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ATOMIC FORCE MICROSCOPY STUDY ON THE EFFECT OF LOW-PRESSURE HYDROGEN PLASMA CLEANING ON STAINLESS STEEL WEIGHTS

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Abstract: Despite the new definition of the Kilogram, physical weights prone to contamination will still be used in the dissemination of the unit. Cleaning is applied to bring the weight surface to a well-defined state to allow predictable adsorption behaviour. Currently used mechanical cleaning methods show poor reproducibility. Therefore, non-contact cleaning techniques such as plasma cleaning have been introduced. In this study, the applicability of low-pressure hydrogen plasma for cleaning stainless steel weights was studied using atomic force microscopy (AFM) and gravimetric weighing. Results show that hydrogen plasma effectively removes surface contamination without damaging the surface. Successive ultrasonic cleaning in ethanol did not considerably reduce surface contamination.

Keywords: AFM, hydrogen plasma cleaning, stainless steel weight, surface contamination

1. INTRODUCTION

The upcoming new definition of the Kilogram will be based on invariant natural constants instead of a physical artefact prone to contamination. However, physical weights will still be used for maintaining the mass unit between realizations and for disseminating the unit to other weights. The realizations will take place in vacuum implying that weights must be transferred between ambient and vacuum. The instability of weights in long term and the effect of vacuum to ambient transition in short term are governed by sorption effects on the weight surfaces. The adsorption of gas molecules and particles on the weight surface depends on the chemical state and the morphology of the outermost surface layer. Thus, a well-defined clean surface is desirable for achieving consistent and predictable adsorption behaviour.

Mass standards are cleaned upon manufacturing and often before periodic calibrations in order to restore the initial surface state. Currently used “mechanical” cleaning techniques, such as the nettoyage-lavage and solvent cleaning, have shown poor reproducibility or effectiveness [1, 2]. These methods are highly dependent on the skills of the operator and the purity of the solvents as well as the cleanliness of the glassware. Therefore, novel “noncontact” cleaning techniques, such as low-pressure hydrogen plasma and UV/ozone cleaning, have been introduced [2, 3].

In this paper, low-pressure hydrogen plasma is applied for cleaning stainless steel weights. Disc weights with naturally accreted contamination were used in the study. The effect of hydrogen plasma on the surface morphology was investigated by means of atomic force microscopy (AFM) and gravimetric weighing. Results show that hydrogen plasma is very effective in removing even thick contamination layers without altering the surface morphology. Successive ultrasonic cleaning in ethanol did not considerable reduce surface contamination.

2. MATERIALS AND METHODS

2.1 Sample weights: Class E_2 stainless steel sample discs (Häfner Gewichte GmbH) were used for the cleaning studies. The weights were manufactured in 1986 and have been used since as mass standards in the mass laboratory of MIKES. Therefore, naturally accreted surface contamination typical for weights used in mass metrology was expected. The weights were 38 mm in diameter and had a nominal mass of 100 g.

2.2 Cleaning: A commercial low-pressure plasma cleaner (Gatan Solarus Model 950) was used for hydrogen plasma cleaning experiments. The operating parameters were: 20 $cm^3 \cdot min^{-1}$ hydrogen flow, 93 Pa base pressure and 50 W RF power. These parameters were found to effectively remove surface contaminants without damaging or removing the bulk of the sample. After successive plasma cleaning trials the sample weight was further cleaned ultrasonically in ethanol. The idea was to find out if there remained surface contamination that could be removed using ethanol. The cleaning procedure was as follows: First, the sample weight was placed on a filter paper inside a clean beaker filled with ethanol. After that, the beaker was placed in an ultrasonic bath for 10 min at room temperature. Finally, the weight was rinsed with distilled water and dried by removing remaining water drops with a lint free cloth.

The same sample weight was cleaned using hydrogen plasma cleaning for 2 min, 8 min and 10 min at a time. After hydrogen plasma cleaning the sample weight was further cleaned ultrasonically in ethanol.

2.3 AFM studies: A commercial AFM (Park systems XE-100) was used for studying changes in the surface morphology upon cleaning. The AFM was operated in noncontact mode. Special silicon probes with wear resistant platinum silicide coating (Nanosensors PtSi-NCH) were used in order to minimize tip blunting. This is important as changes in the tip radius will affect the recorded surface topography and thus making it difficult to observe and interpret changes in surface morphology. The typical tip radius was less than 25 nm and the nominal resonance frequency and spring constant were 330 kHz and 42 N·min^{-1}, respectively.

Topography images of the sample surface were recorded before and after each cleaning experiment in order to evaluate changes in surface contamination. Exactly the same area was found using the AFM's integrated optical microscope. Image resolution was set to 256 x 256 pixels and scan size of 5 µm x 5 µm was used. The imaged surface area was chosen to include grooves, because earlier studies have shown that grooves and pits are preferential sites for contamination [4].

2.4 Image processing: Changes in surface topography due to cleaning were analysed using an image processing method developed for this purpose [4]. Using this method even small nanometre scale changes are clearly visualized. The idea is to subtract topography images before and after cleaning from one another. In order to do so, the images must represent exactly the same surface area and they must be flattened with respect to the same reference plane. For doing this, an iterative step-by-step procedure is performed (figure 1): Step 1: Initial line-by-line flattening is performed for both images. Step 2: The area of interest is cropped from the image and the exact same area is found from the other image by correlation. Step 3: A second line-by-line flattening is performed for the cropped images. Step 4: The images are subtracted from one another. Step 5: Line-by-line flattening is repeated using only topography data points with similar z-values in both images, i.e. reference plane pixels. Steps 4 and 5 are repeated iteratively a few times, so that the z-values included in the next iteration are even closer to each other. After the images have been flattened with respect to the same reference plane, the final image is obtained by subtracting the images from one another. Using this image processing method, changes in surface topography can be clearly seen. A more detailed description of the image processing method is given in [4]. Image processing was performed using MATLAB.

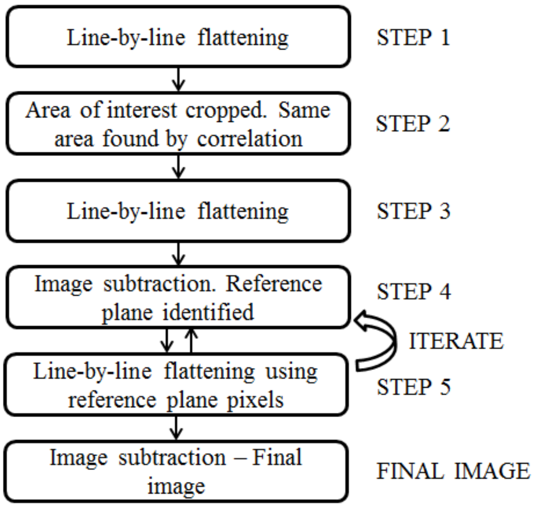

Figure 1. Scheme of the image processing method.

2.5 Gravimetric weighing: Besides using AFM for studying effects of cleaning, also gravimetric weighing before and after each cleaning experiment was performed. Before any cleaning procedure the stability of the sample weight was monitored against a "dummy" weight from the same batch. The "dummy" weight acted as the reference for evaluating the mass changes due to cleaning. Gravimetric weighing was performed using a Mettler Toledo AX1006 mass comparator. The results are given with a resolution of 0.1 µg.

3. RESULTS

The surface morphology of the stainless steel sample disc before any cleaning is shown in figure 2. Parallel grooves seen in the topography images are typical for polished stainless steel weights. These grooves are about 100 nm deep for the sample weight under study. The protuberances seen in the images are identified as surface contamination.

The effects of hydrogen plasma cleaning are clearly seen when comparing the surface topography before (figure 2) and after three cleaning trials (figure 3). A total cleaning time of 20 min (2 min + 8 min + 10 min) using low-pressure hydrogen plasma effectively reduces the amount of surface contamination (protruding surface structures) without altering the bulk surface structure. No considerable reduction in surface contamination was observed after subsequent ethanol cleaning, but instead, additional contamination was observed (figure 4).

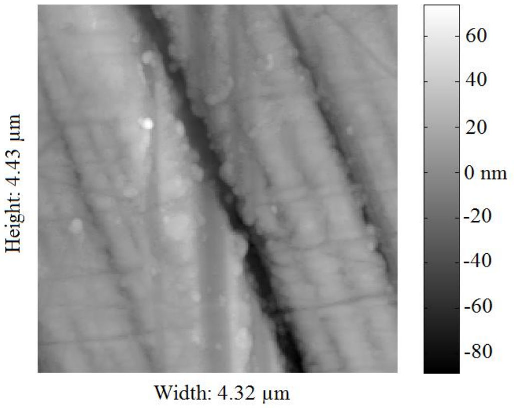

Figure 2. Topography image of stainless steel surface before hydrogen plasma cleaning.

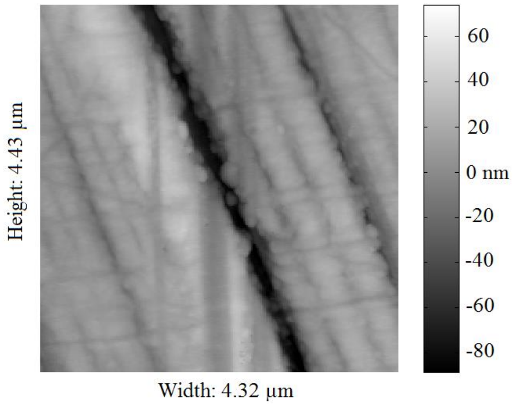

Figure 3. Topography image of stainless steel surface after hydrogen plasma cleaning for 20 min.

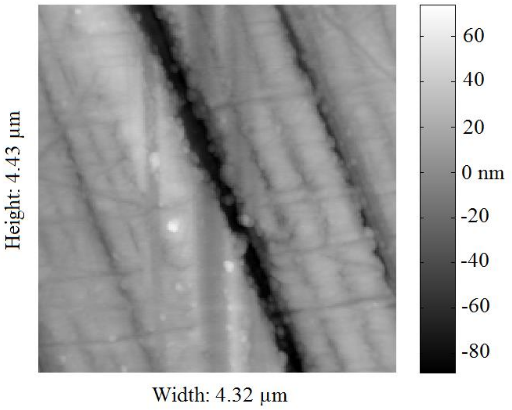

Figure 4. Topography image of stainless steel surface after hydrogen plasma cleaning followed by ultrasonic cleaning in ethanol.

In order to observe nanometre scale changes in the surface morphology, images before and after each cleaning trial were subtracted from each other using the developed image processing method. Dark shaded areas in these images (figures 5 to 8) represent sites were contamination was lost and light areas sites that gained contamination due to cleaning.

Most of the surface contamination was removed during the initial 2 min hydrogen plasma cleaning (figure 5). The initial plasma cleaning removed some of the protuberances, but the majority of the removed contamination was located in the grooves. This is hardly seen from the topography images (figures 2 and 3) as the gray scale covers the whole height range of the image making it hard to detect small changes. A second cleaning trial of 8 min reduces further protuberances as well as contamination located in the grooves (figure 6). However, the changes in surface contamination are less for the second cleaning trial. A third cleaning trial of 10 min had only a small effect on the surface contamination (figure 7). Mainly some contamination located in the grooves was removed. Comparison with subtracted images of consecutive AFM scans (not shown) confirms that the observed changes were caused by cleaning and not by an artefact of the experimental method.

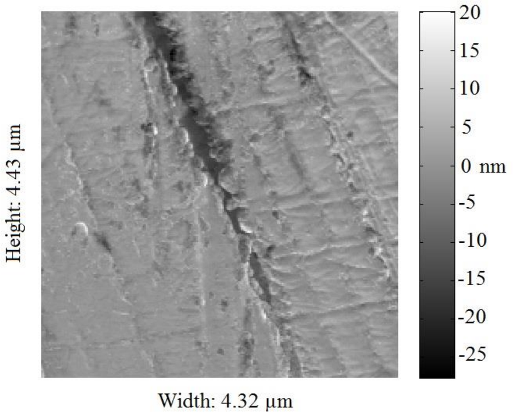

Figure 5. Changes in surface topography after 2 min of hydrogen plasma cleaning.

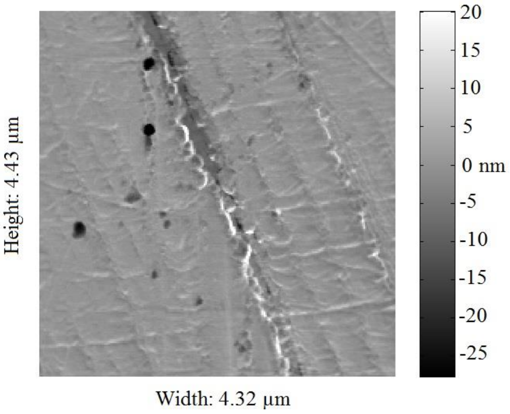

Figure 6. Changes in surface topography after further 8 min of hydrogen plasma cleaning.

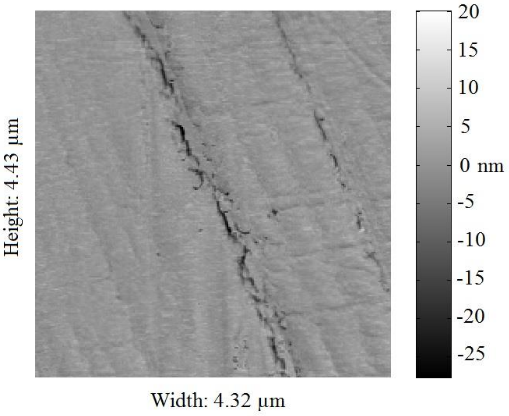

Figure 7. Changes in surface topography after further 10 min of hydrogen plasma cleaning.

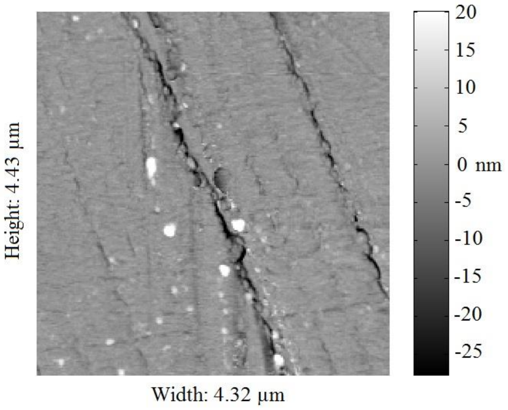

Figure 8. Changes in surface topography after additional ultrasonic cleaning in ethanol.

After hydrogen plasma cleaning the sample was ultrasonically in cleaned in ethanol for 10 min. Ethanol cleaning removed further contamination from the grooves similarly to the last hydrogen plasma cleaning trial (figure 8). However, additional contamination protuberances were observed after ethanol cleaning.

The effect of cleaning was also studied by weighing. From the weighing results (figure 9) it can be seen that the mass reduced by 3 µg upon the initial 2 min hydrogen plasma cleaning. Further cleaning didn't have a measurable effect on the mass of the weight. Ethanol cleaning resulted in an increase of mass of several micrograms (not shown here). Increase of surface contamination was also seen from the AFM image (figure 8). Impurities in the solvent, distilled water or glassware are possible sources of contamination.

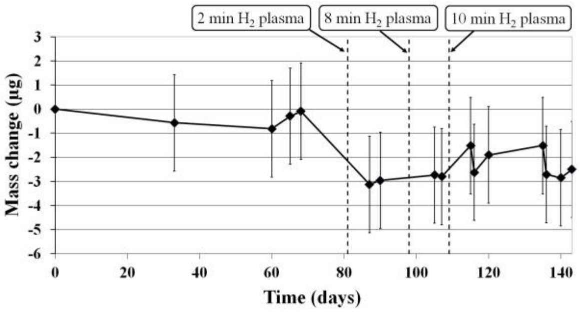

Figure 9. Changes in mass difference between sample and reference weight after successive hydrogen plasma cleaning. Uncertainty of weighing (*k*=1) is shown as error bars.

4. DISCUSSION

Most of the removed contamination was found in the grooves of the surface. This indicates that surface defects such as grooves are preferential sites for adsorption. Because of this, the surface area under study was chosen to include grooves.

From the AFM images showing changes in surface contamination upon plasma cleaning (figures 5 to 7), it can be seen that the removal of contamination is less for each successive cleaning experiment. This indicates that the cleaning effect reaches saturation. Also, it can be seen that no abrasion of the bulk surface occurs. These properties of the cleaning process are vital for achieving repeatable cleaning results and a clean well defined surface.

Further cleaning in ethanol removes some contamination from the grooves, but the effect is in the same order of magnitude as the last plasma cleaning trial. Thus, it seems that ultrasonic cleaning with ethanol is not able to remove any contamination that cannot be removed using hydrogen plasma. Ethanol cleaning, as any solvent cleaning, may however add contamination to the surface if there are any impurities in the solvent, distilled water or glassware. This was observed in our experiments both as a mass increase of the weight and as contaminant protuberances on the surface. Solvent cleaning is highly operator depend as opposed to plasma cleaning, which is a noncontact method in which the cleaning process is well controlled and thus operator independent.

Results of weighing support the findings that most of the contamination was removed already during the initial 2 min plasma cleaning trial. AFM images show that excess plasma cleaning further reduces surface contamination especially in the grooves. This was however not observed by weighing. This can be explained by the fact that grooves, although containing relatively more contamination than flat areas, constitute only a small part of the total surface.

Our results are in good agreement with the results of Marti *et. al.* [5] who applied X-ray photoelectron spectroscopy (XPS) for studying changes in surface chemistry of stainless steel weights upon low-pressure hydrogen plasma cleaning. XPS results show that plasma cleaning effectively removes carbonaceous contaminants without oxidizing the surface. They also found similar saturation behaviour of carbon removal. Our AFM studies additionally confirm that plasma cleaning is non-abrasive. This is essential for preserving the initial mass of standard weights upon cleaning.

Before replacing currently used solvent based “mechanical” cleaning methods, gravimetric studies using 1 kg mass standards has to be performed in order to study the repeatability of cleaning in terms of mass and the long term mass stability after cleaning.

5. CONCLUSIONS

The effect of low-pressure hydrogen plasma cleaning on stainless steel weights was studied using AFM and gravimetric weighing. Hydrogen plasma was found to effectively remove naturally accreted contamination without damaging the surface. Most of the contamination was already removed during the first 2 min of cleaning. Successive cleaning removed less contaminants and saturation of the cleaning process was observed after about 20 min. Further ultrasonic cleaning in ethanol did not considerably reduce surface contamination but instead re-contamination occurred, emphasizing the difficulty of achieving repeatable cleaning results with solvent cleaning. Our studies show that low-pressure hydrogen plasma cleaning is an effective, non-abrasive and operator independent cleaning method which seems well suited for cleaning stainless steel mass standards. However, gravimetric studies on mass stability and repeatability of cleaning are necessary.

ACKNOWLEDGEMENTS

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