temperature for extra safety since the 44% Ir alloy is slightly to the left of the center of the miscibility gap. One can conclude that 600°C is below T_c because of the coherency hardening observed. Thus the experimental T_c for the palladium-iridium system is between 600 and 750°C. This value is much lower than the 1200°C critical temperature predicted

by Cahn's theory.

It was pointed out in the introduction that Cahn's theory explicitly assumes that the average Young's modulus and average strain terms are necessary and sufficient to determine the coherency strain energy. Because of these factors Cahn is able to conclude that the strain energy is independent of wavelength. On the other hand composition fluctuations in palladium-iridium alloys would result in large differences in Young's moduli for volumes of different composition. This would result in strains varying greatly in the lattice. Thus Cahn's assumption, that the average strain per unit composition change is sufficient to describe the strain effects, is inappropriate for palladium-iridium. It is also inaccurate for other cases but the effect of the error would probably not be as large in other systems.

A further point is that the greatest lattice strains would be found in the palladium-rich metal surrounding the iridium-rich clusters. This now means that cluster interface areas are important to the strain energy of the decomposed alloy. This statement is contrary to Cahn's conclusion that the strain energy does not depend upon the wavelength of composition modulations of "spinodally" decomposed alloys. Cahn's conclusion was based upon the assumption that the strains in the lattice were homogeneous. This assumption, of course, is not considered valid for palladium-iridium as noted above. Since the strain energy does depend upon the interface area in a given volume of palladium-iridium alloy, then it also depends upon the wavelength of the composition modulations. Reinforcement of this point lies in the very fact that the wavelength of spinodally decomposed Cu-Ni-Fe was observed by Hillert[3] to increase with aging time. The elimination of interface area could provide the energy to drive the reaction

in this direction, thus indicating its probable importance in the Cu-Ni-Fe system. One may now ask how these conclusions apply to the palladium-iridium results.

First consider the direct effect of the varying Young's modulus in decomposed palladium-iridium metal. Most of the lattice strain would be in the palladium-rich metal, because of its lower Young's modulus. Also, most of the strain in the palladium-rich metal would be expected near the cluster interface. By Eqn. (3) one can qualitatively see that strain (ϵ) would be increased more than E would be decreased. The fact that ϵ is squared in the equation is of paramount importance. Thus, because of the large difference in Young's moduli of palladium and iridium, the result of such a consideration would be more than double of $T-T_c$.

Second, as pointed out, the strain energy would be closely related to the cluster interface area. The importance of this can be appreciated with the help of an illustration. Consider a lamella of metal 150Å×1500Å× 1500Å. If this lamella were divided into one hundred cubes of 150Å edge length, the total surface area of the metal would more than double.

It has already been concluded that the iridium clusters are not of a periodic lamellar nature. Thus one could further conclude that interface areas of decomposed palladium-iridium alloys could be significantly larger than those implied by classic spinodal theory. This could also then increase $T-T_c$.

Thus, instead of the coherent miscibility gap being depressed 300°C by coherency strains, it is easy to appreciate a possible depression of about 800°C. This would set T_c between 600 and 700°C. The result is a better agreement of experiment and theory. Unfortunately a more quantitative treatment of these factors is not possible due to limited data.

In summary there are two main points about the applicability of spinodal theory to the palladium-iridium system. First, although palladium-iridium should presumably be a "spinodal" system, it exhibits coherent precipitation instead. The size and shape of the precipitate is controlled by diffusion distances, surface area considerations, and geometric compatabilities. The last two factors seem to be due to the extreme variations in Young's moduli in this system.

Second, it is emphasized that palladium-iridium is quite a special spinodal system. From it new insights can be gained into spinodals. Thus now one can look at spinodal decomposition slightly differently and more realistically than in the past. It would be well to consider the spinodal decomposition to be a special form of coherent precipitation rather than merely similar to coherent precipitation. The special form being the limit where no activation energy is necessary. One can thus consider the spinodal to be a periodic coherent precipitate and the palladium-iridium system the link between classical spinodal decomposition and classical precipitation.

V. CONCLUSIONS

From this study it can be concluded that the palladium-iridium system does not experience spinodal decomposition at 709°C or 600°C. At 709°C an iridium-rich incoherent precipitate formed. At 600°C two stage hardening was observed and attributed to coherent clusters of iridium-rich metal. The critical temperature of the coherent miscibility gap was concluded to be between 600 and 750°C. Movement of grains at grain boundaries, observed during hardness testing, was concluded to be due to plastic flow of a relatively soft grain boundary precipitate.

The two stage hardening of the alloys aged at 600°C was concluded to be the product of two hardening mechanisms. The first stage hardening was concluded to be due to the extra hardness of the iridium-rich clusters. The second stage hardening was attributed to shear modulus variations or coherency strain effects.

The existing spinodal theory was shown in this study to fail to predict the proper depression of the coherent miscibility gap and the manner of demixing of palladium-iridium. These failures were attributed to the large differences in Young's moduli involved in the palladium-iridium system and to approximations in the theory. The low elastic compliance (high Young's modulus) of the iridium-rich clusters was concluded to prevent iridium-rich metal from forming periodic lamella. It was concluded that the large Young's modulus difference of the two metals resulted in extra strains in the palladium-rich volumes. It was assumed that most of the coherency strain would be near the cluster interface. These two factors affected approximations made by Cahn and allowed qualitative agreement of experiment and theory as to the effect of coherency strains on the critical temperature of the coherent miscibility gap.

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REFERENCES

1. G. Borelius, Trans. AIME 477 (1951).
2. R. Carpenter, Ph.D. Thesis, University of California, Berkeley, UCRL-16609.
3. M. Hillert, Acta Met. 9, 525 (1961).
4. V. Daniel and H. Lipson, Proc. Roy. Soc. A181, 368 (1943).
5. V. Daniel and H. Lipson, Proc. Roy. Soc. A182, 378 (1944).
6. S. Ogawa, Acta. Cryst. 11, 872 (1958).
7. J. Cahn and J. Hilliard, J. Chem. Phys. 28, 258 (1958).
8. J. Cahn, J. Chem. Phys. 30, 1121 (1959).
9. J. Cahn and J. Hilliard, J. Chem. Phys. 31, 688 (1959).
10. J. Cahn, Acta. Met. 9, 795 (1961).
11. E. Raub and W. Plate, Z. Metall. 48, 444 (1957).
12. B. E. Warren, Prog. Met. Phys. 147 (1959).
13. S. D. Dahlgren, Ph.D. Thesis, University of California, Berkeley, UCRL-16846.

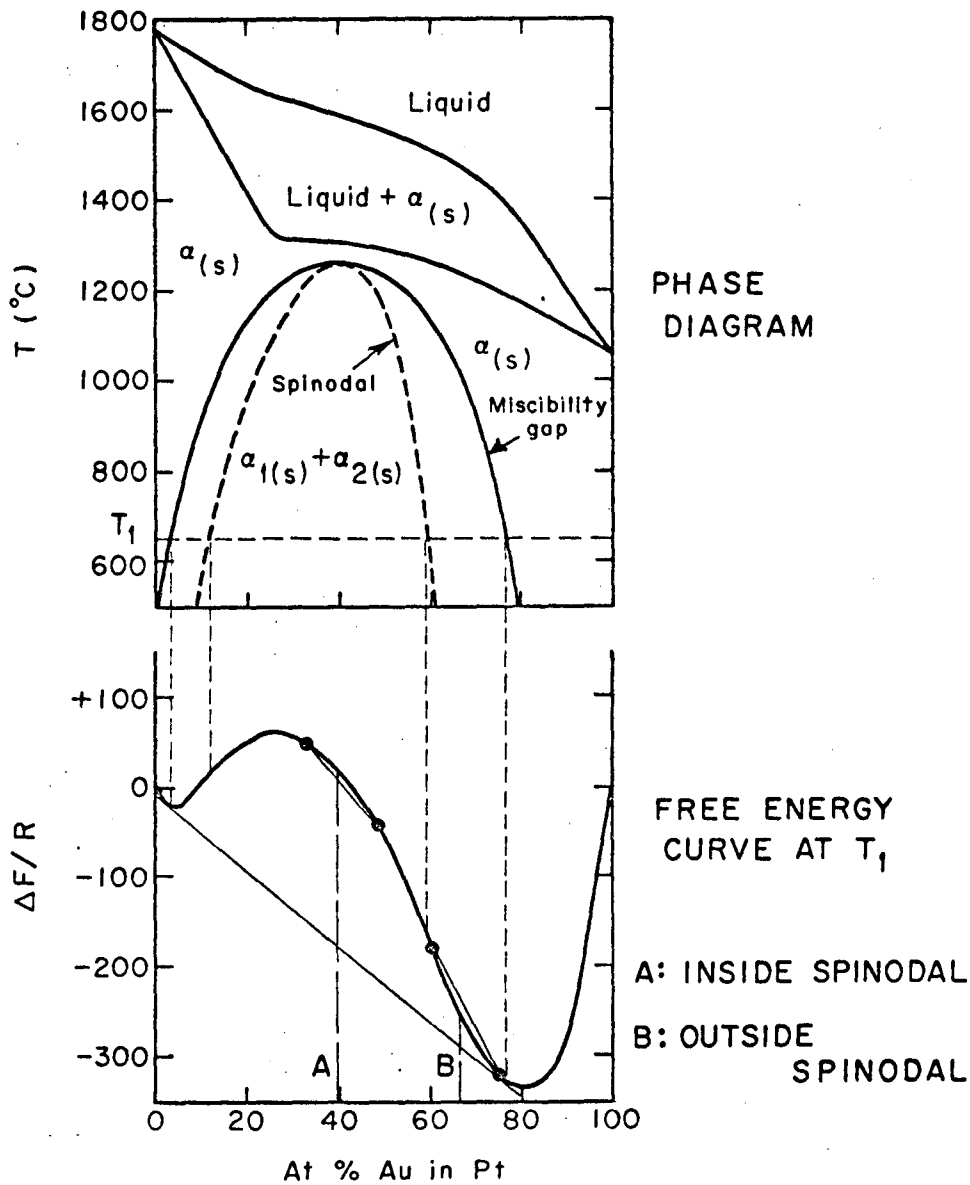

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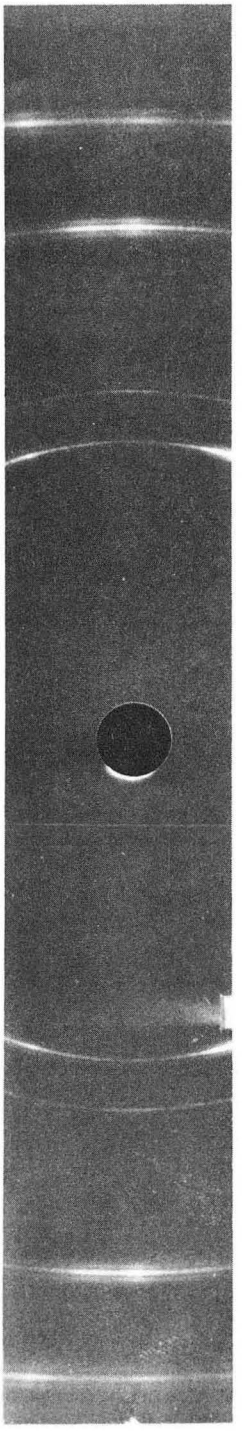
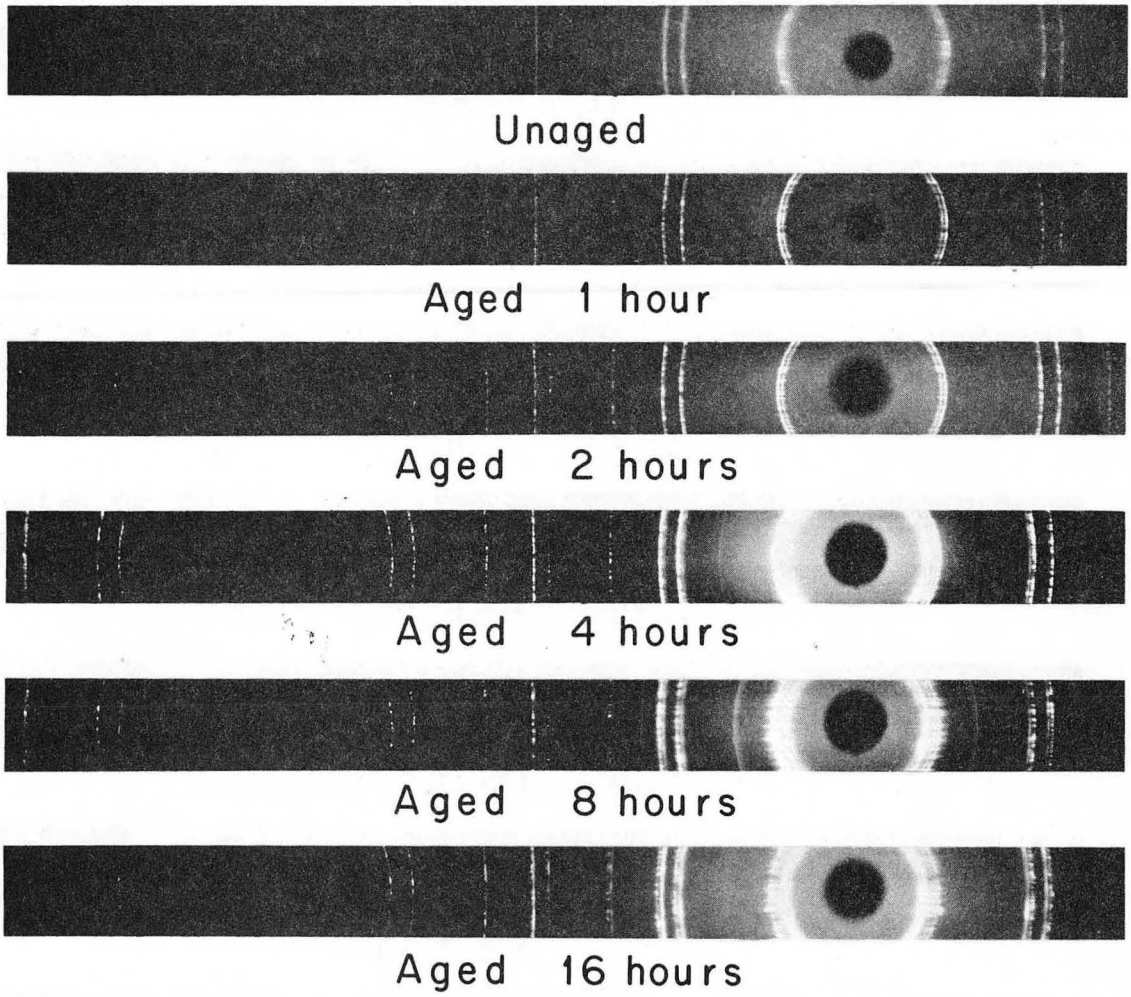
Fig. 1. Phase diagram of gold-platinum alloy system showing spinodal curve. The shape of the free energy vs composition is shown in the figure below for one temperature. The relationship of the free energy curve to the spinodal is indicated by the vertical lines.



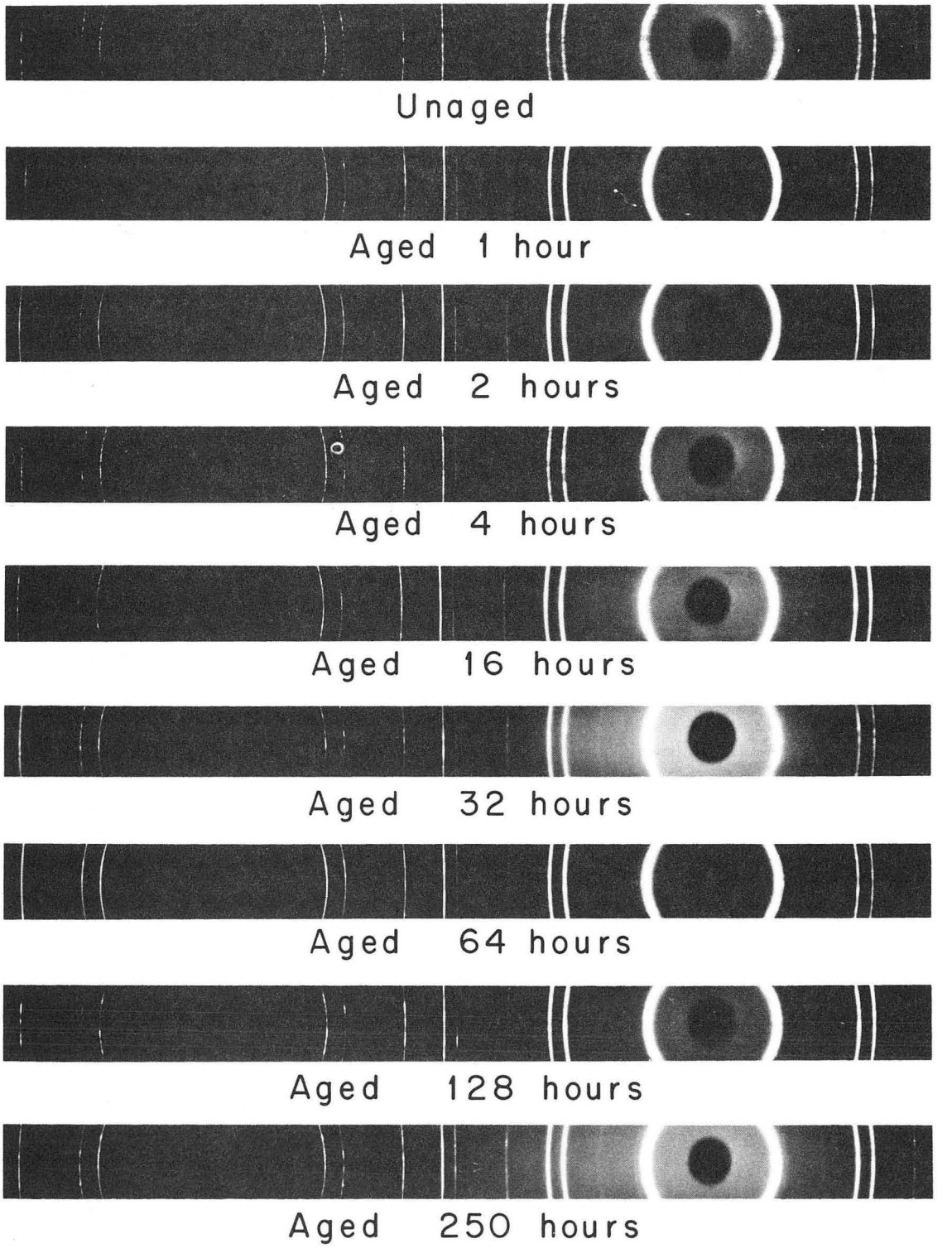
ZN-5244

Fig. 2 X-ray diffraction pattern of quenched and aged Pt-Au alloy showing "side bands" at the sides of the Bragg lines.[2]



ZN-5990

Fig. 3 X-ray diffraction patterns of quenched Pd-Ir alloys aged at 709° showing precipitation of iridium-rich phase with increasing aging times.

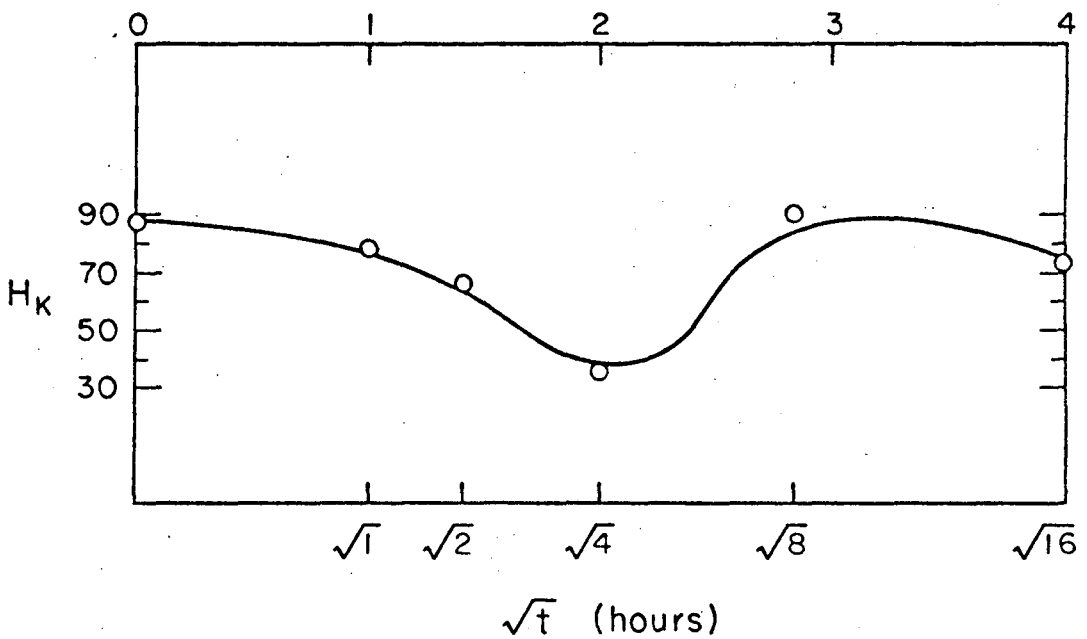


ZN-5989

Fig. 4 X-ray diffraction patterns of quenched Pd-Ir alloys aged at 600°C showing evidence of coherency strains with increasing aging times.

Table 1. Hardness data for quenched and aged Pd-Ir Alloys

Time (hrs)	Hardness (Knoop) Specimens Aged at 709°C	Hardness (Vickers) Specimens Aged at 600°C
0	88	592
1	78	602
2	66	705
4	35.5	666
8	89.5	-
16	72.5	648
32	-	718
64	-	724
128	-	756
250	-	804



MUB-13474

Fig. 5. Plot of Knoop hardness vs square root of aging time of Pd-Ir alloys aged at 709°C.

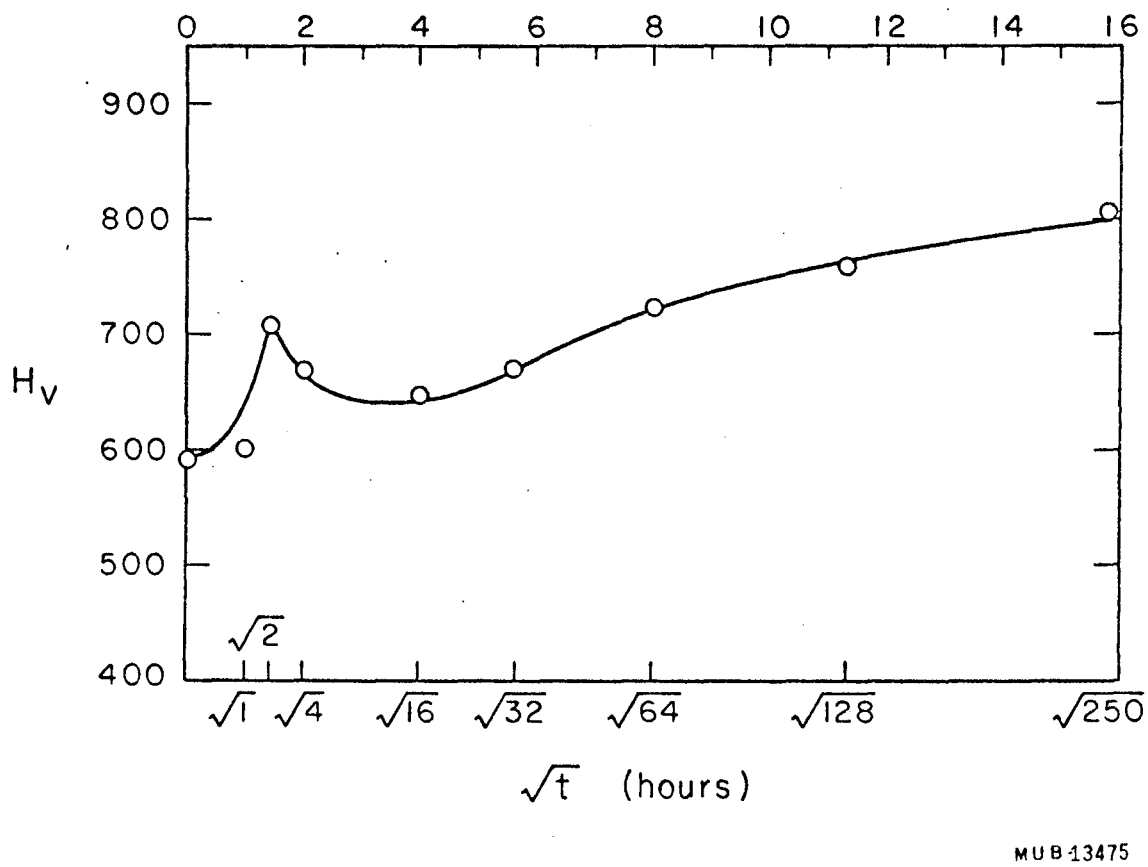
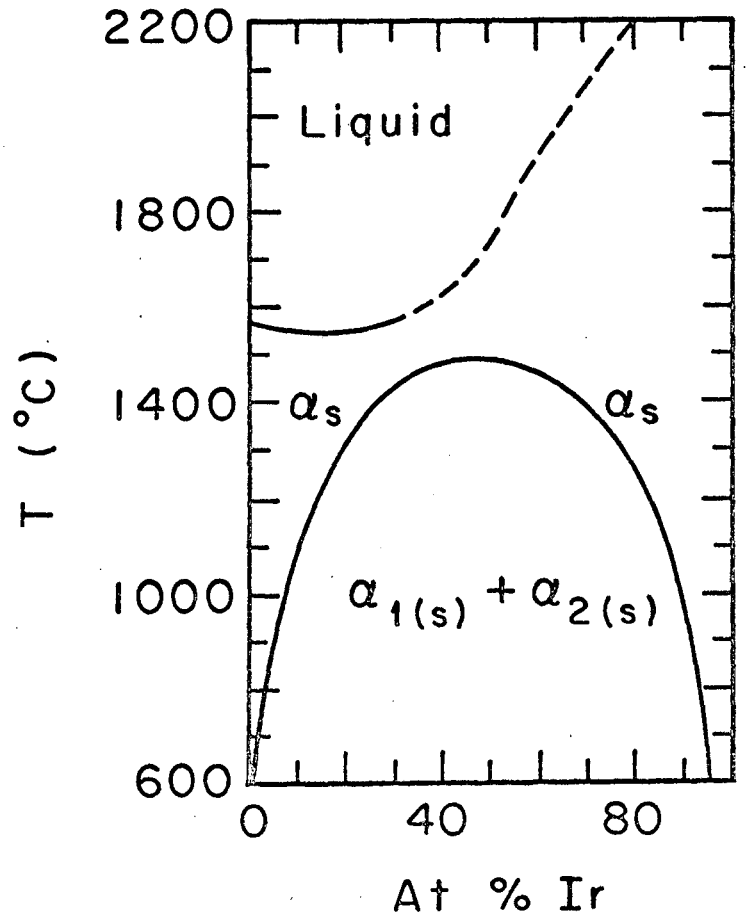


Fig. 6. Plot of Vickers hardness vs square root of aging time of Pd-Ir alloys aged at 600°C.



MUB-13476

Fig. 7. Phase diagram of palladium-iridium system.[11]

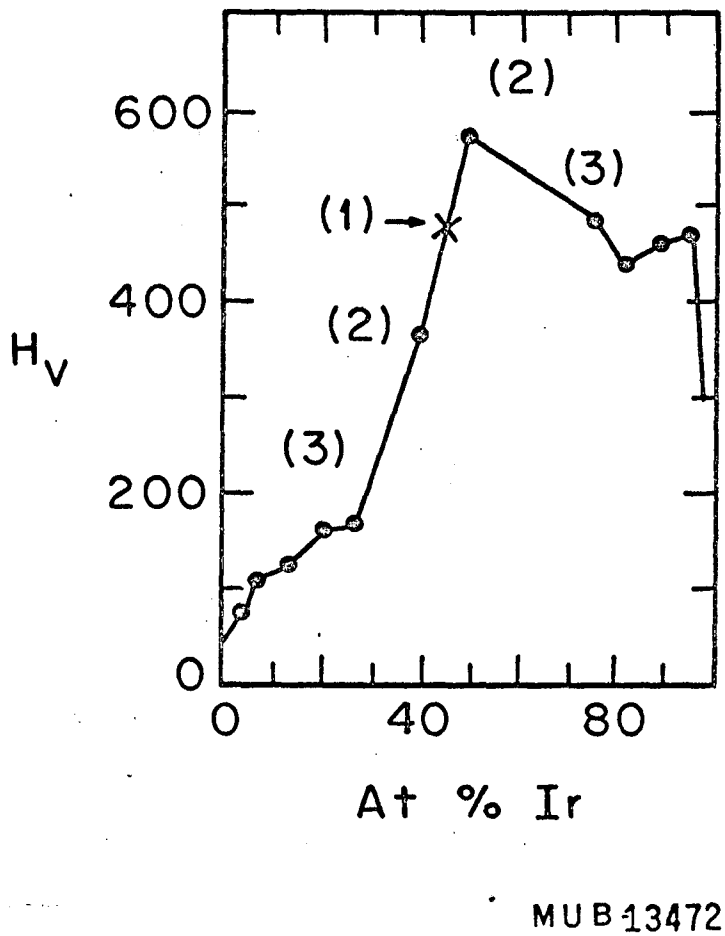
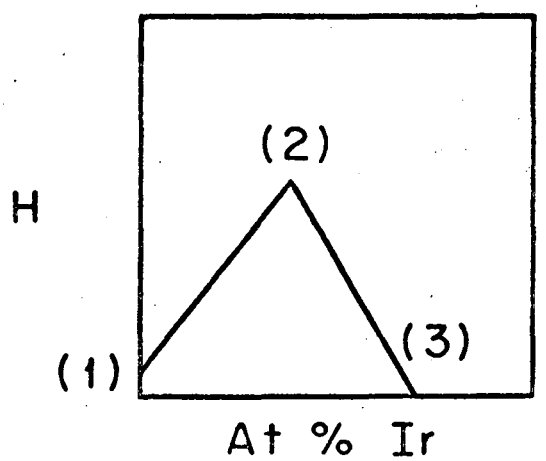
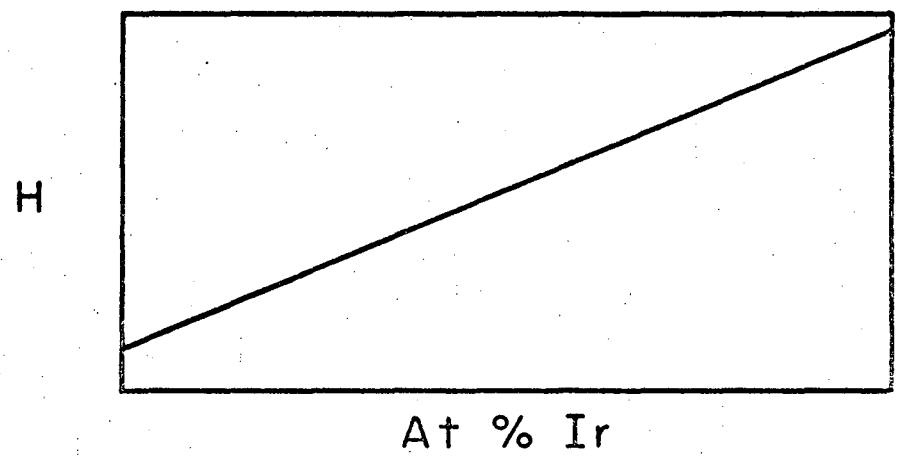


Fig. 8. Plot of Vickers hardness vs atomic percent iridium of solid solution Pd-Ir alloys.[11]



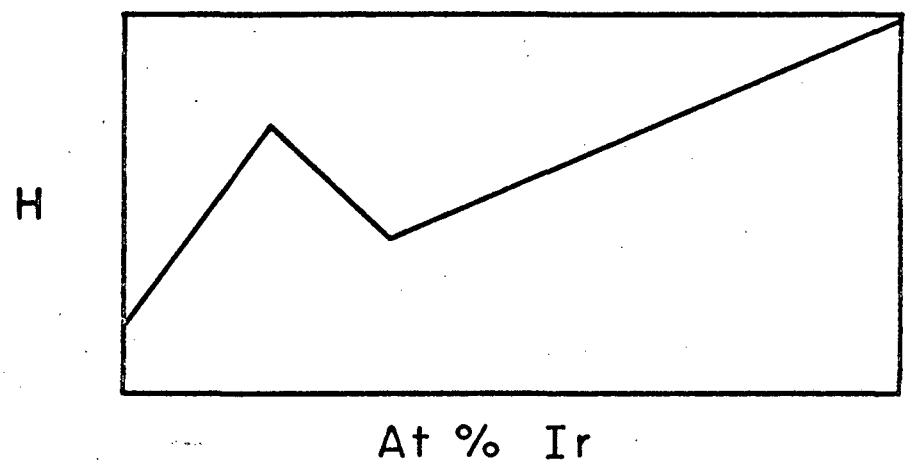
MUB-13473

Fig. 9. Sketch of hardness of Pd-Ir alloy vs composition of iridium-rich clusters, due to hardness of the iridium-rich clusters.



MUB-13470

Fig. 10. Sketch of hardness of Pd-Ir alloy vs composition of iridium-rich clusters, due to coherency strains.



MUB-13471

Fig. 11. Sketch of hardness of Pd-Ir alloy vs composition of iridium-rich clusters, due to both cluster hardness and coherency strain effects.

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