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GROWTH OF MODULATED STRUCTURE IN GOLD-PLATINUM ALLOYS

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## ABSTRACT

The growth of structural modulations during the early stages of precipitation in gold-platinum alloys has been investigated by x-ray diffraction methods. Three different alloys having compositions 60%Au-40%Pt, 40%Au-60%Pt, and 20%Au-80%Pt were investigated over the temperature range 500 to 600°C. It was found that logarithm of modulation wavelength was directly proportional to logarithm of isothermal aging time, and that the apparent activation energy for the reaction corresponds to that for interdiffusion in this alloy system. Loss of coherency, indicated by loss of structural modulation, was found to occur at smaller wavelength near the center of the miscibility gap; this was attributed to a maximum in elastic strain energy caused by coherency strains at the critical composition.

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# I. INTRODUCTION

Gold-platinum alloys are one of the "sideband" group; these alloys, in the central region of the phase diagram, are characterized by a homogeneous single phase stable at high temperatures which decomposes into two other phases having the same crystal structure at lower temperatures.[1] Tiedema et al.,[2] and Van der Toorn[3] investigated the sideband precipitation mechanism occurring in gold-platinum alloys on both sides of the miscibility gap by x-ray diffraction methods. The sidebands were attributed to the presence of periodic modulations of the matrix lattice constant in the cubic axis directions; it was reported that the modulation "wavelength" increased in an undefined way during aging, up to a maximum of about $40a_o$, where $a_o$ is the lattice constant of the quenched matrix.

Hillert et al.,[4] investigated the variation of modulation wavelength in sideband alloys of the iron-copper-nickel system and found a linear relationship between logarithm of wavelength and logarithm of aging time. The maximum wavelength reported in the iron-copper-nickel system was about 100 $a_o$, appreciably greater than in the gold-platinum system. In addition, the coexistence of two tetragonal phases during an intermediate stage of the reaction between the initial sideband stage and final equilibrium has been reported for certain iron-copper-nickel alloys.[5,6]

Guinier[7] has reviewed the experimental data reported for sideband precipitation reactions and concluded that the existence of intermediate stages, such as coexisting tetragonal phases, is markedly dependent on the elastic strain energy associated with the reaction. A measure of the relative strain energy associated with a coherent precipitation (or preprepcipitation) reaction is the difference between

lattice constants of the equilibrium phases. For an iron-copper-nickel alloy of nearly the critical composition this difference is about one-third of that for a gold-platinum alloy of critical composition. Indeed, for gold-nickel alloys, a modulated structure is expected from phase diagram considerations, but it is observed only with difficulty; in this case the lattice constant difference is about 10%.[7,8]

The present work was undertaken to investigate the variation of wavelength with annealing time, the existence of intermediate stages in the overall reaction, and the maximum attainable wavelength in alloys of critical composition as well as on either side of the miscibility gap.

## II. EXPERIMENTAL

### A. Specimen Preparation

All specimens used for diffraction experiments were in the form of 0.020 inch diameter wires, made from induction melted ingots. The alloys were cast into graphite molds and water quenched. The ingots were annealed and then swaged to 0.10 inch diameter, followed by cold drawing to final diameter, with appropriate intermediate annealing treatments.

Gold concentration of the alloys was determined gravimetrically, platinum being obtained by difference. Alloy compositions are given in Table I.

Spectrographic analysis of the alloys showed the major impurities to be Rh (0.04%), Pd (0.07%), and Fe (0.04%). All others were less than 0.01%.

Table I Chemical Analysis of Specimens

| Alloy | Wt % Gold |
|---|---|
| 6A-4P | 60.58 ± 0.01 |
| 4A-6P | 39.45 ± 0.15 |
| 2A-8P | 20.00 ± 0.10 |

## B. Heat Treatments

The specimens were homogenized by direct resistance heating in an argon atmosphere. The homgenization heat treatment was terminated by a helium gas quench. Specimen temperature during homogenization was measured with an optical pyrometer. The emittance correction for non-black body conditions was calculated from simultaneous measurement of specimen temperature by optical pyrometer and thermocouples. Calculated spectral emittance was 0.37 ± 0.02 at 6500Å wavelength (optical) for all alloys. Uncertainty in homogenization temperature measurement is estimated to be ±5°C. Temperature gradients along the specimen were determined pyrometrically. The lengths used for diffraction specimens were taken from the center section of the heated wire and were isothermal within the experimental uncertainty.

Satisfactory homogenization treatments were found to be 1 hour at 1225°C for the 6A-4P and 2A-8P alloys and 1 hour at 1275°C for the 4A-6P alloys. Debye-Scherrer diffraction photographs of specimens homogenized in this way gave sharp f.c.c. patterns; lattice constants calculated for the homogenized and quenched alloys are given in Table II.

Table II Cubic Lattice Constants for Homogenized and Quenched Alloys

| Alloy | $a_o$ (Å) |
|---|---|
| 6A-4P | 4.015 ± 0.002 |
| 4A-6P | 3.980 |
| 2A-8P | 3.954 |

These lattice constants are in good agreement with the variation of lattice constant with composition in quenched gold-platinum alloys reported by Darling, et al.[9]

Specimens were isothermally aged in molten salt baths; aging treatments were terminated by ice-water quenching. Salt-bath temperatures were measured with thermocouples. Aging temperatures are considered accurate within ±3°C of the specified value, except for aging treatments longer than 12 hours, where the uncertainty is ±10°C.

### C. X-ray Diffraction Measurements

The progress of the structural modulation was followed by measurement of the position of sidebands on diffraction patterns of the aged specimens. All diffraction pictures were taken with 114.6 mm diameter Debye-Scherrer cameras, using $CuK_\alpha$ radiation at room temperature. Exposure time was variable depending on whether the primary interest was sidebands or main Bragg lines of the parent phase; the maximum used was 3 hours at 50 KV and 20 ma. The position of the sidebands and main Bragg lines was measured in the usual way, and "wavelengths" characteristic of the modulation size were calculated from the Daniel-Lipson equation:[5]

$$\lambda = \frac{h \tan \theta}{\Delta\theta(h^2+k^2+\ell^2)} \qquad (1)$$

where $\lambda$ = average wavelength in lattice constants

$\theta$ = Bragg angle of matrix line

$\Delta\theta$ = angular displacement between sidebands and main Bragg line

$h,k,\ell$ = indices of parent reflection

Wavelengths were calculated from sideband spacing measurements on (200) and (220) lines of the diffraction patterns. The largest uncertainty in calculated wavelengths resulted from the width of the sidebands; in this work sideband position is defined as the position of maximum density of the sideband, which appeared to be the center. Repeated measurements of sideband position showed the uncertainty in calculated wavelength to be about $\pm 3a_o$. The width of the sidebands is usually attributed to the presence of a spectrum of wavelengths present and is not in strict accord with theoretical treatments of diffraction from a modulated lattice.[2] In the present work the apparent sideband width changed with exposure on the diffraction films because they are a diffuse scattering phenomenon, so it was not found worthwhile to compute the width of the wavelength spectrum, as a function of aging time. The apparent sideband width does, however, decrease with aging time, reaching a minimum at the limit of their existence, so it can be stated qualitatively that the structure becomes better defined with increased aging time.

## D. Results

Isothermal aging treatments were conducted on the three alloys at three different temperatures: 501, 552, and 602°C. Diffraction pictures were taken at periodic intervals during aging, which was continued until sidebands were no longer observed. The wavelengths calculated as a function of aging time for the various alloys and temperatures are tabulated in Table III. The calculated wavelengths are plotted logarithmically with aging time in Figs. 1 to 3.

It is apparent from the curves that the growth of modulation wavelength for the alloy of critical composition (4A-6P) is slower than the rate of the other two alloys. It was also observed that the maximum wavelength attained by the alloy 4A-6P was about $25a_o$, less than the terminal value of nearly $40a_o$ for alloys 6A-4P and 2A-8P.

The diffraction patterns of all the alloys show the same general behavior during annealing; the sidebands appear early in the aging cycle and move toward the main Bragg line of the parent reflection as aging time increases. The diffuse scattering characteristic of sidebands was present on diffraction photographs of the 4A-6P alloy in the homogenized and quenched condition, but was very weak and too diffuse to permit a meaningful calculation of wavelength. There was no indication of diffuse scattering on diffraction photographs of the 6A-4P or 2A-8P alloys in the homogenized and quenched condition.

There are several other differences in the appearance of the photographs at long aging times near the limit of existence of the sidebands. The sidebands for all alloys disappear by evolving into non-radial streaks that intersect the main Bragg lines of the parent reflection; streaking occurs after the sidebands have approached rather

Table III. Wavelength in Lattice Constants for Au-Pt Alloys

| Aging Temperatures (°C) | Aging Times (min) | 6A-4P | 4A-6P | 2A-8P |
|---|---|---|---|---|
| 500 | 0 | | ( ) | |
| | 30 | | 19 | ( ) |
| | 120 | 18 | 19 | 18 |
| | 300 | 22 | 19 | 19 |
| | 480 | 24 | | |
| | 600 | 25 | 20 | 23 |
| | 900 | 28 | 21 | 28 |
| | 1200 | 31* | 22 | 33* |
| | 1500 | | 23 | |
| | 1800 | | 24 | |
| 552 | 0 | | ( ) | |
| | 10 | 16 | 19 | 14 |
| | 30 | 20 | 19 | 16 |
| | 60 | 23 | 20 | 20 |
| | 120 | | 22 | |
| | 180 | 30 | 23 | 28 |
| | 300 | 32 | 25 | 35 |
| | 420 | 36* | | |
| 602 | 0 | | ( ) | |
| | 1 | ( ) | 18 | 16 |
| | 3 | 20 | 18 | 16 |
| | 8 | | 19 | |
| | 9 | 22 | | 19 |
| | 12 | 24 | | 21 |
| | 15 | 24 | 21 | 23 |
| | 18 | 26 | | 24 |
| | 21 | 26 | | 25 |
| | 22 | | 23 | |
| | 24 | 27 | | 26 |
| | 27 | 27 | 26 | 26 |
| | 37 | | | |
| | 60 | 34 | | 36 |
| | 90 | 38* | | 45* |

Table III (Continued)

| | |
|---|---|
| ( ) | Indicates diffuse scattering characteristic of sidebands present, but too weak for accurate measurement. |
| * | Indicates residual sidebands, but intense streaking allows only approximate position measurement. |

closely to the parent Bragg lines and is distinctly different from the appearance of sidebands in early stages of aging. In an earlier investigation of precipitation in the gold-platinum system, it was shown that streaks result from plate type precipitates with {100} habit, formed when the preprecipitates causing the modulation of lattice parameter in one or more ⟨100⟩ directions undergo partial or complete loss of coherency.[2] The present work shows that streaks occur first in the region of the sideband representing the preprecipitates of the equilibrium phase whose composition differs most from that of the quenched, unstable f.c.c. matrix. For example, diffraction patterns of alloy 6A-4P first show streaking the region of the highest angle sideband (i.e., the sideband displaced to a higher diffraction angle than the parent Bragg line angle). The opposite behavior is observed for the 2A-8P alloy; in this case streaking first occurs in the low angle sidebands, which are progenitors of the cubic equilibrium gold-rich phase lines. Streaks appear at about the same time in the region of both high and low angle sidebands on diffraction photographs of the 4A-6P alloy, whose average composition places it at the approximate center of the miscibility gap.

The lattice constants of the equilibrium cubic phases present at 500°C were measured to determine the differences from those of the parent matrices. For the gold-rich equilibrium phase $a_o = 4.047$Å; for the platinum-rich phase $a_o = 3.924$Å. According to variation of lattice constant with composition for gold-platinum alloys, the gold-rich phase contains about 15% platinum.[9] The platinum-rich phase lattice constant corresponds to pure platinum.[9,10] Lattice constant differences between quenched matrices and equilibrium phases are tabulated in Table IV.

Table IV

Difference between matrix and equilibrium cubic phase lattice constants

| Alloy | $\Delta a_{Au\text{-}rich}$ (Å) | $\Delta a_{Pt\text{-}rich}$ (Å) |
|---|---|---|
| 6A-4P | 0.032 | -0.091 |
| 4A-6P | 0.065 | -0.057 |
| 2A-8P | 0.093 | -0.030 |

The lattice constant differences are symmetrical about the critical composition. The sideband that first degenerates to streaks in an alloy of non-critical composition, for example the high angle sideband in alloy 6A-4P, is the sideband representing preprecipitates of the equilibrium phase having the largest $\Delta a$, in this case the platinum-rich phase.

It is also important to point out that no well-defined intermediate stage was observed to exist between sidebands and cubic equilibrium phases in any of the present alloys such as the tetragonal intermediate stages that have been reported in other systems of the sideband type, particularly Fe-Cu-Ni and Cu-Ni-Co.[7] Tiedema et al., observed that distribution of intensity between sidebands bands of a pair for any given Bragg line was unsystematical for their alloys, which were all of non-critical composition. Their calculations attribute the asymmetric intensity to unequal amounts of the two precipitating phases present. The intensity ratio between the sidebands of a pair corresponds approximately to the ratio of the amounts of the phases that will be present at equilibrium, according to the lever law. Integrated intensity measurements were not undertaken in the present work, but inspection of

the diffraction patterns confirmed this observation for the 6A-4P and 2A-8P alloys. The sidebands of a pair appeared to have equal intensity for 4A-6P alloys, in accord with this model. Tiedema et al., have calculated the wavelength of the structural modulations present in a 20% Au-80% Pt single crystal to be ~20 $a_o$ after aging for 15 minutes at 600°C, in good agreement with the present results.

## IV. DISCUSSION

The apparent activation energy for wavelength growth in these alloys was calculated by assuming the process can be represented by an Arrhenius-type equation:

$$S = A\,t\,e^{-Q/RT} \qquad (2)$$

where S = arbitrary fraction of reaction completed, determined by wavelength measurement

A = temperature-independent constant depending on structure

t = reaction time since beginning of measurements

Q = activation energy

R = gas constant

T = absolute temperature

Since there were no indications of different structural changes among diffraction patterns corresponding to alloys of the same average composition when the specimens were in a condition corresponding to the linear sections of Figs. 1 to 3, A was assumed constant within this region. Also within the linear section the fraction completed, S, was assumed equal for a given alloy if the measured wavelength, $\lambda$, was the same at either of the three temperatures investigated. Figure 4 shows log reaction time, t, versus reciprocal absolute temperature. Reaction

times were those required for $\lambda$ to reach 25 $a_o$ for 6A-4P and 2A-8P alloys and $\lambda$ = 20 $a_o$ for 4A-6P alloys. Activation energies were calculated from the slope of Fig. 4 and are given in Table V. The straight line relationship evident in Fig. 4 indicates a single growth process within the sideband stage of the precipitation reaction over the temperature range 500 to 600°C.

Table V. Activation energy for wavelength growth

| Alloy | Q(kcal/mol) |
|---|---|
| 6A-4P | 49.2±2 |
| 4A-6P | 51.9±3 |
| 2A-8P | 49.1±3 |

Bolk[11] has investigated the effect of composition and grain size on diffusion in the Au-Pt system over a temperature range from about 900 to 1050°C. The activation energies for interdiffusion and marker movement with a Pt grain-size of less than $10^{-2}$ cm were determined to be 50.4±5.2 and 45.5±2.3 kcal/mol, respectively. If the Pt grain-size is increased to about $10^{-1}$ mm, the activation energies increase to 55.2±2.6 and 51.0±1.2 kcal/mol respectively; the change was attributed to a contribution to mass transport by grain-boundary diffusion. Bolk also found that the activation energy for marker movement due to grain-boundary diffusion was about 16 kcal/mol; other investigators have reported activation energies for grain boundary self-diffusion in gold and platinum in this range. It appears that the precipitation mechanism in the present work is closely associated with bulk diffusion within the grains; the discontinuous precipitation occurring at grain boundaries is

a competing reaction mechanism.[2] Bolk also found a large Kirkendall effect in the gold-rich region of his diffusion couples, with gold the faster diffusing species. This does not appear to have a noticeable effect in the present work. The temperature dependence of the wavelength growth-rate in sideband alloys of the iron-copper-nickel system (for alloys in the center and in both sides of the spinodal region) was the same as that for lattice diffusion, in agreement with results of the present work.[4] However, the wavelength growth rate with time, at constant temperature, did not show a decrease at the center of the miscibility gap, as found in gold-platinum alloys. Wavelength growth at constant temperature in the iron-copper-nickel alloys was represented by an equation of the form

$$\lambda^m - \lambda_o^m = k\,(t - t_o) \qquad (3)$$

where the subscripts denote the beginning of pre-precipitate formation. Assuming $\lambda_o = t_o = 0$, the value of m was found to be between 4 and 5 for all the alloys. A similar analysis of the present data shows m to be 3.2±0.1 and 4.8±0.3 for the 2A-8P and 6A-4P alloys, respectively, over the temperature range investigated. The growth exponent for the 4A-6P alloys is 9.3±1.0, appreciably higher. It is also to be noted that the maximum wavelengths reported by Hillert et al., for modulated structures in iron-copper-nickel alloy are of the order of 70 to 100 $a_o$, and the highest values did not generally occur in alloys of critical composition.

The difference in wavelength growth rate among the various alloys, and the loss of coherency in gold-platinum alloys at much lower wavelength than in iron-copper-nickel alloys suggests that elastic strain energy is an important parameter in the precipitation process. At the critical

composition after aging for sufficient time at 500°C to produce equilibrium, the misfit between equilibrium cubic phases and quenched matrix in the gold-platinum system is about 3%. For iron-copper-nickel alloys of nearly symmetrical composition aged at 550°C the total misfit is only about 0.9%.[6] Guinier's conclusion that the stability of modulated structures depends on the lattice strain can be extended further, to consider the loss of coherency in the alloy of critical composition, 4A-6P, at a lower wavelength than the other two.

All the alloys in the present work are within the chemical spinodal region of the phase diagram.[12] Cahn has given a description of the morphology to be expected from a spinodal precipitation reaction of known habit plane that enables an approximate calculation of relative elastic strain energy density to be made for alloys in different positions within the spinodal region of the phase diagram. For spinodal decomposition occurring with a {100} habit, the spatial array of gold and platinum rich regions resembles a body-centered cubic lattice, in which regions rich in one component occupy the corners, and regions rich in the other component occupy the centers of the "unit cell."[13] If the enriched regions are nearly spherical, the unit cell edge has length $\lambda/\sqrt{3}$. Assume the alloy is an elastically isotropic solid, that the strain fields of regions rich in one component have negligible influence upon those rich in another, and that the relative amounts of the gold-rich and platinum-rich regions comply with the phase diagram of Darling et al.[1] Then at ~500°C the volume ratios of gold rich:platinum regions are about 3:1, 1:1 and 1:3 for alloys 6A-4P, 4A-8P, respectively. The radius of a strained region enriched in either component is $\sim\lambda/4$. The elastic strain energy associated with such a coherent, spherical

preprecipitate is:[14]

$$\frac{6\mu\, V\, \delta^2}{\left(1 + \frac{4\mu}{3K}\right)} \tag{4}$$

where $\mu$ = matrix shear modulus

$V$ = preprecipitate volume

$\delta$ = lattice misfit parameter equal to $\frac{\Delta a}{a_o}$, where $a_o$ = parameter of quenched and $\Delta a$ = difference between $a_o$ and lattice parameter of preprecipitate

$K$ = preprecipitate bulk modulus

The average elastic strain energy per preprecipitate particle, $\bar{\epsilon}$, is then

$$\bar{\epsilon} = \sum_i \frac{N_i\, 6\mu\, V_i \left(\frac{\Delta a}{a_o}\right)_i^2}{\left(1 + \frac{4\mu}{3K_i}\right)}, \quad i = 1,2 \tag{5}$$

where $N_i$ = volume fraction of $i^{th}$ enriched region and other parameters are as defined above. The elastic strain energy density is then $3\sqrt{3}\,\bar{\epsilon}/\lambda^3$. The elastic moduli of alloys 6A-4P and 2A-8P in the homogenized and quenched condition are $21\times10^6$ psi and $24\times10^6$ psi, respectively.[15] If the elastic parameters of the gold rich and platinum rich regions are taken equal to those of the elements, and the elastic modulus of alloy 4A-6P is estimated to be $\sim22\times10^6$ psi, the strain energy density dependence on position within the spinodal region can be calculated. The calculated values are given in Table VI.

It can be seen that the calculated strain energy of the critical alloy is ~30% greater than the other two, in qualitative agreement with

Table VI. Elastic strain energy density

| Alloy | $3\sqrt{3}\,\bar{\epsilon}/\lambda$ (cal/mol) |
|---|---|
| 6A-4P | 63.8 |
| 4A-6P | 82.6 |
| 2A-8P | 61.8 |

the thesis that elastic strain energy is responsible for the early loss of coherency at the center of the gap. It appears the early coherency loss results when both growing phases have relatively large misfit with the matrix. The calculated strain energies are upper limits, because the $\Delta a$ values were taken from equilibrium cubic lattice constant data, rather than values for the limit of the coherent state. Theoretical calculations show the total free energy change upon precipitation in the gold-platinum system to be on the order of 300 cal/mol,[16] so the strain energies are not of unreasonable magnitude.

The wavelength time curves (Figs. 1-3) imply that the sideband reaction mechanism in the present case is the same as that in iron-copper-nickel case, at least for the alloys 6A-4P and 2A-8P. The reason for the lower slope of alloy 4A-6P is not clear. Cahn's theoretical treatment of spinodal decomposition implies that elastic strain energy will reduce the reaction rate, however this treatment is concerned primarily with the growth in amplitude of the composition fluctuation in the very early stages of the reaction. If the growth in wavelength, which is apparent from the diffraction photographs, is in reality due to preferential amplification of certain (relatively long) wavelengths at the expense of shorter wavelengths, an apparent wavelength "growth" would appear on the diffraction patterns. There is some experimental

evidence to support this point of view: (1) The sidebands become less diffuse as the reaction proceeds, indicating a gradually narrowing spectrum of wavelengths, toward larger values. (2) The interdiffusion coefficient for the gold-platinum alloy system does not show a minimum near the center of the miscibility gap. It increases, rather gradually, from the minimum value at $N_{Au} = 0$ up to $N_{Au} \cong 0.75$, after which it increases more rapidly to a maximum at pure gold.[17] (3) The lower initial slope of the wavelength-time curves implies that stable "nuclei" are present at the beginning of the transformation, therefore the reaction is primarily a growth process.[18] The only apparent cause of a minimum growth rate at the critical composition is a maximum in strain energy, since the gradient energy term is not very dependent upon composition or temperature.[10]

## V. CONCLUSIONS

Isothermal growth of the structural modulation wavelength in spinodal gold-platinum alloys has been found to follow a linear logarithmic relationship for alloys on both sides and at the center of the spinodal region, and the apparent activation energy for the reaction agrees with that for volume diffusion in this alloy system. The reaction mechanism is similar to that found earlier in iron-copper-nickel sideband alloys, but coherency is lost at much lower wavelengths, particularly at the critical composition. The loss of coherency at generally low wavelengths was attributed to higher elastic strain energy, which exhibits a maximum near the critical composition.

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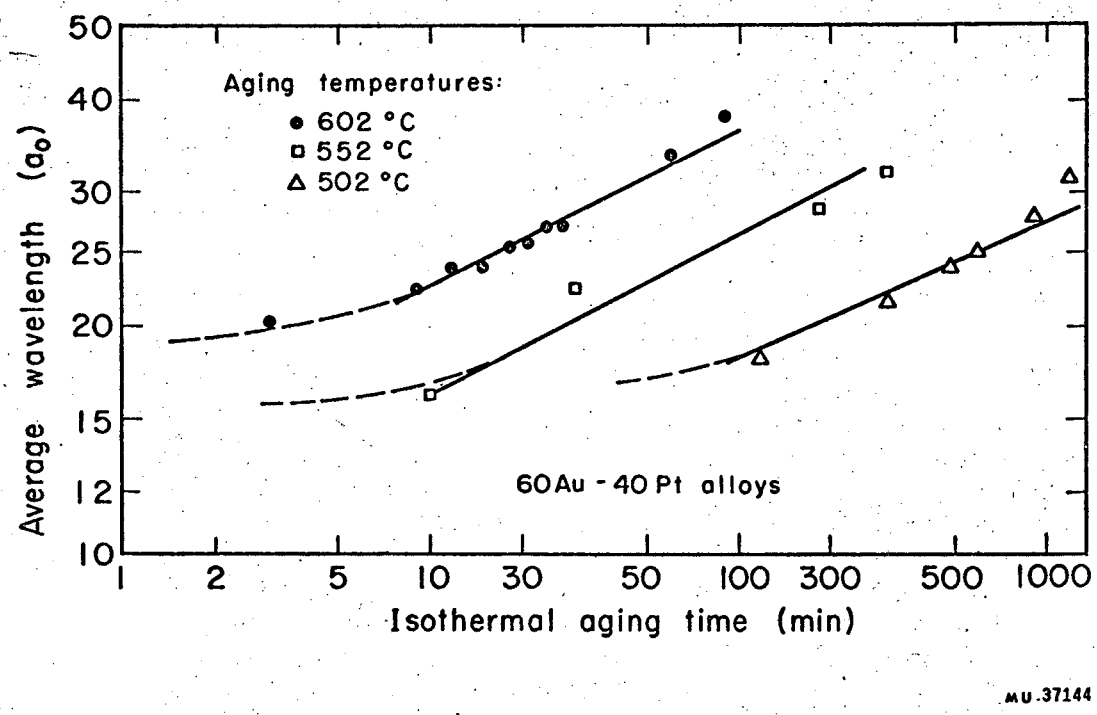


Fig. 1 Isothermal wavelength growth curves for 6A-4P alloys

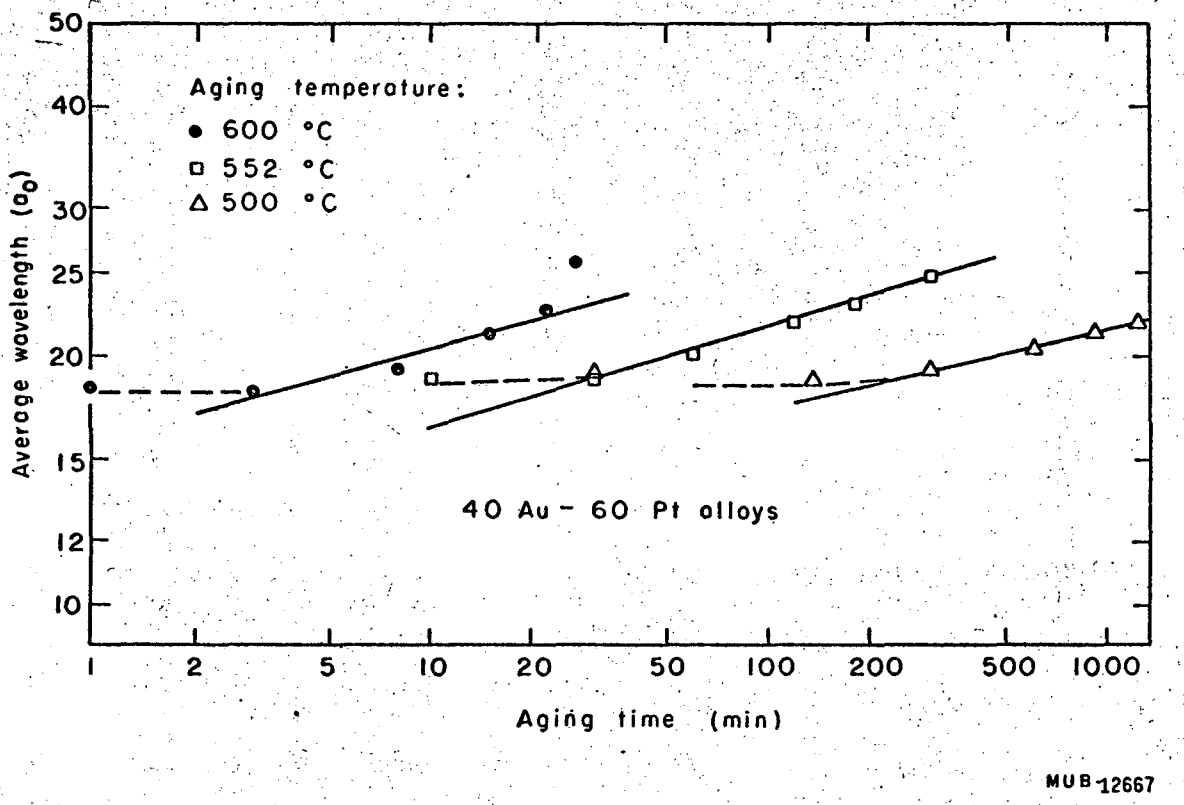


Fig. 2 Isothermal wavelength growth curves for 4A-6P alloys

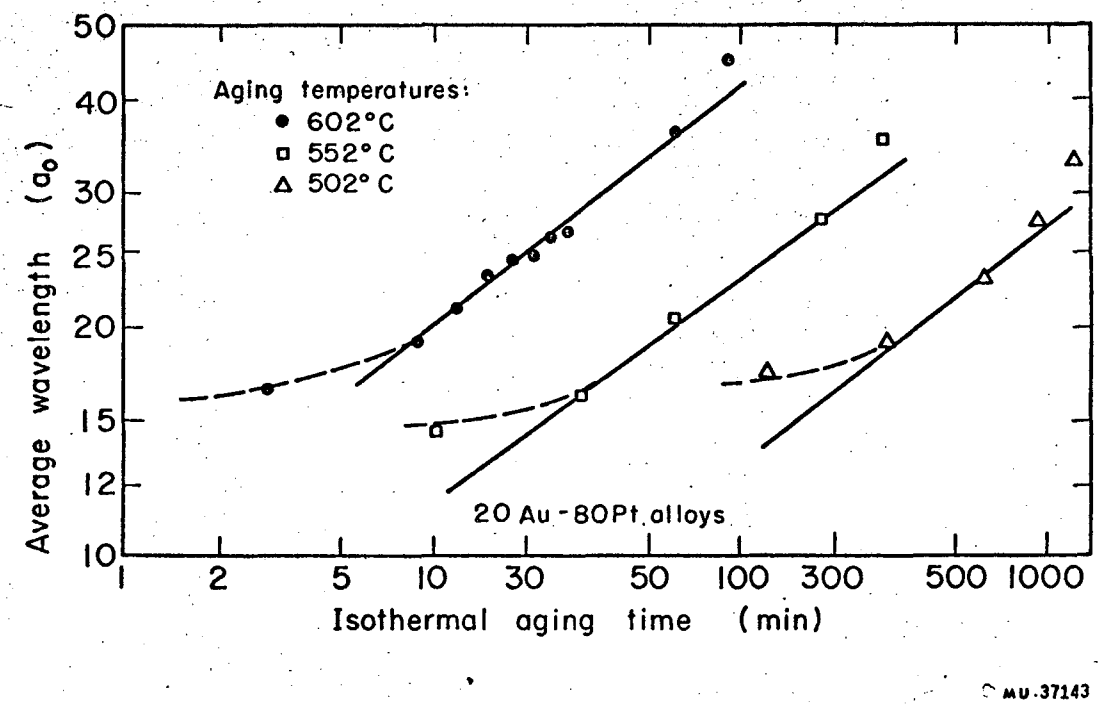


Fig. 3 Isothermal wavelength growth curves for 2A-8P alloys

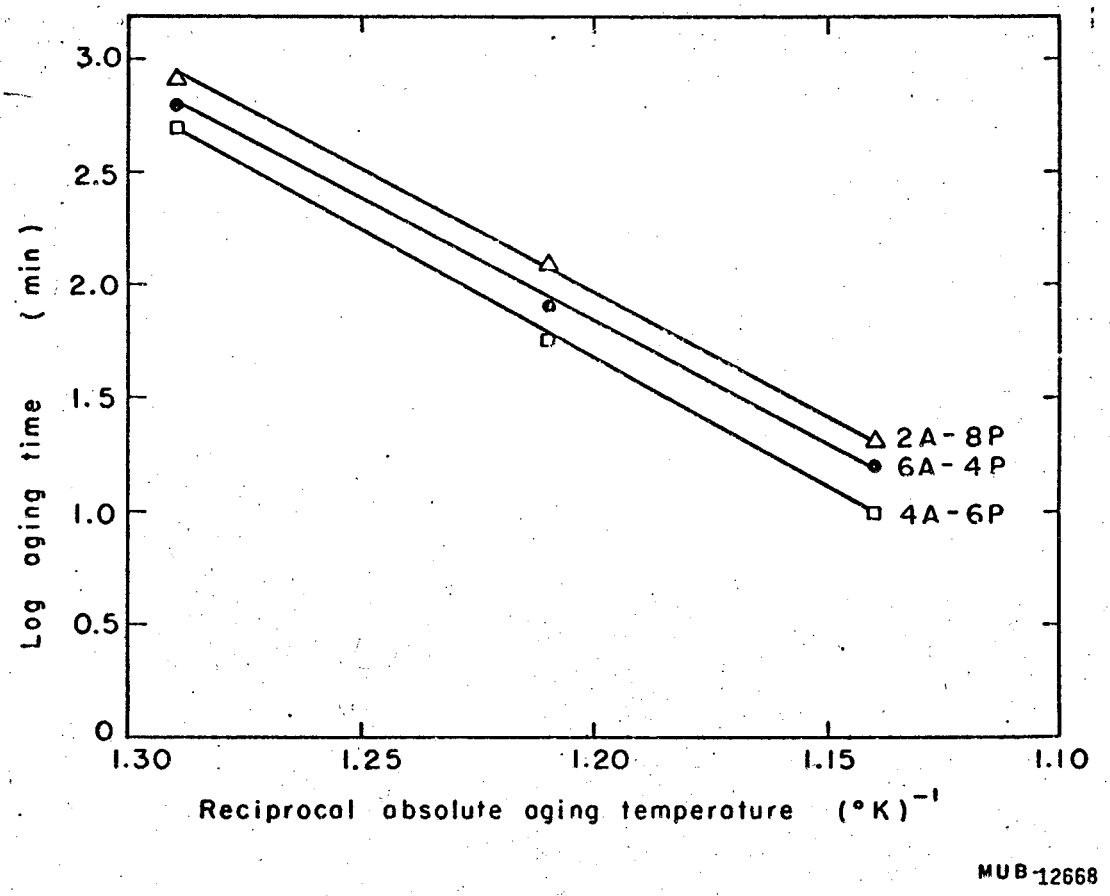


Fig. 4 Isothermal reaction time vs. reciprocal absolute temperature for gold-platinum alloys

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