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Influence of Oxygen Contamination on the Pd–Si Solid-State Reactions Activated by Mechanical Alloying

M. Magini,* F. Padella, P. Delogu, T. Dikonimos Makris, and S. Turtù

ENEA-INN-Numa, CRE-Casaccia, Via Anguillarese, Rome, Italy

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The influence of oxygen contamination on the solid-state reaction (SSR), induced by ball milling, between palladium and silicon, has been investigated by X-ray diffraction and surface anal. X-ray analysis reveals that about 1 wt % of oxygen is able to inhibit the SSR between palladium and silicon, while at higher oxygen content already formed phases are destabilized. The picture merging from photoemission spectra in connection with X-ray analysis indicates that silicon is bonded both to palladium and oxygen at the surface of palladium particles with an increasing silicon enrichment with increasing oxygen contamination.

1. Introduction

In the 1980s mechanical alloying has been largely investigated as a preparative tool able to produce besides the already known oxide dispersion-strengthened (ODS) alloys a large variety of equilibrium and nonequilibrium compounds. As a preparative tool, two factors are fundamental to keep under control the process: the contaminations (from the milling tools and the milling atmosphere) and the energy transferred from the mill to the processed powder.

In a previous paper we have examined the problem of the energy transfer and have been able to rationalize in a coherent picture experimental data coming from different milling apparatuses and different milling conditions.[1] Aim of the present paper is to give some hints about the importance of contaminations coming from the air.

Contaminations, in fact, are often responsible of apparently unexpected phenomena occurring during the milling process, as already reported in literature.

Firstly, Mizutane and Lee[2] explained the partial crystallization of different Ni–Zr alloys, milled beyond the amorphous phase formation, by the presence of oxygen and iron debris. Yvon and Schwartz[3] detected that even traces of iron contaminations modified the phases obtained by milling Al–Ge powders.

The effect of iron contamination is probably less severe than those coming from the air due to seal leaking and to the periodical sampling of the same powder under milling. This is particularly true when dealing with elements known as getters, such as titanium. By milling Ti–Al powders, large contaminations from both oxygen and nitrogen have been detected[4,5] and found that they were responsible of the formation of an fcc phase recognized as (Ti,O)N mixed oxide nitride isomorphous with TiN.[4,6] Further, oxygen contamination was responsible of an apparent "demixing" phenomenon observed by milling for long times the Pd–Si mixture.[7,8]

It is well accepted that the mechanism of SSR by ball milling proceeds through the repeated formation of clean element surfaces at which reactions start up. Reaction with oxygen (or of any other contaminant) is surely favoured by the fresh surfaces formation and therefore strong effects on the SSR by the contaminations are expected.

Moreover, while there is abundant experimental evidence (e.g., from X-ray, SEM, TEM, DSC) about the behavior of the "bulk" of the milled systems investigated, very little has been said about the state of surfaces during the milling process.

We have acquired a good experience with the Pd–Si system which has been milled in a large number of conditions.[1,7–10] The system therefore seems to us suitable to investigate the effect of oxygen contamination on the SSR. The aim has been pursued by monitoring the oxygen content during milling and correlating it with "bulk" (X-rays) and "surface" (XPS-XAES) analysis.

2. Experimental Section

2.1. Ball Milling. The ball milling processes was done by both planetary (Fritsch "Pulverisette 5") and shaker devices (spex 8000). Cylindrical tempered steel vials of 250 cm^3 were employed with the planetary mill. They were sealed with covers provided with O-rings and stopcocks in order to carry out the milling with a slight overpressure of argon gas. Balls of different diameters of the same material of the vials (stainless steel) have been used. The rotation speed of the plate supporting the vials can be varied by a potentiometer and has been accurately measured. In the following, the experiments carried out by the planetary mill can be identified by the rotation speed, expressed in rpm (revolutions per minute), reported in each figure. The shaker mill has a fixed vibration speed an the milling was carried out with its vial closed in air or in argon gas. The experiments carried out by the shaker mill have been identified by the notation "spex" in each figure.

Pure silicon (99.9%, 250 mesh, Fluka) and palladium (99.9%, 60 mesh, Ventron) were mixed to a $Pd_{80}Si_{20}$ composition. The purity of the $Pd_{80}Si_{20}$ starting mixture has been verified by oxygen

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LECO analyser (see below) and has been found to be affected by 0.15 wt % of oxygen giving thus a real composition of $Pd_{79,4}Si_{19,8}O_{0,8}$ with Pd/Si = 4.01.

Iron contamination, after long milling time, has been checked and was lower than 1 wt % (e.g., after 30 h at 300 rpm we detected about 0.5% of iron).

The experimental milling procedure has been described elsewhere.[11] The weight ratio between balls to powder was usually 5.

2.2. X-rays, DSC Measurements and Oxygen Analysis. X-ray diffraction patterns were recorded by an automatic diffractometer (Seifert VI), using Mo Kα radiation. The X-ray specimens were prepared sampling at intervals and spreading out the powder on a 3M adhesive tape. Differential scanning calorimetry (DSC) was performed using a Perking-Elmer DSC 7, working with a scan rate of 40 °C/min and under a constant high purity argon flux of 30 cm^3/min.

Thermal treatments have been carried out directly in DSC or in a tubular oven under argon atmosphere.

To monitor the contamination from air, the oxygen content was analysed with a LECO TC 136 gas analyzer during milling and/or at the end of a given milling process.

2.3. XPS-XAES Analysis. X-ray photoelectron spectroscopy (XPS) and X-ray-induced Auger electron spectroscopy (XAES) analysis were performed using an ESCALAB MKII V.G. spectrometer equipped with a hemispherical energy analyser, the system operating at a base pressure of 10^{-9} mbar. The Al Kα line (without monochromator) at 1486.6 eV was used to record the Pd 3d, Si 2p spectra; Si KLL Auger spectra were excited by the Bremssthralung radiation associated with the Al Kα line. The electron analyzer was operated in the fixed analyser transmission (FAT) mode at a constant pass energy of 20 eV, giving a fwhm of the Ag 3d line equal to 1.2 eV. The cleaning of the samples surface was performed *in situ* by argon ions bombardment with a static ion gun (Ar^+ ions energy equal to 5 kV).

The spectra were acquired for the as received samples and after an argon ions bombardment for a time necessary to reach a constant value of the oxygen content.

A wide scan (0–1000 eV) including all the principal photoelectron transitions relative to every element was acquired for each sample to identify the contamination species, besides the main constituents Si, Pd, and O.

XPS quantification usually is performed by measuring the area of the most intense photoelectron peak for each element, as it is proportional to the concentration, and dividing it by the appropriate sensitivity factor which accounts for the different photoionization cross sections. For these samples, however, the overlapping of the O 1s and Pd 3p transitions (531 and 533 eV) makes it impossible to determine the oxygen content by the usual procedure. Therefore the quantitative analysis was performed only for Si and Pd, measuring the Si 2p and Pd 3d peaks area from the wide scan.

The Si 2p and Si KLL detailed spectra were recorded, with the aim to identify the silicon bonds through the study of the line shapes, the energy positions and especially the Auger parameter (AP), defined as the difference in energy between an Auger peak and a photoelectron peak of the same element. This parameter being strongly dependent on the chemical environment,[12] offers a way to circumvent the difficulty to identify the silicon chemical states by the usual evaluation of the chemical shift. In fact the separation between the Si 2p line energy position of the pure element and of the intermetallic Si–Pd phase (~0.5 eV) is below the energy resolution of the instrument. Thus the different silicon bonds occurring on various samples were identified by measuring the AP and comparing them with those of standard pure silicon (Si [1,1,1]), silicon oxide (SiO_2), and Si–Pd phases (Pd_3Si and Pd_4Si). We obtained 1715.9 eV for pure silicon, 1711.4 eV for the silicon oxide, and 1716.9 eV for both Si–Pd phases, all in good agreement with literature.[13]

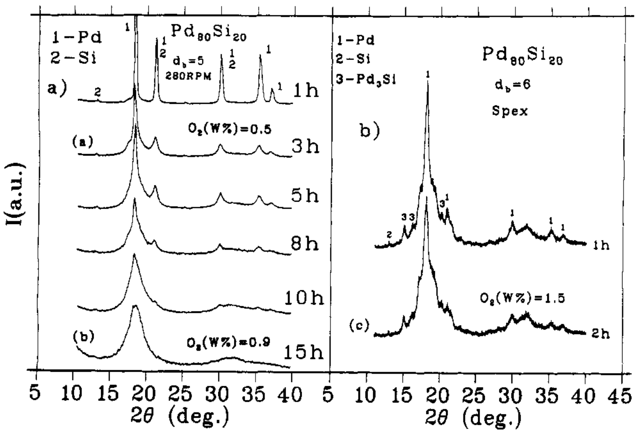

Figure 1. X-ray patterns as a function of the milling time for the $Pd_{80}Si_{20}$ composition. In given milling conditions (indicated hereafter by d_b = ball diameter and rpm = rotation speed in revolutions per minute) the system evolves towards the amorphous phase (a); in others, an intermetallic compound is formed (b). Here, and in the following figures, samples, indicated on the X-ray patterns by letters and by oxygen content (in weight percent), have been selected for XPS analysis (see section 3.3).

A curve-fitting routine was used to decompose the Si 2p line to determine the silicon fraction involved in the intermetallic bond with palladium and the remaining oxidized one, the latter giving also an indication of the variations in the oxygen content for the different samples, since, as explained above, a direct measure of the oxygen concentration was not possible.

3. Results and Discussion

3.1. Solid-State Reactions between Pd and Si. When submitted to mechanical action, palladium and silicon always react. This is certainly true for the $Pd_{80}Si_{20}$ composition, hereafter considered, and is largely true for many other compositions at present under investigation. The $Pd_{80}Si_{20}$ system possesses a peculiarity that we have not been able to detect at the same level of clarity in any other system up to now investigated. Depending on the milling conditions the system clearly follows two different and distinct pathways. The behavior is summarized in Figure 1. Figure 1a shows that, in given milling conditions, the system gradually evolves toward the formation of an amorphous phase. Figure 1b shows that, in other conditions, Pd and Si immediately react to form the intermetallic compound Pd_3Si (in mixture with minor fractions of other intermetallic compounds). The formation of the intermetallic is accomplished in the very early milling stages. The formation of the amorphous phase is gradual but, again, the path is chosen at once since the broadening of the Pd lines, instead of the appearance of the intermetallic lines, is always indicative of the amorphous pathway.

We have already analyzed the energy-transfer conditions allowing one of the two solid-state reactions described as a function of the adopted milling conditions and the reader is referred to ref 1 and 11 for further details. However, we think it useful, for a better comprehension of the following experiments, to resume in Figure 2 the energy map showing the different pathways undergone by the Pd–Si system under different milling conditions.

3.2. Oxygen Competition with Palladium in the Reaction with Silicon. Evidence from X-rays. From thin films literature (see, e.g., ref 14) it is well-known that a thin oxide layer in the metal–Si systems is nearly always

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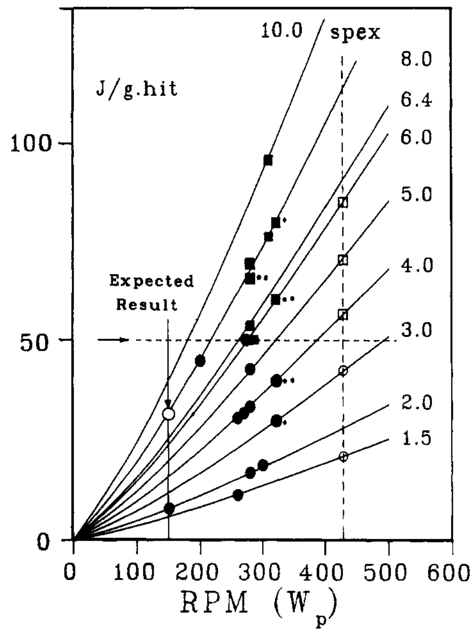

Figure 2. Energy map for the Pd–Si system. The continuous lines represent the energy transferred per hit and per unit of mass (J/g hit) as a function of the rotation speed of the planetary mill in RPM (revolutions per minute) for each ball diameter used (given in millimeters near each curve). Each full and open symbols represent experiments carried out on planetary and shaker mill, respectively. Squares and circles identify the intermetallic and amorphous pathway, respectively. The experiments have been carried out on the $Pd_{80}Si_{20}$ composition with exception of $Pd_{83}Si_{17}$ (◇) and $Pd_{86.5}Si_{13.5}$ (**). For the label "expected result" and the corresponding open circle, see text (section 3.2). For detail on the energy map see ref 1.

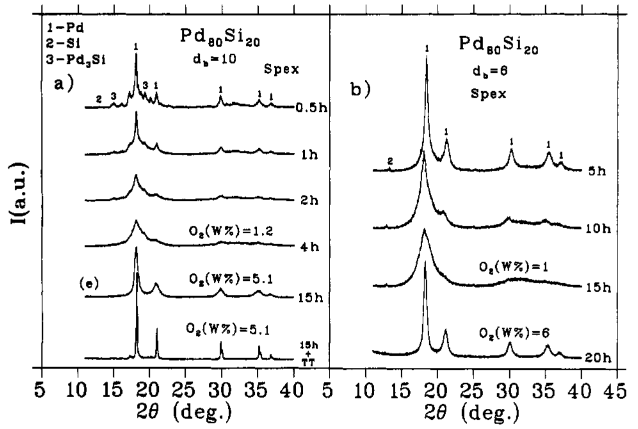

Figure 3. Examples of demixing phenomenon promoted by oxygen contamination in intermetallic (a) and amorphous phases (b).

present at the interface and it is enough to seriously influence the kinetic behavior of silicide formation. Or, if the layer is thick, it can actually change the composition of the first formed silicide.

In the mentioned cases, the amount of oxygen involved may be very low (less than the atomic percent level). In our case much greater contaminations are considered, and its effects on selected examples will be examined in detail.

Already Reacted Systems. By milling for long time without taking care of oxygen pickup, the oxygen will react with silicon *subtracting it* from the already formed phases (amorphous or intermetallic). This is clearly evident in Figure 3.

In the Pd_3Si intermetallic network Pd and Si are directly bonded in the well-defined crystallographic geometry.

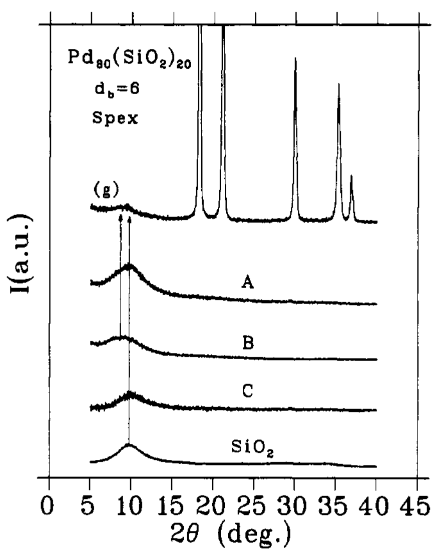

Figure 4. X-ray pattern of the $Pd_{80}(SiO_2)_{20}$ after 10 h of milling. The broad halo at low angle is the contribution from the tape sample supporter and from amorphous Si-O_x (see text). Lower curves: (A) supporting tape plus starting SiO_2; (B) supporting tape alone; (C) difference between A and B. SiO_2: bulk specimen of SiO_2 showing its amorphous nature. Vertical weak lines indicates the position of the maxima from SiO_2 and from the tape.

When the oxygen content increases from about 1% to 5% (see Figure 3a), the silicon atoms are subtracted from the interiors of the ordered domains in order to form *Si–O_x at the surface of the grains*. As a result only the palladium lines are seen at the end of the demixing process since the "bulk" of the system has been destroyed by oxygen. A similar phenomenon occurs if the already formed phase is an amorphous phase (see Figure 3b).

From a thermodynamic point of view, the heats of formation of SiO_2 (880kJ mol^{-1} [15]) and Pd_3Si (150 kJ mol^{-1} [16]) favor the formation of silicon oxide with respect to the already formed intermetallic compound.

From the diffractometric point of view, after the demixing process, silicon is no more detectable. A part from the masking effect of palladium with respect to silicon already described in connection with the very early stages of milling,[7] after the demixing process, silicon is very likely present only at the surfaces of the palladium particles in order to form an amorphous Si–O_x layer (where x can reach at the maximum the value of 2).

A thermal treatment of the demixed sample (see Figure 3a) does only promote the recovery of palladium grain size (i.e., sharpening of the Pd lines) but does not allow detection of silicon.

To better understand the behavior of oxidized silicon, we have purposely examined a $Pd_{80}(SiO)_2)_{20}$ powder mixture where starting SiO_2 instead of silicon has been milled with palladium. After 10 h of milling only palladium lines are seen in the X-ray diffractogram apart from an amorphous halo at small angles due to both amorphous SiO_2 and the scattering from the sample tape holder (see Figure 4).

A specimen containing only the starting SiO_2 spread on the tape gives a broad halo (Figure 4 curve A). Subtracting

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(16) De Boer, F. R., Boom, R., Mattens, W. C. M., Miedema, A. R., Niessen, A. K., Eds.; *Cohesion in Metals*; North Holland: Amsterdam, 1988; Chapter III.

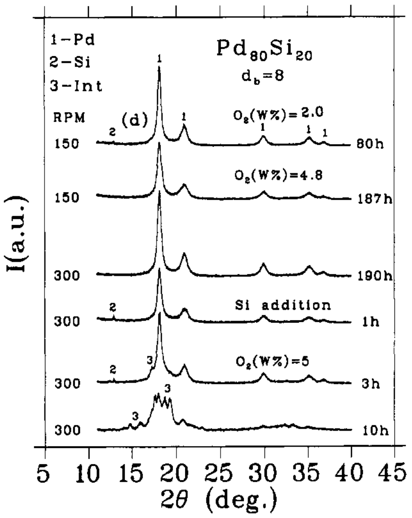

Figure 5. Example of no reaction at all between Pd and Si due to oxygen contamination and influence of fresh silicon addition (see text section 3.2).

Table 1. Real Atomic Composition of a $Pd_{80}Si_{20}$ Sample as a Function of the Oxygen Contamination in Weight Percent

O_2, wt %	stoichiometric composition of nominally $Pd_{80}Si_{20}$
1	$Pd_{75.7}Si_{18.9}O_{5.4}$
1.4	$Pd_{73.6}Si_{18.4}O_{8.0}$
2	$Pd_7{}^{1.7}Si_{17.9}O_{10.4}$
3	$Pd_{68.0}Si_{17.0}O_{15.0}$
4	$Pd_{64.7}Si_{16.2}O_{19.1}$
5	$Pd_{61.6}Si_{15.4}O_{23.0}$
6.6	$Pd_{57.1}Si_{14.3}O_{28.6}$
8	$Pd_{53.6}Si_{15.4}O_{33.0}$
10	$Pd_{49.1}Si_{38.6}O_{28.6}$
12.5	$Pd_{44.0}Si_{11.0}O_{45.0}$

from A the curve B, due to the tape holder alone, we obtain curve C whose maximum and shape fairly well correspond to the pattern of amorphous quartz also reported on Figure 4.

No Reaction at All. We said that palladium and silicon always react when submitted to mechanical action. This is true if the oxygen content is kept at low level otherwise the competing reaction of oxygen with silicon will totally inhibit the silicon–palladium reaction.

An example of no reaction at all is given in Figure 5. In this case the $Pd_{80}Si_{20}$ composition has been firstly milled at a low energy condition (150 rpm and ball diameter of 8 mm) and sampling every 10 h by opening the vial in air (thus allowing some oxygen pickup).

On the basis of the milling conditions, described on Figure 2, we would expect the formation of an amorphous phase. This has been indeed verified with an even lower energetic input as shown in the map of Figure 2 in correspondence of 150 rpm and ball diameter of 2 mm.

In our case it is shown that after 80 or 187 h of milling (see Figure 5) only broadening of the palladium peak lines has been achieved. Increasing the rotation speed at 300 rpm is ineffective: no reaction takes place between Pd and Si. The explanation is given by the oxygen content. It already reaches the value of 2.0 wt % after 80 hours, (i.e., 10% by atoms, see Table 1). In this condition, evidently, the oxygen atoms are enough to saturate, at the surface, the silicon atoms completely hindering thus the Si–Pd reaction.

A further confirmation of this interpretation is given by the subsequent steps shown in Figure 5. If, after 190 h of milling (and an oxygen content of about 5 wt %), we add a proper evaluated amount of fresh silicon, the Pd–Si reaction takes places forming the intermetallic compound expected for this condition of milling (lower curves of Figure 5).

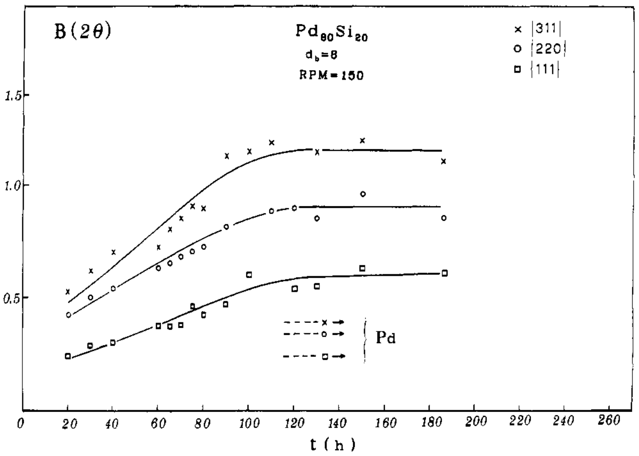

Figure 6. Broadening of the palladium peak lines measured as line width at half-maximum intensity versus the milling time in hours for the experiment of Figure 5. The arrows in the low part refer to the plateau reached with pure palladium. Lines have been drawn through the experimental points for clarity.

The previous example of no reaction at all deserve further comments. When the reaction between Pd and Si is inhibited by the presence of oxygen the line broadening registered on the palladium lines is different from the one observed with pure palladium.

The broadening of the palladium peaks of the experiment of Figure 5 are reported in Figure 6 as a function of the milling time. The widths of the peaks monotonically increase up to saturation values for long milling times. These values are *much larger* than those obtained by milling pure palladium as can be seen from the figure. In other words a much greater crystallite size reduction of the palladium particles can be achieved in the presence of silicon than in absence.

Size–strain analysis by the well-known Warren-Averbach methods has been performed on these samples on a previous paper[17] showing that pure palladium reaches a plateau value around 40 nm while palladium crystallites reaches a few nanometers scale (5–10 nm) in the presence of silicon. Further, the palladium particles in presence of silicon underlie a strain approximately twice the one of pure palladium. All the information obtained, therefore, indicate that even in the case we have called of no reaction the silicon (partially oxidised) is able to "attack" the palladium particles promoting both a crystallite size reduction and an increasing network strain with respect to pure palladium. Therefore silicon *does not react at bulk level* (X-ray) *but does interact* in some way with palladium in agreement with subsequent indication given by surface analysis (see section 3.3).

Very Large Oxygen Contamination. Some milling experiments have been purposely carried out in air in order to introduce large contaminations in the milled mixture. Table 1 shows that from the stoichiometric point of view around 6,6% by weight of oxygen two oxygens for each silicon are introduced so that oxygen beyond this limit cannot be saturated by silicon. The experiment reported

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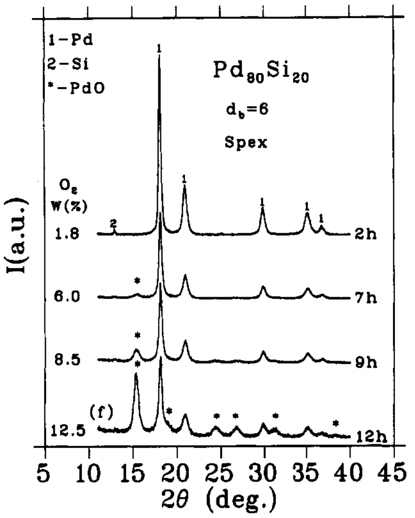

Figure 7. Formation of palladium oxide (Pd-O JCPDS no. 41-1107) due to very large oxygen contamination.

on Figure 7 shows that the onset of formation of palladium oxide just begins around the value of 6% of oxygen. When oxygen reaches 12.5% all the X-ray lines of the Pd-O are clearly seen in the X-ray pattern. In the conditions described above we have been able to promote the formation of the palladium oxide for which the thermodynamic driving force is scarce (ΔH of formation = −90 kJ mol^{-1}).

Comparison with Thermal Activation. The influence of oxygen on the Pd–Si reactions has been verified by thermally activating a sample milled for short time and prone to undergo one of the two typical pathways. The sample of Figure 1 at 1 h (reported in Figure 8a) has been treated on a differential scanning calorimeter up to 650 °C under a flux of air (Figure 8b) and under a flux of Argon (Figure 8c). The treatment in air prevents also in this case the reaction between palladium and silicon while in argon gas the elements, already premilled and intimately mixed, are able to react giving a mixture of intermetallic compounds.

3.3. State of Surfaces. Evidences from XPS-XAES. Selected samples, labeled by letters from a to g in the previous figures, have been analyzed by XPS. A standard sample of $Pd_{80}Si_{20}$ (labeled by s) has been obtained by melting appropriate amounts of the starting elements in a furnace under argon atmosphere. The melt has been slowly cooled at room temperature (2 days), and the formation of the expected equilibrium compounds has been verified by X-ray analysis. Figure 9 shows the Si2p photoemission spectra in order of increasing level of oxygen contamination, and Table 2 summarizes the more relevant results from XPS analysis.

A part from the standard sample which is oxygen free and only shows Si–Pd bond, all the other samples show both Si–Pd and Si–O bonds with no evidence of free silicon (see section 2.3). In all the samples, therefore, *irrespective of the degree of reaction* between Pd and Si, all the silicon atoms, at surface, are engaged with both palladium and oxygen.

From the XPS spectra alone, one cannot establish whether or not the same silicon atoms are *contemporarely* bonded to palladium and oxygen. Indeed, considering the standard sample for the "pure" Si–Pd bond (curve s) and curve g (amorphous SiO_2) for the "pure" Si–O bond, no peak shifts, within instrumental resolution, are detected in the other samples with respect to the reference ones. However, the cross comparison from bulk (X-ray) and surface analysis strongly supports the hypothesis that, at the surface, silicon atoms are *contemporarely* bonded to both palladium and silicon. The curve d, in Figure 9, of the "nonreacted" sample is an exemplification. At the surface level silicon and palladium are electronically bonded as well as silicon and oxygen. If the two peaks of curve d were solely due to the presence of Si–Pd and Si–O bonds in *different locations* of the sample, why should Si and Pd not react, as expected from the milling conditions, in order to form, at bulk level, the intermetallic compound? The answer is that the silicon already bonded to palladium is also bonded to oxygen, and this fact inhibits the reaction to proceed at bulk level, i.e., in the interior of palladium domains.

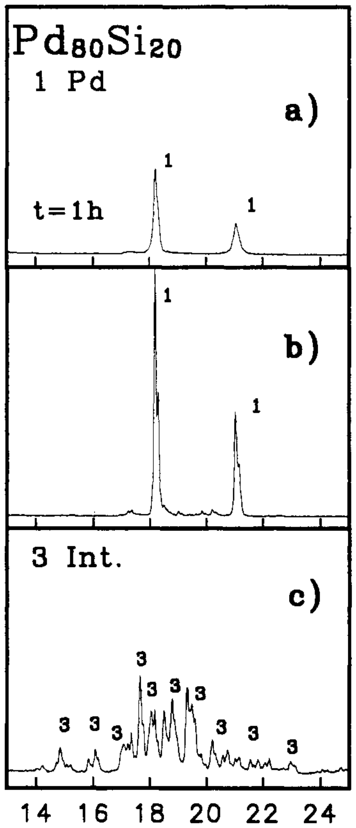

Figure 8. Sample of Figure 1a at 1 h of milling (a) as such and after treatment in DSC up to 650 °C in air (b) and in oxygen atmosphere (c).

The observation from X-ray line broadening (see Figure 6) that even in absence of solid-state reactions some interaction between silicon and palladium particles was to be expected, receives a direct confirmation by surface analysis. The palladium crystallite size reduction may be explained not only by the hardness of silicon acting as a wedge at microscopic level. The presence of surface Pd–Si–O bonds inhibits, in fact, the rewelding process of the fractured surfaces thus allowing the attainment of a lower crystallite size in $Pd_{80}Si_{20}$ than in pure palladium.

Although in a small fraction, palladium silicon interaction is present in the $Pd_{80}(SiO_2)_{20}$ sample (g in Figure 9) indicating thus that during milling some Si–O bonds of SiO_2 have been broken in favor of the formation of Si–Pd bonds. Evidence of broken Si–O bonds in SiO_2 under mechanical action have been already reported by researchers investigating the pathogenicity of silicon prepared by mechanical grinding.[18]

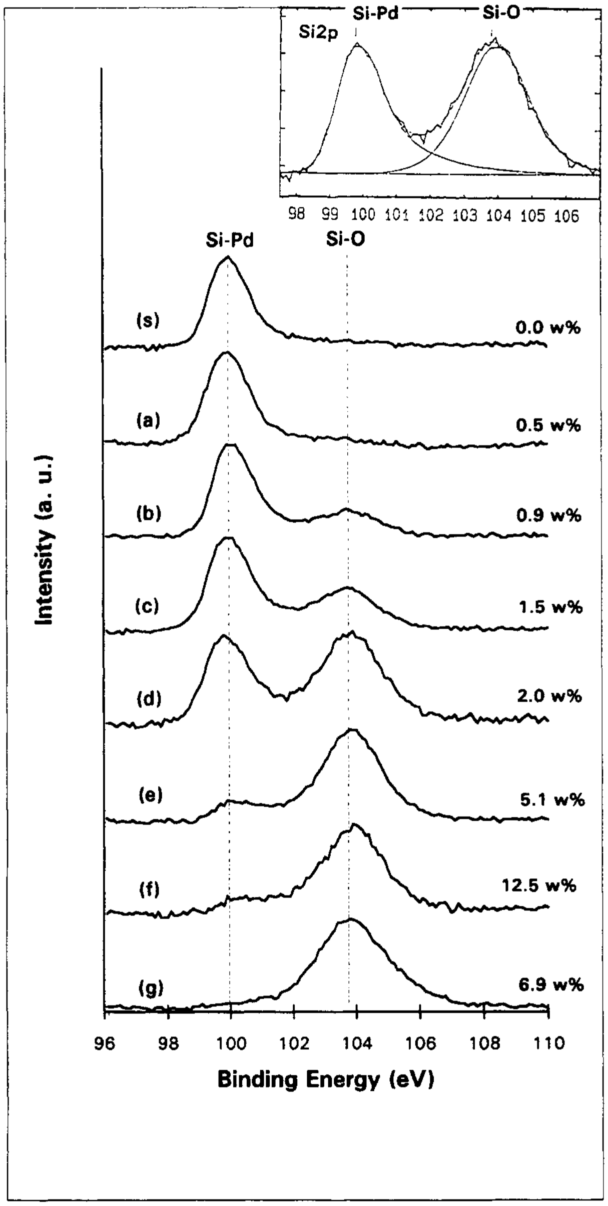

Figure 9. Si_{2p} photoemission spectra for selected samples shown in previous figures (a–g). S represents a standard $Pd_{80}Si_{20}$ alloy obtained by melting procedure (see section 3.3). The Si–Pd and Si–O contributions of the spectra have been separated by fitting procedures (see onset). The oxygen contamination in weight percent is reported on each spectrum.

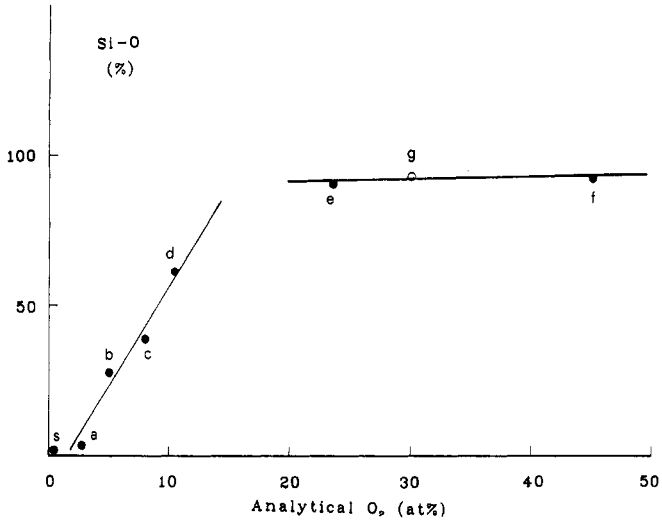

Figure 10. Percents of Si–O (derived from the fitting of the spectra in Figure 9) are shown in function of the oxygen contamination (chemical analysis).

Table 2. Surface Analysis Results for the Samples Indicated in Column 1 Having the Analytical Oxygen Content Reported in Columns 2 and 3 (Values in Parentheses in Column 2 Give the Estimated Errors in Chemical Analysis)[a]

sample	analytical O_2 wt %	analytical O_2 at. %	Si–O, area %	Pd/Si
$Pd_{80}Si_{20}$				
s				4.0
a	0.50 (3)	3.0	3	4.0
b	0.90 (5)	4.9	28	3.3
c	15(1)	8.0	39	3.1
d	2.0 (1)	10.4	61	2.8
e	5.1 (3)	23.4	91	2.2
f	12.5 (6)	45.0	94	2.3
$Pd_{80}(SiO_2)_{20}$				
g	6.9 (3)	30.0	93	1.3

[a] Column 4 gives the area percent of Si–O interaction determined from the deconvolution of the Si2p photoemission spectra given in Figure 9, and column 5 gives the ratio of Pd and Si in atoms.

Since the evaluation of the oxygen content at surface is not possible as we have seen in section 2.3, the correlation between bulk oxygen contamination and the presence of surface oxygen can be evidenced by the Si–O bond registered in the Si2p photoemission spectra (Figure 9).

If we plot the precent of Si–O (column 4 Table 2) versus the analytical oxygen content, we obtain the trends shown in Figure 10. In a first region by increasing the oxygen contamination Si–O rises accordingly. Then, a saturation value is reached at about 90% of Si–O. Samples e and f, having a quite different oxygen contamination (5 and 12.5%), have the same level of silicon bonded to oxygen at surface. Figure 7, indeed, shows that around 6 wt % of oxygen begins the formation of palladium oxide. Therefore oxgyen beyond this limit does not bond anymore to silicon but promotes the Pd–O formation diffusing from the surface to the bulk.

It should noticed that the Si–O percent in samples e–g (see Figure 10) is nearly the same, showing that the silicon saturation in e and f is similar to that of $Pd_{80}(SiO_2)_{20}$, which can be assumed to represent the maximum level of silicon oxidation reachable by milling $Pd_{80}Si_{20}$.

Column 5 of Table 2 gives the atomic ratio of total palladium and silicon. It can be seen from the table that only on the standard oxygen-free (s) and on the lowest oxygen-containing (a) samples, the Pd/Si ratio measured on the surface layer is equal to the nominal composition of Pd/Si = 4. Despite the uncertainty intrinsic to surface analysis, an unambiguous enrichment of silicon, at increasing oxygen level, merges from the Pd/Si ratios. In other words, silicon in the presence of oxygen, tends to stay at the surface of palladium particles irrespective to the degree of reaction undergone by Pd and Si (detectable by X-rays) but depending only on the degree of oxygen contamination. The more the sample is oxidized at bulk level the higher is the silicon enrichment at the surface. Sample f is not an exception to this trend because, as we have said, the extra oxygen with respect to sample e or sample g has been engaged in the formation of palladium oxide.

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(18) Fubini, B.; Giannello, E.; Pugliese, L.; Violante, M. *Solid State Ionics* **1989**, *32/33*, 334.

3.4. Final Comments. From a thermodynamic point of view the reaction of silicon with oxygen (to form e.g., SiO_2) is favored with respect to that of silicon with palladium (to form, e.g., an intermetallic compound). If the oxygen content is kept at low level, that is on the order of 1 wt % (as can be deduced from the actual and other experiments), then the fresh surfaces of palladium and silicon created by milling can react to form an intermetallic compound or an amorphous phase. If the oxygen is not kept under control, then the solid-state reactions between palladium and silicon are inhibited by the competing silicon–oxygen reaction and, at bulk level, we register the behavior, described in Figure 5, of no reaction.

At the surface level, however, we have evidence of a silicon–palladium interaction and the crystallite size reduction of palladium particles in $Pd_{80}Si_{20}$ with respect to the one occurring in pure Pd (see Figure 6 and ref 17) is certainly due to surface silicon. Despite of the detected Si–Pd interaction at surface level, the Si–Pd reaction does not proceed at bulk level so the picture merging is that oxygen engages the silicon, also bonded to palladium, at the surface layer empeding to it a further reaction with palladium.

The preferential affinity to form Si–O than Si–Pd bonds is even more clear considering the "demixed" samples of Figure 3. Here the Si–Pd reactions proceeded at bulk level but the oxygen has been able to promote silicon diffusion from the bulk to the surface thus destroying the previously formed phases.

The ability of a low content of oxygen in both preventing reactions and destabilizing products already formed must be taken in serious considerations by people working on mechanical alloying. Neither palladium nor silicon can be considered as "getters" such as titanium and zirconium, for which even more important problems can likely rise. Controversial claims made in the literature about the achievement of new and/or metastable phases or apparently unexplainable pathways should be carefully reviewed in light of contamination from both air and milling tools.

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