Surface morphology, surface composition and outgassing behaviour of vacuum fired stainless steel

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Abstract. The surface morphology of stainless steel, after low temperature bakeout and vacuum firing, has been studied by atomic force microscopy (AFM) and scanning tunnelling microscopy (STM). The local elemental composition on the surface before and after thermal treatment has been investigated by atom probe (AP) depth profiling measurements. After vacuum firing a significant change of the surface structure and topology is observed by AFM and STM. AP depth profiling analysis results in a noticeable nickel surface enrichment. Since hydrogen recombination is strongly influenced by surface structure and composition the outgassing behaviour is almost controlled by the surface microstructure.

1. Introduction
Stainless steel (SS) is one of the most commonly used constructional materials for vacuum chambers and components. Specialized applications like accelerator and storage ring facilities or the processing of advanced semiconductor devices make need for extreme high vacuum (XHV). If the XHV is to be achieved a reduction of the outgassing rates of the materials used in the construction of the vacuum system is essential [1]. The question of how to reduce outgassing is a challenge to both, the vacuum physicist and vacuum engineer, who must find a cost effective solution between surface treatment, applied pumping and processing time. Beside surface treatment to reduce the surface roughness high temperature vacuum firing became an alternate method and widely accepted practice of reducing the amount of hydrogen dissolved in SS. There is a considerable body of work attempting to describe the hydrogen outgassing behaviour of SS during and after thermal treatment. For the description of the outgassing rate basically two models common as diffusion limited model (DLM) and recombination limited model (RLM) have been discussed [2-10]. Surface states which may greatly influence the outgassing kinetics are not considered in the DLM. The recombination rate of hydrogen atoms approaching the surface from the bulk and desorbing in a second-order process may complete the physical picture. It is well established that the rate of recombination depends strongly on the atomic structure of the surface and is e.g. generally higher on stepped surfaces than on flat close packed planes. In order to gain atomic level information on the real morphology of a SS surface after common bake-out and vacuum firing samples were imaged in the scanning tunnelling microscope (STM) [11]. This previous experiments on AISI 304L SS samples show that the surface reconstructs completely during vacuum firing and large atomically flat terraces bounded by bunched steps and facets are formed. Surface inspection after vacuum firing by Auger electron spectroscopy (AES) gives reason for a composition change indicated by a reduction of the chromium signal in relation to the iron and
nickel signal. Since the information depth of this technique covers several atomic layers not only the top atomic layer of the sample is investigated. The atom probe allows measuring the chemical composition on the surface atomic layer by layer. The quantitative concentration can be obtained directly by counting the detected particles. For this reason the 3D atom probe has been used to investigate the segregation behaviour on SS samples after bakeout and vacuum firing [12].

The goal of this work was to introduce atomic force microscopy (AFM) as additional surface imaging technique to enlarge the field of view and continue the STM studies on small surface regions of interest.

2. Experimental
The main experimental work has been carried out on a combined UHV scanning tunnelling microscope (STM) – atom probe field ion microscope (AP-FIM) apparatus. The STM (Omicron STM-1) is directly attached to the UHV chamber which houses the field ion microscope with time-of-flight mass spectrometer and position sensitive detection of the field evaporated ions (3D atom probe) [13]. An additional preparation chamber equipped with a heating stage (e-bombardment) is attached to the microscope chamber to perform the thermal treatment of the SS samples before STM imaging. Surface inspection after bakeout and annealing can be performed with a cylindrical mirror Auger electron spectrometer (Varian 981). For vacuum diagnostics and outgassing observations a quadrupole mass spectrometer (Balzers QMA 125) is mounted. A unique feature of the particular combined instrument is that it allows a fully-predictive preparation of STM probe tips in situ by FIM which is important for a reliable imaging of complex surfaces [14].

The AFM measurements were performed ex situ in ambient conditions with a Dimension 3100 instrument (VEECO) equipped with a XYZ closed loop scanner and a NanoscopeIVa controller. Images were recorded in contact mode and in tapping mode. The software packages from VEECO and WSxM 4.0 from Nanotec were used for data analysis and representation.

For the STM and AFM studies on surface morphology 1 mm thick SS sheet samples (grade AISI 304L, nominal 18-20% Cr, 8-12% Ni) with glass bead blasted surface finish were used. The small stripes were cleaned chemically in a commercial electrolyte (Struers A2, containing perchloric acid in monobutyl-glycolether), rinsed with iso-propanol and dried in hot air, spot welded on the STM sample holder and transferred into the preparation chamber. The thermal treatment was performed in situ simulating low temperature bake out at 600 K and vacuum firing at around 1300 K.

The specimens for the atom probe analysis were cut from SS wire with almost the same composition as the STM samples (0.125 mm diameter, grade AISI 302, nominal 17-19% Cr, 8-10% Ni). The fine specimen tips were prepared by electro polishing in the same Struers A2 electrolyte and mounted onto a molybdenum loop which allows in situ vacuum firing by resistive heating.

3. Results
3.1. AFM Measurements
From the lapse of time the AFM measurements were carried out ex situ after the experiments in UHV but from the scale of imaged area they should be discussed at the beginning. In figure 1 an AFM micrograph of a SS sample before vacuum firing is depicted. The imaged area of 100 µm x 100 µm gives a reference for the surface morphology after common low temperature bakeout. A corresponding line profile of a 20 µm long section is plotted in figure 3 top. The grooves decorating the grain boundaries are in average 250 nm in depth, the grains within show also a certain roughness with variation in height between several nanometers and up to 50 nm. The AFM micrograph in figure 2 shows the SS sample after vacuum firing. The imaged area is 100 µm x 100 µm of size. A significant change of the surface structure and topology can be observed. The corresponding line profile is plotted in figure 3 bottom. During the high temperature treatment a complete reconstruction of the surface takes place. The surface within the grains become much smoother but the grain boundaries become much more predominate. From the line profile variations in height over 1000 nm can be drawn out. A
closer look to the specific surface structure on the grains is given in figure 4. In this micrograph an area of 10 µm x 10µm is plotted in a 3D representation. Hereby the depth scale is enhanced to give a better visibility of surface features on top of the grains. Driven by minimizing surface free energy closed packed terraces bounded by facets are formed which have been studied in detail by STM.

![AFM micrograph of the SS surface before vacuum firing after bakeout (3h@600K). Image size 100 µm x 100 µm.](image1)

![AFM micrograph of the SS surface after vacuum firing (20min@1250K). Image size 100 µm x 100 µm](image2)

![AFM line profiles of SS surface after bakeout (3h@600K) and after vacuum firing (20min@1250K) taken from Fig. 1 and 2.](image3)

3.2. STM measurements
The investigation of complex structured surfaces by STM makes need for a fully-predictive preparation of probe tips. For this study tungsten tips with a high aspect ratio were used. These were finally prepared to the desired shape by field evaporation in the FIM stage. With the STM a surface area up to 1000x1000nm² can be imaged. This is small compared to the grain size of the SS sheet.
sample. For the thermal treatment the sample must be transferred to the heating stage. For this reason it is practically impossible to inspect the same position before and after firing again. In figure 5 a STM image documenting the change of the surface structure due to the vacuum firing treatment (20min@1250K) is depicted. The STM micrograph is plotted as derivative image with a scan area of 1000x1000 nm². The gap voltage was set to -1 V, applied to the sample. The tunneling current was set to 0.1 nA. The surface exhibits large flat terraces with extensions up to several hundreds of nm which are bounded by characteristic facets. As it can be seen from the line scan these facets have step heights in the range of 10 – 20 nm. According to the previous study [11] the flat terraces are interpreted as (111) planes. The formation of the closed packed (111) planes can be expected from free energy minimization and is e.g. confirmed by the measured height of 0.1 nm of monatomic steps. According to the measured angles in the micrographs and line scans the facets can be interpreted as elements of (100) and (110) planes. This assumption is confirmed by reference measurement on a stepped Ni single crystal with 1,665 nm broad (111) terraces and 0.94 nm high (100) steps earlier used by A. Winkler et al. [15].

**Figure 4.** AFM micrograph (3D) of the SS surface after vacuum firing (20min@1250K). Image size 10 µm x 10 µm, z-scale enhanced.

**Figure 5.** STM micrograph (derivative) of the SS surface after vacuum firing (20min@1250K). Image size 1µm x 1µm.

### 3.3. Atom probe analysis

The depth profile of the SS specimen before vacuum firing shows a uniform distribution of the main alloy components with small statistical fluctuations. In average 17.9±0.3 at% Cr, 7.8±0.2 at% Ni, 70.8±0.6 at% Fe, 0.43±0.05 at% C and 3.1±0.1 at% N were measured which is in good agreement to the nominal composition. In addition a significant amount of hydrogen is found in the time-of-flight mass spectra. Since hydrogen is a main component of the residual gas it is very difficult to assign a certain quantity of the measured ions to hydrogen dissolved in the bulk. The significant changes after vacuum firing can be observed in the concentration profile presented in figure 6. The particular specimen was fired at 900°C for 10s. In the atom probe measurement nickel enrichment is found in the first atomic layer. The chromium concentration in the top layer is found about the bulk concentration. Surprisingly in the second atomic layer in all measured profiles distinct chromium enrichment is found. In the first atomic layer chromium was mainly detected as oxide. The average composition from the third atomic layer up to about 2 nm in depth was found to be 13.7±0.4 at% Cr, 9.5±0.4 at% Ni, 75±1 at% Fe, 0.07±0.03 at% C and 1.5±0.1 at% N. With respect to the samples
without thermal treatment after vacuum firing a roughly 50% lower amount of hydrogen ions have been recorded.

![Figure 6. Composition of surface region of a SS specimen after vacuum firing (20s@1200K), measured layer by layer by 3D atom probe. Only Fe, Cr and Ni depicted.](image)

In order to find a possible explanation for the unexpected concentration profile with chromium enrichment in the second atomic layer model calculations were performed using the thermodynamic concept after Williams and Nason [16]. Since this model is only developed for binary alloys the calculations were performed for the binary systems Fe-Ni, Fe-Cr and Cr-Ni. The corresponding thermodynamic data were taken from ref. [17]. For the system Fe-Ni surface enrichment of nickel is predicted as observed in the atom probe experiment. For the system Cr-Ni driven by the enthalpy of mixing the model predicts alternating enriched Ni and Cr layers. This may explain the observed concentration profile of Ni and Cr within the first 3 atomic layers with Ni peak in the first and Cr peak in the second layer.

4. Conclusions

The high temperature treatment of SS in vacuum leads to a significant change in surface morphology and surface composition and a strong influence on the gas surface interaction can be deduced from the experimental findings. The deep grooved grain boundaries and facets formed by bunched atomic steps represent very active sites for adsorption and recombination. Density function theory (DFT) calculations by Tersoff et al. [18] predict for step sites on (111) planes an energetic level very close to the bulk state. A close up view on the large (111) terraces by STM show that there are a lot of defects too. In an area of 100 nm$^2$ approx. 50 vacancies can be observed and represent additionally active sites for recombination. A further consequence can be deduced from the surface composition. On Fe single crystal surfaces an extremely low sticking coefficient for hydrogen was found by Berger et al. [19] in thermal desorption spectroscopy experiments. In comparison one magnitude higher sticking coefficients for hydrogen on Ni surfaces were found by Winkler et al. [15]. From this data it can be assumed that Ni segregation promotes adsorption and recombination of hydrogen.

From STM and atom probe data it can be concluded that the outgassing behaviour is almost controlled by surface defects and subsurface sites where hydrogen is deeply trapped. The physical picture with surface near deep traps and strongly bound sites may also explain the results by L Westerberg et al. [4] from nuclear resonance and extraction experiments. The similar average H concentrations in a surface near region (0.05 – 0.7 µm in depth) after 24 h long air bake and after 1 h vacuum firing indicate that an oxide layer obviously form similar deep traps than those arise from the surface defects which were observed on the vacuum fired surface. The important role of subsurface sites and deep traps may also explain outgassing experiments by Inayoshi et al. [20] where no significant difference in the outgassing rate between chemical polishing and electro polishing as treatment of the SS surface were found. The specific shape of thermal desorption spectra obtained by Bacher et al [10] gives also a clear indication for the existence of deep level traps.
The recombination of hydrogen atoms to the hydrogen molecule which can finally desorbs is of course the most important step in the outgassing process. From the look on the surface it is hard to understand that the recombination process is limiting the outgassing. The description as a second order desorption process may be not completely correct since in this picture the rate is a function of the coverage. At commonly measured outgassing rates after vacuum firing the corresponding coverage must be below $10^{-8}$ of a monolayer. In the second order desorption model, taking 0.52 eV as activation energy in account, roughly $10^{-4}$ of a monolayer can be desorbed at room temperature which is much more as supplied by diffusion to the surface sites. From this results a more complete description of the outgassing process may be given by a more or less dynamic equilibrium between diffusion, sojourn in different level traps and recombinative desorption.

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