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POSSIBILITIES OF PLATINUM RECOVERY FROM METAL SUPPORTED SPENT AUTO CATALYSTS

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The used auto catalytic converter is a valuable source of platinum group metals, so it is important to have it recycled in order to recover precious metals. World literature describes a number of pyro- or hydrometallurgical methods used for recovery of platinum from used automobile catalytic converters. However, all the methods, available in the literature, are used to recover platinum from ceramic carrier. Among automotive catalysts withdrawn from use, these with metallic carrier constitute quite a big group.

Key words: Precious Metals Group (PGM) metals, metal recovery, spent auto catalysts, metallic carriers.

INTRODUCTION

Nowadays, ecological problems become a priority in many areas of science and industry. Also in the automotive industry, more strict standards for emission of harmful compounds in the form of exhaust gases into the atmosphere introduced. Thus, for several years, installations reducing environmental pollution, commonly referred to as automotive catalysts, are used in cars. In these devices, chemically active elements, especially Precious Metals Group (PGM) - having the ability to convert harmful substances - are used [1].

Their main task is to limit the emission of dangerous substances such as: nitride oxide (NOx), hydrocarbons (CH) and carbon monoxide (CO). As a result, compounds neutral to the environment, such as carbon dioxide, water and nitrogen are obtained at the outlet of catalytic converters [2]. Typical auto catalytic converter is built mainly from metallic or ceramic carrier with porous structure covered with the PGM metals (Figure 1). The most often used are: platinum, palladium and rhodium. Catalytic carrier is wrapped by the fibrous material (to prevent slipping) and closed in a shell made from stainless steel plate. The PGM layer is put on the ceramic carrier (Al_2O_3 with the addition of other oxides e.g. CeO_2 - washcoat), which has the honeycomb structure, that means a dense net of square holes. Such construction increases the active surface, which is the contact zone of catalytic substances (Pt, Pd, Rh) with the exhaust gases, that flow through the channels [3].

For certain applications (reducing light-off, reducing back-pressure, etc), a metallic carrier rather than ceramic one is chosen. It is a commonly known fact that converters with a ceramic substrate cover about 95 % of the total market [4].

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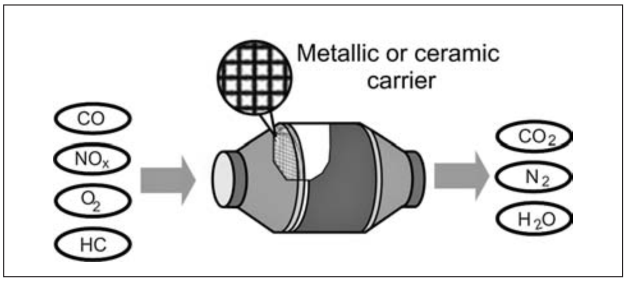

Figure 1 Scheme of auto catalyst

Considering the fact that the metal heats up much faster than ceramics, metal catalysts rapidly reach "working temperature" and quickly purify exhaust gases. At the same time, they are more resistant to damage caused by thermal shock and high temperature (determined by their resistance to 1 300 °C). The advantage of metal supported catalysts is their better thermal conductivity obtained due to high content of platinum [5].

Catalytic converters with metallic carriers – MSC (Metal Substrate Converters) were originally designed for sport and racing cars where low back pressure and reliability under continuous high load is required. This is partially a cost issue. Ceramic carriers are inexpensive when manufactured in large quantities. Metallic cores are less expensive to build in small production runs. Either material is designed to provide a high surface area to support the catalyst washcoat, and therefore it is often called a "catalyst support" [6]. Metallic foil monoliths (Figure 2) are made of FeCrAl [7]. Analysis of chemical composition of this kind of catalytic converters is shown in Figures 3-7 and in Table 1.

The surface of the sample catalysts was analyzed with the use of scanning electron microscope (SEM) equipped with a Hitachi S 4200 the X-ray detector. Accelerating voltage applied during the observation and X-ray microanalysis was 15kV. Microanalysis of the

Figure 2 Real view of catalytic carrier structure

chemical composition was performed by means of EDS method (Energy Dispersive Spectrum).

Unfortunately, such a structure makes it difficult to recover the precious metal contained in these kind of catalyst [7].

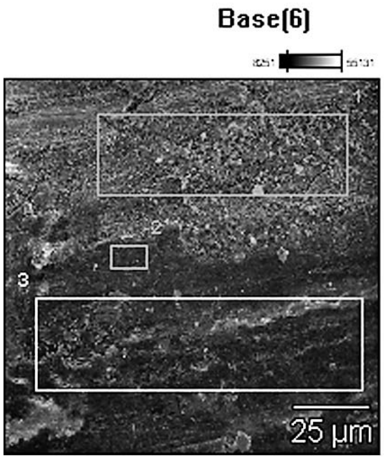

Figure 3 Structure of catalytic converter sample with marked selected areas for X-ray energy spectra (Magnification x450)

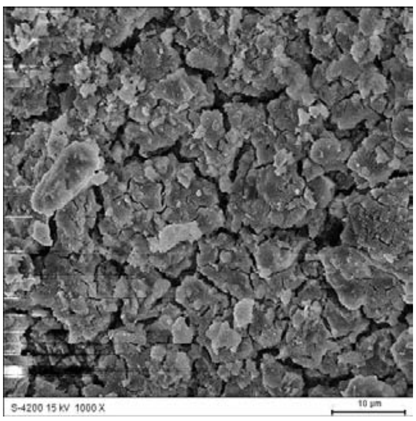

Figure 4 Structure of catalytic converter

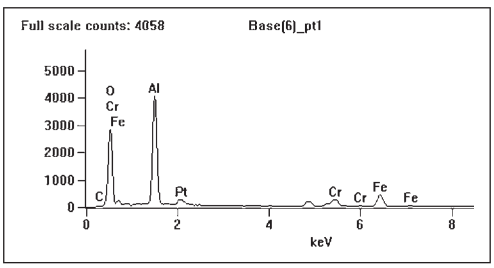

Figure 5 X-ray energy spectra (EDS) at point 1 for sample of catalytic converters

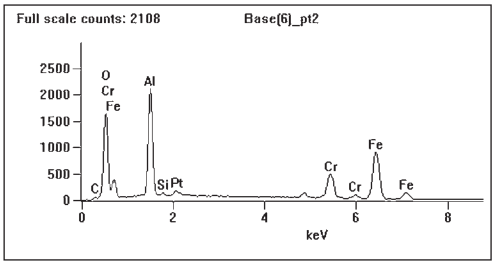

Figure 6 X-ray energy spectra (EDS) at point 2 for sample of catalytic converters

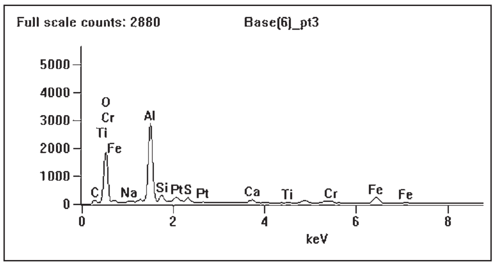

Figure 7 X-ray energy spectra (EDS) at point 3 for sample of catalytic converters

COMPARISON OF METALLIC OR CERAMIC CATALYTIC CARRIER

Consequently, the most important element in the catalytic converter applied not only in automobile industry, but generally in all industries is the material for the converters carrier (metallic or ceramic). The most commonly used are catalytic converters with ceramic carriers.

Table 1 **Chemical analysis for sample of catalytic converter**

Element	Base(6) pt1	Base(6) pt2	Base(6) pt3
	Weight %		
Cr	6,1	11,8	1,8
Fe	18,3	42,8	2,1
Pt	4,5	2,1	5,0
C	0,5	0,7	6,8
O	42,3	24,4	44,2
Al	28,0	18,0	22,4
Si	-	0,3	2,0
S	-	-	1,7
Ca	-	-	1,9
Ti	-	-	1,0

The advantages of ceramic carriers are:

- very high specific surface,
- high corrosion resistance,
- high adhesion of active substances,
- high melting temperature,
- easiness in shaping.

The characteristic features of metallic catalytic carriers are:

- easiness of heat transfer (they are resistant to local overheating),
- small hydraulic resistances,
- high mechanic strength,
- all apparent powder density,
- smaller susceptibility to mechanical damage [8].

The difference between both type of auto catalytic converters is shown in Table 2.

Table 2 **The difference between boths type of auto catalytic converters [7]**

Part of catalyst	Ceramic carrier	Metallic carrier (MSC)
Steel shell	2,900 kg	1,300 kg
Isolation	1,000 kg	0,800 kg
Carrier	0,900 kg	1,300 kg
Washcoat (with PGM)	0,160 kg	0,160 kg
PGM	0,005 kg	0,005 kg
Sum	4,965 kg	3,555 kg
Material for recycling	1,065 kg	0, 155 kg

The efficiency of the metallic and ceramic converters measured by comparing how much gas is converted, is shown in Table 3.

Table 3 **Measured conversion at idle [9]**

Conversion efficiency	Ceramic Carrier (TWC-C - Three Way Catalyst-ceramic)	Metallic Carrier (TWC-M - Three Way Catalyst-metallic)
HC	31,58 %	45,62 %
CO	32,08 %	33,52 %
NO	43,33 %	47,32 %

RECYCLING OF USED AUTO CATALYTIC CONVERTERS

In Europe End-of life–vehicles (ELVs) are a particularly valuable waste source, amounting to more than 9 million tons per year thus they demand to be properly managed [10]. Derective 2000/53/EC gives basis for more sustainable approach and drives to a recovery improvement, in order to reduce waste production from the sector of End-of-Life-Vehicles treatment. This regulation increases in the re-use and material recovery as shown in Table 4.

Table 4 **Targets of ELVs recycling and recovery (Directive 2000/53/EC) [10]**

Year	2006	2009	2015
Re-use and recovery	85 %	80 %	95 %
Re-use and recycling	80 %	80 %	85 %

Catalytic converters are devices that should be periodically regenerated, and eventually replaced. Currently, this increasing number of catalysts (coming from exchanges and also from vehicles withdrawn from the market) should be recovered.

The needs of waste management and high prices of precious metals contained within these wastes, makes the recovery of platinum group metals from used auto catalytic converters potentially profitable. The main problem, in platinum recovery from catalysts, is however its low content within a single catalyst.

The first step to recover PGM metals and especially platinum from used auto catalytic converters (both with ceramic and metallic carrier) is to collect and then dismantle them. After these operations catalytic converter carriers are milled and homogenized. Then chemical analysis is necessary in order to check the level of platinum and other precious metals. Thus, there are numerous pyro-, hydrometallurgical and mixed methods applied in recovering of PGM metals from catalytic converters [11]. Both types of PGM metals recovery methods are complex, multistage, in which the appropriate catalytic converter carrier grinding and primary homogenizing is needed. Then many essential operations are applied and at the end a method, which allows to separate the obtained platinum or other PGM metals from the solution or alloy and refine it/them to the desirable level.However, if recovery of PGM metals to be cost-effective, well over 90 % of these precious metals must be recovered [12-14].

As the precious metals are applied only to certain parts of the converter (washcoat), the first step of recycling process is a mechanically separate the washcoat and PGM from the substrate [15]. The next step is then to homogenize the PGM fraction.

The metallic carrier is shredded by passing it through one or more different types of shredders, hammer mills. This step is preceded by separation of various fractions of steel scrap (such as can-fraction, foil-fraction) from the precious metal containing fraction. There is little information on the recovery of precious metals from spent automotive catalysts with metal carriers in the world literature. The Umicore Precious Metals Refining - one of the world's largest precious metals recycling facilities - has dedicated and highly fully automated shredding line for metallic carriers from spent automotive catalysts in Maxton (USA). This technology allow to achieve a high recovery yield for the washcoat [4].

However, the crushing process can causes problem - a fine dust (obtained after this process) is rich in precious metals [15]. The authors Hensel, Konieczny and Brückhe [15] suggested that it allow to partly separated washcoat from the substrate!

The wash coat can be seperated from the substrate by mechanical means in certain process parameters (difference in form, size and weight mixture of). The end result is that different but homogeneous fractions of high purity are recovered.

The main steps of PGM recovery process from spent automotive catalyst with metallic carrier suggested in paper [15] are:

- Mechanical Reduction - reduction to a defined particle size by means of a shredder.
- Magnetic Separation - metallic fraction is magnetically separated.
- Mechanical After-treatment - the residue of precious metals on the substrate foil is seperated from the steel parts by means of a mechanical separation unit.

All fractions of the wash coat are homogenized. The substrate foil and casing material can be reutilized in steel smelting [15].

CONCLUSIONS

The automotive industry is facing significant challenges as vehicles have considerably environmental impact on all stages of their life cycle [16]. The recovery of PGM metals and especially platinum in the last decade has been growing but is not sufficient. The bigger and bigger demand for platinum causes the growth its price. Considering, however, the existing state of the technological development it is very unlikely that platinum group metals shall be replaced (in automotive industry) by other substitute in the nearest future. So, the recovery of PGM metals from used auto catalytic converters has become very important and catalytic converters very valuable sources of these metals. High purity of recovered metals allows to use then again and does not cause any financial problems.

Acknowledgements

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Note: The responsible translator for English language is M. Kingsford, Katowice, Poland