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Recovery of platinum from the spent auto-catalysts by pyrometallurgy

Recovery of platinum from the spent auto-catalysts by pyrometallurgy

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Abstract. The present article introduce a method of pyrometallurgy to recovery platinum from spent auto-catalysts. In the paper, the effect of binary basicity R (R=CaO/SiO_2) of slag and the parameters of smelting process such as temperature and time of smelting on platinum recovery were researched. The results of this study show the platinum recovery is higher when R should be around 0.5 and smelting temperature of 1773 K as well as smelting time of 4 hours. Under the optimum condition, the recovery rate of platinum is up to 98% by the method presented.

1. Introduction

Platinum is one of the most important metals in the Platinum group metals (PGMS) have been greatly utilized in agriculture, electronic, national defense and other sophisticated industry due to its excellent physicochemical properties [1-4]. Particularly, platinum is widely applied in automotive catalyst to purify automobile exhaust and protect the environment for it has fine catalytic capability. Mineral resources of platinum, however, are extremely scarce on Earth and it is hard to extract platinum from them [5-7]. Meanwhile, large quantities of the secondary resources of platinum-containing are generated with the tremendous growth of scrapped cars in China. As reported, the amount of platinum used for each vehicle is 1~2 g and the platinum content is 1000~2000g/t in spent auto-catalyst [7]. It is necessary to recovery platinum from spent auto-catalysts. The reasons are that the waste catalysts contains not only large amounts of precious metals such as platinum, palladium and rhodium, but also have been listed as hazardous waste by the Ministry of environmental protection of China and the related departments of other countries[8-9]. Therefore, the development of the advanced recycling technology of platinum from spent auto-catalysts is highly necessary.

At present, the technologies of recycling platinum from spent auto-catalysts are mainly divided into hydrometallurgy and pyrometallurgy or combination of both methods [10-12]. Now the industrial method of recovering platinum from spent auto-catalysts is mainly hydrometallurgy which are listed by most literatures published [13-14]. This method recover the platinum by leaching the carrier or platinum in solution including alkaline and acidic solution. But it has many inevitable drawbacks. For example, the method produces much waste water and residue, poor adaptability for leaching material and needs high grade of platinum in raw material [15-16]. However, most of problems which are created by hydrometallurgy can be avoided and have a high recovery rate of platinum by using pyrometallurgy which was described by Peng [17] and Kim [18].

The metal collector method is usually chosen to recovery platinum and other precious metals in pyrometallurgy [15]. The results of smelting mainly depend on the selection of molten slags and parameters in smelting process. Therefore, in this study, the smelting slag system and parameters of melting process are mainly researched and molten slag is expected to form the glassy slag which has little adverse impact on the environment. In this paper, the molten slag system is SiO_2-CaO-Al_2O_3-MgO-FeO and the binary basicity (R= CaO/SiO_2) of molten slag should be less than l. The melting temperature and viscosity of slag system were selected by thermodynamics software of Factsage 6.4 and experiments and then the parameters of smelting were confirmed though experiments.

2. Experimental

All of chemical agents in the experimental process were analytical pure which need to be dried about 12 hours in 473 K and the raw material should be dried under the temperature at 573 K for 5 hours to remove moisture and crushed to about 200 mesh before smelting. The equipment of smelting was molybdenum disilicide heating furnace as shown Figure 1. The graphite crucibles were used to place smelting material, which dimensioned as Φ80mm x 130mm. In single experiment, the total 200 g material (mixture of spent auto-catalysts and some oxides with intensively mixed) was put in graphite crucible. Viscosity of slag was measured by using the viscosity measurement equipment (DN-Ⅱ). The phase compositions of the Pt-Fe alloy obtained and molten slag were analyzed by X-ray diffiraction (X'Pert PRO, PANalytical). The microstructure of the Pt-Fe alloy was analyzed by SEM and EDS (SEM-EDS, SU800). The content of molten slag composition and platinum in the slag were measured by XRF and ICP, respectively.

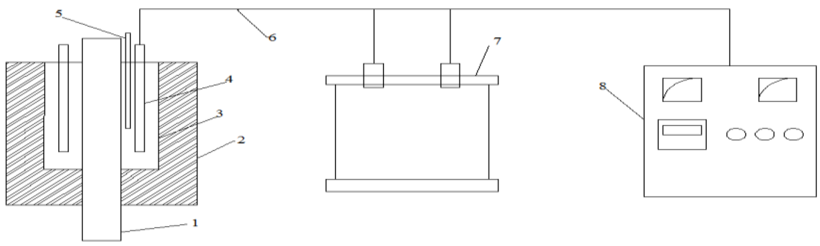

Figure 1. Molybdenum disilicide heating furnace. (1-alundum tube; 2-the furnace shell; 3-the furnace inner wall; 4-heating rod; 5-thermocouple; 6-cable; 7-transformer; 8- temperature control system)

3. Results and discussion

3.1. Influence of molten slag binary basicity on recovery of platinum

In this paper, the melting temperature and viscosity of slag were tested and the recovery rate of platinum were measured under different binary basicity (R= CaO/SiO_2). The melting temperature of selected slag was of a rather small range (1533 K to 1573 K), and the temperature factor has little impact on recovery of platinum. In present study, the influence of slag viscosity and R on the recovery rate of platinum were considered as the main factors and investigated under the same experimental conditions, the results as shown in Figure 2. Figure 2 shows that the recovery of platinum and viscosity of molten slag had the same changing tendency with the variation of R. Meanwhile, there were differences between the smelting of recovering platinum and iron and steel smelting. In iron and steel smelting process, the viscosity of molten slag should be less than 1 Pa·S as possible to smoothly separate of the slag and iron or steel melt. However, in the process of recovery platinum from spent auto-catalysts, the collector will rapidly sink to bottom when the viscosity of slag value was too small which would lead to platinum was not adequately collected and the recovery rate of platinum was lower. It was necessary to keep the binary basicity of the smelting slag system at around 0.5 for achieving higher recovery of platinum.

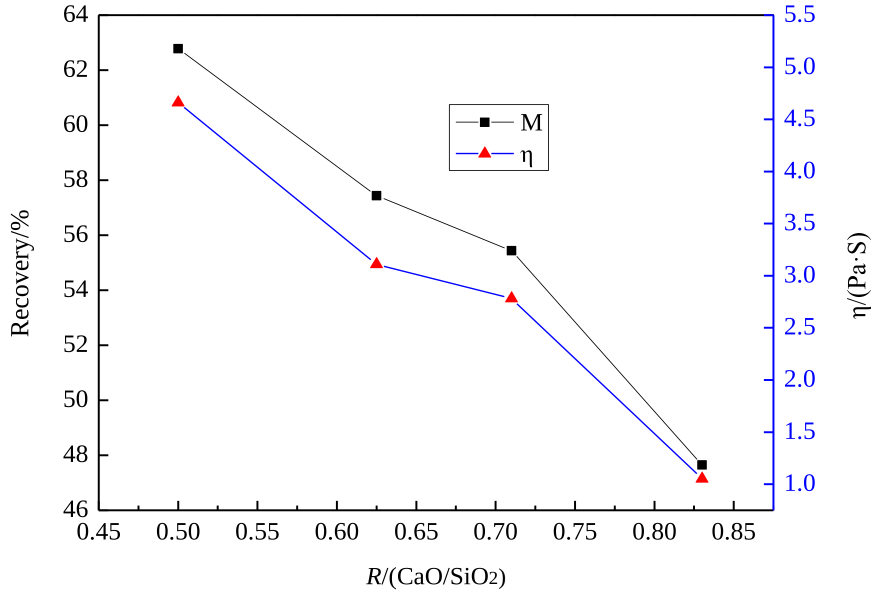

Figure 2. Effect of R(=CaO/SiO_2) on recovery of platinum and the viscosity of slag (smelting temperature of 1673 K and smelting time of 3 hours).

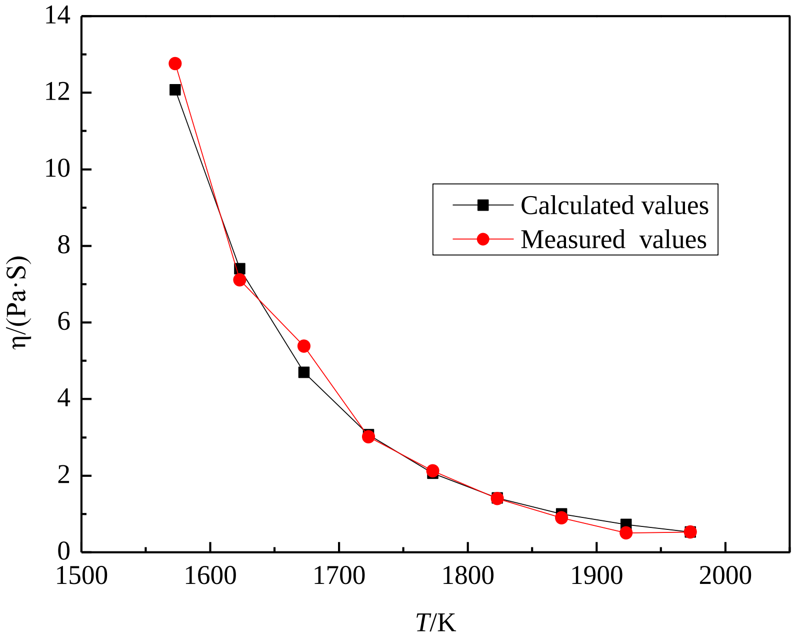

Figure 3. Viscosity curves of measured and calculated values of smelting slag.

In this article, R of smelting slag was maintained about 0.5. The viscosity of molten slag was calculated by Factsage 6.4 and measured by experiments as shown in Figure 3. The viscosity of calculated needed to correct by modified Einstein-Roscoe model [19] as shown Formula 1. Figure 3 shows the differences between calculated and experimental values was very small. Therefore, the parameters of slag calculated by Factssage 6.4 can be used in smelting experiment.

$$\eta=\eta_0(1-af)^{-2.5} \tag{1}$$

Where η is the corrected viscosity of molten slag, the η_0 is the measured viscosity, a is a constant equal to 2.5, the f is the percentage content of solid phase at high temperature.

3.2. *Effects of the parameters of smelting process on platinum recovery*

In the process of smelting, some parameters of technology should be chosen to ensure high platinum recovery and low cost of experiment. In this paper, the parameters of smelting included the amount of collector added, temperature and time of smelting.

In order to recycle platinum from waste catalysts, some collectors needed to be added in the melting and formed alloy with platinum. The influence of the amount of collector added on the recovery of platinum as shown in Figure 4. It could be found that the recovery of platinum increasing from 58% to about 98%with the collector added when the amount of collector is 4 wt% to 15 wt% of waste catalysts, and then the recovery of platinum changing inconspicuously with the collector unceasingly put in the melt. Therefore, the present study taken the amount of collector was 15wt% of waste catalysts as a reasonable parameter which can reduce cost and improve the grade of platinum in Pt-Fe alloy.

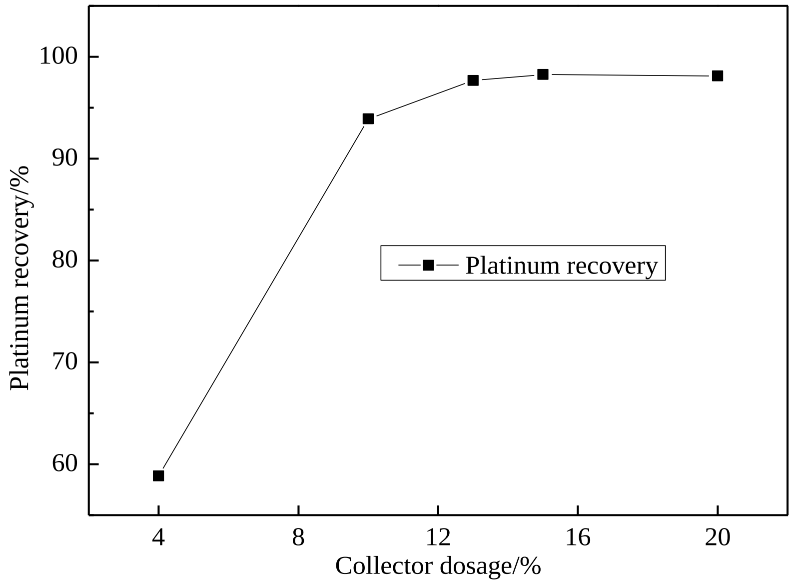

Figure 4. Effect of the amount of collector on the platinum recovery.

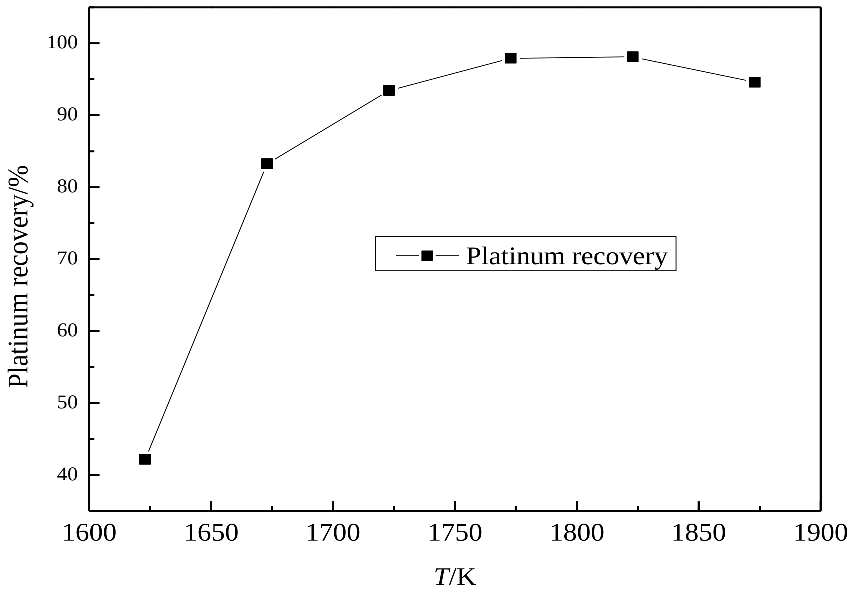

Figure 5. Effect of temperature of smelting on the platinum recovery.

In most pyrometallurgy, the temperature and time of smelting played significant roles in smelting process. It was necessary to choose rational temperature and time of smelting to cut production cost and obtain high recovery of platinum. The effect of temperature and time of smelting on platinum recovery as shown in Figure 5 and Figure 6, respectively. As could be known from Figure 5, platinum recovery increase from 42% to about 98% as the temperature of smelting from 1623 K to 1773 K and then the platinum recovery start to reduce with rising the temperature. The reason was that viscosity of molten slag was small at high temperature so that the collector sink quickly to bottom of melt before collecting adequately the platinum in melt. For the temperature of smelting investigated in the study, the appropriate temperature of smelting was 1773 K. Figure 6 shows that platinum recovery is increasing from 84% to around 98% as time of smelting from 2 hours to 4 hours and then the recovery raises is small when continue to raise the temperature. It could be seen that the time of smelting should keep in about 4 hours in experiment of smelting.

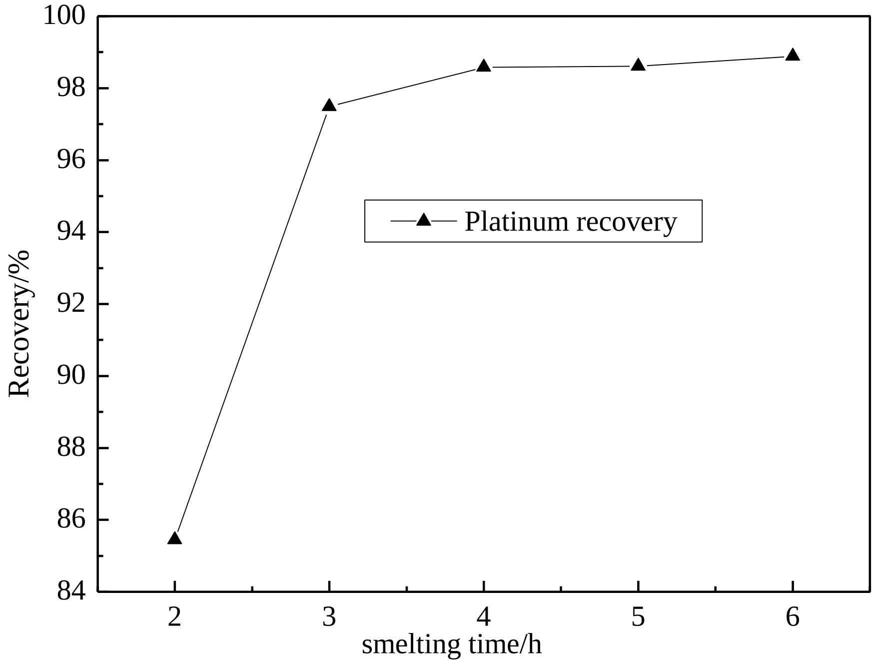

Figure 6. Effect of smelting time on the platinum recovery.

3.3. Analysis of molten slag and alloy obtained after experiment

The molten slag and alloy were analyzed by using related analysis equipment. The chemical composition and its platinum content of slag and its phase as shown in Table 1 and Figure 7, respectively.

It can be found from Table 1 that the main chemical composition of molten slag are SiO_2, CaO and Al_2O_3, the R is about 0.5 which is closed to the expected values and meet the binary basicity value required for glass slag. In addition, the platinum content in the slag is less than 10 g/t. Meanwhile, Figure 7 shows that t the XRD pattern of molten slag is in accordance with amorphous. It could be known the slag was glassy state which achieves the requirements and objectives of previous expected.

The Pt-Fe alloy obtained after experiment of smelting was analyzed by XRD and SEM, the results were shown in Figure 8 and Figure 9, respectively. Figure 8 shows that the phase composition of alloy obtained are mainly iron and some trace elements such as sulphur, silicon and oxygen. The Platinum is not found because its content and grade is very small in Pt-Fe alloy. But the platinum can be discovered by SEM-EDS in the alloy. From Figure 9, it can be seen that the alloy obtained mainly contains the platinum and iron. The oxygen element was found in alloy due to mild oxidation of the alloy surface. Other elements included aluminum might be doped in sampling. The consequences of analyzing indicated the results of smelting experimental and prospective had little difference. The production of method presented in this paper could be used to recovery the platinum from spent auto-catalysts.

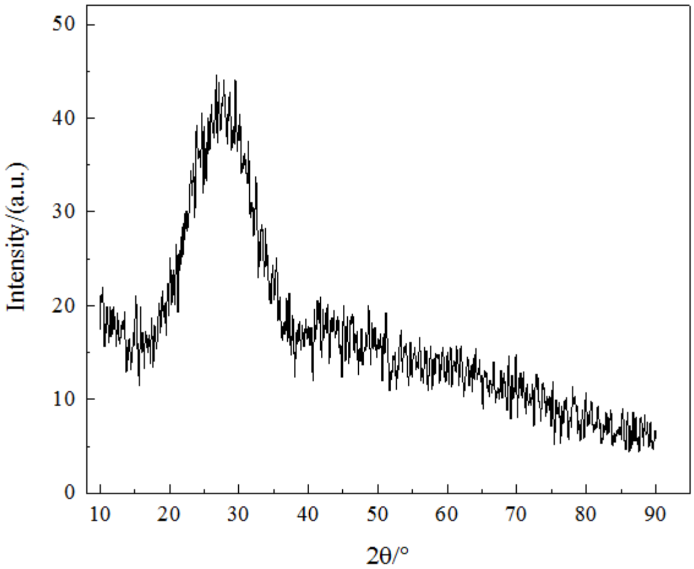

Figure 7. XRD pattern of molten slag after smelting experimental.

Table 1. The chemical composition of molten slag.

Chemical composition	SiO_2	CaO	Al_2O_3	MgO	FeO	Pt
Mass fraction/%	52.66	23.79	15.91	4.23	1.44	<10g/t

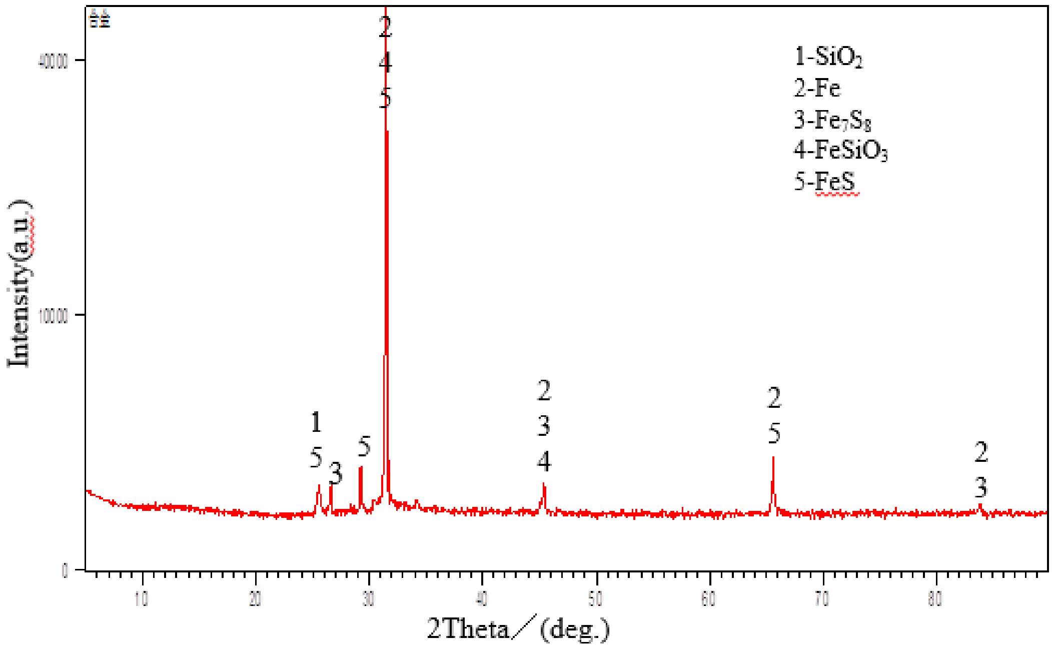

Figure 8. XRD pattern of Pt-Fe alloy obtained after experimental.

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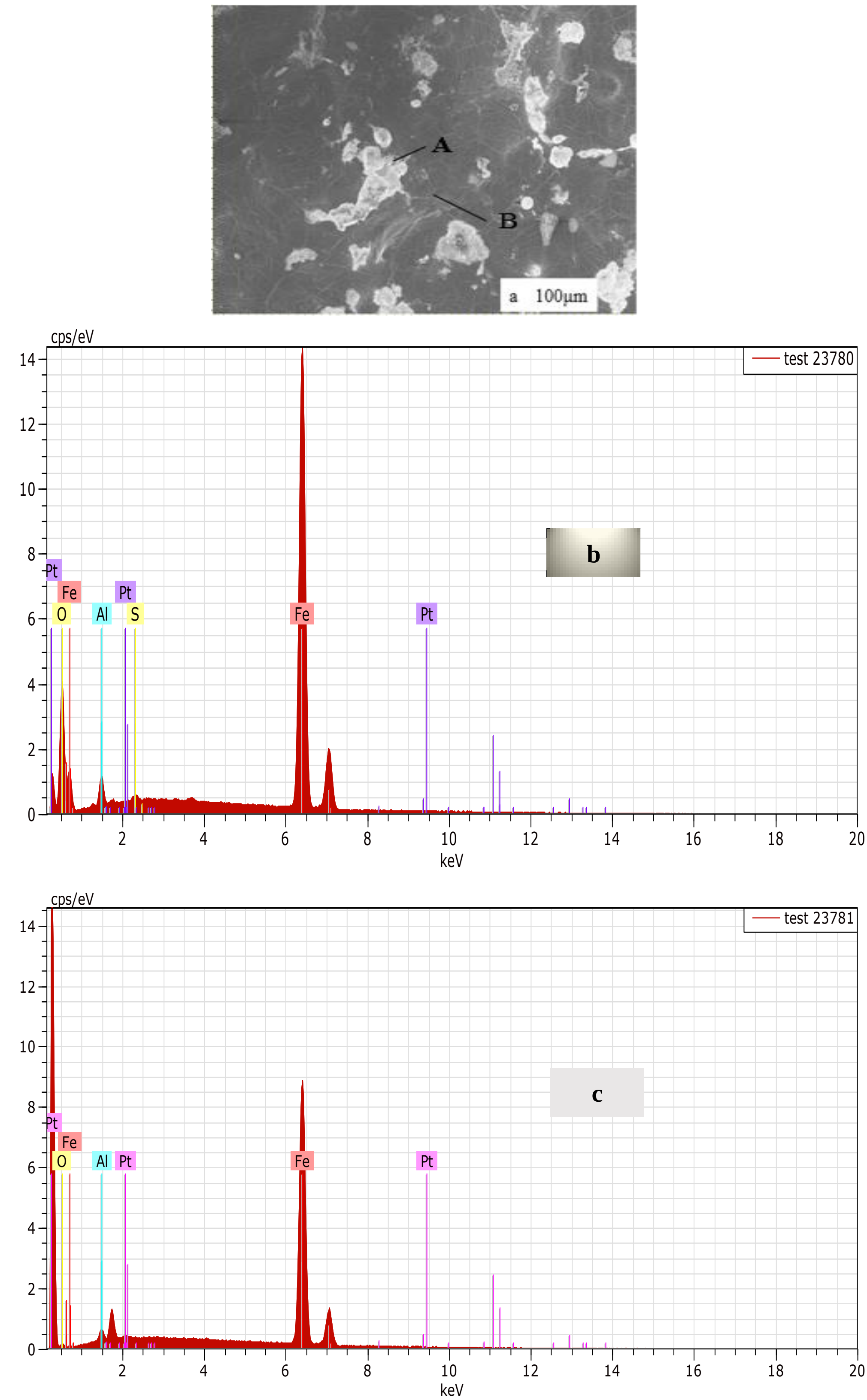

Figure 9. SEM image (a) and the results of EDS (b, c) of alloy after smelting experimental.

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4. Conclutions

(1) Effect of the R(=CaO/SiO_2) on the platinum recovery in spent auto-catalysts were researched by experiments. It can be known the platinum recovery was higher when the R values at about 0.5.

(2) The parameters of amount of collector, temperature and time of smelting in smelting process were 15wt% of raw material, 1773 K and 4 hours, respectively.

(3) The samples included slag and alloy obtained after smelting experiment were analyzed and compared with the expected results. It can be found the related targets of slag and alloy were reached. This methods of pyrometallurgical presented in this paper can be used to recovery platinum from spent auto-catalysts.

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