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CHEMICAL CLEANING OF METAL SURFACES IN VACUUM SYSTEMS
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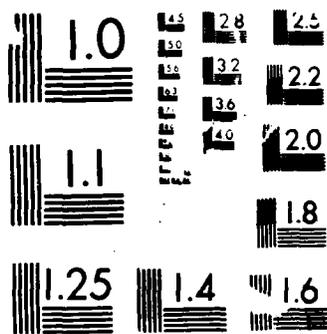
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Chemical Cleaning of Metal Surfaces in Vacuum Systems
by Exposure to Reactive Gases

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Abstract

Chemical surface cleaning procedures for metals using oxidation/reduction cycles by exposure to oxidizing (O_2 , NO) and reducing (H_2 , NH_3) gases are summarized and are briefly discussed for iron, nickel, palladium, copper and silver surfaces. We also present data on the reduction of gaseous contaminants in a stainless steel UHV system by flowing nitric oxide through the system during bake-out.

Introduction

Preparation of a chemically and structurally defined surface is a prerequisite for the study of the physical and chemical characteristics of clean metal surfaces and for experiments on the interaction of gases with these metals. Even if the nominal purity of the bulk metals used to prepare the specimen is of the highest quality, it is unavoidable that bulk impurities present (in the ppm range) will segregate and enrich on the surface during heating cycles in vacuum. Cleaning procedures of the samples, therefore, typically involve extended cycles of ion bombardment and heating in vacuum to deplete the subsurface region of the specimen from those bulk impurities.

In this communication we summarize alternative cleaning methods for

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metal surfaces using reactive gases. A comprehensive review of the preparation of atomically clean surfaces has been given by Musket et al. /1/, where a compilation of cleaning procedures published before early 1981 can be found. Cleaning procedures involving oxidation/reduction cycles by reactive gases have been included in this review. Since then, some of the reactive gas cleaning procedures have been extended to other metals and have been refined and more carefully evaluated for some materials. Examples from our laboratory (Fe, Ni, Pd, Cu, Ag) will be discussed in this article. A compilation of the reactive gas cleaning procedures, including those already summarized in ref. 1, is given in Table 1.

Finally, we will summarize the procedures used to clean vacuum systems by flowing nitric oxide through the system during bake out.

Before specific metal substrates to which reactive gas cleaning procedures have been applied are discussed, we want to point out some general advantages (and disadvantages) using this technique.

The obvious advantage of using reactive gas exposures rather than ion bombardment is that no surface damages are induced as in the case of sputtering. For some metals (such as chromium), however, oxygen exposure to remove contaminants such as carbon or sulfur leads to the formation of very stable surface oxides which can lead to a reconstructed surface layer and can only be removed by repolishing the crystal /2/.

A further advantage of oxidative/reductive cleaning of surfaces is that due to the presence of the oxidation/reduction agent, a chemical potential gradient for the segregation of contaminants is induced. That enhanced segregation is induced by the reactive gases is evident by comparing the times necessary to deplete the contaminants by oxida-

tion/reduction cycles (on Ni and Fe) and the total sputtering time to achieve the same depletion level of bulk contaminants in the sample /3/.

Gases employed in oxidation/reduction cycles are typically oxygen and hydrogen. It was found, however, that NO (instead of O₂) and NH₃ (instead of H₂) are more effective for cleaning of nickel surfaces, obviously because the dissociation efficiency of these gases (which is a necessary prerequisite for the surface reaction) is higher than for O₂ and H₂ molecules. Pressures and temperature have to be adjusted such that the surface reaction rate in the oxidation and reduction of the contaminants matches the rate of surface segregation of the bulk impurities. The exact parameters have to be experimentally determined for each substrate and might differ for different crystallographic orientations of single crystal specimens /4,5/.

Iron

Iron is a notoriously difficult metal to clean because of the problems associated with obtaining samples of low impurity levels in the bulk. The common impurities are carbon, sulfur, oxygen, nitrogen, phosphorus and chlorine. Depletion of these contaminants can be achieved by prolonged sputtering at elevated temperatures /6/. Caution is necessary, however, to stay below the α - γ phase transition temperature of 1183 K of pure iron. Since high levels of bulk impurities lower the phase transition temperature the sputtering rate has to be high enough to continuously deplete the selvedge in order to avoid enrichment of the impurities and subsequent reconstruction of the crystal surface /7/.

In a previous publication we described our results on cleaning an iron {211} crystal by reduction in 1 atm of hydrogen at T = 713 - 733 K /3/. It was found that after 100 hours of hydrogen treatment the con-

centration of impurities (C, O, S) were reduced to a stationary low level. It was suggested that the remaining contamination might be caused by gaseous contaminants present in our preparation chamber. In view of more recent careful studies by T. J. Vink et al. /4/ on the reduction of oxidized Fe(100) by hydrogen it is possible, however, that the remaining level of contaminants is due to a higher stability against reduction by hydrogen. Vink et al. observed, by ellipsometry, that a thick oxide layer can be reduced in 2×10^{-2} torr of hydrogen at crystal temperatures of 473 - 643 K, and that oxygen dissolved in the subsurface region diffuses to the reaction interface and is depleted. However, the reduction of a single monolayer of oxygen on Fe{100} was not possible with hydrogen at pressures of up to 10^{-2} torr and exposures of up to 6×10^7 L. Contrary to their findings on Fe{100}, they observed a complete reduction of an oxide layer on a Fe{110} crystal, emphasizing that the reaction is face specific /5/. These studies also revealed that the rate determining step for the reduction process is the activated dissociation of hydrogen on an oxygen site.

The higher stability of a surface oxide, as compared to the bulk oxide, follow the general observation that surface compounds are more stable than the respective bulk compounds. This has been discussed for the stability of surface nitrides on iron by Ertl, Huber and Thiele /7/. Therefore, the final reduction of oxygen on a Fe{100} surface requires a more reactive agent than molecular H_2 , such as acetylene /8/.

Although no studies of iron have been performed on single crystals, it is suggested that also N_2/H_2 mixtures might prove to be an effective reducing agent for ironoxide. In surface science studies on the reduction of a commercial iron ammonia synthesis catalyst /9/ it has been

found that the oxide is reduced to the metal in a N_2/H_2 gas mixture with a ratio between 1:2 to 1:3 at a pressure of 600 - 700 torr and temperature between 623 - 673 K. If the reaction is performed in a batch reactor, the ammonia formed will nitride the iron surface and lead to a protective nitride layer preventing heavy oxidation if the sample is exposed to air. That iron crystals, nitrated by exposure to ammonia, are protected to some extent from bulk contamination during exposure to air has been reported previously /3,10/.

It is finally noted that an identical hydrogen treatment (1 atm, 650 K) on a Fe/Mn single crystal was not successful in removing a stable surface oxide. Sputtering was necessary to remove the surface oxide layer /2/.

Nickel

Typical bulk impurities of nickel are O, S, C. In particular, carbon and sulfur turn out to be a persistent contamination segregating onto the surface when the crystal is heated. As summarized by Musket et al., oxygen treatments followed by hydrogen reduction of the remaining oxide have been applied widely to remove residual carbon. Removal of sulfur was achieved by ion bombardment at elevated temperatures /11/. As described by us previously /3/, sulfur can be oxidized on a Ni(110) surface with oxygen ($p \sim 10^{-7}$ mbar) at 1000 K. It turned out, however, that the use of nitric oxide is, by about a factor of 10, more efficient than the use of molecular oxygen in the removal of sulfur. Nitric oxide may also be used to remove carbon at $T \sim 600$ K, but no comparative studies have been done with oxygen as an oxidizing agent. Subsequent removal of the oxide can be done by exposure to hydrogen ($p_H = 10^{-6}$ mbar $T \geq 640$ K) /3/ or, alternatively, by ammonia. In reference /12/ we pre-

sented data on the reduction of a surface oxide on a Ni{100} surface with NH_3 . About 370 L were sufficient to remove the oxide completely leaving a $c(2 \times 2)$ nitrogen overlayer. Removal of the nitrogen overlayer and production of a clean surface is achieved by flashing the crystal to $T \sim 1000 \text{ K}$ /12/. By a comparison to exposures necessary for the removal of the oxide by hydrogen at $T \sim 670 \text{ K}$, it follows that reduction by NH_3 is more efficient.

The reason that NO and NH_3 are more effective in oxidation of sulfur and reduction of oxygen must be that both gases dissociate more easily than O_2 and H_2 on the contaminated nickel surface. The availability of atomic oxygen and hydrogen are necessary prerequisites for the surface reactions leading to the removal of the impurities. From an inspection of the bond energies for NO (630 kJ/mol) and O_2 (498 kJ/mol) it would follow that O_2 is more easily dissociated. That H_2 dissociates more easily than NH_3 ($\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$) would also follow from a comparison of the respective bond energies of 436 kJ/mol versus 460 kJ/mol for the latter. Therefore, the higher activity cannot be related to the dissociation energies of the molecules, but must be caused by a different catalytic activity of the substrate towards dissociation of NO and NH_3 as compared to O_2 and H_2 .

The reason for the high catalytic activity of NO and NH_3 follows from an inspection of the possible reaction mechanisms leading to dissociation. If dissociation would occur by impact from the gas phase, the bond strength argument mentioned above would suggest that O_2 and H_2 are more reactive. However, if dissociation occurs via a molecular precursor of the respective gases, the residence time of the molecules on the surface (and therefore their stationary coverage under reaction con-

ditions) will determine the overall rate of dissociation. It is well established from adsorption studies that both NO and NH₃ are much more strongly adsorbed than O₂ and H₂, and therefore their residence time (which can be calculated from the Frenkel equation) will be significantly longer leading to a higher dissociation probability. A detailed discussion of the kinetics of dissociation via a molecular precursor state can be found elsewhere. /13/ In the context of the present paper, we would like to point out that the choice for the gaseous oxidation/reduction agent used in chemical cleaning procedures of surfaces cannot only be based on the dissociation energy of the gaseous molecule, but must also consider the adsorption energy of the molecular reaction gases on the surfaces to be cleaned.

Palladium

In palladium, the most persistent bulk impurity is carbon which will consistently segregate to the surface at $T \sim 500$ K. The detection of carbon impurities by Auger Electron Spectroscopy commonly available in UHV systems is complicated due to the overlap of the Pd M_{4,5} N_{2,3} N_{4,5} signal with the carbon Auger signal at 272 eV. In a recent LEED /14/ and TPD /15/ study, it was reported that even Ar-ion bombardment at $T \sim 1000$ K for 400 hours was not sufficient to remove the carbon completely as evidenced by LEED I(E) curves and TPD experiment of CO. Only after extensive oxidation/reduction cycles (using O₂ and CO) was a carbon free surface obtained. /14/ This clean surface was observed to undergo a phase transition at $T \sim 250$ K which was not detectable on the contaminated surface. /14/

Copper and Silver

A copper {111} was cleaned by heating to 800 K in 1.3 mbar of O₂

for 5 minutes to remove carbon and sulfur. The remaining surface oxygen was subsequently reduced by heating in 3 mbar of H₂ at 800 K for about the same time. This cycle was repeated 5-7 times and resulted in a carbon and sulfur free surface as judged from the XPS spectra. Occasionally some residual oxygen persisted after this treatment, especially after the crystal was exposed to more extensive oxygen treatment to produce CuO and Cu₂O surface species /16/. This residual oxygen was removed by argon ion sputtering (1 keV, 850 K).

A polycrystalline silver sample was effectively cleaned of carbon contamination by cycles involving exposure to 0.5 mbar of oxygen at 673 K for about three minutes followed by flashing to 900 K /17/.

NO Treatment of Stainless Steel Vacuum Chambers

We finally discuss our results by flowing nitric oxide through a stainless steel vacuum chamber during bake-out in order to reduce the background carbon monoxide and hydrogen pressure. Those procedures were first applied by J. Pritchard (Queen Mary College, University of London) to achieve vacuum conditions suitable to maintain an impurity free surface for the time necessary to record infrared reflection absorption spectra of weakly chemisorbed molecules. A recipe for treating a "clean" vacuum system, i.e. a UHV chamber used for adsorption studies only, was described in reference 3. In this procedure, nitric oxide is flown at a pressure of $\sim 5 \times 10^{-7}$ mbar through the system during the final stages of bake-out (T \sim 470 K). As monitored by a mass spectrometer, kept at lower temperatures, initially no nitric oxide but high levels of nitrogen, water, and carbon dioxide are detected. The appearance and continuous increase of the m/e = 30 signal (typically 30-180 min) indicates that most of the carbon and hydrogen containing contaminants

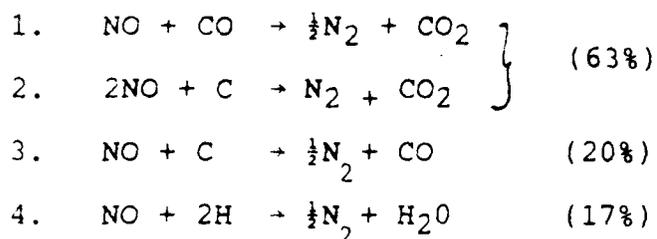
have been removed from the walls of the vacuum chamber, and the nitric oxide flow is terminated. More important than achieving an excellent base pressure, the mentioned NO treatment reduces the displacement of contaminants from the walls during long exposures of adsorption gases, in particular, when adsorption isotherms or isobars are recorded. This procedure has been applied successfully by other groups /18/.

The data presented below were taken in a stainless steel UHV system used to measure, by a Knudsen cell method, the vapor pressures of 4-aminophenyl ether (ODA) and 1,2,4,5 Benzenetetracarboxylic anhydride (PMDA). As a result of those experiments, the vacuum chamber was heavily contaminated with carbonous residues providing a steady supply (during the time of our cleaning procedures) of carbon and oxygen as well as hydrogen from the fragmented organic molecules. The partial pressure of selected gases were continuously monitored with a mass spectrometer (amu 1-300) interfaced to a computer during bake-out with and without flowing NO through the system which was pumped with a 360 l/s turbomolecular pump. Nitric oxide with the nominal purity of 99.0% (Matheson Gas Products) was used for the experiments.

In Fig. 1, we plotted selected data for the intensity of selected masses for (i) residual gases during bake out of the vacuum chamber at 453 K, (ii) with a NO pressure of 4.7×10^{-7} mbar flowing through the system, (iii) $5\frac{1}{2}$ hours later with NO at 4.7×10^{-7} mbar and (iv) after increasing the NO partial pressure to 3.3×10^{-6} mbar 8 min later.

During regular bake-out of the vacuum chamber at 453 K the typical gas background of a hot stainless steel chamber (CO, CO₂, H₂O, CH₄, ..) was observed. Upon introduction of nitric oxide to the system, an additional source of oxygen is provided leading to an enhancement of oxi-

dation reactions on the walls. This can be seen by comparing the intensities before and after introduction of NO at $P_{NO} = 4.1 \times 10^{-7}$ mbar to the hot system in Fig. 1. A comparison of the intensities shows that the hydrogen partial pressure (amu 2) is only marginally affected, whereas drastic increases in amu 14-18 and, in particular, in the CO₂ partial pressure (amu 44) is detected. Peaks at amu 28 and 30 are due to N₂, CO and NO, and those at 14, 15 and 16 to N⁺ and doubly ionized N₂, CO and NO, respectively. It is straightforward to associate the increase in amu 18 and 17 with the production of water. (Note that the ratios of amu 18/17 are almost identical with and without NO when the semi-logarithmic scale is considered.) Peak at amu 16 is associated with the production of methane and oxygen resulting from the fragmentation of NO in the mass spectrometer. A closer inspection of the peak ratios reveals that CO₂ is the predominant reaction product resulting from the reaction of NO with the walls of the chamber. The mass spectra indicate that the following reaction occurs on the hot walls.



Spectra taken 5½ hours after introduction of NO show a pronounced decrease in reaction products, indicating a depletion of contaminants. However, increasing the NO pressure by an order of magnitude (to 3.3×10^{-6} mbar) again enhances the wall reactions. From such pressure jump experiments, the approximate probabilities of reaction 1 + 2, 3 and 4 occurring as given above were calculated, normalized to a NO consumption

of 100%. Clearly, the predominant wall reaction produces CO_2 , either from adsorbed CO or carbonous residues on the walls. Less probable are the reactions producing CO or H_2O , but it should be remembered that these data were taken in a heavily contaminated UHV system and might not reflect the reaction probabilities in systems with a different history. Also, in "clean" vacuum systems, a short NO treatment (30 min - 2 hrs) results in a typical reduction of residual gases by a factor of ~ 2 , whereas for heavily contaminated systems the improvement in final vacuum conditions requires an accordingly longer treatment. We finally note that a NO treatment is more effective than a treatment with pure O_2 , presumably due to the same reasons as have been discussed in the context of chemical cleaning for residual surfaces.

Summary

We briefly reviewed chemical cleaning procedures for metal surfaces used subsequently in surface science studies and included more recent results from our laboratory. The procedure to improve vacuum conditions by flowing nitric oxide through the hot vacuum chamber during bake out has been summarized and the reactions taking place on the walls of the system have been qualitatively discussed.

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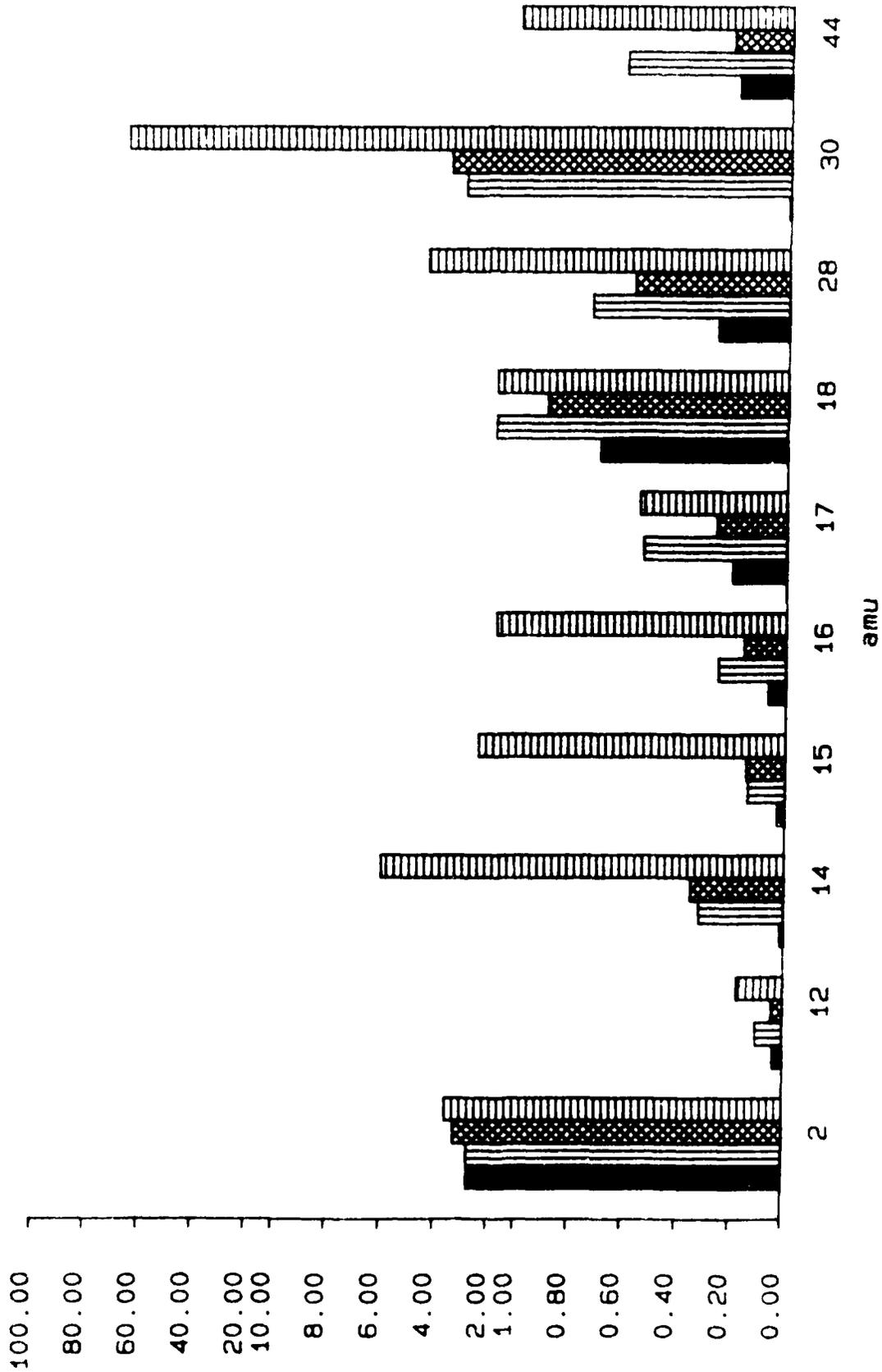
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Figure Captions

Fig. 1. Intensities of selected masses during bake-out of a vacuum system without and with NO flowing through the chamber.



- T=453 K, p=4.4x10⁻⁸ mbar
- ▨ NO gasinlet T=453 K, p=4.7x10⁻⁷ mbar
- ▩ after 5 1/2 h T=453 K, p=4.7x10⁻⁷ mbar
- ▧ T=453 K, p=3.3x10⁻⁶ mbar

Table 1: Cleaning of metal surfaces by gas exposure

Material	Major Impurities	Oxidation cycles	Reduction cycles	Comments
<p>I, F denotes intermittent or final heating to remove surface oxides Arf, Arf denotes intermittent or final cleaning by Ar ion bombardment</p>				
Co (poly)	S, O, Cl, C, N	Heat in oxygen 1.3x10 ⁻⁶ mbar, 900 K		Arf, F /19/
Co (100)	S, O, Cl, C, N	Removal of carbon by heating in oxygen ca. 3x10 ⁻⁶ mbar, 900 K	Removal of oxygen by heating in hydrogen	Alternative oxygen removal by Arf. Oxygen pressures > 2x10 ⁻⁵ mbar leave oxide on the surface /20/
Cu (100)	C, O, S, Cl, N	Removal of carbon and sulfur by heating in oxygen 1.3 mbar, 800 K	Removal of surface oxide by heating in hydrogen	
Cu (111)	C, O, S, Cl, N	Removal of carbon and sulfur by heating in oxygen 5 min, 1.3 mbar, 800 K	Removal of oxygen by heating in hydrogen 5 min, 3 mbar, 800 K	5-7 cycles, eventually occurring oxygen removed by Arf /16/
Au (poly)	C, S, Ca	Heating in oxygen 24 h 6x10 ⁻⁵ mbar, 1000 K	Heating in hydrogen 8 h 6x10 ⁻⁵ mbar, 1000 K	Series of I, oxidation and reduction cycles for an already Ca free surface /22/
Au (100)	C, S, Ca	Heating in oxygen 6x10 ⁻⁷ mbar, 673 K		Various combinations of I or Arf (Ca removal) and oxidation over a long period of time /23/
Au (111) + its vicinals	C, S, Ca	Removal of carbon by heating in oxygen 10 h 10 ⁻⁷ mbar, 973 K /28/		Including oxidation /24/ in I and Arf cycles
Ir (poly)	C, O, N, S, P	Repeated heating in oxygen for several h 1.3x10 ⁻⁶ mbar, 1590 K		Arf /25/ or cycles of Arf and F /26/
Ir (100) (2x1)	C, O, N, S, P	Heating in oxygen 5-10 min, 7x10 ⁻⁸ to 1.3x10 ⁻⁷ mbar, 1200-1590 K		Cycles of I and oxidation /27/
Ir (100) (1x1)	C, O, N, S, P	Oxidation of the prepared reconstructed surface by dosing 10-20 LA oxygen ca. 7x10 ⁻⁸ mbar, 475 K or 670-670 K	Removal of the oxygen by heating in hydrogen ca. 10 ⁻⁷ mbar, 400-700 K, or 20 LA T<400 K or in CD 300 LA, T<400 K /29-33/	Arf followed by alternative cycles of I and oxidation produces a reconstructed (5x1) surface /29-37/
Ir (110) (2x1)	C, O, N, S, P	Heating in oxygen several min, 7x10 ⁻⁸ mbar - 1.3x10 ⁻⁷ mbar, ca. 800 K		It is important to heat the surface to ca. 600 K at some point during the oxidation
Ir (111)	C, O, N, S, P	Heating in oxygen 7x10 ⁻⁸ mbar - 1.3x10 ⁻⁶ mbar, 800-1100 K		Repeated cycles of I and oxidation until the surface was stoichiometrically clean /36-45/
Ir (755)	C, O, N, S, P	Heating in oxygen several min, 7x10 ⁻⁷ mbar, 770-870 K		Repeated cycles of Arf /54, 55/, I and oxidation /36, 42, 47-53/
				F /51, 52/

(continued)

Material	Major Impurities	Oxidation cycles	Reduction cycles	Comments
Fe (poly)	C, S, O, N, P, Cl			No details listed, but all investigators used hydrogen pretreatment /58, 57/ to remove impurities that form volatile hydrides
Fe (100)	C, S, O, N, P, Cl	Oxygen exposure 0.5-10 LM, 770 K	"Titration" of oxide with acetylene /58, 59/ or by heating in either oxygen or water vapor ca. 10-6 mbar, 770-870 K /60/	Ar-I, oxidation and reduction cycles /71/ Combination of chemical cleaning with Ar-I
Fe (110)	C, S, O, N, P, Cl	Oxygen treatment several h, 7x10-8 mbar, 970 K	Hydrogen treatment 1000 mbar, 850 K Heating in hydrogen for long periods ca. 10-4 mbar, 1070 K Heating in hydrogen 100 h 1013 mbar, 713-733 K	Combination of chemical cleaning with Ar-I /51/ Combination of chemical cleaning with Ar-I /62/ Combination of chemical cleaning with Ar-I /63/ Ar-I /3/
Mo (poly)	S, C	Removal of carbon (as CO) and sulfur by heating in oxygen 1.3x10-6 mbar, 1100-1500 K		Ar-I or I /64-66/
Mo (100)	S, C	same treatment as Mo (poly)		Cycles of either Ar-I, I and F together with oxidation /67-68, 71-74/ I /70/
Mo (110)	S, C	Removal of carbon and sulfur by initial oxygen treatment ca. 7x10-6 mbar, 1700 K Removal of carbon and sulfur by heating in oxygen ca. 10-6 mbar, 1200-1800 K		I /68, 75-76.
Mo (111)	S, C	Removal of carbon and sulfur by initial oxygen treatment ca. 7x10-6 mbar, 1800 K	Oxide removal by heating in hydrogen 10-4 mbar, 1800 K	Reduction step appears negligible, can be substituted by I /71/
Mo (112)	S, C	Removal of carbon and sulfur by heating in oxygen ca. 7x10-6 mbar, 1700 K Removal of carbon by oxygen treatment as outlined under Mo (poly)		I /68/ - prolonged heating may lead to irreversible scattering to (112) planes /78/ F /79/

(continued)

Material	Major Impurities	Oxidation cycles	Reduction cycles	Comments
Ni (pol)	C, S, O	Removal of carbon by heating in oxygen 1000 s ca. 10 ⁻⁷ mbar, 900 K	Oxide removal by heating in hydrogen 1000 s ca. 10 ⁻⁷ mbar 900 K	Cycles of ArI and I combined with oxygen and hydrogen treatment /80, 81/
Ni (100)	C, S, O	Removal of carbon by heating in oxygen 7x10 ⁻⁹ to 7x10 ⁻⁶ mbar, 920-1200 K		Chemical cleaning (for ca. 0.05 wt carbon) with cycles of ArI and I /82-87/
		Removal of carbon by heating in oxygen 7x10 ⁻⁹ to 7x10 ⁻⁶ mbar, 920-1200 K	Oxide removal by heating in hydrogen 10 ⁻⁷ to 10 ⁻⁴ mbar 920-1400 K	Cycles of ArI and I combined with oxygen and hydrogen treatment /98-104/
			Reduction of surface oxides to water by heating in ammonia 370 LA, 650 K	F to remove surface nitride /12/
Ni (110)	C, S, O	Removal of carbon by heating in oxygen 820-1070 K /83, 105/ or 670-870 K /106-108/		Cycles of ArI and I combined with oxygen treatment
		Removal of carbon by heating in oxygen 820-1070 K	Oxide removal by heating in hydrogen 1000 s, ca. 10 ⁻⁷ mbar, 900 K	Residual oxygen after oxidation removed by hydrogen treatment /98, 101, 102, 109-112/
		Removal of carbon and sulfur by heating in nitric oxide 20 LA, 8x10 ⁻⁶ mbar, 1000 K	Oxygen removal by heating in hydrogen 10 ⁻⁶ mbar, 176-40 K	After initial oxygen and hydrogen treatment no depletion in sulfur, 14 h of oxidation (NO) and reduction cycles lead to a clean crystal /3/
Ni (111)	C, S, O	Removal of carbon by heating in oxygen 10 ⁻⁶ mbar 800-1170 K		Cycles of ArI and I combined with oxygen treatment /82, 83, 88, 113-117/ - Some authors used long oxygen treatments followed by repolishing the crystal /113-115/
		Oxygen adsorption at ca. 300 K		F effective in removing carbon /84, 98, 118, 119/
			Removal of residual oxygen by heating ca. 10 ⁻⁶ mbar, 820-1300 K	/98, 101, 102, 111, 120-122/
Nb (pol)	C	Decarburization by heating in oxygen 1.3x10 ⁻⁶ mbar, 2000 K		F /123/
Nb (110)	C	Oxygen treatment similar to Nb (pol)		F /124/
Pd (pol)	C, S	Heating in oxygen 1.3x10 ⁻⁶ mbar, 1000 K		F or ArF /125, 127/ most effective conditions - Lower oxidation and anneal temperatures resulted in a sample that exhibit sulfur segregation above 600 K /126/
Pd (110)	C, S	Traces of carbon removed (as CO and CO ₂) by heating in oxygen ca. 3x10 ⁻⁷ mbar, 800 K		F /128/

(continued)

Material	Major Impurities	Oxidation cycles	Reduction cycles	Comments
Pd (110)	C, S	Removal of carbon by heating in oxygen at 600 K	Oxygen removal by heating in CO oxidation to CO ₂ at 800 K	Ar-I, I, oxidation and reduction cycles /14/
Pd (111) + (210)	C, S	Heating in oxygen 1.3x10 ⁻⁶ mbar, 1000 K similar to Pd (poly)		Ar-I, F - Complete carbon removal required additional oxidation - I cycles /129-134/
Pt (poly)	C, Ca, P, S, Si, Cl, O	Removal of carbon by heating in oxygen 10 min. 3x10 ⁻⁶ mbar, 1300 K		I, Ar-I, F /135/
Pt (100)	C, Ca, P, S, Si, Cl, O	Removal of carbon by heating in oxygen 10 ⁻⁷ to 10 ⁻⁵ mbar, 1000-1300 K		One or more cycles of oxidation and I /136, 138-140/ - and addition of Ar-I /137, 141-145/
Pt (111)	C, Ca, P, S, Si, Cl, O	Removal of carbon by heating in oxygen 15 n 7x10 ⁻⁶ mbar, 1173 K		F /141/
Pt (111)	C, Ca, P, S, Si, Cl, O	Carbon removal by heating in oxygen 10 ⁻⁷ to 10 ⁻⁶ mbar, 973-1300 K		One or more cycles of oxidation and Ar-I (to remove Ca) - Different surface structures can be obtained /146-148/
Pt (100)	C, Ca, P, S, Si, Cl, O	Removal of carbon by heating in oxygen 7x10 ⁻⁶ mbar, 673-1273 K		One or more Ar-I, oxidation and F /137, 143/
Pt (100)	C, Ca, P, S, Si, Cl, O	Removal of carbon by heating in oxygen 3x10 ⁻⁷ mbar, 643 K		Ar-I /144/
Pt (100)	C, Ca, P, S, Si, Cl, O	Removal of carbon by heating in oxygen		F /138, 139, 140/
Pt (112) (113) + (133) + (122) + (121) Cl, O	C, Ca, P, S, Si	Heating in oxygen		F /150/
Pd (poly)	C, Cl, C, N	Heating in oxygen ca. 2-24 h 10 ⁻⁶ mbar, 2000-2500 K		F /151-155/
Pd (100)	C, Cl, C, N	Heating in oxygen 2.7x10 ⁻⁶ mbar, 1470 K		Ar-I, oxidation and F until clean /156/
Pd (100)	C, Cl, C, N	Heating in oxygen ca. 2 min. 10 ⁻⁷ to 10 ⁻⁶ mbar, 2500-2770 K		Several F to obtain annealed surface /151, 157, 159/
Pd (100)	C, S, B, O, Si, Ni	Carbon removal by heating in oxygen 10 ⁻⁷ to 10 ⁻⁶ mbar, ca. 1270 K	Heating in hydrogen to remove surface oxides ca. 10 ⁻⁷ mbar, ca. 600 K	Cycles of Ar-I, oxidation, I and reduction until clean - this treatment leads eventually to boron depletion /159, 160/

(continued)

Material	Major Impurities	Oxidation cycles	Reduction cycles	Comments
Rh (110)	C, S, B, O, Si, Mg	Carbon removal by heating in oxygen 7x10 ⁻⁸ to 10 ⁻⁶ mbar, 670-1300 K		Cleaning by combination of ArI, oxidation and F /161, 162/
Rh (111)	C, S, B, O, Si, Mg	Carbon removal by high temperature oxygen treatment ca. 10 ⁻⁷ mbar		F /160, 163, 164/
Ru (101)	C, S, O	Heating in oxygen 10 ⁻¹⁵ s 7x10 ⁻⁸ to 1.3x10 ⁻⁷ mbar, 1300-1500 K		Repeated oxidation and F cycles /165-176/ - ArI /168, 174, 176/
Ru (110)	C, S, O	Heating in oxygen 10 ⁻⁷ to 10 ⁻⁶ mbar ca. 1500 K	Complete oxygen removal by heating in hydrogen ca. 7x10 ⁻⁷ mbar, 1400-1500 K	F /177, 178/
Ru (110)	C, S, O	Heating in oxygen 10 ⁻⁷ to 10 ⁻⁶ mbar ca. 1500 K	Repeated cycles of oxidation and F /179-181/	
Ag (poly)	S, C, O, Cl	Carbon removal by heating in oxygen 3 min, 0.5 mbar, 673 K		F /17/
Ag (111)	S, C, O, Cl	Heating in oxygen		F /182, 183/
Te (poly)	S, C, O	Carbon and sulfur removal by heating in oxygen 10 ⁻⁷ mbar, T>2000 K		/184/
Te (100)	S, C, O	Heating in oxygen 1.3x10 ⁻⁶ mbar, 2300 K		F /185/
W (poly)	C	Carbon removal by heating in oxygen 10 ⁻⁷ to 10 ⁻⁶ mbar, 1500-1800 K	Removal of tungsten oxides by heating in hydrogen 2 min, 7x10 ⁻⁷ mbar, 2200 K /184/	Removal of oxides by F /186-190/ or F and ArF /192/
W (100) + (110) + C (111) + (112)		same treatment as outlined under W (poly)		F /183-221/
U (poly)	S, Cl, P, O, C	Chemical treatment in oxygen 30 min, 10 ⁻⁷ mbar, 1070 K	Reduction in hydrogen 10 min, 10 ⁻⁷ mbar, 1070 K	This procedure removes phosphorous and sulfur but leaves some oxygen on the surface /222/

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