CONTROL OF PLASMA CHEMICAL PROCESSES
BY RAMAN SPECTROSCOPY

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INTRODUCTION

Raman spectroscopy which has been particularly intensively
developing in the recent decades, finds application in the
solving of a wider range of problems. A complex of works on
the development and application of this particular method in
the study of some units of the low-temperature plasma genera-
tors and the products of plasma technology has been carried
out in the Alma-Ata Power Institute.

An outline of the investigations carried out is given
below.

EXPERIMENTAL EQUIPMENT

In the investigation the Raman scanning microprobe is made
use of which represents a combination of a microscope with
the Raman-scattering spectrometer thus ensuring a high loca-
ality of the investigation up to 1 m. The excitation of
spectrum was effected by a green line of 514.5 nm of the la-
sor on the argon ions of variable power. The spectra were re-
corded by the photoelectric method on a tape diagram.

RESULTS AND DISCUSSION

I. Cathodes of refractory metals (Zr, Hf, W) are the main
units of various electric arc devices which determine their
life-time. That is why at present essential attention is
paid to the theoretical and experimental investigation of ca-
thode units, that requires attracting new experimental me-
thods to study the processes on the cathode surface.

The data obtained by us /1/ show that the laser Raman
spectroscopy offers ample opportunities in the investigation
of electrodes of the plasmatrous treated by plasma.

Raman spectroscopy as a method of indestructive and non-
penetrating control makes it possible directly analyse the
thin layers on the surface without preliminary preparation.
At the same time at using the laser to excite the spectrum a
ray penetrates into the depth up to several hundreds of ang-
strom, thus reliably giving the unique information about the
molecular structure of a substance and the structure of a
crystal lattice.
In particular, this method has been employed by authors to investigate zirconium thermochemical cathodes of plasmo-tron after their plasma treatment. It should be noted that such investigations appear interesting because they are also involved in a wider problem of the Raman spectroscopy: observation of the phonons on metals and alloys — this is a new field for this method, similar information is practically not available in the literature /2/.

The thermochemical cathode under study was a zirconium insert with the diameter of 3 mm built in flush with a copper water-cooled casing. Plasmotron cathodes were studied immediately after their operation with different parameters.

Visually at the large magnification the cathode surface is divided into several clearly distinguishable zones, an appropriate Raman spectrum was obtained for each of them.

To obtain standards, the Raman spectra for metal zirconium and its oxide were recorded as well. They were used for evaluation of the composition of a substance on the cathode surface. These experiments enabled to evaluate the composition of the substance formed on the cathode surface after its treatment by plasma /3/. The distribution of zirconium oxide by the radius of the insert surface is given in Fig. I. The investigation of the film composition and structure by the depth is carried out in a similar way, if a cross-section of cathode is made.

**Distribution of zirconium oxide by the radius of the zirconium insert in the plasmotron cathode**

![Graph](image-reference)

**Fig. I**

2. Application of the laser microprobe of Raman is prospective when investigating the coatings obtained by plasma spraying likewise corrosive films on various surfaces, etc. /4/.

Prospects of using the Raman spectoscopy method in this trend are shown by us with the example of determining the corrosive film composition on the surface of the steel pipeline parts having been influenced by corrosive media /5/. The spectra of seven samples were obtained within the frequency region of 200-2000 cm⁻¹. Pipe cuts were placed directly in the laser ray without any preparatory operations.

Analysis of corrosive films was carried out basing on preliminarily recorded standard Raman spectra of all ferrum oxides. The identification of spectra of the samples analysed allowed to conclude that in the majority of cases a multicomponent film forms on the surface of the samples (See Table 1).

If we take into account that Fe²⁺ is a primary corrosion product, and Fe³⁺ is the final one, it is possible to estimate the degree of oxidation of individual samples and suppose some conclusions about the kinetics of the oxidation process in
each particular case.

Table 1

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Standard description</th>
<th>Composition of corrosive film</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HY-79 dist. water 300°</td>
<td>C + FeO + Fe₂O₃</td>
</tr>
<tr>
<td>2</td>
<td>HY-56 dist. water 30°</td>
<td>FeO</td>
</tr>
<tr>
<td>3</td>
<td>HY-19 air 20°C</td>
<td>FeO + Fe₃O₄</td>
</tr>
<tr>
<td>4</td>
<td>HY-100</td>
<td>FeO + Fe₂O₃ + Fe₃O₄</td>
</tr>
<tr>
<td>5</td>
<td>C 20 air 300°C</td>
<td>FeO</td>
</tr>
<tr>
<td>6</td>
<td>C 20 solution &quot;B&quot; 300°C</td>
<td>FeO</td>
</tr>
<tr>
<td>7</td>
<td>0,8x16H10T dist. water 300°C</td>
<td>FeO + Fe₃O₄</td>
</tr>
</tbody>
</table>

Scanning on the surface makes it possible to evaluate the change of the film composition, and the analysis by the layers shows the distribution of separate components by the thickness of an oxide layer.

3. Another field, where we have successfully applied Raman spectroscopy, is the investigation of microstructure of refractory materials, obtained by the method of plasma synthesis. As the refractories represent complex objects, a number of specific difficulties arise in their investigation by the Raman spectroscopy. First of all, it is a heterogenic material, which components are characterized by absolutely different chemical, mechanical and thermal properties.

Structurally, refractories consist of a solid part and pores. The solid part, in its turn, comprises grains, entirely consisting of crystal phases as well as the zones of glassy and amorphous states. Individual grains represent crystal structures which contain impurities and inhomogeneities and there is a derable disordering. All this results in that the vibrational frequencies can differ from the frequencies of vibration for large monocrystals and the lines are considerably broadened.

The availability of impurities can cause not only the appearance of new lines in the spectrum, but the substantial changes, alternating a space group of the crystal.

The spectra of two samples are given in Fig. 2 which were mineralogically defined as sphene (titanite), but one of them differed from the other in that it was of yellow colour due to impurities. It is seen on the figure that the spectra of these two varieties differ greatly.

The Raman study of refractories is also based on obtaining standard spectra of separate mineral components available in refractory materials. On this basis the identification of any phase in the refractory at any stage of its reception is carried out. At the same time in the practice of obtaining the refractories the cases are observed when depen-
depending on the conditions the crystals of different spatial groups are formed indistinguishable by diffraction data, i.e. the Raman spectroscopy has a definite advantage over traditional methods.

Fig. 2. Raman spectra of the two varieties of titanite.

All this is realized in the development of a new, objective and indestructive method of the analysis of refractories, that allows to study the phase composition of zones with dimensions up to 1 m in a short time (about 0.5 hr) whenever standard spectra are available.
REFERENCES


