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The contamination of nickel surfaces during oxidation in fused silica reaction vessels

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In many experiments involving the high temperature oxidation of nickel in fused silica reaction vessels the final oxidation products have been found to include silica as β-cristobalite. Prior to oxidation the nickel was decarburized by exposure to oxygen followed by hydrogen reduction of the remaining oxide film. The silicon of the silica was transferred from the vessel walls to the specimen as silicon monoxide formed by the reduction of the silica by the carbon monoxide produced during the decarburization step. The silicon monoxide was reduced at the metal specimen by residual carbon to form silicon which then dissolved in the nickel. Detectable contamination of the surface took place during subsequent oxidation when the silicon was preferentially oxidized at the surface. The reaction of carbon monoxide with the silica tube was enhanced by devitrification caused by previous high temperature (> 700° C) treatment. Contamination could be avoided if the tube was never heated above 700° C and was minimized at 900° C by more complete decarburization of the specimen.

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1. Introduction

An integral part of a systematic study of the oxidation of nickel at low pressures involved the preparation of reproducible, clean, oxide-free surfaces prior to exposure to oxygen. A standard procedure adopted in this laboratory to prepare such surfaces consisted of decarburizing the surface layers of the nickel by brief oxidation at low pressure followed by an extended heat-treatment in vacuum, during which residual carbon in the nickel reacted with the oxide to form carbon monoxide. The oxide film remaining after the heat-treatment was then reduced with hydrogen leaving the specimens in the required "hot-bare" condition [1] for subsequent oxidation. It was convenient to carry out this pre-treatment with the specimen contained in a fused silica reaction tube heated by a conventional electric furnace. It was discovered, however, that at 900° C the metal surface became contaminated with silicon[*]. Since the source of the contamination appeared to be the reaction vessel a series of experiments was made to establish the precise conditions for contamination and the mechanism by which the process occurred. The information thus obtained defined criteria which had to be met so that silicon contamination could be avoided during the pre-treatment of nickel specimens for future oxidation experiments using silica reaction vessels.

2. Experimental

The nickel was zone-refined, cold-rolled polycrystalline sheet, 0.025 cm thick[†], whose analysis was as follows: C 7, O 14, F 4, Si 1, C4 1, Fe 10[‡] (all in ppm atomic). The samples were prepared by chemical polishing in an acetic/nitric sulphuric/phosphoric acid mixture [2] and electropolishing in 67% sulphuric acid [3]. The oxygen[§], hydrogen[§], and carbon monoxide[‖]

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[*] In what follows the word "silicon" will be used in a non-specific sense, i.e. it will not define the chemical or physical state unless otherwise indicated.

[†] Supplied by Materials Research Corporation, Orangeburg, New York.

[‡] All other impurities less than 1 ppm.

[§] Supplied by J. T. Baker Chemical Co.

[‖] Supplied by Matheson of Canada Ltd.

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TABLE I Summary of results.

Temperature (°C)	Pre-treatment	Curve type	Silicon analysis	
			X-ray emission (μg/cm^2)	X-ray fluorescence*
700	Hot-bare	I	0.022	+
700	Hot-bare†	II	n.d.‡	–
700	Hot-bare§	I	0.14	+
700	Carbon monoxide	I	0.16	+
700	Hydrogen (10^{-5} torr)	I	0.072	+
700	Hydrogen (1 torr)	I	0.031	+
900	Hot-bare	I	0.030	n.a.‖
900	Hot-bare†	II	n.a.	–
900	Hot-bare¶	II	n.a.	+**

*“+” indicates silicon present, “– ” indicates silicon below the limit of detection.
†New quartz tube.
‡“n.d.” indicates not detected.
§Specimen was annealed in argon at 1100°C.
‖“n.a.” indicates not available.
¶Specimen was heated in vacuum for 16½ instead of 2½ h after brief exposure to oxygen at 10^{-3} torr pressure.
**This value for silicon is just above the limit of detection.

used were 99.997, 99.999 and 99.5% minimum purity respectively. Oxidation kinetics were determined using an ultra-high vacuum microbalance assembly [4]. Gas pressures were controlled and stabilized as described previously [5] and the gas composition was monitored using a Varian partial pressure gauge mass spectrometer.

The specimens were prepared for oxidation using the hot-bare pre-treatment, namely they were exposed to oxygen at 10^{-3} torr pressure for about 15 to 30 sec after a vacuum of less than 5×10^{-8} torr had been achieved at a temperature of either 700 or 900°C. This formed oxide equivalent to a uniform film about 100Å thick, which was in excess of that required to decarburize the specimen completely. The system was evacuated and the sample was heated for a further 2½ h in vacuum, during which time partial decarburization occurred. The temperature was then lowered to 600°C and hydrogen was admitted at 1 torr pressure for a period of 5 min in two successive doses to reduce the remaining oxide. The hydrogen was removed and the specimen was raised to the original temperature. The specimens were oxidized in 10^{-5} torr oxygen for from ½ to 1 h; the experiment was terminated by physically lowering the furnace while maintaining the gas pressure at 10^{-5} torr.

After removal from the apparatus some of the samples were immediately analysed for silicon using an electron excited X-ray emission technique [6, 7]. The limit of detection for silicon was considered to be 0.005 ± 0.002 μm/cm^2. The presence or absence of silicon thus determined was confirmed subsequently by X-ray fluorescence. The limit of detection for this technique was 20 ppm atomic. The X-ray emission technique gave values for silicon concentrated at the specimen surface (to a depth of about 200Å), whereas the fluorescence method determined both the superficial and in-depth contributions (to a depth of about 3000Å).

A comparison of the silicon analyses obtained by both X-ray methods showed that in general the data were consistent, i.e. the presence or non-detection of silicon by the first method was confirmed by the second. The good consistency of the two sets of data placed reliability on the X-ray fluorescence data where the corresponding X-ray emission results were not available.

Replicas were taken from the surfaces of most of the samples and were examined by electron microscopy to identify the surface structure of the silicon contamination. Selected samples were also examined by reflection electron diffraction.

3. Results

The kinetic curves obtained during oxidation at

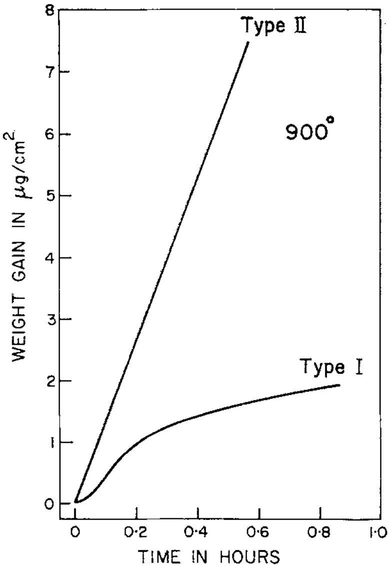

Figure 1 Oxidation kinetics at a temperature of 900° C for a contaminated specimen (Type I) and an uncontaminated specimen (Type II).

10^{-5} torr and 700 and 900° C were divided into two types, I and II. A typical type I curve obtained at either 900 (Fig. 1) or 700° C showed an initial short period of increasing rate followed by a longer decreasing rate portion. In contrast, type II kinetics consisted of a constant rate at 900° C (Fig. 1) and a very slowly decreasing rate at 700° C. X-ray analysis of samples oxidizing to give type I kinetics (Table I) indicated that silicon contamination had occurred, whereas type II behaviour was associated with silicon-free surfaces. The contaminated specimens had been pre-treated and oxidized in a silica tube which had already been used at 900° C for several hours (a so-called "aged" tube). Silicon-free samples were obtained only when the reaction vessel was new, or had not been heated to a temperature above 700° C.

Liberation of carbon monoxide occurred during the decarburization step of the pre-treatment, suggesting that this gas might be responsible for the contamination of the nickel samples. A specimen was therefore heated in an aged tube in pure carbon monoxide at 700° C and 10^{-5} torr for 1 h, removed from the system, analysed for silicon and then oxidized at 700° C in 10^{-5} torr oxygen for 1 h. After the carbon monoxide treatment the amount of silicon was barely detectable by either X-ray method but after oxidation it was much larger than had been obtained using the hot-bare pre-treatment (Table I).

When the decarburization step was extended by heating for 16½ instead of 2½ h in vacuum after the brief exposure to oxygen carbon removal from the specimen was much more complete. The silicon contaminated surface of such a specimen was removed by electropolishing away about 5 μm of metal; upon subsequent oxidation at 10^{-5} torr the amount of contaminant on the surface was found to be reduced to a barely detectable level (Table I).

The 600° C hydrogen reduction step of the pre-treatment using an aged tube did not lead to silicon contamination even though hydrogen is a reducing gas like carbon monoxide. When, however, specimens were heated in hydrogen for 1 h at 700° C either at 1 torr or at 10^{-5} torr and then subsequently oxidized they were found to be contaminated with silicon though not to the same extent as the specimen which was heated in carbon monoxide (Table I).

Sample contamination did not take place at 900° C in vacuum alone ($< 5 \times 10^{-8}$ torr) after heating for 1½ h in an aged quartz tube even though the background gas was about one-third carbon monoxide and one-third hydrogen. The subsequent oxidation of one such specimen at 900° C and 10^{-5} torr for 1¼ h in a separate all metal UHV system produced an uncontaminated surface.

Another method which has been used for preparing specimens prior to oxidation involved annealing them at 1100° C for 1 h in a fused silica tube, which had been evacuated with a rotary oil pump and then backfilled with argon to 30 torr pressure. After electropolishing to remove about 25 μm of metal one such sample was given the hot-bare pre-treatment followed by oxidation at 700° C and 10^{-5} torr for 1 h. It was found to be contaminated to a much greater extent than a specimen which had undergone the same pre-treatment and oxidation, but which had not been given an argon anneal (Table I).

3.1. Topographical examination

Electron optical examination of replicas taken from the surfaces of specimens oxidized at 900° C showed the contaminant to exist as discrete overgrowths approximating to spherical segments in shape. These overgrowths were readily distinguishable from the much larger nickel oxide crystallites and were distributed around the edges of the crystallites (Fig. 2a),

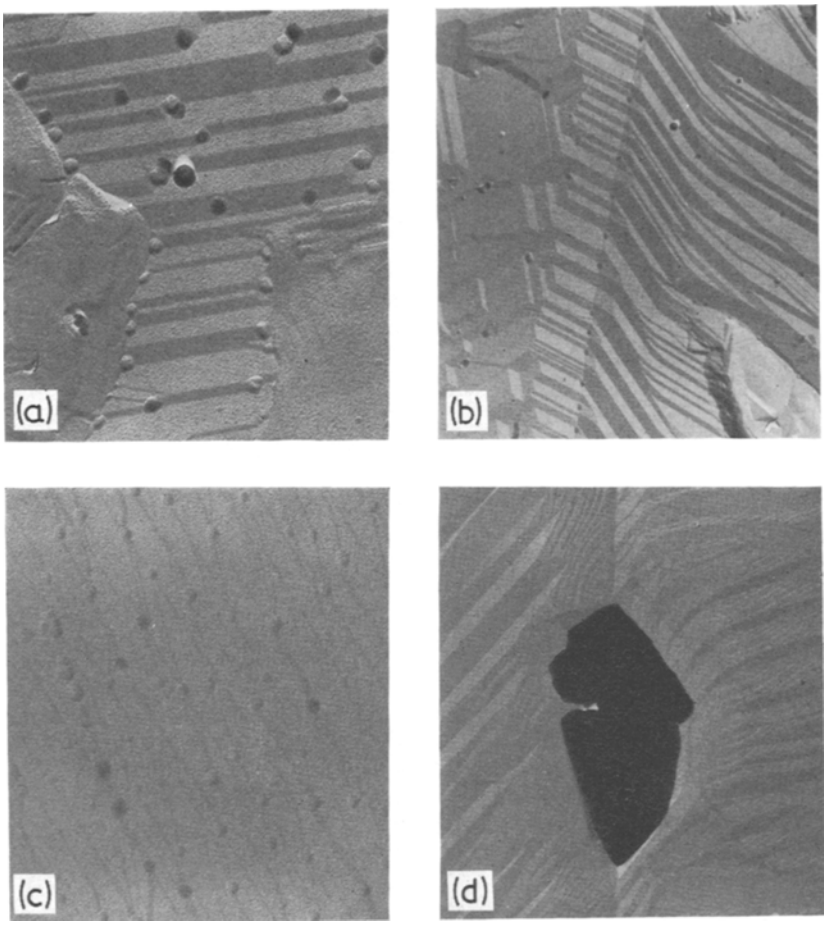

Figure 2 Replicas of the surfaces of specimens oxidized at 900°C: (a) magnification: × 20000; (b) magnification: × 8000; (c) magnification: × 30000, contaminated specimens; (d) magnification: × 16000, uncontaminated specimen.

along the junctions of metal grain boundaries (Fig. 2b), and on facet steps in the areas between the crystallites (Fig. 2c). Their size and number varied with the orientation of the metal substrate grain. The maximum diameters were about 2500Å with the average value being in the range 500 to 1000Å.

The overgrowths were always observed for any measurable level of contamination at 900°C; when silicon was not detected or was at a very low level they were not observed (Fig. 2d). The non-oxide covered areas were still faceted as in the contaminated case. In contrast at 700°C the contaminant was never seen even when the amounts detected were similar to or greater than those at the higher temperature (Fig. 3a). The areas between the oxide particles were always rougher and more faceted than those of an uncontaminated specimen (Fig. 3b). Treatment of specimens contaminated at 900°C with concentrated hydrofluoric acid for 5 sec removed the overgrowths usually without leaving any evidence of where they had existed. The silicon level as determined by X-ray fluorescence dropped to below the limit of detection. These results suggested that the contaminant was present as silica. Definitive electron diffraction patterns due to silica were only obtained from the surfaces of relatively heavily contaminated samples. The d-values from the semi-rings observed fitted those of β-cristobalite.

4. Discussion

The results of this study have shown that surfaces of nickel specimens became contaminated with silica most probably in the form of β-cristobalite

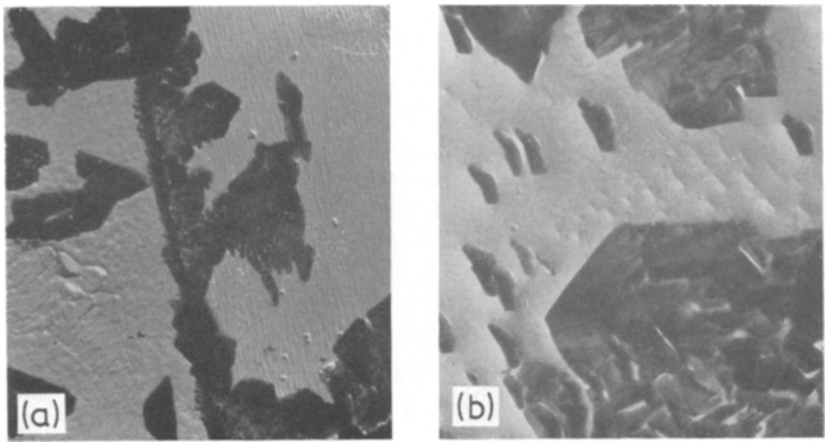

Figure 3 Replicas of the surfaces of specimens oxidized at 700°C: (a) magnification: × 4000, contaminated specimen; (b) magnification: × 8000, uncontaminated specimen.

after oxidation at 10^{-5} torr and 700 or 900°C. This occurred because they had been heated in an aged silica reaction vessel in the presence of carbon monoxide which was liberated during the decarburization step of the pre-treatment. Contamination did not occur when a new quartz tube was used; continued ageing at 900°C however, eventually led to contamination of the nickel. The rate of oxidation for such a contaminated specimen was much less than that of an uncontaminated one.

Deliberately increasing the carbon monoxide concentration by heating the sample in pure carbon monoxide greatly increased the amount of silica found after oxidation. When the concentration of carbon monoxide was relatively low, such as during heating in vacuum, silicon was not detected on the sample. When the specimen was more completely decarburized prior to the pre-treatment the amount of carbon monoxide produced upon exposure to oxygen at 900°C was considerably reduced as was also the level of contamination even in the presence of an aged silica tube.

It is well known that silica reacts with reducing gases such as carbon monoxide and hydrogen to form gaseous silicon monoxide but at much higher temperatures than those of the present study [8, 9]. The ageing of the silica tube is accompanied by devitrification, which may be one of the reasons for its reactivity towards these reducing gases at the temperatures used in this study. The most likely reactions that may occur between the hot silica tube and the carbon monoxide or hydrogen are the following:

$$SiO_2(s) + CO(g) = SiO(g) + CO_2(g) \quad (1)$$

$$SiO_2(s) + H_2(g) = SiO(g) + H_2O(g) \quad (2)$$

The value of the free energy change for these reactions is positive at either temperature. A relatively high concentration of carbon monoxide coupled with the removal of silicon monoxide by reaction with the specimen would however favour these reactions in the forward direction.

It is suggested that during the decarburization step at low pressures gaseous silicon monoxide was produced according to reaction 1. The most likely reaction of this gas with the specimen is with the carbon dissolved in the metal according to

$$SiO(g) + [C]_{Ni} = [Si]_{Ni} + CO(g) \quad (3)$$

The silicon thus formed appeared to dissolve in the exposed bare metal since it was barely detectable by X-ray emission on the surface of the specimen which was analysed immediately after the carbon monoxide treatment; the amount dissolved was also undetectable by X-ray fluorescence. During the subsequent oxidation this dissolved silicon was concentrated on the surface by diffusion and was oxidized to form silica as β-cristobalite; it was then readily detected by either X-ray method.

Crystalline β-cristobalite was also found by Garmon [10] on the surface of nickel single crystal spheres, when these were heated in Vycor (96% silica glass) reaction vessels at temperatures as low as 500°C under oxidizing conditions at pressures of 2×10^{-6} torr for periods of 1 h or more. It was also found that contamination was most common when the

Vycor tube had been aged to the point of devitrification. Similar overgrowths of silica were observed also on the surface of oxidized copper single crystal spheres [11]; the topography of such surfaces bore a close resemblance to that found in the present study for samples oxidized at 900°C (Fig. 2). In the case of the specimen pre-annealed in argon the contamination had occurred as a direct result of this treatment. At 1100°C the silicon appeared to have diffused into the metal to a considerable extent since contamination of the surface took place during subsequent specimen pre-treatment and oxidation even after the prior removal of a substantial amount of metal.

5. Summary and conclusions

The preparation of clean, oxide-free, silicon-free nickel surfaces for subsequent oxidation by a pre-treatment involving decarburization of the metal by exposure to oxygen and then reduction of the excess oxide film by hydrogen was possible using silica reaction vessels only if these latter were never heated to temperatures above 700°C. Carbon monoxide was generated during the decarburization step and this gas reacted with a silica tube which had been heated for more than a few hours at 900°C. Silicon contamination of the samples resulted when the above pre-treatment was carried out at 900°C. Contamination may be avoided at temperatures above 700°C if the nickel is completely decarburized, so that carbon monoxide is not produced when the metal is exposed to oxygen.

The contamination of specimens by silica is aggravated by the fact that most high temperature apparatuses involve heating both the silica-containing reaction vessels as well as the specimens. Such contamination could be avoided by heating only the specimen using techniques such as infra-red radiant or induction heating, in which the walls of the reaction vessel are kept relatively cool.

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