

Annealing Characteristics and Strain Resistance of 99.93 wt.% Platinum

IMPLICATIONS FOR THE MANUFACTURE OF PLATINUM ARTEFACTS

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In industrial applications, platinum is often used in the form of the nominally pure metal, since impurities and alloying elements may adversely affect both its working characteristics and its stability against corrosion, at both ambient and high temperatures. Low strength, typical of a metal of this purity, is accepted in industrial products despite being a significant disadvantage. To optimise the technical parameters for the thermal and mechanical processing of platinum, knowledge is required of its rheological characteristics, including deformation resistance.

There has been much recent interest in the technical literature in the rheological features of platinum alloys for jewellery applications (1, 2). By contrast, in industrial applications, platinum is often used in the form of the nominally pure metal, since impurities and alloying elements can adversely affect its working characteristics (3, 4). 99.93 wt.% pure platinum is used in Russia, for instance, to produce heat- and chemical-resistant crucibles.

To comply with the Russian State Standard GOST 13498-79 (5), platinum must be at least 99.93 wt.% pure (i.e. the overall total impurity content is not more than 0.07 wt.%). Palladium, rhodium, iridium and ruthenium impurities must not exceed 0.04 wt.% in total, and the upper limits (in wt.%) for other impurities are as follows: silicon 0.005, iron 0.01, gold 0.008 and lead 0.006. It should be noted that unlike alloys, the mechanical characteristics of pure metals depend strongly on their impurity content, which must be determined experimentally.

99.917 wt.% pure platinum test samples were prepared for the present work. Impurity levels (in wt.%) were analysed as follows: Pd 0.06, Rh 0.01, Ir 0.007, Si 0.001, Fe 0.003, Au 0.001 and Pb 0.001. The chemical composition of the platinum test samples was therefore close to that required by GOST 13498-79.

The test blanks for the current work were obtained by means of cast moulding a platinum bar 50 mm thick and hot forging at 900 to 1530°C, with subsequent cold rolling of the sheet material. The thicknesses of sheets obtained by rolling of the 25 mm forged blanks were 1.25, 0.83, 0.71, 0.63 and 0.56 mm. The forged blanks underwent annealing in a batch furnace at a temperature of 1000°C for 40 minutes, so as to achieve recrystallisation. This temperature was initially assumed to be high enough to ensure complete recrystallisation (2). Using such a high annealing temperature industrially is controversial, since it can adversely affect the structure of the metal and some of its working characteristics.

In determining the force/energy parameters for processes involving pressure working, the strain resistance, σ_s , is understood to be a function of the strain state of the sample, in terms of compression and degree of strain (6). The deformation resistance is considered in terms of the uniaxial compression or tension of the sample under conditions of plastic deformation. It was assumed that during cold deformation, the deformation resistance depends only on the geometric parameters of the change in shape.

In order to plot hardening curves as a function of deformation, starting at zero, the original material must be fully recrystallised. To establish the

transition temperature for recrystallisation, experiments were set up to determine the yield limit as a function of the annealing temperature. An initial shear strain Λ was determined by varying the compression $\varepsilon\%$ of the blanks during cold sheet rolling (i.e. in the flat deformed condition), and calculated by Equation (i):

$$\Lambda = 2\ln(b_0/b_1) \quad (i)$$

where b_0 and b_1 are the sample thicknesses before and after rolling, respectively. We also defined:

$$\varepsilon\% = 100\Delta b/h_0 \quad (ii)$$

where $\Delta b = b_0 - b_1$.

Using the generalised deformation characteristic Λ allows for summation as the deformation accumulates. This approach is also compatible with the majority of computer programs for calculating stress-strain characteristics.

The prepared platinum strips were rolled to a final thickness of 0.5 mm on a mill with 300 mm diameter rollers, imparting them with varying degrees of cold working. Flat ten-fold samples were then cut from the sheets, with their long axes oriented along the rolling axis. The samples were then annealed at temperatures from 200 to 1100°C.

Tension tests were conducted on an “Instron 1195” machine, using a traverse speed of 1 mm min⁻¹, and the Vickers hardness HV5 was measured. Hardness is plotted against annealing temperature in Figure 1, the legend for which is given in Table I.

Results of Hardness Testing

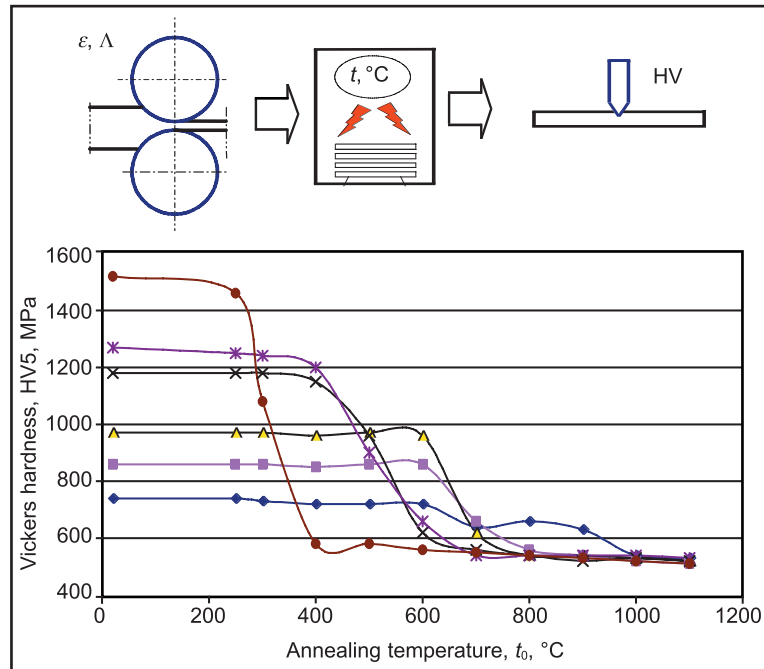
The experimental results showed that the Vickers hardness of platinum can vary very considerably within the wide range 500–1500 MPa, depending upon the degree of strain. It should be noted that standard references (e.g. (7)) give the Vickers hardness of platinum of technical purity, in the annealed state, in the range 350–420 MPa; calculation from the HV value in Reference (8) gives

Table I

Legend for Figure 1

Symbol	Λ (averaged data)	h_0 , mm	h_1 , mm
◆	0.15	0.560	0.520
■	0.40	0.630	0.515
▲	0.68	0.710	0.505
×	0.97	0.830	0.510
*	1.91	1.250	0.480
●	7.78	25.000	0.505

Fig. 1 Experimental schematic and results for measurement of dependence of Vickers hardness, HV5, for 99.93 wt.% platinum on annealing temperature, t_0 , and initial degree of shear strain, Λ (averaged data). See Table I for legend



392 MPa. This spread of values is explained by the varying chemical composition of the platinum samples tested; in the present work, the platinum contained 0.01 wt.% rhodium as the principal strengthening element.

Figure 1 shows that full annealing is reached on heating to 400°C if the metal is cold-worked to the high degree of shear strain of 7.78 (compression $\varepsilon\% = 97.96\%$). With decreasing initial deformation, the annealing point shifts towards higher temperatures. Thus, with a degree of initial shear deformation greater than 0.4 (compression 18%), the annealed state is reached at temperatures above 700–800°C. At lower degrees of compression, the metal can be softened only by heating to above 1000°C.

Figure 2 shows the dependence of the annealing temperature t_0 of platinum on initial shear strain. Regression analysis gives Equation (iii) for this dependence, with a correlation coefficient of 0.982:

$$t_0 = 695 - 141 \ln(\Lambda) \quad (\text{iii})$$

Minimising the annealing temperature on the basis of the degree of deformation in the metal is technologically significant, since at higher annealing temperatures, collective recrystallisation occurs and grain size increases, and the plastic characteristics are adversely affected. The decrease in recrystallisation temperature with increasing shear strain may be explained in terms of an accumulation of internal energy in the crystal lattice during cold working.

This stored energy derives from heating during the annealing process. As a result, the annealing temperature may be lower for hardened than for unhardened metal.

Deformation Resistance

The sheet material used for the present experiments was prepared by repeated rolling of flat platinum samples. The results of tension tests provided values of yield strength corresponding to uniaxial tension, and hence the deformation resistance σ_s .

There are two principal methods for determining deformation resistance. In the first, flat specimens are rolled on a mill to a range of thicknesses. The specimens are then subjected to uniaxial tension tests, so as to determine the conventional yield strength. This is an empirical parameter, defined in terms of the stress which will produce a given degree of conventional strain. $\sigma_{0.2}$ is defined as the stress to produce 0.2% conventional strain. It is usually assumed that $\sigma_s = \sigma_{0.2}$, since both parameters refer to the start of plastic deformation. The advantage of this method is that no neck is formed, and high degrees of plastic deformation are therefore attainable.

The second method is uniaxial tension testing, during which true (not conventional) stress and deformation are measured. Plots of σ_s vs. either $\varepsilon\%$ or Λ are obtained. A disadvantage of this method is that a neck is formed, and large deformations can-

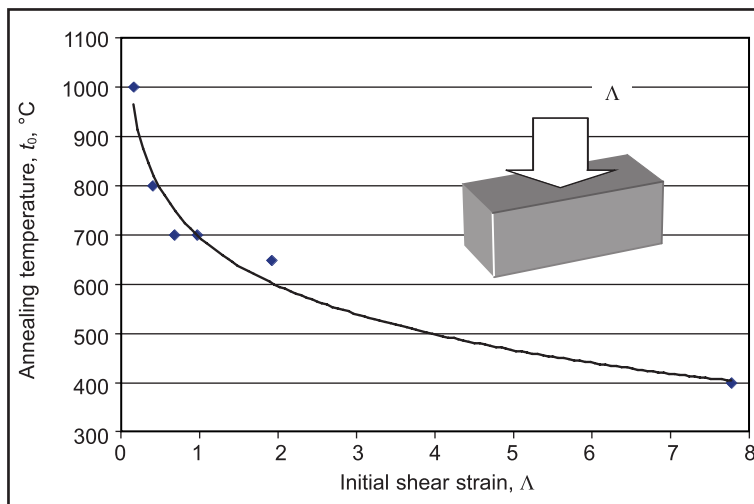


Fig. 2 Influence of initial shear strain, Λ , on annealing temperature, t_0 , of 99.93 wt.% platinum

not be achieved. In this work, $\sigma_{0.2}$ is taken as a measure of the stress at which plastic deformation begins under uniaxial tension. σ_s is adopted for stress-strain calculations in which the stress condition is not one of uniaxial tension. Experimental measurements have provided results for $\sigma_{0.2}$ as a function of the degree of preliminary hardening.

Different researchers employ a variety of factors in evaluating metal hardening. Here, we consider deformation in terms of: the shear deformation, Λ , given by Equation (i):

$$\Lambda = 2\ln(b_0/b_1) \quad (i)$$

and the relative compression ε_0 , given by Equation (ii):

$$\varepsilon_0 = 100\Delta b/b_0 \quad (ii)$$

In order to plot hardening curves for metals in the cold state, it is important, where possible, to measure accurately the nominal yield strength of the metal in the unhardened state.

Experiments in processing semi-finished platinum products showed that the conventional yield strength of the material is rather variable, by contrast with its tensile strength. Plots of the dependence of $\sigma_{0.2}$ on the initial shear deformation and the annealing point (Figure 3) showed that

GOST 13498-79 grade platinum may have a yield strength anywhere in the range 50 to 230 MPa, depending on its thermomechanical processing history. The yield strength decreases with increasing annealing temperature.

It was found that, at lower annealing points (600 to 700°C), the dependence of $\sigma_{0.2}$ on Λ shows a maximum in the range $\Lambda = 0.8$ to 1.5, corresponding to $\varepsilon_0 = 30$ to 50%. At higher temperatures, $\sigma_{0.2}$ decreases monotonically with increasing Λ . At annealing points in excess of 1000°C, the prior cold working of the metal ceases to have an effect. Under softening conditions, $\sigma_{0.2}$ takes a characteristic value of 60 MPa, and this was treated as a constant in the regression equations.

The experimental results may be explained as follows. At low annealing temperatures, $\sigma_{0.2}$ increases with increasing Λ , because the metal has been subjected to hardening by cold rolling. Under these conditions, annealing has little softening influence. However, if Λ rises to between 0.8 and 1.5, annealing has sufficient influence to soften the metal. $\sigma_{0.2}$ therefore decreases again, and the curve shows a maximum. If the annealing temperature is over 800°C, the curves show no maxima, because the influence of annealing is sufficient for full softening, without taking into account the energy of plastic

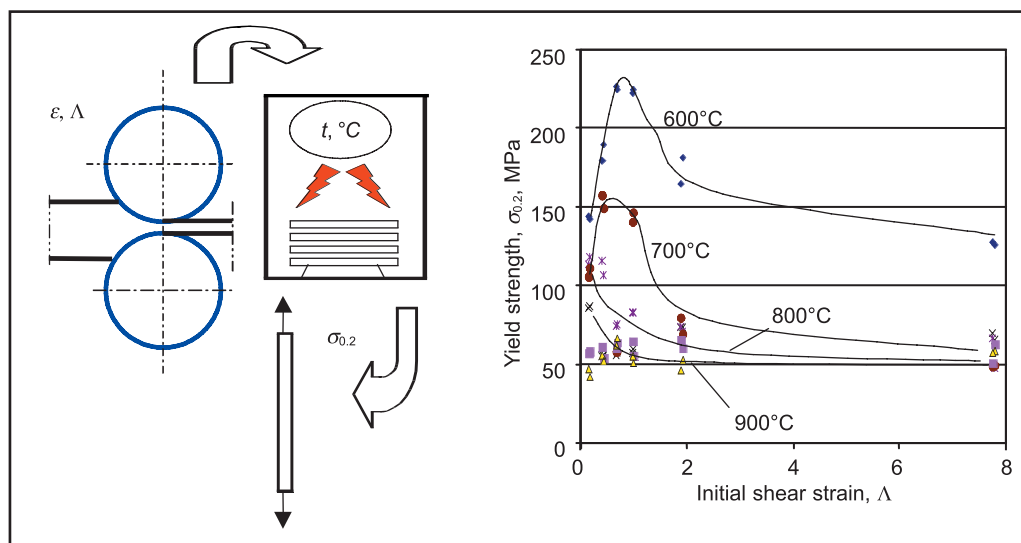


Fig. 3 Experimental schematic and results for measurement of dependence of conventional yield strength, $\sigma_{0.2}$, for 99.93 wt.% platinum, on initial degree of shear strain, Λ , and annealing temperature, t_0 : \blacklozenge 600°C; \bullet 700°C; \ast 800°C; \times 900°C; \blacksquare 1000°C; \blacktriangle 1100°C

deformation.

The practical significance of this observation lies in the possibility of choosing annealing regimes to obtain the desired metal characteristics. For example, in some industrial applications, pure platinum is used as a fabrication material, in spite of the low strength of products made from it. Improved products with greater strength, desirable for vessels and crucibles, may be achieved through plastic deformation and partial annealing.

Effect of Annealing Temperature on Grain Size

Higher annealing temperatures increase grain size. This effect is particularly evident at temperatures over 900°C, where it is attributable to collective recrystallisation (Figure 4). A fine crystal structure is preferred for the deep forming of vessels and crucibles.

The dependence of conventional yield strength on shear deformation for Pt 99.93 is shown in

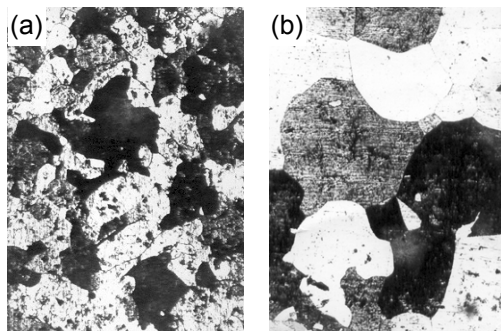


Fig. 4 Structure of 99.93 wt.% platinum ($\times 100$) after cold rolling at $\Lambda = 1.91$ ($h_0 = 1.250$ mm, $h_1 = 0.480$ mm) and annealing for 40 minutes at: (a) 800°C; and (b) 1000°C

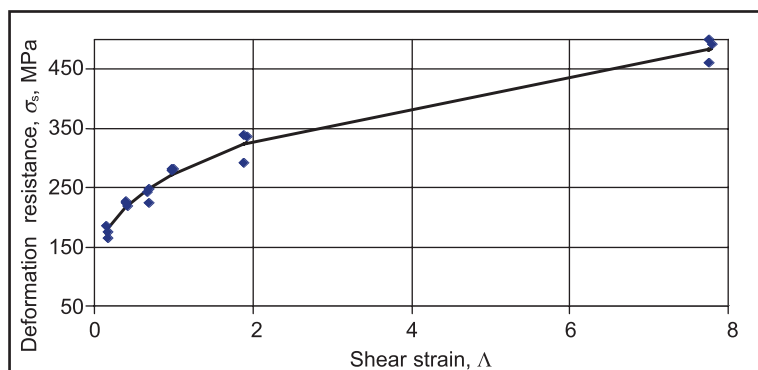


Fig. 5 Dependence of deformation resistance, σ_s , on shear strain, Λ , for 99.93% platinum

Figure 5, which indicates that the deformation resistance of the metal may vary between 60 and 460 MPa. Depending on the case selected, linear regression analysis gave Equations (iv)–(vi) for the hardening curve:

$$\sigma_s = 60 + 214\Lambda^{0.334} \quad (\text{iv})$$

$$\sigma_s = 60 + 269\epsilon^{0.334} \quad (\text{v})$$

$$\sigma_s = 60 + 39.8\epsilon\%^{0.481} \quad (\text{vi})$$

The amount of strain, ϵ , is given by $\epsilon = \ln(h_0/h_1)$. The correlation coefficient of regression for Equations (iv) and (v) is 0.9873, and for Equation (vi), 0.9726. These values indicate that the approximations are satisfactory. Determining the exponent in Equation (iv) enables the degree of deformation in platinum under draw-forming to be predicted. In accordance with plasticity theory, the sheet retains its shape without necking, if the exponents in Equations (iv) or (v) are high enough.

Stress-Strain Analysis

Stress-strain conditions during the deformation of platinum crucibles have been calculated by finite-element methods (9). Figure 6 shows the results for deep drawing of a product of thickness S , using a die of radius r_m . The shear deformation Λ shows a non-uniform distribution, with its maximum at the punch radius. There are two shear deformation maxima along the radius of the sample, which correspond to the two hardening maxima.

These investigations of annealing regimes and hardening conditions have practical implications for the production of platinum vessels at the

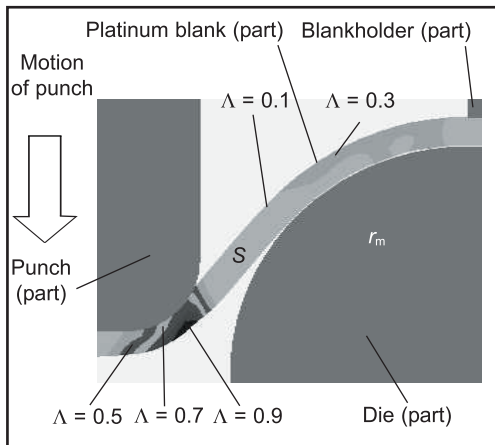


Fig. 6 Detail of stress-strain calculation for deep drawing of platinum at $r_m/S = 8$

Ekaterinburg Non-Ferrous Metals Processing Plant, Russia. The plant produces chemically stable platinum crucibles in a range of shapes (see Table II). A selection is shown in Figure 7.

Conclusions

The annealing temperature range for 99.93 wt.% platinum is 400–1000°C, and depends on the degree of cold working. Annealing is possible at

400°C if the shear strain Λ is at least 7.78, or the relative compression $\epsilon\%$ is at least 97.96%.

Annealing at temperatures higher than 900°C increases grain size; this is attributable to collective recrystallisation. Depending on the strain condition, the preferred annealing temperature range is therefore 400 to 800°C.

The conventional yield strength $\sigma_{0.2}$ depends non-linearly on the degree of shear deformation. This has been analysed in terms of hardening by a regression analysis.

At low annealing temperatures, $\sigma_{0.2}$ increases with increasing Λ , because the metal has been subjected to hardening by a cold rolling process. However, if Λ rises to between 0.8 and 1.5, annealing is sufficiently powerful to soften the metal. $\sigma_{0.2}$ therefore decreases, and the curve shows a maximum.

The strain resistance of 99.93 wt.% platinum ranges from 60 to 460 MPa as Λ increases from 0 to 7.78.

The data obtained in the present work allow stress-strain relations to be calculated as a function of deformation for semi-finished platinum artefacts.

Table II

Dimensions of Some of the Shapes of Platinum Crucible Produced by Ekaterinburg Non-Ferrous Metals Processing Plant, Russia

Diameter, mm	Height, mm
8	8.5
28	22
38	128
42	30
135	150

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Fig. 7 Chemically stable platinum crucibles. (The red coloration is a reflection of the background.)

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