Modeling the alumina cleaning by means of high temperature evaporation into vacuum

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Abstract. Considering a porous granule to be an ensemble of solid micro-particles the mathematical model is developed for the high temperature vacuum cleaning of alumina from ferrous impurity. Three parts of the process are identified: the diffusion in solid, the evaporation into vacuum and the filtration through pores into outer space. The model found to be consistent with available experimental data. Analytical solutions on the level of solid micro-particles might be instrumental for the treatment of experimental data.

High purity alumina is greatly valued in the production of light-emitting diodes, substrates of microchips, implants, articles of jewellery and so on. A possibility to get alumina of 99.997% purity by means of vacuum evaporation was demonstrated experimentally in [1, 2]. The process goes on because under the working temperature range (less than the alumina melting point by 100–200 K) saturation vapor pressure of impurities is much higher compared with alumina. The raw alumina produced by hydrothermal oxidation of aluminium is loaded with a bunch of impurities. The greatest problem among them is a ferrous impurity, because the concentration of iron is one among the upper values and its saturation vapor pressure is the lowest value. That’s why the cleaning of alumina considered in this paper is limited by evaporation of iron. A withdrawal of iron atoms from alumina powder is considered here on three levels. On the outer level there is a container filled with powder and exposed for some time to high temperature in a vacuumized space. On the next level the particles of powder are considered as porous granules comprised by solid micro-particles. The iron vapor leaving the surface of micro-particle percolates at first through the pores between micro-particles and next through the pores of powder. On the last, third level an evaporation of iron contained as impurity in the solid particle into the space of pores is considered.

1. Model definition
The percolation of iron vapor through the layer of powder with thickness L along the Z-axis (figure 1) under typical values of temperature and pressure is a Knudsen diffusion governed by equation

$$\frac{dp_Z}{dz} = -\frac{R_g}{M} \frac{J_Z}{D_K}, \quad D_K = \frac{2}{3} \frac{R_p}{R_Z} \sqrt{\frac{8R_g T}{\pi M}}$$

or

$$\frac{dp_Z}{dz} = -\frac{3 \nu T}{8 R_p} J_Z, \quad (1)$$
where \( J_Z \) – vapor flux along the Z-axis, \( p \) – pressure, \( T \) – temperature, \( M \) – atomic weight of iron, \( R_g \) – gas constant, \( R_{pZ}^p \) – equivalent radius of pores, \( D_K \) – Knudsen diffusion coefficient, \( v_{TP} \) – thermal velocity of vaporized iron atoms. Mass conservation equation for this case looks like:

\[
\frac{dJ_Z}{dz} = N_S J_Y^1,
\]

(2)

where \( N_S \) – specific surface of the powder \( \text{cm}^2/\text{cm}^3 \), \( J_Y^1 \) – vapor flux through the surface of porous granules of the powder. A boundary value problem for two ordinary differential equations (1) and (2) is on hand. Boundary conditions:

\[
z = L \rightarrow p_Z = p_0,
\]

\[
z = 0 \rightarrow J_Z = 0
\]

(here \( p_0 \) is the vacuumized space pressure).

![Diagram](image)

**Figure 1.** Three levels of the model.

The flux \( J_Y^1 \) in (2) results from the solution of similar problem on the Y-level (figure 1). On this level the momentum equation is similar to (1):

\[
\frac{dp_Y}{dy} = -\frac{3\nu_T}{8R_Y^p} J_Y.
\]

One-step approach to this equation is:

\[
p_Y^1 - p_Y^0 = -\frac{3\nu_T R_Y}{16R_Y^p} J_Y^1.
\]

(3)

The complementing mass conservation equation is:

\[
J_Y^1 S_Y = V_Y N_S^0 J_{Fe}^1, \quad J_Y^1 = \frac{R_Y}{3} N_S^0 J_{Fe}^1.
\]

(4)

New symbols used in (3) and (4) are: \( R_Y \) – radius of porous granule, \( R_Y^p \) – equivalent radius of pores between micro-particles, \( N_S^0 \) – specific surface of the porous granule \( \text{cm}^2/\text{cm}^3 \), \( J_{Fe}^1 \) – vapor flux through the surface of micro-particle, it results from the solution of the boundary value problem on the X-level.

The iron vapor flux from within micro-particle through the surface is governed by the solid state diffusion in alumina:

\[
J_{Fe}^1 = D \frac{\rho_{Fe}^0 - \rho_{Fe}^1}{R},
\]
where $\rho_{Fe}^0$ – an average density of ferrous impurity in the micro-particle, $\rho_{Fe}^1$ – iron density at the surface of micro-particle, $D$ – diffusion coefficient, $R$ – radius of micro-particle.

The evaporation from the surface into imperfect vacuum is governed by the Hertz-Knudsen equation [3]:

$$J_{Fe}^1 = \left(\frac{\rho_{Fe}^1 p_{Fe} - p_0}{\rho_{Fe}^0}ight) \frac{1}{\nu_T},$$

where $\rho_{Fe}^0$ – an initial uniform density of ferrous impurity, $p_{Fe}$ – saturation vapor pressure of iron (its relative density taken into account), $p_0$ – pressure outside the micro-particle (depends on the embedment of micro-particle into the porous granule or into depth of powder). Elimination of $\rho_{Fe}^1$ from the last two equations gives the sought-for formula for the vapor flux through the surface of micro-particle:

$$J_{Fe}^1 = \frac{\rho_{Fe}^0 - \rho_{Fe}^1 p_0}{\nu_T p_{Fe} + \frac{R}{D}}.$$  (5)

This flux determines an abatement of iron density in the micro-particle:

$$\frac{d\rho_{Fe}^0}{dt} = \frac{3}{R} J_{Fe}^1.$$  (6)

Getting together the last two formulae one has the equation describing the process of cleaning:

$$\frac{d\rho_{Fe}^0}{dt} = \frac{3}{R} \frac{\rho_{Fe}^0 - \rho_{Fe}^1 p_0}{\nu_T p_{Fe} + \frac{R}{D}}.$$  (7)

The rate of the process depends on the current density of the impurity, on the backpressure, on the temperature driven evaporation factor and on the diffusion factor (mainly on the micro-particle size). For the constant backpressure (it occurs only for the detached micro-particle) there is an analytical solution:

$$\frac{d\ln(\rho_{Fe}^0 - \rho_{Fe}^1 p_0)}{dt} = \frac{1}{\chi}, \quad \chi = \frac{R}{3} \left(\nu_T p_{Fe} + \frac{R}{D}\right),$$

$$\rho_{Fe}^0 - \rho_{Fe}^1 p_0 = \rho_{Fe}^1 \left(1 - \frac{p_0}{p_{Fe}}\right) \exp\left(-\frac{t}{\chi}\right).$$

Modeling of the process of cleaning of the powder means a handling of equations (5) and (6) for an ensemble of micro-particles forming a layer of porous granules of greater radius. The backpressure for the particular micro-particle comes as a result of the solution of boundary value problem at the given time step. Specialization of pressure goes from level $Z$ to level $X$ – $p_Z \rightarrow p_Y \rightarrow p_0$. In the backwards direction goes the specialization of vapor flux – $J_Z \leftarrow J_Y^1 \leftarrow J_{Fe}^1$.

2. Test run

Decreasing of iron concentration with increasing exposure time was calculated for micro-particle in two environment: in solitary state and in the center of porous granule with radius $R_Y = 1$ mm. Initial iron concentration is 450 ppm, working temperature – 1750°C. Temperature dependence of the diffusion coefficient for iron in alumina is imported from [4]:

$$D = 1.336 \times 10^{-8} \exp\left(-\frac{298000}{R_g T}\right) \quad [m^2/s],$$

where $R_g = 8.3147$ J/mol K. On the figure 2 solid lines indicate that micro-particle is in the center of porous granule, dashed lines show the results for detached micro-particle. Two values
were considered for the radius of micro-particle $R$: 0.8 and 1.5 $\mu m$. For $R = 0.8 \mu m$ ppm of solitary micro-particle falls 10 times after 1000 seconds, for the embedded micro-particle the same fall occurs after 4 times greater time span. To be precise Knudsen diffusion takes more time than the leaving the micro-particle. The situation is different for $R = 1.5 \mu m$.

3. Powder cleaning example

Full capability of the developed model is demonstrated using the initial data given in table 1. Results of modeling are displayed on figures 3 and 4.

![Figure 2](image)

**Figure 2.** Final ppm versus time of exposure.

| Table 1. Initial data |
|-----------------------|
| **Quantity** | **Dimension** | **Value** |
| Working temperature | $^\circ C$ | 1750 |
| Vacuum pressure ($p_0$) | torr | 1e-5 |
| Powder layer thickness ($L$) | mm | 40 |
| Radius of porous granules ($R_Y$) | mm | 1 |
| Radius of micro-particles ($R$) | $\mu m$ | 0.8 |
| Initial Fe concentration | ppm | 450 |
| Process time ($t$) | sec | 7200 |

Figure 3 shows profiles of iron vapor pressure along the depth of alumina powder in the units of vacuum pressure. Zero-marked thick line shows the initial pressure profile. Every next line shows the state after 720 seconds time span.

Figure 4 show profiles of iron concentration along the depth of alumina powder. Zero-marked line shows the initial uniform distribution of the concentration. Every next line, corresponding to the time increased by 720 seconds, shows the remarkable loss of iron, and after the tenth step it disappears almost completely.
4. Comparison with experiment

Experimental facility for the production of high-purity aluminum oxide and methods for samples examination are described in [5]. Samples with full set of measured data are gathered into the table 2. Initial concentration of ferrous impurity is 450 ppm for all samples. Figures in the column marked “Av. d, mm” are considered to be values of doubled radius of porous granules. Admitted that diffusion coefficient from [4] is trustworthy, and equivalent radius of pores between micro-particles is approximately equal to the radius of micro-particles, the mathematical model leaves unique parameter to be identified using experimental data. It is radius of micro-particles $R$. Procedure of minimizing the normal deviation of calculated values of final Fe ppm from experimental values leads to the value $R = 0.8 \mu m$. The quality of identification is demonstrated by the figure 5. Unfortunately the table 2 doesn’t mention the depth of powder layer where the sample is taken from. One has to consider that they all are taken from the surface of powder. It means that only two levels of the model are used when the comparison with experiment was performed.

5. Conclusion

The mathematical model is developed for the high temperature vacuum cleaning of alumina from ferrous impurity. It consists of three one-dimensional models sharing common information. They are identifying three levels of handling the alumina to be cleaned: Z-level – powder of porous granules, with Z-axis along the depth of layer; Y-level – ensemble of solid micro-particles forming
Table 2. Samples with measured final Fe ppm

| Sample number | $T$, °C | Exposure time, h | Fe, ppm | Av. $d$, mm | Vacuum, Torr |
|---------------|---------|-----------------|---------|-------------|-------------|
| 55            | 1600    | 2               | 169     | 3.3         | $5 \times 10^{-6}$ |
| 74            | 1600    | 6               | 23.8    | 3.3         | $4.5 \times 10^{-6}$ |
| 53            | 1600    | 10              | 33.1    | 3.1         | $4 \times 10^{-6}$  |
| 41            | 1750    | 2               | 48.5    | 2.9         | $4 \times 10^{-5}$  |
| 57            | 1750    | 2               | 34.7    | 2.9         | $3 \times 10^{-5}$  |
| 11            | 1750    | 2               | 59.9    | 2.2         | $3 \times 10^{-5}$  |
| 17            | 1750    | 4               | 24.9    | 2.2         | $1.5 \times 10^{-5}$ |
| 20            | 1750    | 6               | 49.1    | 2.2         | $3 \times 10^{-5}$  |

Figure 5. Comparison of measured and calculated values of final Fe ppm for 8 samples from the Table 1 (white columns – experiment, hatched columns – calculation).

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