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Abstract

Full Text

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ON THE MECHANISM OF DISSOLUTION OF PHASES IN THE Au–Pt SYSTEM

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It is known that gold with platinum forms a continuous series of solid solutions, which, upon lowering the temperature in a certain concentration range, decompose into gold-rich (α_2) and platinum-rich (α_1) phases (^{1}). Transformations in the solid state were studied by Johansson and Linde (^{2}). They indicated the existence of ordered phases of the type Au_3Pt, PtAu, and Pt_3Au in various temperature intervals. However, subsequent investigations did not reveal the existence of such ordered phases, and only in 1951 Grube, Schneider, and Esch (^{1}), carrying out an x-ray study of the transformations, found an ordered phase of composition Au_3Pt (α' phase) below 1000°. The parameter of the α' phase after annealing at 900° increases from 3.873 Å for an alloy with 5 at.% Pt to 3.918 Å for an alloy with 25 at.% Pt. The most detailed study of the gold–platinum system and measurement of the lattice parameters was carried out by the authors (^{3}). They showed that the parameters of alloys in the single-phase region deviate only slightly from the line corresponding to Vegard' s law. These same authors refuted the presence of the ordered phases indicated in work (^{2}).

Fig. 1. Change in the parameters of the α_1 and α_2 phases for alloys with 10 and 25 at.% Pt as a function of quenching temperature

In the present work, alloys of gold with platinum containing 10 and 25 at.% platinum were investigated. The alloys were prepared from gold plates of 99.99% purity and platinum plates of 99.8% purity in a high-temperature tungsten furnace under vacuum in corundum crucibles. The ingots were forged in the cold state and remelted again. This treatment was repeated four times, after which the alloys were subjected to homogenizing annealing in vacuum at 900° for 70 hours. From part of the alloys, rods of each composition, 0.4–0.5 mm in diameter, were turned on a lathe; after etching off the surface layer, they were again annealed at 900° for 30 hours and then slowly cooled from this temperature over 10 hours. The lattice parameters of the alloys were determined

Fig. 2 graph

Figure 2: Fig. 2 graph

simultaneously in a back-reflection camera and in a VRS-3 camera of diameter 142.4 mm using Cu K_α radiation, from the 333 doublet at an angle $\theta \approx 81^\circ 20$ for the α_2 phase and from the 422 doublet at an angle $\theta \approx 74^\circ 13$ for the α_1 phase. The values of the parameters, densities, and a number of other quantities for all alloys are summarized in Table 1.

The investigation of the alloys was carried out by the method of successive quenchings;

described earlier in work (ˆ4). In the present case, three series of specimens were studied simultaneously. The specimens of the first series, after heating to the corresponding temperature, were instantaneously quenched. The specimens of the second series were subjected to a 3-minute anneal followed by quenching, and the specimens of the third series were quenched after a 10-minute holding time. For specimens with 10 at.% Pt this process was repeated from 100° to 875°, and for alloys with 25 at.% Pt from 100° to 1050° at intervals of 15-25°. At room temperature, the X-ray diffraction patterns of alloys of both concentrations, together with the intense lines

Fig. 2. Change in the width of line 333 of the α_2 phase, the microhardness H, the background of the X-ray diffraction pattern S, and the density ρ as a function of the quenching temperature of an alloy with 25 at.% Pt

of the α_2 solid solution based on gold, contain weak lines of the α_1 solid solution of gold in platinum. At the same time, as is seen from the data of Table 1, the solubility of platinum in the gold lattice is much greater. Thus, for example, in the alloy with 10 at.% Pt about 9 at.% Pt is dissolved in the gold lattice, while the platinum-based solution contains about 3 at.% gold. From the equilibrium diagram it is evident that, at first, increasing the temperature sharply increases the solubility of platinum in gold, whereas the solubility curve of gold rises almost vertically. Therefore, in alloys quenched from 100°, after a 3-minute holding time, a reduction in the parameters of the α_1 phase is observed, caused by the transfer of Pt atoms into the lattice of the α_2 solid solution. Figure 1 presents the parameters of the α_1 and α_2 phases, as well as of all intermediate states, for alloys with 10 and 25 at.% Pt. A periodicity is clearly visible in the course of the parameters. The reason for this periodicity will be discussed below. The value of the parameter for alloys with 10 at.% Pt reaches 3.913 Å, whereas for alloys with 25 at.% Pt the smallest value of the parameter is 3.917 Å. Each time the parameter of the α_1 phase falls to this extremely low limiting value, the width of line 333 of the main phase gives a maximum (see Fig. 2), thereby marking the state of maximum lattice distortion.

Figure 2 presents the curves of microhardness H, the background of the X-ray diffraction pattern S, the width of line 333 of the α_2 phase, and the density ρ as

Fig. 4. Diagram of intermediate states arising during the mutual dissolution of phases in the Pt—Au system

Figure 3: Fig. 4. Diagram of intermediate states arising during the mutual dissolution of phases in the Pt—Au system

functions of the quenching temperature. The density of the alloys was measured 5 min after quenching, and then after 1, 2, 24, and 48 h. The point is that the density of the alloy changed sharply after quenching and then, after 24 h, and sometimes after 48 h, assumed its stable value. These stable values are plotted on the graph. In addition, the graph shows density values measured shortly after quenching. The distances between them have been hatched for clarity. The greatest discrepancies in the density values are obtained where substantial changes occur in the alloys. In those places where these changes are absent, discrepancies between the density values are almost absent.

Above 100°, the solubility of gold in platinum also slowly begins to increase. The flux of gold atoms, tending toward the grain boundaries, meets the flux of platinum, creating zones rich in gold. The formation of these interlayers of a new phase occurs in the lattice planes of Au—Pt, as

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Fig. 3. Appearance and movement of diffusion halos on X-ray diffraction patterns of alloys with 10 (I) and 25 (II) at.% Pt near the 422 and 333 mμ lines of the main phase

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Fig. 1. Laue photograph of a rutile pseudomorph after ilmenite. Taken perpendicular to (0001)

as around the corresponding lines in the X-ray pattern diffuse halos already appear at 190° (the effect of two-dimensional diffraction), gradually forming into lines. Indexing these lines in the cubic system is possible with the parameter 4.065 Å, i.e., with the parameter of a lattice containing only about 3 at.% Pt. The appearance of diffuse lines can be observed especially well near lines 333 and 422 of the main phase. In Fig. 3 the arrows indicate the appearance and displacement of diffuse lines near lines 333 and 422 for alloys with 10 and 25 at.% Pt as a function of the quenching temperature. The separation of gold-rich formations and the appearance of new lines correspond to a sharp decrease in the width of line 333 of the main phase (Fig. 2), a fall in its intensity, and a decrease in the background of the X-ray pattern. As Fig. 1 shows, the parameters of the α_1- and α_2-phases decrease somewhat in this process, then remaining unchanged over a certain temperature interval. During this period dissolution of the intermediate-phase formations occurs, accompanied by broadening of the lines on the X-ray patterns and by an increase in the background. All diffuse lines then disappear.

Fig. 4. Diagram of intermediate states arising during the mutual dissolution of phases in the Pt–Au system

Table 1

Alloy no.	*Pt* , wt.%	*Pt* , at.%	Parameter of α_2-phase, Å	Parameter of α_1-phase, Å	Density, ρ	Microhardness, H
1	10.2	10	4.055	3.921	19.9	5.45
2	25.15	25	4.047	3.921	20.2	6.1

As a result of this dissolution, the gold atoms pass into the platinum-rich solution, increasing its parameter to 3.916 Å for the alloy with 10 at.% Pt and to 3.920 Å for the alloy with 25 at.% Pt. Platinum atoms, conversely, enrich the gold-based solution, thereby causing a reduction of the parameter and an increase in microhardness and density (see Fig. 2).

This ends the first period of redistribution of gold atoms into the platinum lattice and, conversely, of platinum atoms into the gold lattice, occurring by means of the formation of intermediate, gold-rich interlayers (zones). The process of such redistribution of atoms by means of the formation and dissolution of an intermediate phase upon increasing the temperature is repeated periodically. This periodicity of the process is reflected not only in regular oscillations of the lattice parameters, but also in changes in the line width, density, and other physical characteristics of the alloys.

The second period of transformations proceeds analogously to the first, and dissolution of platinum atoms and a decrease in the parameter of the α_1-phase begin again. Periodic repetition of this process leads to the appearance of definite quantitative ratios of atoms in the unit cells of both phases. As a result of this, in alloys with 10 at.% Pt, in the temperature interval 500–600°, stratification of the α_1-phase into solid solutions α_1 and α_1' occurs (see Fig. 1). The lines of these phases are so weak that it is impossible to carry out any analysis of their intensities. Therefore in Table 2 only the squares of the sines of the reflection angles are compared. Already at 590°, as a result of equalization of the concentrations of the solid solutions, the lines begin to merge, forming a single phase. It should be noted that stratification of platinum-based solid solutions with a very low value of the parameter, which has

place in alloys with a content of 10 at.% Pt in the temperature interval 500-600°, is not observed in alloys with 25 at.% Pt. However, above 700° in alloys of both concentrations the lines on the X-ray patterns corresponding to the α_1 phase split. Its lattice becomes tetragonal, with parameters $a = 3.920$ Å, $c = 3.900$ Å and $c/a = 0.99$,

Table 2

hkl of the α_1 phase	$\sin^2\theta$, found	$\sin^2\theta$, calc.	*hkl* of the α_1' phase	$\sin^2\theta$, found	$\sin^2\theta$, calc.
111	–	–	111	0.118	0.116
200	0.159	0.157	200	0.155	0.154
220	0.313	0.312	220	0.309	0.308
311	–	–	311	0.425	0.424
331	0.742	0.740	331	0.736	0.734
420	0.779	0.779	420	0.773	0.771
422	0.932	0.933	422	0.925	0.925

and its intensity almost becomes equal to the intensity of the principal phase.

Table 3 gives the calculation of the X-ray pattern of an alloy with 25 at.% Pt quenched from 750°. The squares of the sines of the reflection angles were calculated from the lattice constants given above. The observed intensities were obtained by photometry of the X-ray pattern. The intensity calculation was carried out approximately, taking into account only the Lorentz and polarization factors. With further increase in temperature, owing to dissolution of the intermediate-phase formations, disordering of the α_1 phase occurs. The tetragonality of the lattice disappears. It again becomes cubic. Its parameter increases, while the parameter of the α_2 phase decreases. In alloys with 10 at.% Pt, already at 875° their parameters begin to approach each other for the formation of a homogeneous solid solution. In alloys with 25 at.% Pt the α_1 phase dissolves completely only after holding for several hours at 1050°. As a result of its dissolution and enrichment of the α_2 phase with Pt atoms, the latter separates. A solid solution with parameter 4.017 Å (the α_2' phase) arises.

Table 3

hkl of the α_{1T} phase	$\sin^2\theta$, found	$\sin^2\theta$, calc.	*I*, found	*I*, calc.	*hkl* of the α_{1T} phase	$\sin^2\theta$, found	$\sin^2\theta$, calc.	*I*, found	*I*, calc.
111	0.117	0.116	30	50	222	0.463	0.463	20	10
200	0.154	0.154	27	18	400	0.616	0.616	15	5
002	0.157	0.156	7	10	331	0.732	0.732	40	22
220	0.308	0.308	35	18	133	0.738	0.735	5	12
022	0.312	0.310	10	15	420	0.773	0.772	45	16
311	0.424	0.424	40	22	024	0.779	0.776	5	14
113	0.430	0.427	10	12	422	0.926	0.925	50	42

Equalization of the concentration between the α_2 and α_2' phases leads to an ordered structure of the type Au_3Pt, and then to a homogeneous solid solution.

Fig. 4 gives a general scheme of the mutual dissolution of phases in the Pt—Au system. Observation of superstructure lines in the Pt—Au system is difficult. However, from approximate geometrical considerations it may be concluded that the α_1' phase, which arises in the interval 500-600°, is an ordered phase of the Pt_3Au type, whereas tetragonalization of the lattice occurs as a result of ordering with the composition PtAu.

Thus, along the path of mutual dissolution, the phases in the Pt—Au system pass through a series of ordered states, exactly as was shown by us in the case of the Ni—Au system ([4],[5]). In the light of the present investigation it becomes clear why the ordered phases found in work ([2]) were not observed in subsequent investigations. The point is that Pt_3Au, PtAu, and Au_3Pt in this case are not stable phases existing in a definite temperature interval, but only ordered states arising along the path of mutual dissolution of phases.

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