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INFLUENCE OF THE ELEMENTAL COMPOSITION AND CRYSTAL STRUCTURE ON THE VACUUM PROPERTIES OF Ti-Zr-V NON-EVAPORABLE GETTER FILMS

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Abstract

Non-evaporable thin film getters based on the elements of the 4th and 5th columns of the periodic table have been deposited by sputtering. Among the about 20 alloys studied to date, the lowest activation temperature (about 180 °C for a 24-hour heating) has been found for the Ti-Zr-V system in a well-defined composition range. The characterization of the activation behavior of such Ti-Zr-V films is presented. The evolution of the surface chemical composition during activation is monitored by Auger Electron Spectroscopy (AES) and the functional properties are evaluated by pumping speed measurements. The pumping speed characteristics are quite similar to those already measured for commercially available NEG materials, except for the much lower saturation coverage for CO. This inconvenience, which is due to the smooth surface structure of these films, can be counteracted by increasing the roughness of the substrate.

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1. INTRODUCTION

Providing the vacuum level required for particle accelerators/storage rings is made difficult by the small vacuum chamber conductance and by the degassing induced by surface bombardment. An effective solution to this problem can be obtained by coating the whole inner wall of the vacuum pipe with non evaporable getter (NEG) films. After "in situ" activation by baking, these films provide a large pumping speed and also a much lower dynamic and static degassing when compared to traditional structural materials.[1,2] Several getter coatings composed of elements of the 4th and 5th columns of the periodic table have been produced and tested. The lowest activation temperature, 180 °C for a 24-hour heating, has been obtained for a TiZrV alloy,[3,4] sputter deposited from a cathode made of intertwisted wires of the constituent elements. To check if other compositions can provide a lower activation temperature, a dedicated sputtering system was developed and samples of different concentrations of these three elements have been deposited.[5] The region of composition in the ternary phase diagram, which corresponds to the lowest activation temperature, was identified by monitoring the surface composition by Auger Electron Spectroscopy (AES) during the activation process.[5] Analysis by X-ray diffraction (XRD) revealed that all the samples in that region present a grain size below the detection limit of the instrument (5 nm).[5] In the present contribution the functional properties of such NEG films on copper substrates are investigated by pumping speed measurements, while the surface composition and the crystal structure are studied by AES and XRD, respectively.

2. SAMPLE PREPARATION AND DEPOSITION

A three-cathode DC magnetron sputtering system, in which the 50 mm diameter V, Ti, and Zr targets are individually powered, is adopted to produce most of the samples. A bake-out of the system at about 150 °C for 12 hours allows a base pressure in the order of 10^{-9} Torr to be attained before deposition. The typical Ar discharge pressure is $5 \cdot 10^{-3}$ Torr. The power applied to the targets ranges from 20 W to 200 W. The deposition rate is typically 0.1 nm s^{-1} and the maximum temperature of the samples during deposition is below 100 °C. The thickness of the deposited film is between 1 μm and 2 μm.

In order to test the reproducibility of the pumping speed measurements, identical samples are needed. To approach at best this situation, three samples are produced in the same coating process making use of a sputtering system with an intertwisted wire cathode as described in reference 1.

Two substrate geometries are used. The first, for AES analysis, consists of 316LN stainless steel and OFE copper platelets (14 mm x 10 mm), the second, for pumping speed measurements, consists of 120 mm diameter OFE copper disks. Prior to coating, the stainless steel samples are simply cleaned in a detergent aqueous solution, while the copper disks are chemically polished.[6] Rotation of the copper disks during deposition is necessary in the three independent cathodes sputtering system to obtain a concentration variation lower than 3% over the whole layer. The samples are dry-air vented after deposition and then mounted in the measuring systems or stored under vacuum. For each coating run, a sample is analyzed by Energy Dispersive X-ray spectroscopy (EDX) in order to obtain its chemical composition.

3. SAMPLE CHARACTERIZATION

3.1 Analysis by Auger Electron Spectroscopy (AES) and X-Ray diffraction (XRD)

The details of the experimental set-up are described in reference 5. Spectra are acquired in the direct EN(E) mode (figure 1a). All direct EN(E) spectra are normalised prior to peak

intensity measurements in order to eliminate the influence of instrumental parameters such as fluctuations in beam current and detector efficiency. For the present study all EN(E) spectra are normalized to the same background intensity value at 600 eV kinetic energy. O-KLL peak areas are calculated from the direct spectra by subtracting, as a crude approximation, a linear background between 499 eV and 518 eV. In a similar way C-KLL peak areas are calculated by setting a linear background between 200 eV and 285 eV. Since the peak-to-peak height in the derivative spectra is strongly affected by line-shape changes related to graphite to carbide transformation, the measurement of peak areas of C-KLL is mandatory in order to draw conclusions about the amount of C on the surface of NEG materials.[7]

Numerically differentiated dEN(E)/dE spectra (figure 1b) were used to follow the changes in the Zr MNV line-shape, which indicates the degree of activation of the TiZrV surface. The peak at 147 eV (named Zr metal in figure 1b) grows when the surface oxide is more and more reduced, whereas the component at 141 eV, characteristic for Zr in ZrO_2,[8] decreases. The ratio between these components has been used previously[5] to qualify the activation temperature of TiZrV films of different composition. A similar splitting between metal and oxide Auger peak occurs for Ti-LMV,[9] but because of the high kinetic energy of the Ti-LMV electrons the two peaks cannot be resolved with the energy analyzer used for the present study. Similarly, the energy shift between metal and oxide LMV transition of V is narrower than the resolution of the analyzer at the corresponding kinetic energy.[10]

Sample heating in the vacuum system of the Auger electron spectrometer is achieved by radiation from a hot filament.[5] The sample can be clamped to the heated OFE copper plate by means of a copper frame, which partly covers the sample surface. The frame is tightly fixed to the sample plate by four screws so as to provide good thermal contact between sample and sample plate. The sample temperature is measured by two thermocouples with an accuracy of ± 3 °C.

The vacuum chamber of the Auger electron spectrometer is unbaked not to change the initial sample conditions and the total base pressure before the surface treatments is 10^{-9} Torr (N_2 equivalent), H_2 being the dominant gas followed by water vapor (about $2 \cdot 10^{-10}$ Torr). During sample heating the total pressure in the experimental vacuum chamber increases to about $4 \cdot 10^{-8}$ Torr at 350 °C, again with H_2 as the main gas followed by H_2O ($\sim 4 \cdot 10^{-9}$ Torr) and CH_4 ($\sim 4 \cdot 10^{-9}$ Torr). The partial pressures of CO and CO_2 during sample heating at 350 °C are in the order of 10^{-9} Torr. Baking the UHV system would not significantly reduce the sample contamination, since most of the outgassing during thermal treatment is generated by the sample heater.

The surface of the NEG alloys are first analyzed in the as-received state (after deposition and an air exposure lasting about 1 hour) and then after "in situ" heating for 1 hour at a given temperature. The rate of temperature increase is in the order of 10 degrees per minute. The heating temperatures are 120 °C, 160 °C, 200 °C, 250 °C, 300 °C and 350 °C.

The crystal structure and the size of the crystallites are investigated by XRD as described in reference 5.

3.2 Pumping speed measurements

Pumping speed measurements are performed by means of a standard Fisher-Mommsen dome[11] pumped by a turbo-molecular pumping station which provides an effective pumping speed in the dome of about $10 \, l \, s^{-1}$ for H_2.

The coated copper disk is clamped between the Conflat flanges of the measuring dome pump opening. It can be heated up to 400 °C by means of an external heater or water cooled; its temperature is measured by means of a thermocouple, pressed between the steel flange and the disk.

After pump-down, the measuring system is baked at 250 °C for about 20 hours, while the copper disk is maintained at a temperature lower than 80 °C by water cooling to avoid NEG activation and, hence, unduly pumping of the gases released during the bakeout. Then, just before the end of the bakeout, the sample is heated at 120 °C for 2 hours while the heating of the rest of the system is gradually decreased. The base pressure obtained after cooling at room temperature is in the 10^{-10} Torr range.

Pressure measurements are performed by means of two Bayard-Alpert gauges. They are "in situ" calibrated by comparing their readings to that of a previously calibrated gauge.

In a standard measuring cycle, the samples are heated for 2 hours at a given temperature and the pumping speeds for individual gases and gas mixtures are measured after cooling down the sample to room temperature. The investigated temperature range spans from 120 °C to 325 °C in steps of 25 °C or 30 °C without intermediate air venting. During pumping speed measurement, the pressure on the injection side of the dome is usually in the 10^{-8} Torr range, but it may be up to two orders of magnitude higher when large gas quantities must be injected to achieve surface saturation. To avoid accumulation of CH_4 and rare gases, which are not pumped by the NEG, during gas injection the system is pumped with the turbomolecular pump.

The surface capacity and the influence of the surface load of given gas on the pumping speed of another one are measured by pumping known quantities of a base gas and injecting small quantities of a sample gas. This procedure is described in more detail in a previous paper.[12]

4. EXPERIMENTAL RESULTS

4.1 AES and XRD results

The AES results for a heating cycle of a 1.2 μm thick film on copper are presented in figure 1. The in-depth composition of this sample is Ti32Zr16V52 (at %) as determined by EDX. This composition lies in the low activation temperature region of the TiZrV alloy composition.[5]

By heating at increasingly higher temperatures the oxygen line (O-KLL at 512 eV in figure 1a) decreases continuously indicating that the surface oxide is progressively reduced. Changes in line-shapes are distinguished at best in the derivative spectra of figure 1b. The Zr line-shape (Zr-MNV at 141 eV-147 eV) is modified during the thermal treatment and the component at 147 eV is already visible at 160 °C. Its continuous increase indicates the evolution from the oxidized to the metallic surface.[8]

After heating at 200 °C the carbon line (C-KLL at 272 eV) changes its shape (figure 1a), as a result of the modification of the chemical state of carbon from graphite or adsorbed hydrocarbons to carbide.[13] The evolution of the intensity (peak-area) of C-KLL is presented in figure 2. The intensity already increases after heating at 120 ºC for 1h with respect to the value for the as-received sample and starts to decrease above 250 ºC only. The behavior is similar for all TiZrV coatings that exhibit activation at relatively low temperature, independently of the copper or stainless steel substrate material. Moreover, the behavior does not depend on the amount of carbon initially present on the as-received surface.

Finally, the Cl intensity (Cl-LMM at 181 eV) increases continuously upon heating. This increase has been generally observed upon heating of NEG thin films both on copper and stainless steel substrates.[5]

The activation process of several TiZrV thin films on copper has been analyzed by AES and their behavior is identical to that observed on stainless steel substrate. The results are summarized on figure 3a.

The X-ray diffraction patterns are the same for the films deposited on copper and on stainless steel substrates as shown in figure 3b.

4.2 Pumping speed results

The results of the preliminary measurements reported here concern only the composition Ti32Zr16V52 at %, (figure 3) obtained by using a cathode made of intertwisted 1 mm wires.

The spread of pumping speed of three identical samples for CO and H_2 as a function of the heating temperature is shown in figures 4a and 4b. The onset of the CO pumping speed is between 150 °C and 180 °C and a large increase is observed between 180 °C and 200 °C up to a value corresponding to a sticking probability of about 0.5. Then the CO pumping speed remains nearly constant up to 300 °C and finally it keeps increasing again above 325 °C. The highest values of the sticking probability are close to 0.75.

Measurable sticking probability for H_2 are always obtained after a 2 hours heating at a temperature between 180 °C and 200 °C. This is in agreement with data obtained with long coated chambers[3] when considering the different heating time. The maximum of the pumping speed for H_2 is obtained between 230 °C and 250 °C and it corresponds to a value of the sticking probability close to $1 \cdot 10^{-2}$. For higher heating temperatures, up to 300 °C, the pumping speed decreases to about a half of the attained maximum value, and then it increases again above 325 °C.

It is of great practical importance to assess how the surface load of a gas influences the NEG film pumping speed for other gases. Figure 5a shows the results obtained (for the case of CO as base gas, and H_2 and N_2 as sample gases) after sample heating at 325 °C; results obtained at lower heating temperature have similar behavior. In the same way, figure 5b shows the results obtained for N_2 as base gas, and CO and H_2 as sample gases.

The results obtained as a function of the CO load clearly indicate that this gas strongly reduces the pumping speed of the other gases as already observed for St101 and St707 getter strips.[12,14] The loading of only $1 \cdot 10^{14}$ molecules cm^{-2} is enough to reduce the pumping speed of H_2 and N_2 by a factor of two, while that of CO is only slightly reduced. N_2 blocks only partially the pumping of H_2 and does not affect the CO pumping at all; here again the behavior is identical to that reported for St101 and St707 getter strips. Since H_2 does not remain on the getter surface, but diffuses in the film even at room temperature, its pumping does not affect the pumping of other gases.

The maximum values of the sticking probabilities for CO are quite similar to those obtained for commercial NEG strips,[14, 15] whereas the CO saturation coverage is about a factor 50 lower. As reported in a previous paper[4] this feature is due to a very smooth surface structure. A higher saturation value can be obtained by increasing the roughness of the substrate prior to coating. Figure 6 shows that by a non-optimised chemical etching of the Cu disk before deposition, the saturation coverage can be increased by about a factor four. A quantitative evaluation of the roughness, obtained by laser dynamic focussing over a distance of 1.75mm, indicates that the average roughness Ra and maximum roughness Rt are 0.08 μm and 0.59 μm respectively for the film deposited on the smooth substrate and to 0.35 μm and 2.64 μm for that deposited on the chemically etched one.

5. DISCUSSION AND CONCLUSIONS

The comparison with previous results[5] obtained from TiZrV films on stainless steel, indicates that the activation behavior is the same for these different substrates.

X-ray diffraction analysis of the coatings on stainless steel and copper as a function of NEG in-depth composition demonstrates that all the samples exhibiting activation at low temperature do not present signs of crystalline structure at 5 nm resolution (figure 3b).

The evolution of the C-KLL intensity during thermal treatment is not well understood yet. Its increase might be an artefact due to contamination by residual gas or by outgassing from components of the sample-holder during the heating cycle. Investigations using different configurations for the sample mounting are in progress to clarify this point.

As far as chlorine is concerned, this element is known to be present as impurity in many transition metals (0.5 ppm weight in the Ti target used for the NEG deposition, as revealed by Glow Discharge Mass Spectroscopy) and to be prone to surface segregation. The source of Cl might also be the substrate, since the presence of Cl has been detected by AES on the surfaces of the as-received copper and stainless steel substrates.

The onset and the strong increase of the pumping speed for both H_2 and CO between 150 °C and 250 °C is clearly related to the decrease of the surface O content detected by AES. In the same way the additional increase of the pumping speed at the highest heating temperatures (above 325 °C) could be related to the depletion of the surface carbon content as shown in figure 3.

Unfortunately the information extracted from the AES spectra alone does not justify the decrease of the H_2 pumping speed between 250 °C and 300 °C. This pumping speed reduction was not recorded for any other NEG film with higher activation temperature.[14] A similar behavior had been observed for the St707 commercially available NEG strip[14] at about 500 °C. In this case, the loss of pumping speed was imputed to annealing effects leading to a reduction of surface and bulk defects, and so to a decrease of the surface reactivity and of the apparent diffusion coefficient.[16] In the present case, however, X-ray diffraction analysis has not shown any structural change on small samples heated in vacuum up to 350 °C, therefore indicating that if any annealing or structural change occurs it should be limited to a nanometric scale which is out of the reach of the used instruments. Because of the relatively small gas surface capacity of these coatings the effect of contamination due to the system outgassing during the heating cycles cannot be excluded.

Studies are in progress in order to prove or falsify these two possibilities. Structural analysis at higher resolution will be performed by using Electron Transmission Microscopy, while the possible effect of surface contamination due to system outgassing will be reduced by increasing the area of the getter film sample used for pumping speed measurements by mechanical machining or chemical etching the sample substrates prior to coating.

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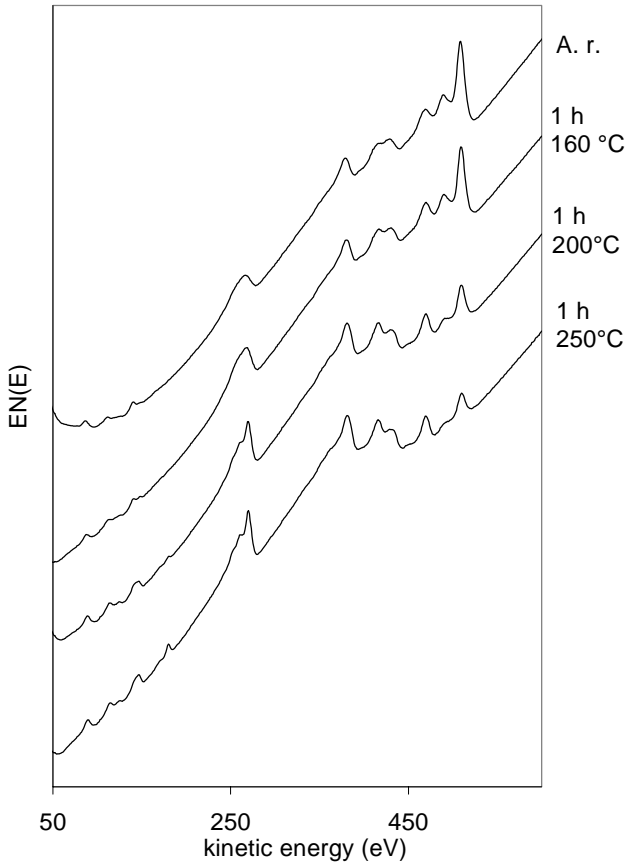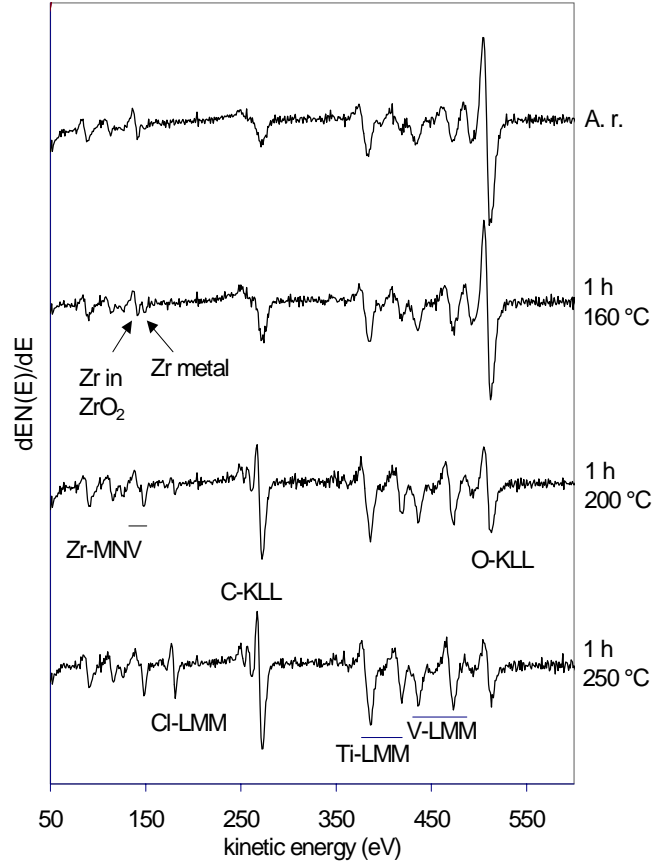
Figure 1: Direct EN(E) (Figure 1a) and derivative dEN(E)/dE (Figure 1b) Auger electron spectra of a Ti32Zr16V52 (at. %) film on copper substrate, as-received (A. r.) and after heating for 1hour at various temperatures.
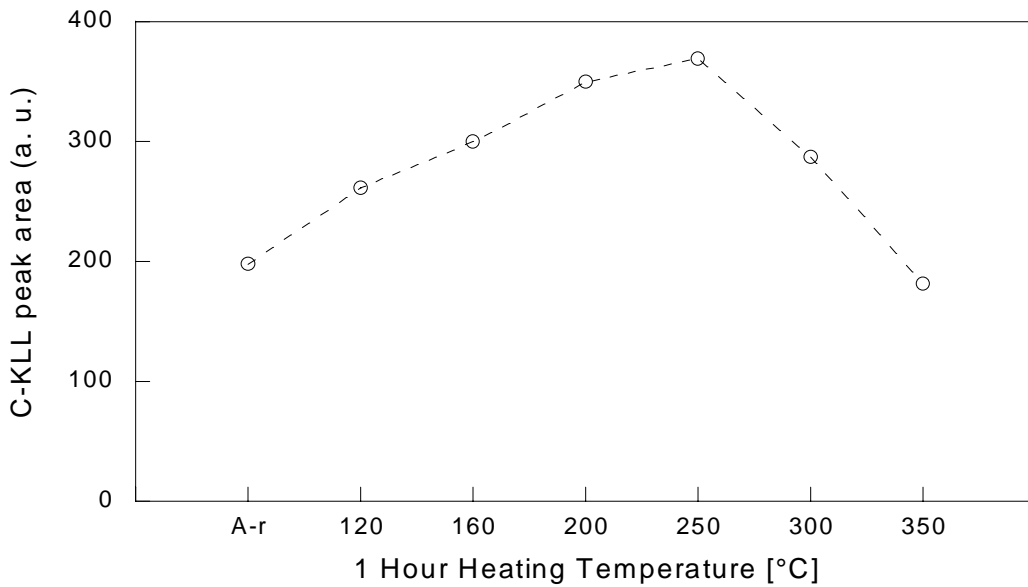

Figure 2: C-KLL peak-area variation of a Ti32Zr16V52 (at. %) film as a function of the heating temperature.
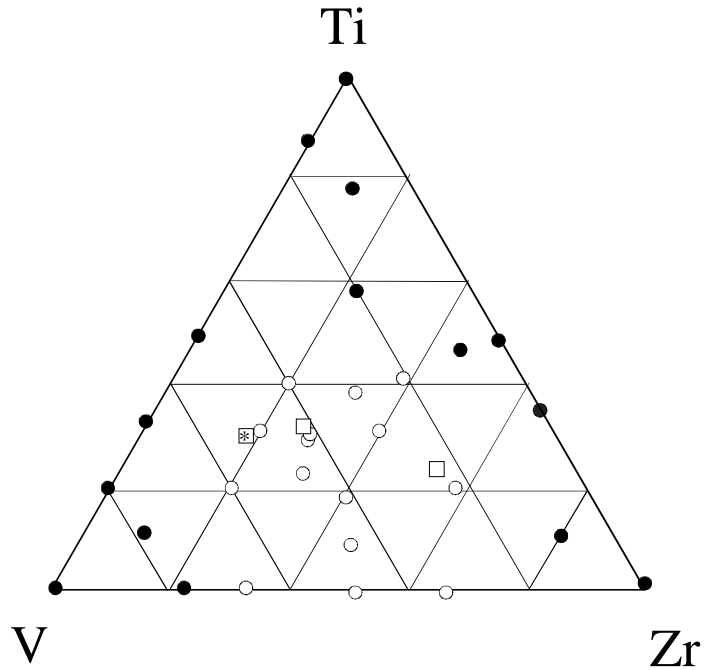
Figure 3a: Quality composition map of Ti-Zr-V films based on the value of the ratio of Zr metallic to Zr oxide peak-to-peak height. The samples with the ratio above 0.5 after 200 °C heating for 1 hour are indicated with empty symbols, the others with black ones. The circles correspond to stainless steel substrates and the squares to copper. The star indicates the composition Ti32Zr16V52 (at. %) adopted for pumping speed measurements.
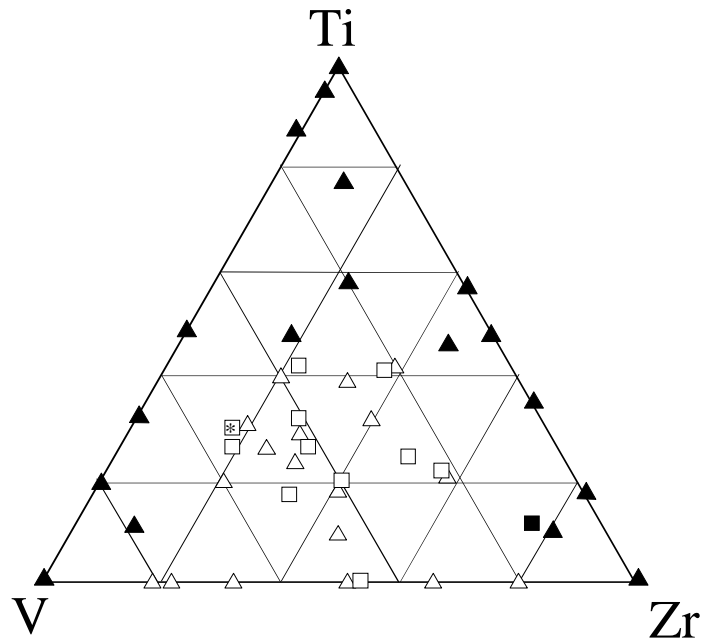
Figure 3b: Structure composition map of TiZrV films based on the crystal grain size. The black symbols represent the samples with grains larger than 100 nm, and the empty ones represent samples with a grain size below 5 nm. The triangles correspond to stainless steel substrates and the squares to copper. The star indicates the composition Ti32Zr16V52 (at. %) adopted for pumping speed measurement.
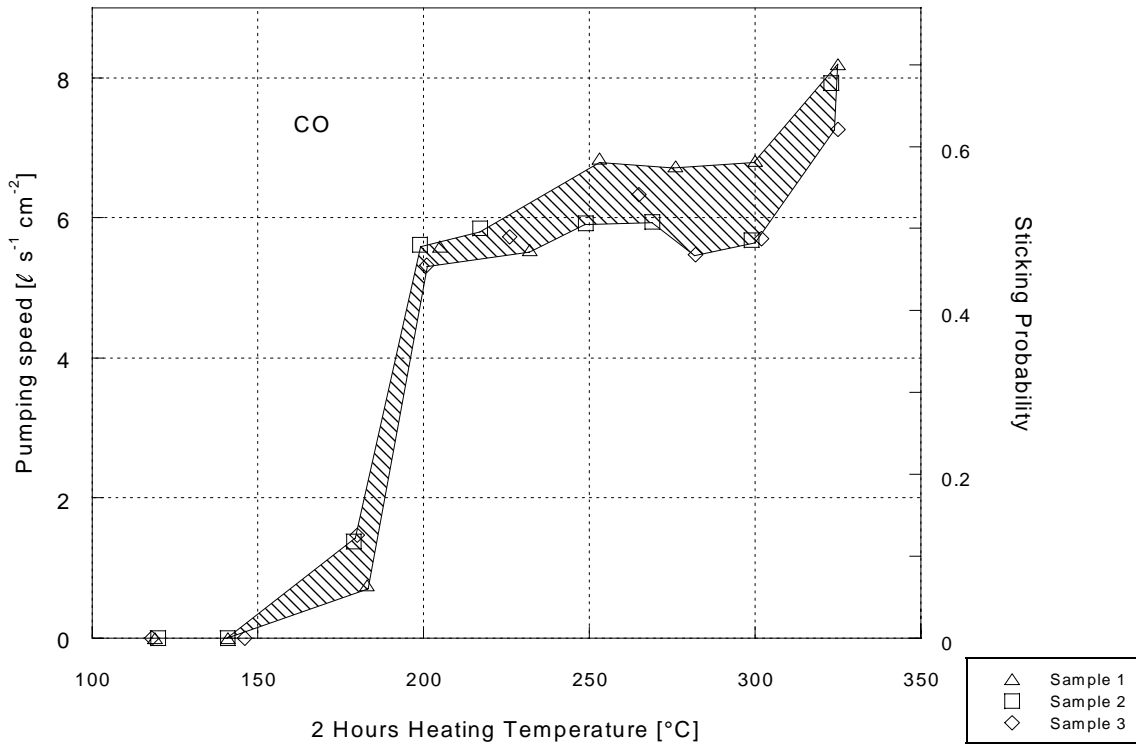
Figure 4a: Pumping speed of CO as a function of the heating temperature for samples of composition Ti32Zr16V52 (at. %). Three samples produced during the same coating process have been measured in order to test the reliability of the pumping speed measuring apparatus.
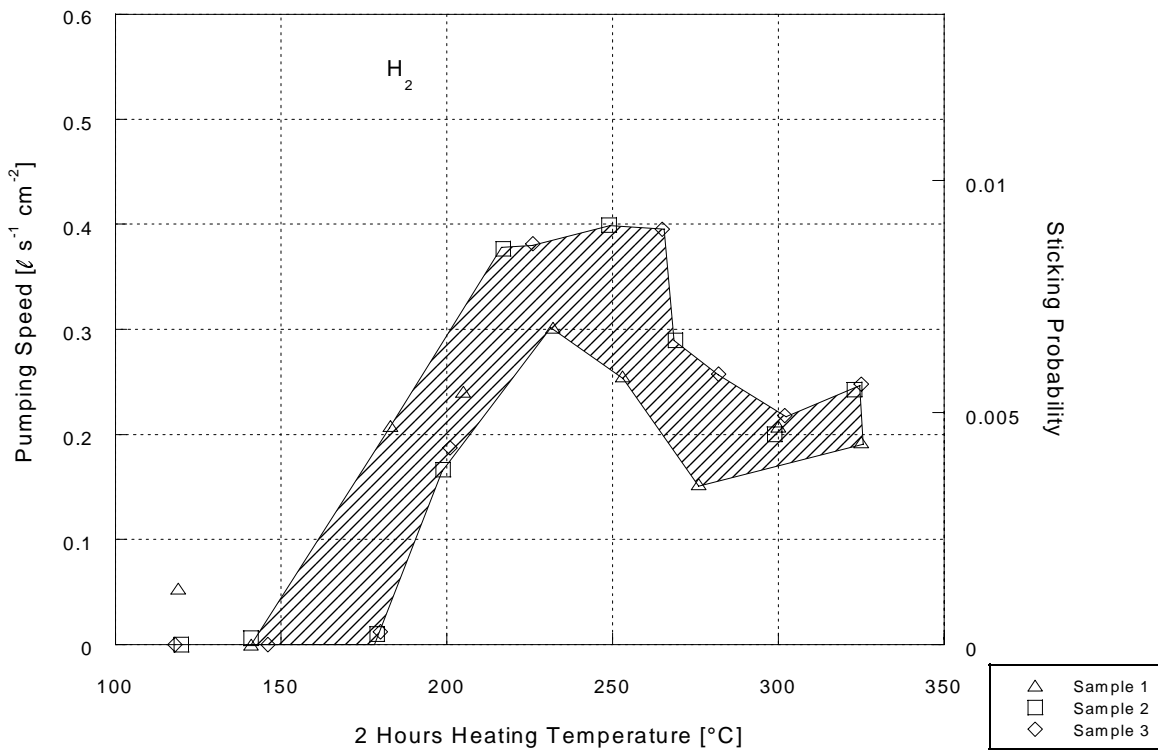

Figure 4b: Pumping speed of H_2 as a function of the heating temperature for the same samples of figure 4a.
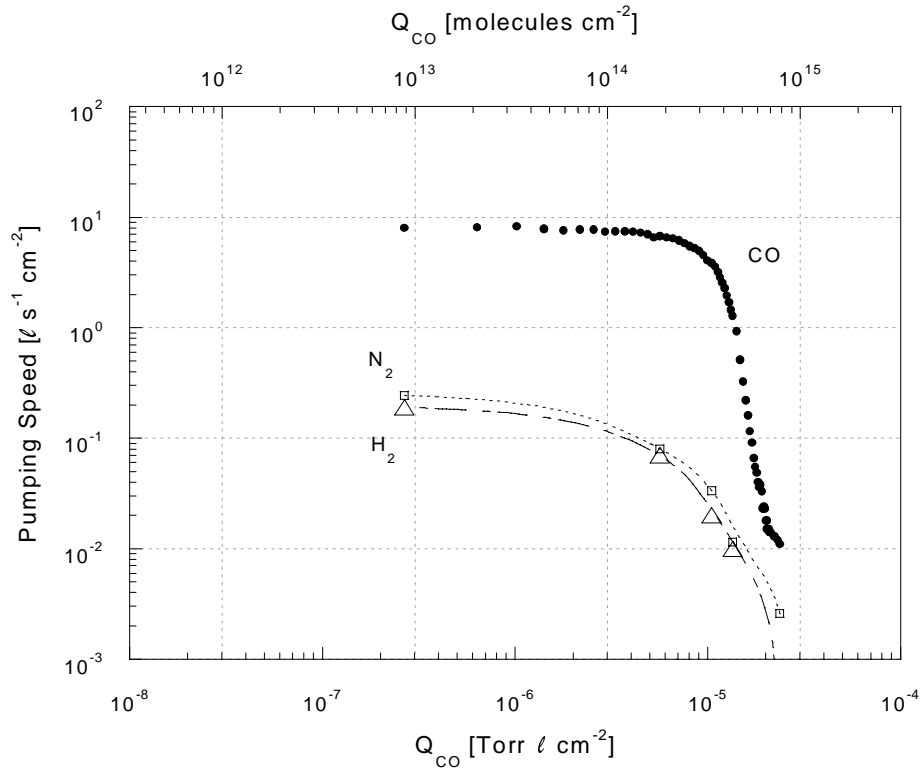
Figure 5a: Pumping speeds measured for a Ti32Zr16V52 (at. %) sample with CO as base gas and H_2, N_2 as sample gas after sample heating at 325 °C for 2 hours.
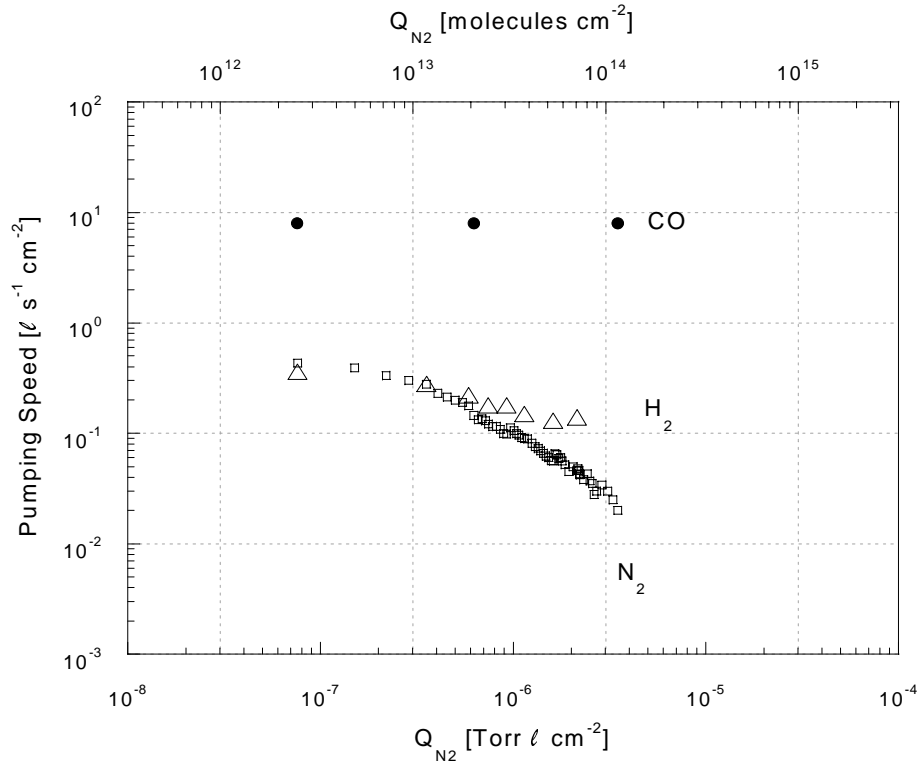

Figure 5b: Pumping speeds measured for a Ti32Zr16V52 (at. %) sample with N_2 as base gas and H_2, CO as sample gas after sample heating at 350 °C for 2 hours.
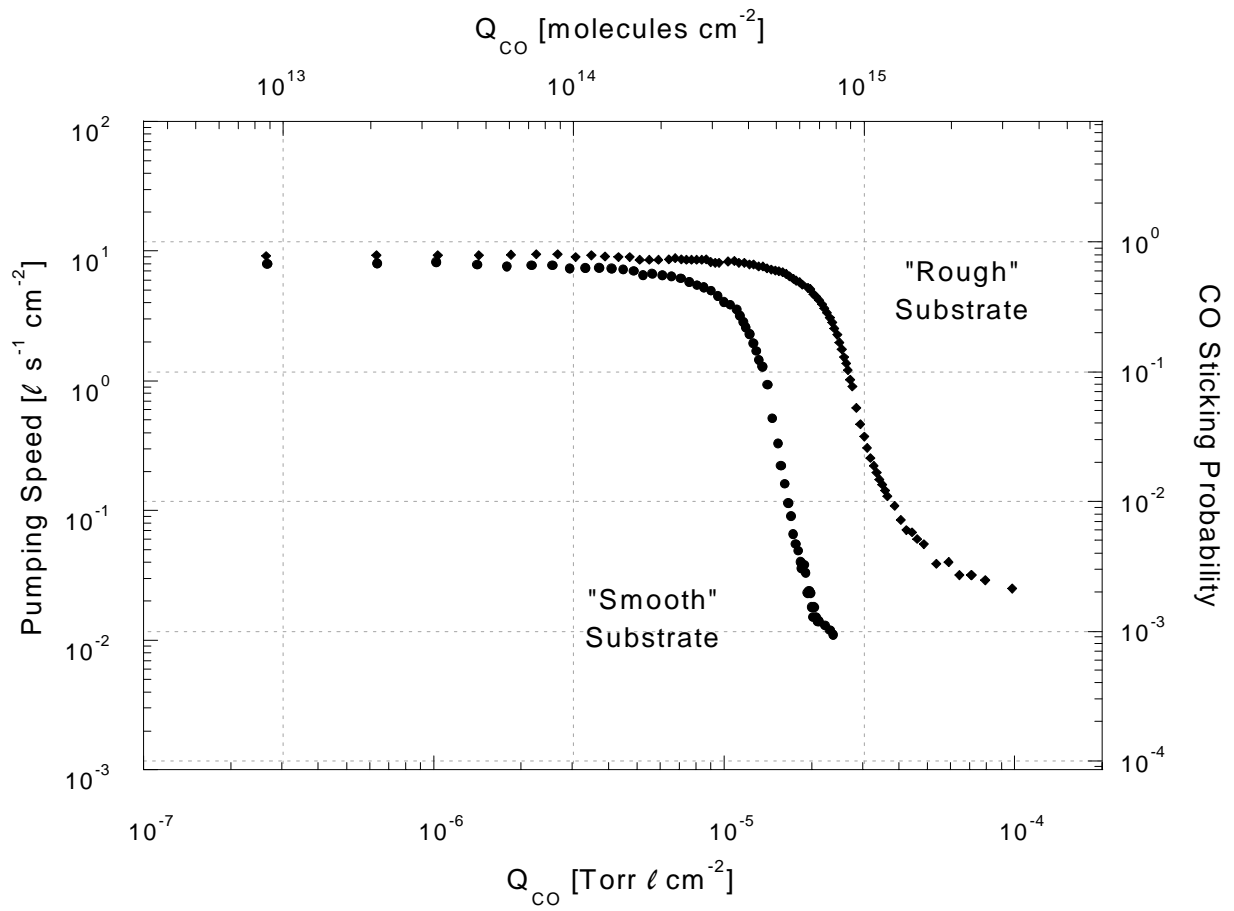
Figure 6: Pumping capacity for CO of a smooth and a rough Ti32Zr16V52 (at. %) sample after heating at 325 °C for 2 h