Modelling the parameters of powder material for the pyrometallurgical refining of platinum alloys

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Abstract. The process of a garnishing layer formation during the pyrometallurgical refining of platinum alloys in the presence of alumina-based powder material has been investigated. The dependencies of the garnishing layer thickness on the alumina powder dispersity and the bulk density have been established. The optimal parameters of powder material have been determined based on the computational and experimental data.

1. Introduction

Platinum group metals (PGM) are widely used in various industries due to their high heat resistance, thermal and corrosion resistance. For the rational use of precious metals, a significant proportion of PGM is obtained from secondary sources [1]. The advantage of non-affinity pyrometallurgical processing of raw materials in contrast to hydrometallurgical purification processes is to reduce the number of technological operations. The resulting alloys in terms of technological and operational properties meet all the requirements for the technical products [2].

Pyrometallurgical purification of platinum-rhodium alloys from Cu, Fe, Ni, Sn, Co, Mo and V impurities is carried out in an open-type induction melting non-rotating installation. The purification process is performed using the backfilling with the Al₂O₃-based powder and oxygen blowing. The metal refining is based on the interaction of impurity elements contained in the melt with the powder material resulting in the formation of a garnishing layer [3]. Oxidative refining involves the partial oxidation of melt components with a higher affinity for oxygen and the transition of oxide forms to the garnishing layer [4].

Different crystal edges of the powder particles can melt at different temperatures [5]. Therefore, when studying the melting process of the substance, it is possible to obtain different dependences of the melting temperature on the inverse radius. It is well known that the surface melting occurs before the melting of the entire particle [6]. This phenomena may affect the accurate determination of the melting point. The thermodynamic driving force of the surface melting process is the reduction of surface energy Δσ. By varying the dispersity of the powder, it becomes possible to control the thickness of the resulting garnishing layer, and therefore, the rate of refining, which is a relevant task.

In this paper, a numerical method predicting the thickness of the garnishing layer has been developed depending on the powder particle size. The method is based on the thermodynamic dependence of the melting temperature on the particle size established by Pavlov [6].
\[ T = T_\infty \left( 1 + \frac{3\Delta \sigma}{r \Delta H(T_\infty)} \right), \]

where \( \Delta \sigma \) - change of the surface energy during the solid-liquid transition, \( T_\infty \) - the melting temperature of bulk material, \( r \) - radius of the particles, \( \Delta H \) - change of enthalpy during melting of bulk material.

2. Experimental details
The Al\(_2\)O\(_3\)-based powder with different dispersity was used to study the effect of the particles size on the rate of pyrometallurgical refining. The specific surface area of the powder was determined by the Brunauer-Emmett-Teller (BET) method based on the data of sorptometric analysis. The bulk density of powders 1 and 2 was determined by weighing a certain volume of material (by the method of measuring cylinders or vessels) [4].

The bulk density \( \rho_{\text{bulk}} \) was calculated by the formula:

\[ \rho_{\text{bulk}} = \frac{(m_1 - m_2)}{V}, \]

where \( m_1 \) - the mass of the graduated cylinder with the material; \( m_2 \) - the mass of the graduated cylinder; \( V \) - cylinder volume.

3. Results and discussion
Figure 1 shows isotherms of N\(_2\) adsorption-desorption at 77 K for the samples of powder material. The isotherms have capillary-condensation hysteresis (mismatch of adsorption and desorption branches of the isotherm in the area of capillary condensation), which indicates the presence of end-to-end mesopores in the sample.

![Figure 1](image)

**Figure 1.** Isotherms of N\(_2\) adsorption-desorption at 77 K for Al\(_2\)O\(_3\) samples (filled points – adsorption, empty points - desorption)

Pore size distributions were calculated using BET. Results are shown in figure 2. The obtained values of the specific surface area and the specific pore volume are given in Table 1.

| Geometrical parameters Al\(_2\)O\(_3\) samples 1 and 2 |
|------------------------------------------------------|
| Sample | Specific surface area, m\(^2\)/g | Total specific pore volume, ml/g |
|--------|---------------------------------|---------------------------------|
| 1 (channel F) | 0.458                           | 0.004                           |
| 2 (channel E) | 0.395                           | 0.003                           |

Pore size distributions were calculated using BET. Results are shown in figure 2. The obtained values of the specific surface area and the specific pore volume are given in Table 1.

According to the data presented in figure 2 the pores are small compared to the particle size and are less than 0.01 %.
 Certain bulk density ($\rho_{\text{bulk}}$) for powder 1 is 2.1008±0.0146 g/cm$^3$, and for powder 2 is 2.0744±0.0104 g/cm$^3$. Assuming that the powder particles have a spherical shape, it is possible to calculate the melting point depending on the radius of the particles.

The obtained calculated dependences are shown in figure 3. From Figure 3 it can be seen that with a decrease in the radius of the particles in the range of 1 – 50 µm, the melting temperature decreases by less than 1 °C. For particles with a radius of less than 0.1 µm, the melting temperature begins to plummet with a decrease in the radius. Thus, at a particle radius of 1 nm melting temperature is halved and is 1089 °C.

The refining process occurs in the active surface layer of Al$_2$O$_3$ particles. The thickness of this layer can be determined with the knowledge of the particle melting temperature using the equation [5]:

$$h = \frac{T_\infty \Delta \sigma}{(T - T_\infty) \Delta H(T_\infty)}$$

where $\Delta \sigma$ - change of the surface energy during the solid-liquid transition, $\Delta \sigma = \Delta \sigma_{(Al_2O_3)}$, $T_\infty$ - the melting temperature of a bulk material, $T$ - the melting point of the particle radius $r$, $\Delta H$ - change of enthalpy during the melting of a bulk material.

Figure 3. The melting point of Al$_2$O$_3$ depends on the particle size from 10 to 500 µm (a) and from 0.001 to 0.1 µm (b).

Figure 4 shows the obtained calculated dependence of the active layer thickness of the particle on its size.

The bulk density of the powder material correlates with the size of its particles. This indicator can be used in industrial conditions to determine the specific surface area.
Figure 4. Dependence of the active layer thickness of the particle on its radius

Figure 5 shows the dependence of bulk density on particle size obtained based on the approximation of experimental values of the bulk density of powder samples 1 and 2 in accordance with GOST [7].

Figure 5. The dependence of the bulk density of the powder particle radius

The obtained calculated data were used to determine the active volume of powder material, which is involved in the reaction with impurities in the refining process. The obtained dependence of the specific active volume on the particle radius is shown in figure 6.

Figure 6. Dependence of the specific active volume on the particle radius (the dashed line represents the region of the optimal values of the particles radius for the pyrometallurgical refining)

In accordance with the obtained dependence, as the particle size decreases and, as a consequence, the specific surface area increases, the active volume of powder material increases, which leads to an increase in the refining rate [4].

The fraction of the active volume of powder material significantly depends on the size up to the particle radius of about 100 µm. With a further increase of the particle radius, the change of the active volume does not exceed 1%. At the same time, the decrease in particle size leads to a decrease in the melting temperature of the bulk material. In this regard, the use of particles with the radius smaller than
10 nm is impractical for the pyrometallurgical purification, since the melting temperature of particles will be much lower than that of the metal melts. In addition, the industrial production of powders with particles whose radius is less than 50 microns without contamination is more complicated.

![Image of "sintered" (garnishing layer) channel Al₂O₃ after refining](image)

Thus, the optimal values of the particle radius of Al₂O₃-based powder material for pyrometallurgical refining lie in the range of 10-100 µm.

It should also be noted that the powder bulk density increases when mixing two fractions of different sizes. In this regard, there is also an increasing active volume of the powder material (Fig. 6 and Table 2). From Figure 7 it can be seen that the thickness of the garnishing layer for powders of different dispersity (and bulk density) varies. Table 2 presents the geometric parameters of the resulting channel.

### Table 2 Parameters of sample of channels E and F

| Parameter                                | Sample |
|------------------------------------------|--------|
|                                           | E      | F      |
| Particle diameter, mm                    | 50     | 50     |
| Channel length, mm                       | 170    | 170    |
| The thickness of the painted layer, mm   |        |        |
| upper                                    | 9      | 10     |
| middle                                   | 10     | 11     |
| bottom                                   | 13     | 14     |
| The thickness of the active layer, mm    |        |        |
| upper                                    | 11     | 12     |
| middle                                   | 12     | 14     |
| bottom                                   | 16     | 18     |

### 4. Conclusion

A numerical simulation of the fraction of the active volume of bulk material based on aluminum oxide in the process of refining platinum alloys under induction heating is carried out.

The results allowed us to determine the optimal geometric parameters (particle size and bulk density) of the bulk material.

### References

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