

DECOMPOSITION REACTIONS IN GOLD-PLATINUM ALLOYS AND THEIR  
EFFECTS ON STRENGTH AND FRACTURE CHARACTERISTICSE. R. Parker, R. W. Carpenter, and V. F. Zackay<sup>†</sup>

## INTRODUCTION

Gold and platinum are highly ductile, face centered cubic metals, relatively weak in their pure states. They form a continuous series of solid solution alloys at elevated temperatures, but upon cooling separate into two saturated solid solution phases within the composition limit shown in the phase diagram of Fig. 1.

When a homogeneous single phase alloy, having a composition such that at lower temperatures it will transform to two phases, is cooled from the  $\alpha$  phase field into the two phase region, precipitation occurs. On Fig. 1 the miscibility gap is divided into two regions by the dotted lines (which are not phase boundaries): (1) a central region between the dotted lines and (2) an exterior region bounded by dotted lines and the two phase region boundary. The significance of the dotted lines, which are called spinodal curves, is related to the nucleation process which initiates the solid state precipitation reaction. When the metastable homogeneous alloy lies in that part of the two phase region bounded by the spinodal curves, it has been shown that nucleation of the precipitating phases takes place rather uniformly throughout the volume of the solid and on a very small scale; for an alloy transformed in the non-spinodal section of the miscibility gap, the precipitation reaction has been shown to occur more slowly and with a less geometrically uniform array of precipitating particles.<sup>1-6</sup> In an oversimplified sense, spinodal decomposition can be termed "homogeneous solid-state nucleation" and the general case of non-spinodal nucleation and growth is identified with heterogeneous nucleation. Thus spinodal decomposition is a special case of general nucleation and growth precipitation reactions and the two processes, heterogeneous and homogeneous nucleation, are competitive within the spinodal region. The distinction in definition between the two is made in terms of chemical thermodynamics, neglecting strain and interfacial free energies, as shown in the free energy diagram of Fig. 1.

The free-energy curve for the metastable homogeneous alloy, at some temperature  $T_1$  within the two phase region, is concave downwards between the inflexion points, which are the spinodal points at  $T_1$ . The locus of spinodal points at all temperatures in the two phase region are the dotted spinodal curves shown on the phase diagram. Because of the downward concavity, composition fluctuations in an alloy with average composition between the spinodes will lower the Gibbs' free energy of the system and thus they are stable and will continue to grow. An alloy with average

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composition in a region of upwards concavity of the free-energy curve exhibits the opposite behavior. There a small composition fluctuation causes an increase in the free energy and is unstable; it tends to disappear. The composition fluctuation in this region must be large in order to lower the system free energy; this amounts to an energy barrier for nucleation and is analogous to the concept of a critical nucleus required for the growth of a precipitate particle in most nucleation and growth precipitation reactions.

Of specific interest in the present investigation was the effect of spinodal decomposition on the mechanical behavior of alloys. As had been previously noted in the literature, alloys transformed within the spinodal composition limits are often brittle. The brittle behavior and potentially high strength of such materials is of great interest. One purpose of this investigation was to determine, if possible, the cause of the brittleness and to evaluate the hardening process.

#### EXPERIMENTAL RESULTS

Two alloys were used -- one containing 80% platinum and 20% gold, the other containing 40% platinum and 60% gold. Figure 2 shows a typical microstructure of the 40% platinum - 60% gold alloy when annealed for a long time within the miscibility gap; the annealed alloys are ductile and their work hardening characteristics are those normally observed for face centered cubic solid solutions. The room temperature stress-strain curve for the 40% platinum - 60% gold alloy, annealed for 97 hours at 980°C, is shown in Fig. 3. The strength is at the level one might expect for such an alloy, but the elongation, which was only 11%, is considerably lower than values normally obtained with face centered cubic solid solutions. The ductile nature of the fracture is shown in the photograph of Fig. 4.

The tensile specimens used in this investigation were 0.020 inch diameter wires, this small diameter was used in order to facilitate quenching from the solid solution range above the miscibility gap. However, reactions occur so rapidly in this alloy system that it turned out to be impossible to suppress the nucleation and growth of the second phase in the 80-20 alloy, even with cooling rates as high as 3400°C/second. The quenched alloy, instead of being a ductile, supersaturated solid solution as expected, was extremely brittle and had no measurable elongation in a tensile test. The fracture strength was of the order of 130,000 psi. Figure 5 shows that the fracture in this material was intergranular. Microscopic examination of a polished section revealed that the second phase had formed at the grain boundaries and that the path of the fracture was through this phase. Microhardness readings showed that within the grains of the matrix the Vickers hardness had reached a value of about 410. (Microhardness values are given in Table 1 for a number of different conditions for the two alloys investigated.) The composition of the grain boundary phase forming in the 80-20 alloy was estimated from the phase diagram to be approximately that of the 40-60 alloy. Subsequent tests on the 40-60 alloy quenched from the solid solution region did produce a ductile condition which fractured through the grains, and the strength of the quenched material was found to be approximately 130,000 psi, as is shown in Fig. 6. In the 40-60 alloy the kinetics of decomposition were such that significant amounts of the second

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phase did not form at the grain boundaries and the material failed with a shear-type fracture, as can be seen in the photograph of Figs. 7 and 8.

The structure of the 80-20 alloy in the quenched condition consisted of hard, strong grains cemented together with a relatively weak, thin layer of a ductile gold-rich phase (see Fig. 9). The fracture was "brittle", even though this second phase was inherently ductile. However, since it had much lower strength than the matrix material, it deformed plastically at low stress levels. Because of its small volume, the grain boundary phase did not contribute significantly to the overall elongation of the test piece before it reached its ultimate limit of plastic deformation and fractured. Thus the brittle behavior of this alloy could be attributed to a peculiar microstructure in which two somewhat ductile phases coexisted in an unusual geometry, with the stronger one being the large bulk of the material in the form of grains, and the weaker one being a ductile boundary phase which failed by shear at a stress too low to cause significant plastic flow in the grains. This condition is analogous to a soft soldered lap joint of two steel strips, in which the thickness of the solder is small. When such a joint is pulled apart in a tensile test, the overall deformation is very small even though both the steel and the solder, when tested separately, would exhibit substantial amounts of ductility prior to failure.

In the 80-20 platinum-gold alloy, it was evident that grain boundary precipitation was occurring at a rate competitive with "spinodal" decomposition. Christian<sup>1</sup> has shown that the ratio of the free energy required to form a grain boundary nucleus to that needed to form a homogeneous nucleus decreases as the ratio of the grain boundary energy to the interphase boundary energy increases. When the ratio of grain boundary energy to interphase boundary energy is more than 0.9, nucleation at grain corners is the fastest; when this ratio is between 0.9 and 0.6, the nucleation rate at grain edges is the most rapid, whereas if it is between 0.6 and 0.25, grain boundary surface nucleation will become predominate. Below 0.25, the only effective nucleation is random. Evidence of early nucleation and growth at grain edges can be seen in Fig. 9, along with substantial, but thinner, grain boundary precipitation. In systems of this kind where segregation of like atoms occurs spontaneously at lower temperatures, it is not unreasonable to expect partitioning of an alloying element at grain boundaries, even at temperatures above the miscibility gap. Consequently, it is not unreasonable to expect that the "nucleation" occurring at grain boundaries did not require significant composition fluctuations beyond those that pre-existed due to the partitioning of gold atoms at the solution temperature. To check the possibility of the growth rate being rapid enough to account for the formation of a grain boundary film, calculations based on measured diffusion coefficients taken from the literature were made. With a diffusion coefficient of  $4 \times 10^{-9}$  cm<sup>2</sup>/sec, even with a cooling rate of 3400°C/second, it is possible for a film of the second phase 400 atoms thick to form as the alloy cools through the temperature range between 1150° and 850°C. Even such a thin film would be wide enough to have accounted for the weak grain boundaries in this material. The photomicrograph of Fig. 9, and other similar observations made during the course of the investigation, indicated that the films formed during the heat treating process were actually much wider than was

indicated by the diffusion calculations. Since it seemed to be virtually impossible to quench the 80-20 alloy without producing the brittle condition caused by grain boundary precipitation, attention was thereafter concentrated on the 40% platinum - 60% gold alloy.

As was mentioned previously, the 40-60 alloy could be quenched from the solid solution range without the formation of a significant grain boundary network. This condition was found to be consistent with diffusion data, which showed that the diffusion rate of platinum (which would have to diffuse and concentrate at the grain boundaries to form a platinum-rich grain boundary phase in this alloy) was approximately two orders of magnitude lower than that of gold in platinum.<sup>9</sup> Thus the 40-60 alloy could be successfully quenched and aged for different lengths of time in order to determine the characteristics imparted by decomposition at a temperature below the spinodal. The solution treating temperature selected was 1225°C and the aging temperature was 510°C. The stress-strain curve for an alloy aged one hour at 510°C is shown in Fig. 10. The high strength and very low ductility are in sharp contrast with those produced by solution quenching alone. Of particular interest is the very high rate of strain hardening exhibited by the quenched and aged alloy. The hardening rate is much too high to be accounted for on the basis of ordinary dislocation interaction hardening. Consequently, a more detailed study of the structure produced by decomposition below the spinodal was undertaken and a theoretical basis was developed for the strain hardening characteristics. The solid curve in Fig. 10 is the experimental curve and the small circles near the upper end are those points calculated on the basis of the theory evolved which will now be described.

#### DISCUSSION

In alloys quenched from the solid solution range to below the spinodal curve, even small fluctuations of composition cause a decrease in free energy, and small regions where the fluctuations occur become stable and grow with time. Such small regions of non-uniform composition disturb lattice periodicity and can be detected by x-ray diffraction when the scattering power of the atoms is quite different or when the distance between atomic planes varies with composition. In the case of gold-platinum alloys, the scattering power of the two atoms is nearly the same; therefore, differences in the x-ray diffraction pattern in the early stages of aging must result from variations in lattice constant from point to point in the diffracting crystals. Such effects have been studied by a number of investigators. During the early stages of transformation, "side bands" appear on the diffraction pattern. Side bands are diffuse lines adjacent to the main Bragg lines of the homogeneous solution. A typical powder pattern with side bands is shown in Fig. 11.

When the segregated regions are close together in the lattice, the side bands are relatively far from the Bragg lines. The distance from center to center of segregated regions is called the "wavelength" of the structure, and measurement of the position of the side bands relative to the position of the parent Bragg line can be used to calculate a wavelength,  $\lambda$ , for an alloy in a particular condition. For the purpose of computations, it can be assumed that the composition varies sinusoidally with distance

in the lattice. Since evidence in the literature indicates that the lattice parameter is very nearly proportional to the composition for gold-platinum alloys in the solid solution state, the variation in lattice parameter can be taken as being proportional to the concentration at any point in the lattice. At 500°C the equilibrium gold-rich phase contains only 20% platinum, whereas the platinum-rich phase contains 98% of this element. The difference in the lattice parameters of alloys of these two compositions is about 0.115Å units, and a homogeneous solid solution containing 40% of platinum would have a lattice parameter of 4.014Å. The maximum shear strain possible due to mismatching lattices would be  $\Delta a/a$ . Plastic flow causes a lattice mismatch, and the lattice shear strain as a function of plastic deformation can be represented by the following equation when  $nb$  is small compared with  $\lambda$ :

$$\gamma = \gamma_{\max} \sin 2\pi \frac{nb}{\lambda} \quad (1)$$

or

$$\gamma = \gamma_{\max} \sin 2\pi \frac{n}{\lambda'}$$

where  $\gamma$  is the lattice disregistry shear strain produced by the passage of  $n$  dislocations of Burger's vector,  $b$ , through the lattice.  $\gamma_{\max}$  is equal to  $\frac{\Delta a_{\max}}{2a}$ , and  $\lambda$  is the wavelength in angstrom units of the composition fluctuation, and  $\lambda'$  is the number of Burger's vectors per wavelength,  $\lambda$ . Substituting in the  $\Delta a_{\max}$  value of 0.115Å and a lattice constant value of 4.019Å, yields the following equation

$$\gamma = 1.43 \times 10^{-2} \sin 2\pi \frac{n}{\lambda'} \quad (2)$$

The internal stress produced by the lattice disregistry would thus be given by

$$\tau_i = (G) (1.43 \times 10^{-2}) \sin 2\pi \frac{n}{\lambda'} \quad (3)$$

or

$$\tau_i = 1.15 \times 10^5 \sin 2\pi \frac{n}{\lambda'}$$

where  $G$  is the shear modulus, taken in this case as  $8 \times 10^6$  psi, and  $\tau_i$  is the internal shear stress. The "flow stress",  $\tau_F$ , required to cause plastic deformation is

$$\tau_F = \tau_i + \tau_y = \tau_y + 1.15 \times 10^5 \sin 2\pi \frac{n}{\lambda'} \quad (4)$$

where  $\tau_y$  is the elastic limit, or macroscopic yield stress.



Calculations based on Eq. (4) show that the passage of a single dislocation into a lattice in which the wavelength is 100 Burger's vectors would produce a resisting shear stress, due to the peculiar kind of work hardening characteristic of this kind of system, of about 4,000 psi, or an increase in the tensile stress of about 8,000 psi. If this picture accurately represents the behavior of a material of this kind, then it is easy to understand why the stress-strain curve should exhibit the extraordinarily high rate of work hardening.

The next problem is to compute the strains corresponding to the stresses indicated by the above equation. The macroscopic shear strain measured on the specimen as a whole would be equal to  $n$ , the number of dislocations passing on a given slip plane, divided by  $y$ , the distance between slip planes. Based on the assumption that in this material, as in most others, the distance between slip planes is approximately 1 micron, or 4,000 Burger's vectors, then both the shear strain and the tensile strain can be calculated for each value of  $n$ . Thus for a given wavelength such as, for example, 100, the stress increment above the yield strength corresponding to a given plastic strain can be calculated. This has been done for the 40% platinum - 60% gold alloy, quenched from 1225°C and aged one hour at 510°C; the stress-strain curve is shown in Fig. 10. The calculated points are shown as small circles on this figure, and they correspond to a wavelength of 140 Burger's vectors chosen, because diffusion calculations had shown that for one hour at 510°C the average wavelength should be about this value. The observed values of stress and strain in the plastic range versus those calculated are in remarkably good agreement.

Several questions remain to be considered, among which are what happens to the shape of the stress-strain curve as a function of time of aging, and why, in the case of alloys such as the one just mentioned, should the material be brittle. The main factor that contributes to brittle behavior in these alloys is the precipitation of a phase at the grain boundaries. If the grain boundary film could become thick enough in the 40% platinum - 60% gold material, then the same kind of brittleness described previously for the 80% platinum - 20% gold alloys could result. Since platinum would be the diffusing species in the gold-rich alloy, it should be possible to estimate the distance that platinum atoms could diffuse and concentrate in one hour at 510°C. Estimates based on such calculations indicate that if zero time is required for nucleation at grain boundaries, then a layer 100 or more atoms thick could be formed in one hour at 510°C. Thus there seems to be very reasonable grounds to assume that the grain boundaries are weakened by the collection of platinum atoms. If this were the cause of the failure, the failure path should have been intergranular and the stress required for fracture should have been of the order of the strength of the platinum-rich solid solution alloys, which would be somewhat higher than that of gold-rich solid solution alloy. This indeed seems to be the case. The fracture stress was about 180,000 psi, and the fracture was intergranular, as the photograph in Fig. 12 shows.

The effect of aging time must also be considered. Two possibilities exist: the wavelength could increase with time, or the wavelength could remain substantially constant and the degree of segregation could increase gradually and continuously during the early stages of aging. Continued concentration of atoms in the segregated regions might reasonably be expected to occur at a fairly rapid rate. Once segregation has started, atoms of the clustering species would tend to leave such regions less frequently than they approached because of the stronger bonding in the concentrated regions. Consequently, segregation should increase with time. In very long periods of time, regions of shorter wavelength would tend to disappear and those of longer wavelength would grow.

A stress-strain curve made on a specimen aged for twenty hours is shown in Fig. 13. In this curve it can be seen that the rate of strain hardening is even greater than it was in the specimen aged for only one hour at 510°C. This would seem to indicate that a further concentration of atoms had occurred, with the concentration gradients becoming steeper but the wavelength remaining about the same. Grain boundary fractures occurred in both the one-hour and 20-hour aged specimens. Figures 14(a) and 14(b) show that significant grain boundary precipitation had occurred in both cases.

#### CONCLUSIONS

- (1) In this investigation, which is consistent with earlier observations, it has been shown that the mechanical properties of alloys in which there is a miscibility gap in the alloy system can become very brittle when quenched from the solid solution range, even though the solid solution phases themselves, if tested independently, would be relatively weak but ductile.
- (2) The fractures follow grain boundaries, which is an unusual condition in high purity solid-solution type alloys.
- (3) A grain boundary precipitate of a weak but ductile material was the cause of the brittleness. Because the volume of material was so small, the plastic strain measured on the macroscopic specimen was small.
- (4) A second important feature of such alloys is that within the crystal a hardening process occurs such that the material, when deformed, strain hardens at an extremely rapid rate. In an analysis of the rapid strain hardening phenomenon, it was concluded that the passage of dislocations in a lattice in which there was a variation in lattice parameter ranging from a maximum to a minimum in a relatively short distance (such as, for example, 100 atoms) would cause very rapid strain hardening to occur. A stress-strain curve based upon a calculation of the internal stress that would be developed as dislocations moved in such a lattice was in good agreement with an actual stress-strain curve.
- (5) The analyses and observations reported herein indicate that a very potent hardening process occurs in certain "solid solution" alloy systems, and that if such reactions can be controlled, then it may be possible to produce a new class of useful alloys.

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TABLE I

VARIATION OF HARDNESS WITH AGING TREATMENT FOR GOLD-PLATINUM ALLOYS

80 Pt - 20 Au Alloy							
	(515°C)			(685°C)			
Aging Time *	0	5	60	0	5	10	15
H <sub>v</sub> **	406	525	572	406	525	585	521

40 Pt - 60 Au Alloy							
	(510°C)						
Aging Time	0	30	60	120	130	600	1200
H <sub>v</sub>	314	493	483	493	514	514	464

\* Expressed in minutes  
 \*\* Vickers Hardness, 25 gram load

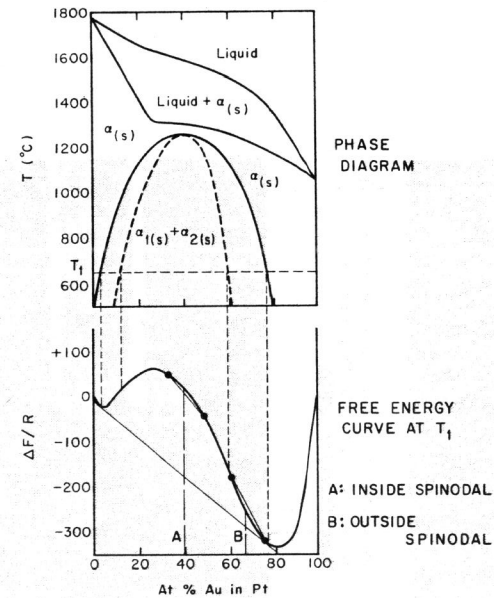


Fig. 1 Phase diagram of platinum-gold alloy system showing spinodal curve. The shape of the free energy vs composition is shown in the figure below for one temperature. The relationship of the free energy curve to the spinodal is indicated by the vertical lines.



Fig. 2 Photomicrograph of ductile 40% Pt - 60% Au alloy annealed 97 hours at 980°C. Magnification 280X

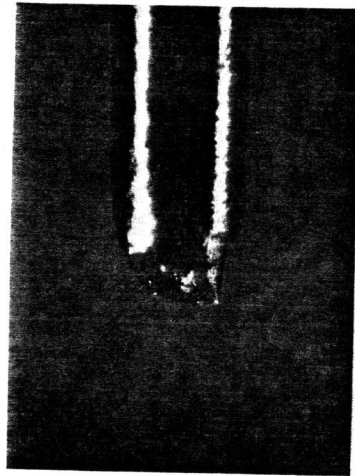


Fig. 4 Photograph of fractured 40% Pt - 60% Au alloy specimen. Stress-strain curve shown Fig. 3. Magnification 9X.

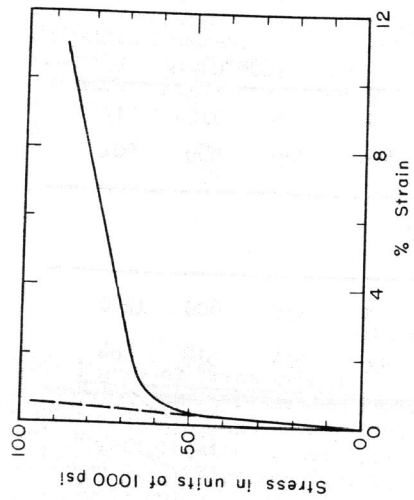


Fig. 3 Room temperature tensile stress-strain curve for 40% Pt - 60% Au alloy annealed 97 hours at 980°C.

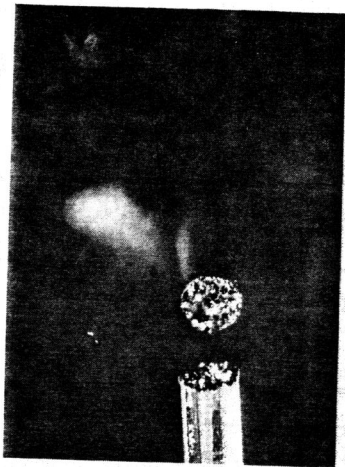


Fig. 5 Photograph of 80% Pt - 20% Au alloy rapidly quenched from 1300°C and broken at room temperature. Magnification 9X.

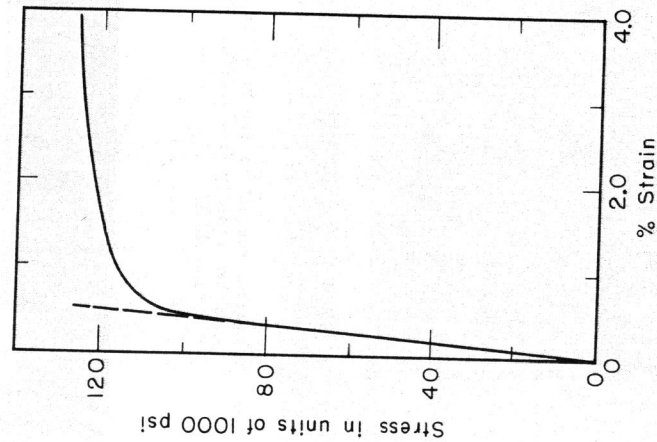


Fig. 6 Room temperature tensile stress-strain curve for solution quenched (from 1225°C) 40% Pt - 60% Au alloy.

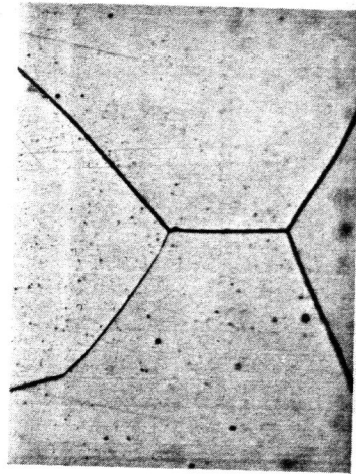


Fig. 7 Photomicrograph of 40% Pt - 60% Au alloy quenched from 1220°C, showing very small amount of grain boundary precipitate. Magnification 280X

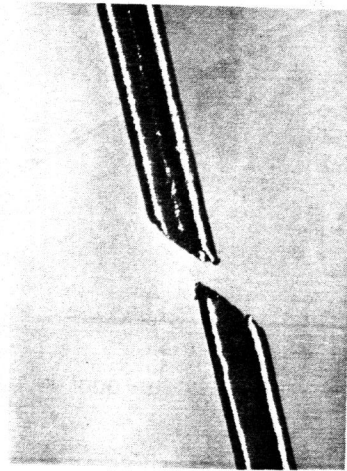


Fig. 8 Photograph showing ductile fracture of quenched 40% Pt - 60% Au specimen. Magnification 9X.



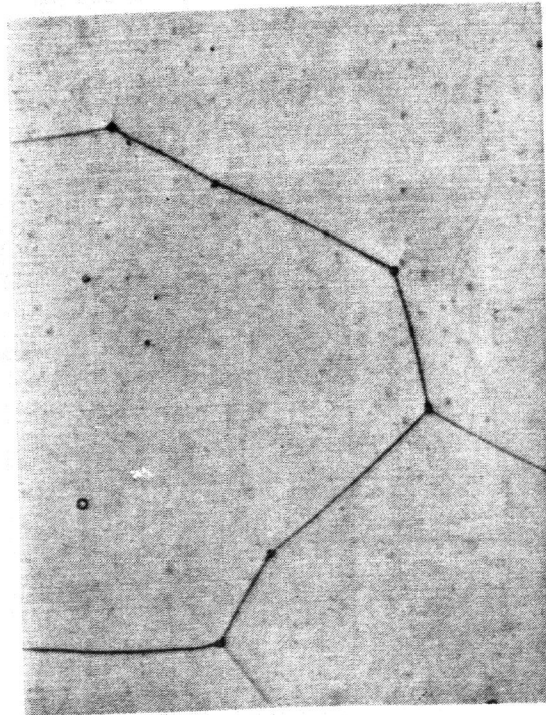


Fig. 9 Photomicrograph of 80% Pt - 20% Au, quenched rapidly from 1300°C. Magnification 440X.

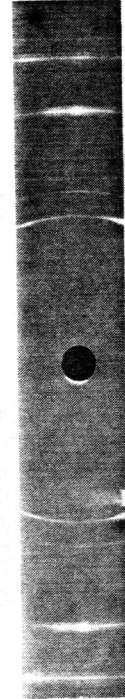


Fig. 11 X-ray diffraction pattern of quenched and aged Pt-Au alloy showing "side bands" at the sides of the Bragg lines.

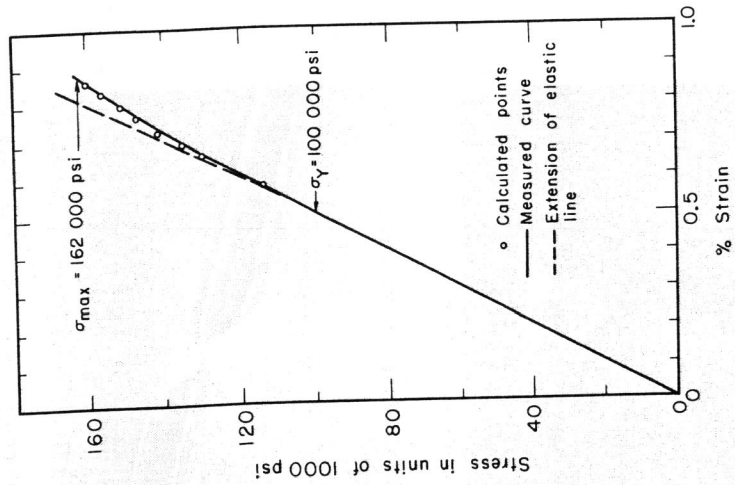


Fig. 10 Room temperature tensile stress-strain curve for 40% Pt - 60% Au alloy quenched from 1225°C and aged one hour at 510°C.

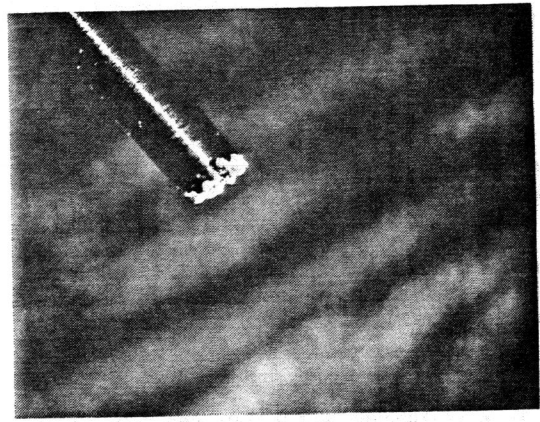


Fig. 12 Photograph of quenched and aged 40% Pt - 60% Au specimen showing brittle intergranular nature of fracture. Magnification 10X.

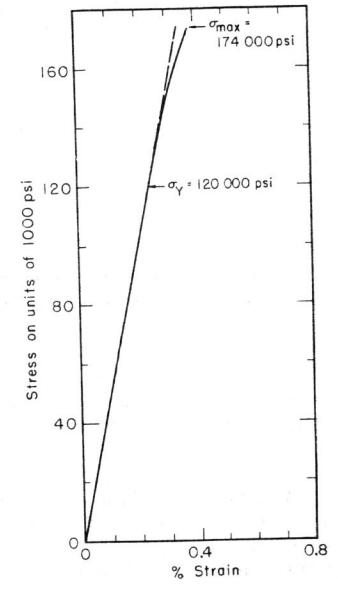


Fig. 13 Room temperature tensile stress-strain curve for 40% Pt - 60% Au alloy quenched from 1225°C and aged 20 hours at 510°C.

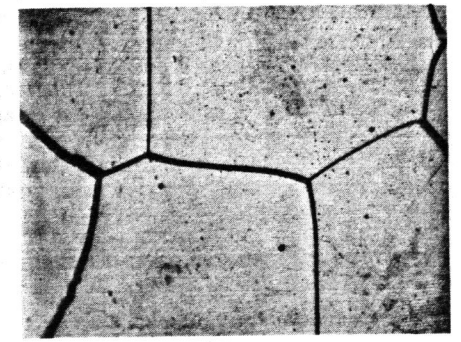
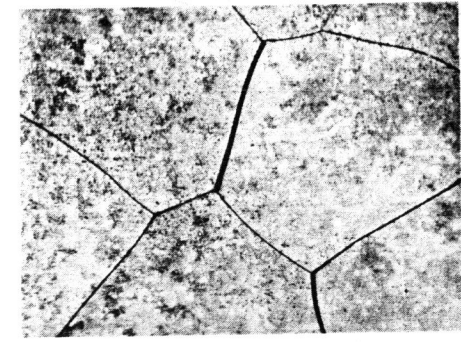


Fig. 14 Photomicrograph showing grain boundary precipitate in 40% Pt - 60% Au alloy quenched from 1225°C; (14a) aged one hour at 510°C, (14b) aged 20 hours at 510°C.