Release of Water and Hydrogen during Outgassing of Some Materials

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An outgassing (vacuum annealing) procedure was used in combination with mass spectrometry to study gas release from pure copper, pure silicon, an Al97Mg alloy, and type 316 stainless steel. This paper focuses on the possibility of separating the different contributions to the total outgassing of a sample that has undergone a typical surface preparation procedure. These contributions have been divided into (1) release from bulk, (2) species introduced in grinding, and (3) species due to air exposure at room temperature. The reaction chamber was made of quartz and stainless steel, and the water release from these surfaces was measured separately. In air exposure of the reaction chamber walls, an uptake corresponding to one to two monomolecular layers of water was measured. This water layer was 85% desorbed in vacuum after 120 h at room temperature. The detection limit of the method is ~50 ppb hydrogen, and all samples investigated contained hydrogen in the 1000 ppb range. The species introduced during grinding were considerable, except for silicon. A significant hydrogen release was found for silicon and Al97Mg as a result of air exposure at room temperature, but not for copper or type 316 stainless steel.

1. Introduction

OUTGASSING in ultrahigh vacuum (UHV) is widely used in studies of materials, both for measurement of species on the surface by thermal desorption spectroscopy (Ref 1) and for measurement of dissolved species in bulk metals by the Ransley method (Ref 2) or the hot extraction method (Ref 3). However, these methods cannot unambiguously separate the surface preparation from the bulk as the source in the outgassing procedure. A very common species studied with these methods is hydrogen, since even low bulk concentrations can have a pronounced effect on the properties of materials. For example, in metals hydrogen embrittlement is a common cause of failure of construction materials, and in oxides a high proton content increases the electrical conductivity and lowers the protective ability (Ref 4).

This paper describes a technique and experimental procedure to distinguish and quantify the surface contribution from the bulk contribution to the overall gas release. The materials examined were pure copper, pure silicon, an Al97Mg alloy, and type 316 stainless steel. They were all polycrystalline and in the as-received condition.

2. Experimental Method

2.1 Apparatus and Experimental Procedure

In principle, the apparatus has three parts: a gas handling system, a reaction chamber (see Fig. 1), and a mass spectrometer (MS) in UHV. The reaction chamber is directly connected to

the MS, which has a base pressure below 10^{-7} Pa (10^{-9} mbar). The three parts are separated by UHV valves. The apparatus is described elsewhere in detail (Ref 5). It has earlier been used to study oxidation of metals (Ref 6) and oxygen exchange reactions (Ref 7) where the reaction chamber was virtually closed with a negligible inlet to the MS. In this way, gas consumption and release due to surface-gas reactions were quantified. In this study the gas release from the sample is measured by means of continuous outpumping of the reaction chamber. Hence, the apparatus is used for thermal desorption where several mass numbers (partial pressures) are measured versus time: 2 (H_2), 18 (H_2O), 28 (CO, N_2, C_2, H_4, ...), 32 (O_2), and 44 (CO_2, C_2H_4O, ...). The mass numbers 28 and 44 will not be discussed in detail, since they can contain several species that are difficult to distinguish from each other.

First the reaction chamber was evacuated with a rough pump for 10 min to a pressure of ~10^{-3} mbar and then pumped with an ion pump via the MS for 30 min at room temperature. Thereafter, the temperature was raised to 100, 200, 300, and so on, every 30 min by using an external furnace. Partial pressures were continuously measured with the MS, and time/temperature responses were thereby obtained. Figure 2 shows the result upon heating the reaction chamber in the absence of a sample. In this and later figures the background pressure in the MS has been subtracted. The pressure in the reaction chamber was in the 10^{-4} to 10^{-2} mbar pressure range during outgassing. After ~5 min virtually all residual air was pumped away, as interpreted from the decrease of masses 28 and 32 in the inset diagram in Fig. 2. This means that after ~5 min the gases
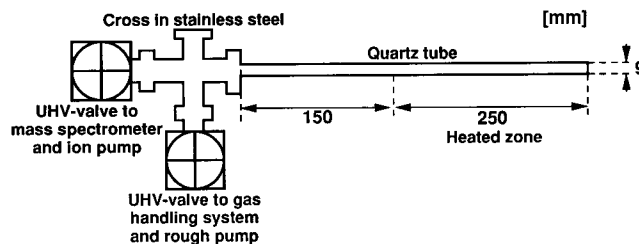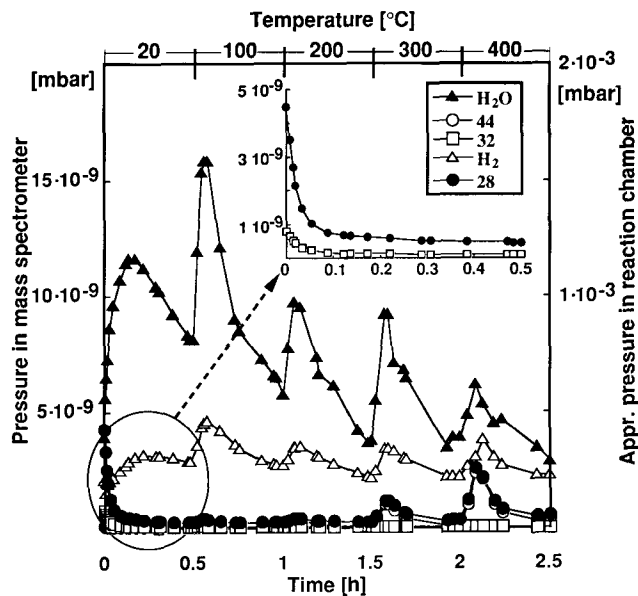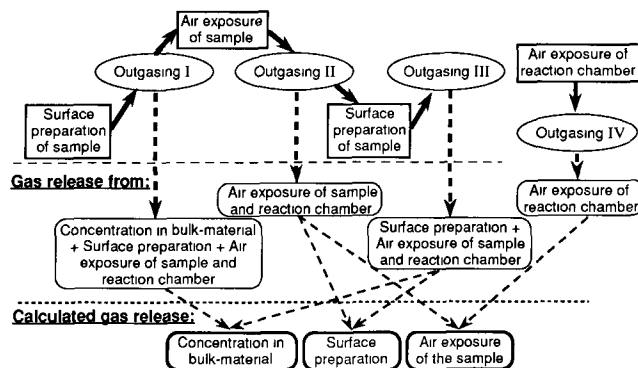

Fig. 1 Reaction chamber

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monitored came only from the sample and the reaction chamber.

The gas release from the samples when exposed to vacuum at different temperatures can be divided into three sources: species in the bulk material, surface preparation, and exposure to the surrounding atmosphere—in this case, ambient air. To separate these sources from each other the experimental scheme shown in Fig. 3 was used. The surface preparation consisted of mechanical grinding with 1200-mesh SiC paper in air and cleaning ultrasonically in 99.5% ethanol. The air exposure was made after the sample had been outgassed by letting ambient air (relative humidity of 30 to 40%) into the reaction chamber for 5 min. The air was subsequently evacuated using the procedure described earlier. The studied samples are described in Table 1. The highest temperature used in this study was set by evaporation of the studied material. This was 400 °C for $Al_{97}Mg$ alloy and copper, 700 °C for type 316 stainless steel, and 900 °C for silicon.
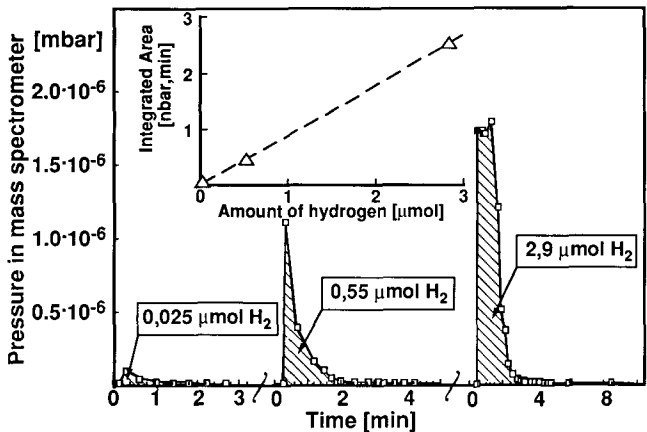
2.2 Calibration

The amount of a gas pumped away can be calculated from the partial pressure and the pump rate. However, many parameters—such as age of the pump, geometry of the reaction chamber, and measurement of pressure—influence the nominal values of the pump rate and pressure. Therefore, a calibration was performed. The gases pumped with the ion pump via the MS were measured as pressure versus time, where an integration corresponds to amount of gas. This amount was determined from the measured pressure in the reaction chamber, where both volume and temperature are known. By letting different amounts of gas be pumped out of the reaction chamber by the ion pump via the MS, a relation between the integrated pressure-time curves and the amount of gas can be established, as illustrated in Fig. 4 for hydrogen. As can be seen, this relation is linear:

$$C = \frac{A}{n} \qquad \text{(Eq 1)}$$

where C is a constant (mbar · min · μmol^{-1}), n is the amount (μmol), and A is the integrated area (mbar · min). In the same way, calibration curves were made for H_2O and CO_2 (Fig. 5). Table 2 gives values for C and the detection limits; these limits depend on pump rate, background in the UHV chamber, and background in the reaction chamber. The relatively high detection limit of H_2 is partly due to a high background in the UHV

Fig. 2 Outgassing of the reaction chamber in the absence of a sample

Fig. 3 Outgassing scheme and principle of separating the different contributions to the overall gas release

Table 1 Chemical composition and sample size

Material	Composition, wt %	Size, mm
Aluminum (type 5xxx)	2.5 Mg, 0.15-0.5 Cr + Mn, bal Al	1 × 8 × 50
Copper	99.99 Cu	0.1 × 30 × 60
Silicon	99.999 Si	1 × 10 × 50
Type 316 stainless steel	18 Cr, 12 Ni, 2.7 Mo, max 0.05 C, bal Fe	0.5 × 8 × 65

Fig. 4 Calibration of H_2 at room temperature. Pressure of H_2 in MS versus time for outpumping of 0.025, 0.55, and 2.9 μmol H_2 in reaction chamber. Inset diagram shows integrated pressure-time values (equivalent to hatched area) versus 0.025, 0.55, and 2.9 μmol H_2 in reaction chamber.

chamber, and the high detection limit of H_2O from the sample is due to water release from the reaction chamber walls. The values for mass 28 in Table 2 have been estimated.
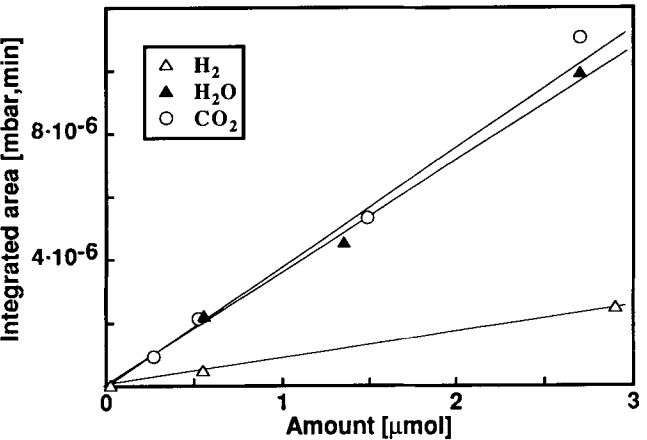
3. Results and Discussion

3.1 Outgassing of the Reaction Chamber in the Absence of a Sample

The outgassing of the empty reaction chamber after 5 min air exposure is shown in Fig. 2. The outgassing of the reaction chamber contains information about the water adsorbed on the walls of the reaction chamber (stainless steel and quartz). We are primarily interested in two questions: (1) the amount of water adsorbed on the walls after 5 min air exposure and (2) how much of this amount will desorb at room temperature. The total amount of water adsorbed on the heated zone was determined experimentally in Fig. 6 to ~260 nmol. This amount corresponds to the area under the filled triangles minus 65% of the area under the dashed line (hatched area). The value of 65% is derived from the fact that the heated zone (70 cm^2) constituted 35% of the reaction chamber walls (200 cm^2).

An outgassing was made at room temperature for 120 h, where the first 6 h is indicated as the dashed line in Fig. 6. After

Table 2   Values for C in Eq 1 for H_2, H_2O, CO_2, and 28, detection limit of respective gas, and detection limit in outgassing of sample

Gas	C, mbar · min · μmol^{-1}	Detection limit of respective gas, ng	Detection limit of sample content, ng
H_2	1.0×10^{-6}	20	100
H_2O	3.6×10^{-6}	5	500
CO_2	3.6×10^{-6}	10	100
28	$~4 \times 10^{-6}$	~10	...

120 h the same outgassing procedure at elevated temperatures was performed (filled circles in Fig. 6). The amount released was calculated from the area under the filled circles to *~40 nmol. The fraction of water left on the reaction chamber is assumed to be the same as the fraction left on the heated zone (40/260 = 15%) after outgassing for 120 h at room temperature. Then ~15% was left on the walls of the reaction chamber after outgassing for 120 h at room temperature, and consequently ~85% of the amount of water had been released. Still, after 120 h a measurable release rate from the reaction chamber was found at room temperature. By extrapolating the outgassing for 120 h at room temperature to infinity, an additional ~15% of water was estimated to be released. By comparing this ~15% with the previous calculated ~15%, one can conclude that virtually all the water uptake in the air exposure will be released at room temperature.

The total water release from the reaction chamber was ~10 μg. By assuming a density of ~1 g/cm^3 of water and using the effective inside area of the reaction chamber, an average thickness of ~1.6 monolayer water on the walls of the reaction chamber was calculated. In general, the properties of the first monolayer are very different from bulk water, and bulk properties are obtained only after the third monolayer (Ref 8). The evaporation of bulk water (Ref 9) is very fast upon exposure to vacuum (10^{-3} mbar), so any water adsorbed exceeding three monolayers should desorb in the 10 min of rough pumping. Therefore, the maximum number of released monolayers expected is three, which is in approximate agreement with the average of ~1.6 monolayers measured in this study.

The inset diagram in Fig. 2 shows that the residual air is readily pumped away since both 28 (N_2) and 32 (O_2) decrease rapidly. After ~5 min the gas released comes only from the re-
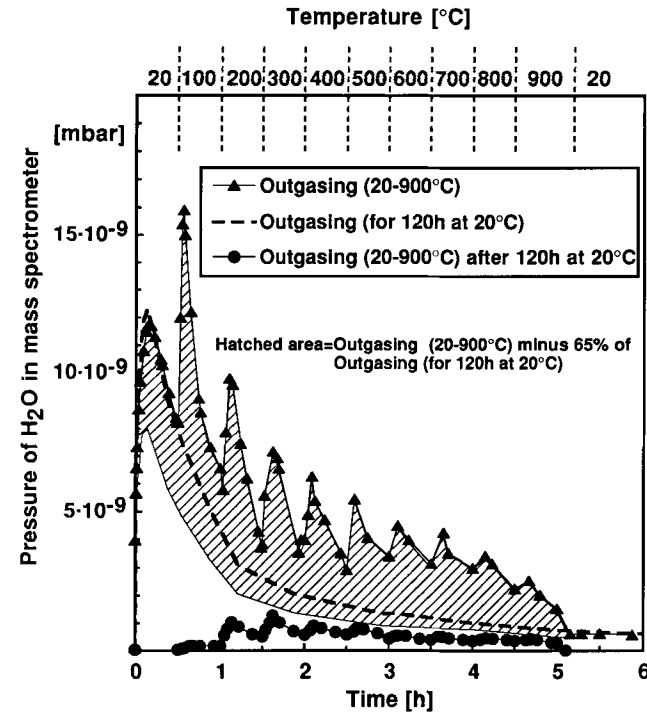

Figure 5. Calibration of H_2, H_2O, and CO_2, integrated area vs. the amount of respective gas in the reaction chamber.

Fig. 5   Calibration of H_2, H_2O, and CO_2, integrated area versus amount of respective gas in reaction chamber


Fig. 6   Outgassing of H_2O from the reaction chamber

action chamber and the sample. In contrast to the rapid decrease of 28 and 32, there was an increase of H_2O, which emphasizes that the water desorption is not ruled by the pump rate. The desorption kinetics can also be viewed as the fraction between water released and the total amount water adsorbed versus time. This was 15% after 0.5 h, 50% after 9 h, and 85% after 120 h at room temperature. At temperatures up to 200 °C, the major outgassing species are H_2O and H_2 from the reaction chamber. Above 200 °C, CO and CO_2 also are released.

3.2 Outgassing of Samples

When a sample is introduced into the heated zone of the reaction chamber, significant increases in all partial pressures occur. As an example, outgassing data for type 316 stainless steel sample treated according to protocol III from Fig. 3 are shown in Fig. 7. The high partial pressure of H_2 at 400 °C is partly due to reaction of the metal with H_2O. This is evident in Fig. 8, since the partial pressure of H_2O becomes lower than the release from the empty reaction chamber (outgassing IV) above 400 °C. Consequently, there is a consumption of water in the reaction chamber, which is described by the reaction:

$$xMe + yH_2O \rightarrow Me_xO_y + yH_2 \qquad (Eq\ 2)$$
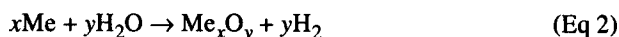
The stainless steel sample was examined with x-ray photoelectron spectroscopy before and after outgassing, and the oxide growth was estimated to ~3 nm. A similar reaction with water was found for $Al_{97}Mg$ and silicon, but for silicon this occurred above 600 °C. The hydrogen content in these
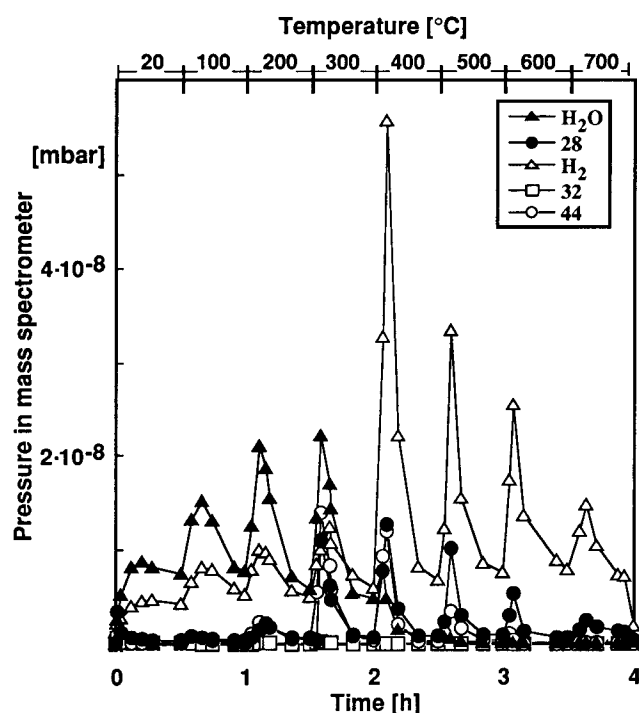
reaction products was probably low since the temperature was high (Ref 10).

By comparing outgassing protocols I to IV with one another in Fig. 8 according to the scheme in Fig. 3, the "origin" of desorbed species can be found. As an example, the partial pressure of H_2O after outgassing I and III was essentially the same, suggesting that the bulk metal contains no H_2O. Figure 8 also shows that air exposure has a small effect on the stainless steel (comparing II and IV), which agrees with the general view that an inert chromium-rich oxide is formed on stainless steels. The other measured mass numbers can be treated in the same way. By integrating the pressure versus time curves for the different
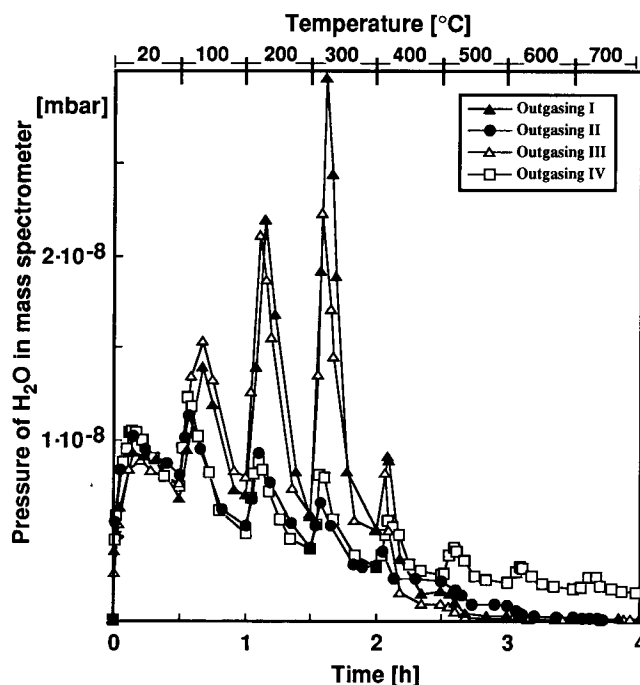

Fig. 8 Outgassing of H_2O from type 316 stainless steel sample treated according to four different protocols

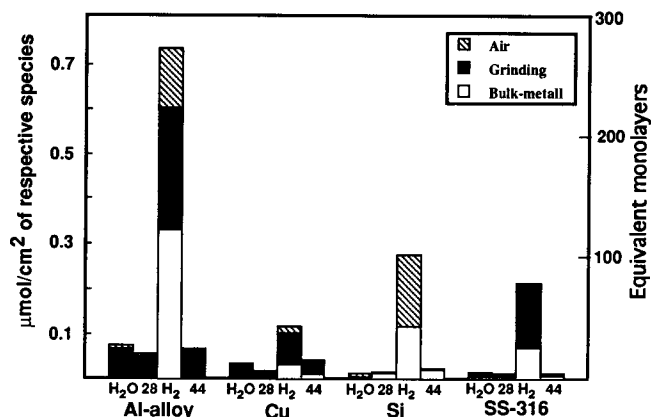**Fig. 7** Outgassing data from type 316 stainless steel sample treated according to protocol III (Fig. 3)

Fig. 9 Release of different gases from bulk due to grinding and air exposure. Based on outgassing in accordance with the scheme in Fig. 3 of $Al_{97}Mg$ and copper to 400 °C, type 316 stainless steel to 700 °C, and silicon to 900 °C. (One monolayer is assumed to equal 1.5×10^{15} atoms/cm^2.)

Table 3 Equivalent concentration in bulk material measured as gas release of different species

Material	Species, ppm (wt)			
	H_2	H_2O	28	44
Type 316 stainless steel	0.8	0.3	0.6	1.2
Copper	1.3	1.3	0.1	7.3
$Al_{97}Mg$	3.5	...	...	...
Silicon	1.0	0.4	0.5	1.3

materials and normalizing to surface area, Fig. 9 is obtained. For hydrogen the equivalent numbers of monolayers were very high, especially for the $Al_{97}Mg$ alloy; this is interesting to consider.

Grinding contributed significantly to the gas release for the "soft" materials—$Al_{97}Mg$ and copper—but was negligible for the "hard" silicon.

For all materials, a measurable hydrogen content was found in the bulk (Table 3). For the case of $Al_{97}Mg$, the measured concentration (3.5 ppm) exceeds the solubility of hydrogen in pure aluminum (Ref 11) by two to three orders of magnitude. This "disagreement" can likely be explained by the presence of magnesium, which is a very strong hydride former (Ref 12).

4. Summary and Conclusions

A method based on mass spectrometry in combination with heating of a sample in vacuum has been used to measure low concentrations of hydrogen in pure silicon, pure copper, an $Al_{97}Mg$ alloy, and type 316 stainless steel. The method can distinguish between gas release from bulk and from the surface (species introduced in surface preparation). The possibility of distinguishing between these two is important since surface preparation was found to significantly contribute to the total gas release. Two different methods of surface preparation have been used: a grinding procedure and a 5 min air exposure. The gas releases, corresponding to mass numbers, 2, 18, 28, 32, and 44, were measured and quantified. The following conclusions can be drawn:

- The method can be used to measure hydrogen content in metals and oxides.
- The detection limit of the method is 100 ng for H_2, 500 ng for H_2O, and 100 ng for CO_2. This corresponds to a hydro-

gen content of <50 ppb (wt) for most materials (~5 cm^3 sample volume).

- Outgassing of different materials gives a "fingerprint" of masses 2, 18, 28, 32, and 44 versus time and temperature.
- All samples contain bulk hydrogen: 0.8 ppm (wt) in type 316 stainless steel, 1.3 ppm (wt) in pure copper, 1.0 ppm (wt) in pure silicon, and 3.5 ppm (wt) in the $Al_{97}Mg$ alloy. In $Al_{97}Mg$, this greatly exceeds the solubility of hydrogen in pure aluminum.

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