Separation of PGMs Bearing Alumina Phase from Cordierite in Spent Automobile Catalyst by Thermal Shock

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Abstract

Spent automobile catalyst is an important secondary resource of PGMs but the present recycling technologies require high energy-consumption. It is of much important to enrich the PGMs with some energy saving physical separation methods. This catalyst is usually composed of cordierite lattice which is covered by PGMs bearing coat layer. We adopted heating-quenching process as a pre-treatment of subsequent selective grinding and compositional concentration. It was found that micro-cracks were generated in the coat layer and the interface of the two phases and that some part of the coat layer was detached from the cordierite substrate. This paper analyzes the mechanism of these phenomena by using mathematical calculation and FEM simulation.

Key words: Automobile catalyst, PGM, Quenching, Heat transfer, FEM

1. Introduction

Environmental catalysis and its pertinent technologies have been attracted much attention in the past decades. Gasoline powered vehicles have increased the demand for platinum group metals (PGMs) consumption worldwide. During the course of its use, the catalytic materials of the converter are thermally shocked and disturbed by repeated low and high temperature cycles. This leads to the gradual loss of catalytic activity because the active surface area of the catalyst in the converter is diminished, and there is a need for replacement of the used catalytic converter. Several million spent catalytic converters are disposed annually worldwide\textsuperscript{1}, each containing about 0.5–1 g of platinum and 1–2 g of all PGMs\textsuperscript{3}.

Butler (2011)\textsuperscript{2} reported that 49.4 wt% of Pt, 79.7 wt% of Pd, and 68.4 wt% of Rh was applied in automobile catalysts in 2011. Although, the lifetime of the catalysts is limited and must be replaced by fresh catalysts, the natural resources of PGMs are also limited and their demand is increasing because of their extensive use for catalysis, electronic devices, biomedical devices, etc. Therefore, the PGMs recovery from the automobile catalysts is expected with energy saving and cost effective methods.

There are a large number of recovery methods of PGMs from spent catalysts reported in the literatures\textsuperscript{3–6}. The NIPPON PGM Co., Ltd.\textsuperscript{3} recovers the PGMs using copper capture in an arc-furnace, called “Rose Process”. Angelidis and Skouraki (1996)\textsuperscript{4} examined Pt recovery from spent Pt-NiO/Al\textsubscript{2}O\textsubscript{3} industrial catalyst by using a mixture of aluminium chloride solution and dilute nitric acid as an oxidant instead of aqua regia. Mhaske and Dhadke (2001)\textsuperscript{5} extracted PGMs from spent automobile catalysts using extracting agent (Cyanex 921) in from aqueous hydrochloric acid media. However, all these PGMs recovery methods did not pay attention to physical concentration of PGMs as a pre-treatment of these metallurgical processes, then, the economic feasibility is low. Because of the double-deck structure of automobile catalysts, in which cordierite lattice is covered by PGMs contained coat layer mainly composed of alumina and ceria phases, pre-treatment of separating coat layer from cordierite phase...
could concentrate PGMs and save the processing energy to one third or fourth in PGMs recycling industry. Some papers were published from our laboratory to concentrate the PGMs bearing coat layer from the cordierite phase in the past. The objective of this paper is the separation of coat layer from cordierite and concentration of PGMs by applying heating-quenching process.

Thermal treatment of ores has been extensively researched to improve comminution efficiency by changing their physical and chemical properties. It is reported that such process can also change the magnetic and dielectric properties of minerals to improve separation efficiency. However, limited research attempt has been made to study on the mechanism of micro-crack generation by thermal treatment and the micro-crack effect on the comminution and liberation of product. In this paper, we intended to analyze the heat conduction and micro-crack generation by thermal stress in the heating-quenching process in order to separate the coat layer from cordierite phase.

2. Experimental

The spent automobile catalysts investigated were three-way catalyst, which were mainly composed of 75 wt% of cordierite (Mg$_2$Al$_4$Si$_5$O$_{18}$) and 25 wt% of coat layer, mainly composed of alumina and ceria phases. PGMs in several 10 nm particles were distributed in the coat layer of fine alumina and ceria aggregates.

In our experiments, lump catalyst samples, in several cm size, were first heated in an electric furnace at 600°C for 1 h to decompose unburned carbon covering the coat layer, then washed and dried at 105°C for 1 h. Then, the samples were heated in an electric furnace again at different temperatures (600, 700, and 800°C) for about 10 min. After the heating, samples were taken out from the furnace and rapidly soaked into cool water (at 20°C). As quenching is a transient process, the samples were soaked into water in a parallel direction along the lattice structure of catalyst, which could make water flow swimmingly through the bores in the lattice. Finally, the samples were separated into two parts: one was large lumps which kept the original lattice structure and was taken out from water with tweezers, and the others were fine powders broken off from the lump samples and dispersed into water which were collected by drying the entire water.

The effect of heating-quenching process was evaluated (a) by checking the micro-crack generated in the coat layer and the interface between coat layer and cordierite phase with microscope, (b) by measuring micro-Vickers hardness, with AKASAI hardness tester, of the feed and the quenched samples heated at different temperatures, and (c) by XRF and ICP-FA analyses to obtain the grade and recovery of coat layer and PGMs in finer fractions after quenching.

3. Results and Discussion

One of the main parameters of our interest in quenching is the shape of micro-fracture and hardness change in the coat layer, and PGMs grade/recovery of various samples, in the conditions of different heating temperatures. Some of the results are shown in Figs. 1, 2.

Fig. 1 is a microscopic images of the sample after quenching: (a) is feed sample, (b) and (c) are the exterior and sectional views of the quenched samples heated at 800°C. It shows that a part of coat layer is fractured by heating-quenching process, especially at thinner part of the coat layer, where a part of the layer is broken out from cordierite as shown in (b), but the coat layer at thick part at the corner is not broken, which suggests that quenching cannot give an enough effect of separating all the coat layer from cordierite phase, but can introduce a lot of micro-cracks along the interface and in the coat layer as shown in (b) and (c).

All the quenching results show that the higher heating temperature before quenching leads to increase the thickness of coat layer to be broken, the fact of which we confirmed by measuring the weight loss of the lump samples after quenching. The largest weight loss, 4.1 wt%, of the sample was achieved after heating at 800°C. This result
indicates that the force applied by the quenching is larger than the adhesive force at the alumina/cordierite interface and that the effect is more remarkable at higher heating temperature. The detailed reason of the phenomenon will be described later.

Fig. 2 shows the change in the micro-Vickers hardness of coat layer and cordierite phase heated at different temperatures.

![Figure 2: Change in micro-Vickers hardness of coat layer and cordierite phase before and after heating-quenching process heated at different temperatures.](image)

4. Mechanism of heating-quenching process

4.1 Equations considered

The heating-quenching in this experiment is a process of thermal transfer, there are two processes: One is heating process: The samples are slowly heated from the room temperature to predetermined temperatures (600, 700 and 800°C) in the furnaces, the direction of heat conduction is from the surface of coat layer to the inside. Second is quenching process: The samples heated were rapidly cooled by soaking into water (at 20°C), in which the heat must be lost from the surface of coat layer.

Heat conduction in the above two processes gives temperature gradient and thermal stress to the sample. The basic law used to determine the thermal energy flow in the transient heat conduction is Laplace equation, which is given as Eq.(1)

\[ \rho c_p \frac{\partial T}{\partial t} = \lambda \text{div}(\text{grad}T) + \phi \]  

(1)

The \( \phi \) is the inner heat source, but there is no heat source in our cases, so the \( \phi \) is zero. The \( \lambda \) is the coefficient of heat transfer.

Under the condition that the \( \rho c_p \) is constant, the thermal diffusivity \( \alpha \) is defined as

\[ \alpha = \frac{\lambda}{\rho c_p} \, . \]

In the quenching process, the differential equation of thermal conduction in the 2D modeling can be calculated as:

\[ \frac{\partial T}{\partial t} = \alpha \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) \]  

(2)

In the quenching process, the initial condition, \( T_0 \), is set at 600, 700, and 800°C. The heat flux is lost from the sample edge to surrounding water by heat convection, so the boundary conduction is given by,

\[ h \left[ T(x, y, t) - T_0 \right] = \left( \frac{\partial T(x, y, t)}{\partial x} + \frac{\partial T(x, y, t)}{\partial y} \right) \bigg|_{x, y = \Gamma} \]  

(3)

The \( h \) is the surface coefficient of heat transfer at the coat layer surface \( \Gamma \), which directly contacts with quenching water.
The eq. (3) is discrete time domain according to Galerkin\(^\text{9}\) FEM method as follow:

\[
\sum_{c=1}^{M} \int \rho c N_i^c \frac{\partial T_i^c}{\partial t} dx dy + \sum_{c=1}^{M} \int \left( \frac{\partial N_i^c}{\partial x} \frac{\partial N_i^c}{\partial y} + \frac{\partial N_i^c}{\partial y} \frac{\partial N_i^c}{\partial x} \right) T_i^c dx dy = 0 \quad (4)
\]

In the quenching process, the strain is induced by temperature gradient among cells in the model, assuming that the targeted cell is restrained by adjacent cells and isotropically expanded. The stress in the cell can be determined using Hooke law

\[
\sigma_i = \frac{eE}{1-2\nu} = \frac{\alpha E}{1-2\nu} (T_{ni} - T_{0i}) \quad (5)
\]

Where \(\sigma_i\) is the strain of the cell \(i\), \(\alpha_i\) is the thermal expansion coefficient of the cell \(i\), \(T_{ni} - T_{0i}\) is the temperature difference between final and initial, \(E_i\) is the Young modulus of the cell \(i\), and \(\nu\) is the Poisson ratio.

The force induced by thermal strain of one cell in the 2D model can be given by:

\[
F_{ix} = \sigma_i \cdot S_x = -\frac{\alpha_i E}{1-2\nu} (T_{ni} - T_{0i}) \cdot S_x \quad (6)
\]

\[
F_{iy} = \sigma_i \cdot S_y = -\frac{\alpha_i E}{1-2\nu} (T_{ni} - T_{0i}) \cdot S_y \quad (7)
\]

Where \(F_{ix}\) and \(F_{iy}\) represent the componential forces in the \(x\) axis and \(y\) axis of the cell \(i\), respectively.

In order to obtain mechanically equilibrium state in the quenching process in all the cells in this double-layer model, the mutual bound model of stress and strain induced thermally is necessary, based on the force equilibrium in this 2D model as shown below:

\[
\sum_{i} F_{ix} = \sum_{i} F_{iy} = 0 \quad (8)
\]

### 4.2 Model considered

For analyzing thermal-stress distribution of the catalyst in heating-quenching process, we applied FEM simulation by using the ABAQUS 6.11, 2D modeling software, which is well known as a powerful software. We analyzed the heating-quenching process in the area of one unit cell (hole) of the catalyst, in order to reduce simulation work load and increase the speed of calculation because the catalyst has a symmetrical structure for all the cells. The sample model was made in true cell sizes. The thickness of coat layer in a cell is largely different as shown in Fig. 3: approx. 10 \(\mu m\) at the thinnest part in the middle of the cell, and 80 \(\mu m\) at the corner. The cordierite is quadrangular unit cell, with thickness of about 200 \(\mu m\).

In the thermal-stress model, the relevant parameters include the apparent density, thermal conductivity, specific heat capacity, thermal expansion coefficient, Poisson ratio and Young modulus of the alumina (in the coat layer) and cordierite phases in the catalyst, which were sited from different papers\(^{9-13}\). Specific properties are shown in Table 1. Although, the properties are temperature depending, we assume that properties were constant at any temperature.

FEM modeling here was composed of four main steps described below more in detail.

1. **Thermal stress analysis in the heating process:**
   - The temperature in the heating process changes slowly and the sample was kept in a predetermined temperature for 10 min, then the final temperature of coat layer and cordierite phase are considered to be the same. The initial temperature is set at the room temperature of 20\(^\circ\)C and the final temperature was set at 600, 700 and 800\(^\circ\)C in each batch test, the conditions of which were used in this model to calculate the thermal-stress generated in coat layer and cordierite phase.

2. **Transient heat conduction during quenching process between coat layer and cordierite phase:** Simulation was undertaken as a shell heat transfer model with the element type...
Table 1 Thermal and mechanical properties of the alumina and cordierite in catalyst

|                     | Alumina phase | Cordierite phase |
|---------------------|---------------|------------------|
| Apparent density, (kg/m³)\(^{17,20}\) | 3900          | 2530             |
| Apparent thermal conductivity, (W/m·K)\(^{18}\) | 30            | 1.5              |
| Apparent specific heat capacity, \(c_p\) (J/kg·K)\(^{16}\) | 1200          | 1000             |
| Apparent thermal expansion coeff., (10\(^{-6}\)·K\(^{-1}\))\(^{18}\) | 8.1           | 1.3              |
| Apparent Poisson’s ratio, (-)\(^{19,20}\) | 0.25          | 0.31             |
| Apparent Young modulus, \(E\) (GPa)\(^{17,19}\) | 139           | 40               |

Fig. 4 Thermal-stress distribution (800°C) in the heating process in the area of half-hole cell (a) and along the coat layer surface at various heating temperatures (b).

meshed to be “heat transfer” type in the ABAQUS, the surface coefficient of heat transfer of the coat layer was set at 1000 W/(m²·K) and the water temperature in the quenching process was 20°C. The history files contained the nodal temperature (NT), element temperature (ET) and all the energy (heat) magnitudes. We carried out three times simulation for different initial temperature conditions, 600, 700 and 800°C, to analyze the effect of heating temperature on the temperature gradient of the sample.

(3) Thermal stress calculation by temperature distribution in transient heat conduction: In order to obtain the stress distribution, the model was stepped in the “thermal general calculation mode” of the ABAQUS to carry out thermal-stress analysis using the dynamic temperature distribution which was calculated by transient heat conduction. The strain and stress were contained in the history files. We chose three typical points to check the stress change with time in the model which were the thinnest part of coat layer, thickest part (at the corner) of coat layer, and the part of cordierite at which the largest force was generated.

(4) Shear force generated at the interface of coat layer and cordierite: In the result of thermal-stress distribution, a section of interface, which contains three cells near the middle of coat layer, was selected to get the shear force changed with quenching time at various heating temperatures for different heating temperature.

4.3 Temperature-stress distribution calculated by FEM simulation

4.3.1 Stress distribution in heating process

In order to determine the effect of heating temperature on the thermal-stress of coat layer and cordierite phase, FEM modeling was undertaken firstly for an unheated sample, setting the initial temperature at as room temperature, and at the final temperatures of 600, 700, and 800°C, respectively.

The model thermal-stress distribution obtained at 800°C heating is shown in the Fig. 4 (a). It can be seen that the stress of coat layer is all compressive and that of cordierite phase is tensile. The compressive stress at the region A, the thinnest part of coat layer, is higher than other areas. In order to clarify the stress change in the coat layer and to check the effect of heating temperature on
the stress, we chose a line of surface area of the coat layer (shown in Fig. 4 (a)) and showed the stress distribution along this line in Fig. 4 (b).

We can see from the figures that, (1) the stress generated in the coat layer is compressive in all the area and that in cordierite phase is all tensile but the magnitude is not so high, (2) the stress increases sharply from the corner to the central part in a cell and the stress becomes higher as increasing heating temperature, and that the largest stress at 800°C heating is approx. 230 MPa. However, there is no fracture even at the central part in the practical experiments. It is considered that the stress induced only by heating did not reach to the compressive strength for the breakage.

4.3.2 Transient temperature distributions in quenching process

The change in temperature distribution with time in the “half-hole model” is shown in Fig. 5 (a), (b) and (c) at different elapsed time after the start of quenching. We selected three typical points as shown in the Fig. 5 (a): point A and B are in the coat layer, and point C is in the cordierite phase. In the Fig. 5 (d), the temperature gradients of three points are indicated. It can be seen that thermal flux transfers from coat layer (alumina) surface into water at the beginning of quenching, and gradually comes out from adjacent area of alumina phase into the surface. Temperature of coat layer decreases at first, especially at the area of thinner parts, then, the temperature of cordierite phase decreases with passing time. Change in temperature and the gradient are variable at different area and passing time. This results indicate that (a) the thermal flux which comes from cordierite to coat layer creates the temperature gradient in coat layer and cordierite in quenching process, (b) the surface area of coat layer, A and B, has higher temperature gradient than the inside of cordierite phase, (c) the thinner part of coat layer, A, shows the highest temperature gradient as shown in Fig. 5 (d).

4.3.3 Thermal-stress distributions in quenching process

Thermal stress distribution after 800°C heating and quenching, obtained from FEM simulation using the ABAQUS, is shown in Fig. 6 (a). The thermal stress is generated by temperature change, which has calculated at previous step, so the model was set heating temperature as initial condition firstly, then assigned the temperature distribution data with time in the model, to calculate the thermal stress. Temperature distribution in quenching process is transient as mentioned in the previous
section, then, the thermal stress is also changed with time and location. Fig. 6 (a) shows the stress distribution in the case of heating at the time of 0.5 s after quenching. We can see that tensile stress is generated in the coat layer and compressive stress in the most area of cordierite phase, and the highest tensile stress are generated at the thinnest part of coat layer. The Fig. 6 (b) shows the stress generated at the three reference points shown, A, B and C, as a function of time, the points of which are at the thinnest part and corner of coat layer, and in cordierite phase. We can recognize that the stress increases shapely within the time of 0.15 s after the start of quenching. It also shows that the higher stress is generated by higher heating temperature for all the points.

4.3.4 Shear force change at the interface with time

As mentioned above, thermal-stress distribution was changed with time in the quenching process and the highest tensile stress was generated in the point A, where is the thinnest part in the coat layer, and this simulation suggested the strength of coat layer (alumina phase) was over its tensile strength (50 MPa), then the fracture was generated at the point A.

Fig. 7 (b) shows the summation of shear forces of the three cells which are located in the vicinity
of the central part shown in Fig. 7 (c), as a function of time. The shear force was sharply increased from zero to the maximum for all the heating temperature, and slowly dropped with time. Since the shear force is made by the stress change of coat layer (tensile) and cordierite phase (compressive), the point A should be broken much easier than other points. The shear force after the breakage (at the time of maximum shear force) is gradually decreased with passing time to the end of quenching at about 0.5 s.

Conclusions

In order to concentrate PGMs in the coat layer from spent automobile catalysis, we applied heating-quenching process and clarified the mechanism of the effect of thermal shock by using hardness test, mathematic analysis and FEM simulation. Heating-quenching process gave a significant influence on the concentration of PGMs bearing coat layer (mainly alumina phase) from cordierite substrate. It is concluded that this process could promote the direct breakage of coat layer and generation of micro-cracks in coat layer and of large cracks at the interface of coat layer and cordierite phase. The micro-Vickers hardness of coat layer was once increased in the heating process but decreased in the quenching process, which indicated the heating-quenching process had a positive effect for the subsequent selective breakage of PGMs bearing coat layer. Mathematical analysis and FEM simulation could make clear that the thermal tensile stress is generated in the coat layer, especially at the thinnest part, in the transient thermal transfer process of quenching owing to the temperature gradient and the difference of thermal expansion ratio of the two phases. We also clarified that only compressive stress was applied to cordierite phase in the quenching process.

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