

Electroless plating of polymers: XPS study of the initiation mechanisms

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This paper deals with polymer metallization by the electroless process. Previous studies in the authors' laboratory have shown the interest of plasma surface treatments of polymers before chemical metallization and the significant role they play towards the chemisorption of a catalyst (Pd^{2+} ions). Three different processes are used to activate the polymer surface for electroless deposition: namely, the one-step process using a mixed SnCl_2 – PdCl_2 solution, the conventional two-step process using SnCl_2 , then PdCl_2 , and a new simplified process (using only PdCl_2), previously proposed by the authors. According to the process utilized a variable initiation time is observed before metal deposition takes place in the metallization bath. The surface phenomena occurring on the polymer during this initiation time are studied by XPS through the chemical form of palladium adsorbed on the surface and through changes in the Pd surface concentration. A reaction mechanism relative to the initiation of the metallic ion reduction is proposed.

Keywords: *electroless plating, polymer metallization, plasma, palladium, surface treatment*

1. Introduction

The electroless plating of polymers by nickel or copper is possible on condition that catalytic sites are created on the surface to be metallized. These sites are constituted by palladium nuclei chemisorbed in solution. Different methods have been proposed to perform this chemisorption: the conventional two-step process which uses, successively, dilute solutions of SnCl_2 then PdCl_2 [1–8], and the one-step process which uses a mixed SnCl_2 – PdCl_2 solution [5, 6, 9]. The authors have recently proposed [10–12] a simplified method which utilizes a dilute PdCl_2 solution acting directly on a substrate whose surface carries nitrogenated groups grafted by NH_3 or N_2 plasma treatment. In the same way, a catalytic activation by PdCl_2 was used by Hamaya *et al.* [13] on glass substrates previously treated in an aminosilane solution and by Burrell *et al.* [14] on polyetherimide. All these methods lead to the adsorption of tin/palladium or palladium nuclei which are not always catalytically active. This subject has been much debated in the literature [1–9, 13, 15] and the problem of the reaction mechanisms is far from being solved. The aim of this work is to study, by X-ray photoelectron spectroscopy (XPS), the substrate surface modifications which occur just preceding the metal deposition (a Ni–P film in the present case).

2. Experimental details

Sheets of polycarbonate of industrial quality 50 mm × 10 mm × 1 mm were degreased with ethanol

in an ultrasonic bath, then treated by O_2 or NH_3 plasma. The reactor used was fitted with two parallel electrodes and powered with a radio frequency (13.56 MHz) generator. The experimental conditions as follows: pressure (100 mTorr), gas flow rate (100 sccm), generator power density (0.5 W cm^{-2}), treatment duration (30 s).

The sensitization solution contained 0.1 g dm^{-3} SnCl_2 and $0.1 \text{ cm}^3 \text{ dm}^{-3}$ concentrated HCl, the activation one 0.1 g dm^{-3} PdCl_2 and $3.5 \text{ cm}^3 \text{ dm}^{-3}$ concentrated HCl. The mixed solution, prepared according to Osaka *et al.* [15], contained 12 g dm^{-3} SnCl_2 , 0.25 g dm^{-3} PdCl_2 , $60 \text{ cm}^3 \text{ dm}^{-3}$ concentrated HCl. After each treatment period of 3 min the samples were thoroughly rinsed in distilled water.

The metallization bath consisted of 36 g dm^{-3} NiSO_4 , $6 \text{ H}_2\text{O}$, 10 g dm^{-3} $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, $29 \text{ cm}^3 \text{ dm}^{-3}$ lactic acid, $< 0.1 \text{ g dm}^{-3}$ thiodiglycolic acid and was operated at pH 5 and 85°C .

XPS was performed with a RIBER SIA 200 spectrometer using a nonmonochromatic magnesium source and a take-off angle of 25° with respect to the sample surface. All spectra were referenced to the C1s signal at a binding energy of 285 eV representative of the C–C and C–H bonds.

3. Results and discussion

Polycarbonate substrates were subjected to O_2 or NH_3 plasma treatment, then made catalytic by each of the three above-mentioned processes: namely, by the conventional one-step process A (3 min in the SnCl_2 – PdCl_2 mixed bath, then water rinsing) after O_2

and NH_3 plasma treatment, by the two-step process B (3 min in the SnCl_2 solution and water rinsing, then 3 min in the PdCl_2 solution and water rinsing) after O_2 plasma treatment, and by the one-step process C proposed by the authors (3 min in the PdCl_2 solution) after surface treatment by NH_3 plasma. It was shown [10–12] that a polycarbonate surface treated by O_2 plasma cannot chemisorb palladium directly, but only through preliminary or simultaneous tin chemisorption. Details on the latter process, and on the related reaction mechanisms, are given elsewhere [10–12]. However, the main results obtained by XPS analysis are briefly recalled here to aid the subsequent discussion. Figure 1A represents the XPS survey spectra of an ethanol degreased polycarbonate sample (a), of the same treated for 1 min by O_2 and NH_3 plasma ((b) and (c), respectively). The O_2 plasma treatment increases the oxygen surface content and NH_3 plasma grafts nitrogen on the polymer surface. Figure 1B concerns the same samples subjected to the sensitization (SnCl_2)/activation (PdCl_2) treatment. As expected, the ethanol degreased sample (a) does not adsorb any chemical species on its surface. On the

other hand, the sample carrying exclusively oxygenated functionality (b) chemisorbs both Sn and Pd species, the former in larger proportion than the latter, while the sample carrying both oxygenated and nitrogenated functionality (c) chemisorbs only palladium. These results show that the sensitization step by SnCl_2 is useless when the substrate surface carries nitrogen. Indeed, treatment by PdCl_2 alone grafts palladium species directly onto nitrogen atoms.

From the present results longer or shorter initiation times, depending on the surface treatment and catalytic process used, are always observed before the metal deposition takes place. These times range from 2 to 40 s (Table 1). A similar phenomenon is mentioned by some authors who have generally measured longer initiation times, namely, from 10 to 10^4 s [6], 10 min [13], from 140 s to 1 h [16, 17]. Two questions arise: (i) what factors determine the duration of the induction period, and (ii) what happens at the solid/solution interface during initiation. Paunovic answered the first question and showed that the type and concentration of the ligand complexing the metallic ions determine the duration of the induction period, the latter reaching the mixed potential at which the metal deposition occurs. Finding an answer to the second question is the aim of this work.

Considering the thermodynamic reactions likely to occur in solution, it is clear that the H_2PO_2^- ions can reduce Pd^{2+} . Indeed, the normal potential of the redox couple $\text{H}_2\text{PO}_3^-/\text{H}_2\text{PO}_2^-$, which is given by the relation $E^\circ(\text{V}) = -0.5 - 0.06 \times \text{pH}$, is -0.8 V at pH 5, while that of the Pd^{2+}/Pd couple is $E^\circ(\text{V}) = +0.99$. Some authors [2–4, 9] consider that the Pd^{2+} ions adsorbed on the surface are reduced to Pd(0) by H_2PO_2^- ions. However, during such a reaction which takes place at the substrate/solution interface, can the Pd^{2+} ions involved in bonds with the substrate behave as ions in solution and, if they are reduced to Pd(0), how are they bonded to the substrate? In the hope of answering this question, the surface of the substrate was analysed *ex situ* by XPS at the end of the initiation time, despite the possible oxidation of the surface during its short stay in air. The Pd 3d spectra were recorded for samples activated by the processes B and C. Figure 2 represents five spectra. Three of them (a, b, c) characterize polycarbonate samples treated by O_2 plasma then successively by SnCl_2 and PdCl_2 (process B). Spectrum (a) corresponds to a sample which was kept as it stood (after O_2 plasma then process B) to be used as a reference, spectra (b) and (c) to the same sample as (a) treated

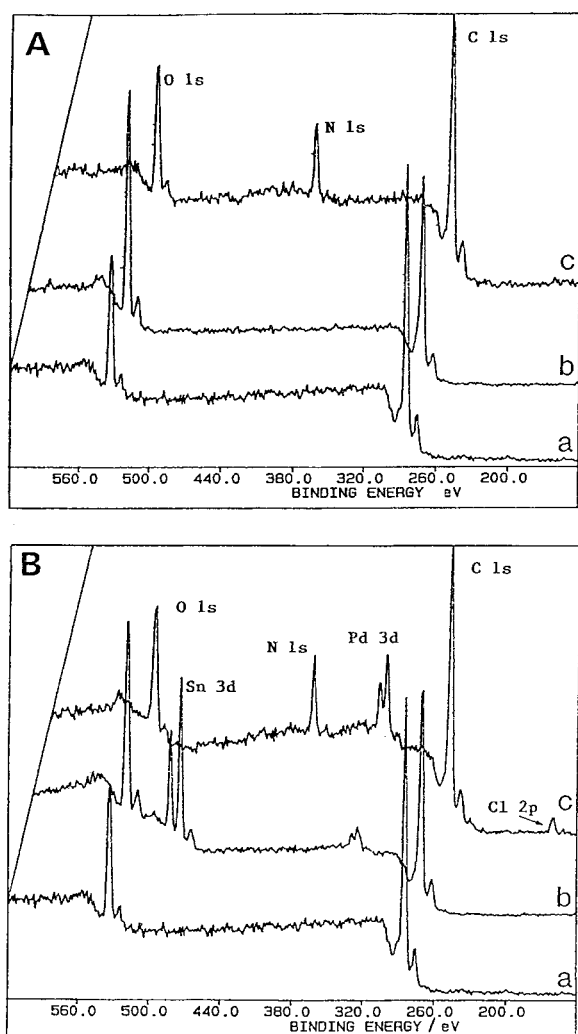


Fig. 1. XPS survey spectra of polycarbonate samples: (A) ethanol cleaned (a), the same treated by O_2 (b) or NH_3 (c) plasma; (B) after activation by the conventional two-step process (SnCl_2 then PdCl_2 treatments).

Table 1. Initiation time before metal deposition for different surface treatments and catalytic processes

Surface treatment	Catalytic process	Initiation time/s
O_2 plasma	A	40
NH_3 plasma	A	8
O_2 plasma	B	2
NH_3 plasma	C	12

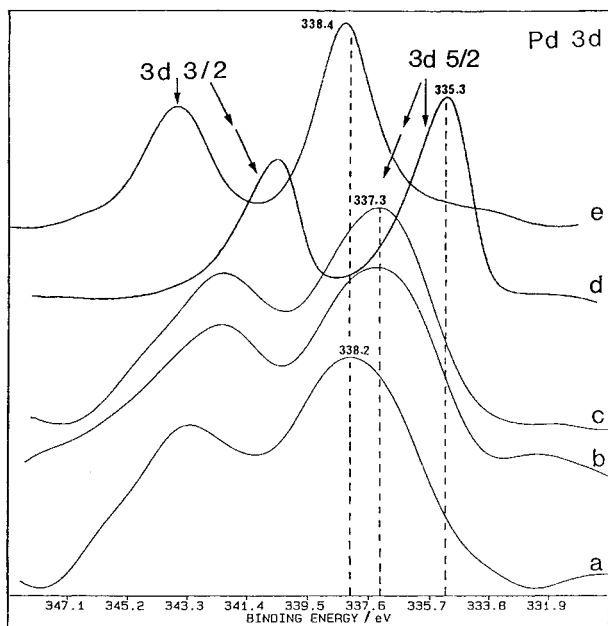


Fig. 2. Pd 3d spectra of polycarbonate samples treated by O_2 plasma then by B process ($SnCl_2$ then $PdCl_2$): (a) sample for reference subjected to the previous treatment, (b) and (c) the same as (a) treated for 2 s in the plating bath (b), in a reducing hypophosphite solution (c); (d) and (e) palladium in the metallic and Pd^{2+} form, respectively.

for 2 s (duration of the initiation time), respectively, (b) in the plating bath and (c) in a solution containing only the reducer used in the plating bath at the same concentration ($0.1 \text{ M dm}^{-3} \text{ NaH}_2\text{PO}_2$ at pH 5 and 85°C). For comparison, spectra (d) and (e) are due to metallic palladium and $PdCl_2$, respectively. After the catalytic process, the palladium species, adsorbed together with chlorine atoms [10], are present on the surface in the Pd^{2+} form (spectrum (a)). Both post-treatments ((b) and (c)), performed for 2 s lead to similar effects and the corresponding Pd $3d_{3/2,5/2}$ spectra show a spin doublet energy shift of 0.90 eV towards lower binding energies with respect to spectrum (a). This shift corresponds to a decrease of the Pd oxidation step and the corresponding peak may be considered as the sum of two contributions: a large one due to Pd^{2+} , a small one due to Pd(0). This slight spectral modification observed *ex situ* during the initiation time characterizes the beginning of the Pd^{2+} reduction.

Similar studies were performed using the simplified one step process (C) comprising an activation by $PdCl_2$ after a surface treatment by NH_3 plasma. Figure 3 gives the Pd 3d spectra obtained for (a) a polycarbonate sample kept as it stood (after NH_3 plasma then process C) to be used as a reference, (b) the same as (a) treated for 12 s (duration of the initiation time) in the plating bath, (c) the same as (a) treated for 12 s in a hypophosphite bath as previously indicated, (d) the same as (c) but treated for 10 min in the same bath. For comparison, spectra (e) and (f) correspond to metallic palladium and $PdCl_2$, respectively. Table 2 gives the surface composition determined by XPS for (a) to (d) samples. At first, it

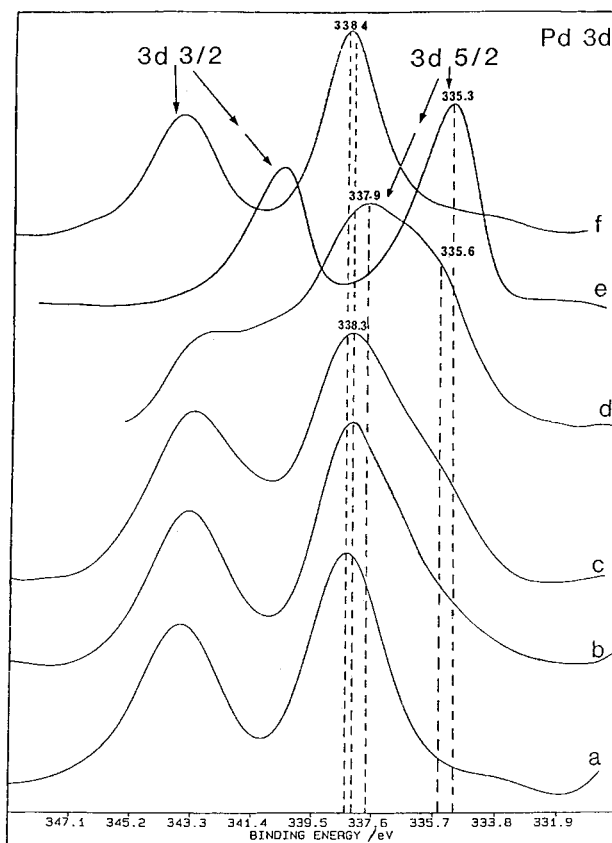


Fig. 3. Pd 3d spectra of polycarbonate samples treated by NH_3 plasma then by C process ($PdCl_2$): (a) sample for reference subjected to the previous treatment, (b) (c), (d) the same as (a) treated (b) for 12 s in the plating bath, (c) and (d) for 12 s and 10 min, respectively in a reducing hypophosphite solution; (e) and (f) palladium in the metallic and Pd^{2+} form, respectively.

appears that the $[Pd]/[Cl]$ ratio is particularly high so that the charge of the Pd^{2+} ions is not only compensated by Cl^- but also by OH^- ions. This is suggested by the Pourbaix diagram of palladium. On the other hand, a significant palladium loss is noted during the initiation time for samples (b) and (c). A prolonged stay in the hypophosphite reducing solution results in a significant loss of both palladium, nitrogen and carbon (sample (d)). The surface layers being partly removed, the underlying oxygen is therefore less masked and its concentration, in the depth probed, increases. However, this concentration exceeds the oxygen content in sample (a). A possible explanation is the adsorption of phosphate ions resulting from the redox reaction (Pd^{2+} reduction) instead of the N-Pd species dragged to the solution. Spectra (b) and (c) in Fig. 3 show a very slight broadening and energy shift of the Pd $3d_{5/2}$ peak towards lower binding energy with respect to spectrum (a). The peak broadening is very weak for spectrum (b), more significant for spectrum (c) on which it appears as a shoulder at 335.6 eV (energy characteristic of metallic palladium). A prolonged immersion in the NaH_2PO_2 solution emphasizes the modifications of the Pd $3d_{5/2}$ peak (spectrum (d)). The latter are due to the partial reduction of Pd^{2+} to Pd(0). However, the maximum of the peak envelope,

Table 2. Surface composition of polycarbonate samples: (a) subjected to NH_3 plasma treatment then to C catalytic process ($PdCl_2$); (b–d) as for (a) but subjected to reduction for 12 s in the Ni–P bath (b) for 12 s in NaH_2PO_2 (c) and for 10 min in NaH_2PO_2 (d)

Surface treatment	Atomic concentrations/%				
	C	O	N	Pd	Cl
(a) NH_3 pl. + $PdCl_2$	68.2	18.2	10.8	2.2	0.6
(b) (a) + “Ni–P” (12 s)	66.8	20.3	10.6	1.7	0.6
(c) (a) + NaH_2PO_2 (12 s)	67.2	20.5	10.3	1.7	0.3
(d) (a) + NaH_2PO_2 (10 min)	61	32	6	1	0

which is located at 338.3 eV (spectra (b) and (c)) or at 337.9 eV (spectrum (d)) (energies mainly characteristic of Pd^{2+}), shows that most of the palladium present on the surface is in the Pd^{2+} form. The question of whether the *ex situ* XPS analyses characterize the real processes occurs. It seems that a partial oxidation of the samples during their short stay in air is possible, particularly for samples (b) and (c) immersed for a short time in the reducing solution. Nevertheless, it may be thought that only the Pd^{2+} ions, which have been reduced during the initiation time, are capable of initiating the deposition reaction. If this is the case, the samples previously treated in the hypophosphite solution then immersed immediately in the plating bath without intermediary wiping, would give rise to an immediate deposition of the Ni–P film. This, however, is not so and additional time is necessary (13 to 15 s) for the deposition to initiate. An attempted explanation of this new induction period will be given in the following.

There is still considerable controversy on the question of whether palladium acts as a catalyst in the Pd^{2+} or $Pd(0)$ form and in the latter case how the reduction occurs. Some authors, such as Cohen *et al.* [2], Chow *et al.* [3], Tsukahara [9] and Sharp [4] consider that the stannous ions reduce the palladium ions to finely divided metallic palladium nuclei or to a palladium layer and that this metallic palladium initiates the autocatalytic process. On the other hand, Sard [1] suggests that the metallic Pd particles present on the surface result from an adsorption, after reduction (in the $PdCl_2$ solution itself) of Pd^{2+} ions adjacent to the interface, by Sn^{2+} ions being dragged through the $PdCl_2$ solution. De Minjer [5] argues, on the basis of ellipsometric measurements, that no metallic Pd is present on the surface and that the Sn–Pd complex formed at the sensitization/activation time reduces the Ni^{2+} ions. Other authors such as Meek [6], Hamaya *et al.* [13], Kiflawi *et al.* [7] consider that the reduction of Pd^{2+} species adsorbed on the surface is performed by the $H_2PO_2^-$ ions of the electroless bath during initiation and that it is a necessary step for obtaining the catalytic agent. In addition, Hamaya *et al.* [13] have chemisorbed, from a $PdCl_2$ solution, palladium species on a glass substrate previously treated by an aminosilane, and have immersed the samples in a solution containing $H_2PO_2^-$ ions at 80 °C for 30 min. They have shown by XPS that, after this treatment, palladium species were present in the metallic form and that the Ni–P film

deposition immediately occurred upon immersion in the plating bath. They concluded that palladium must be in the metallic form to catalyse the reaction, while de Minjer [5] considers that the metal is a very bad catalyst for Ni deposition. Finally, Baylis *et al.* [8] suggest the existence of a specific interaction between the Ni^{2+} ions and the $[Sn(IV), Pd(II)]$ species adsorbed on the surface, without $Pd(0)$ being necessary for catalysing the deposition initiation. In an attempt to clarify this problem, we have tested the catalytic activity towards Ni^{2+} reduction, of different forms of palladium: Pd^{2+} ions ($PdCl_2$ solution at 0.1 g dm⁻³), palladium black (highly divided Pd (0) supplied by Sigma) and palladium foil cleaned in an HCl solution. In three different plating baths (100 cm³) at 85 °C we have added, under stirring: (i) three drops of $PdCl_2$ that is to say about 9 µg Pd (bath 1), (ii) 9 µg of palladium black (bath 2), (iii) one palladium foil 10 mm × 10 mm × 0.01 mm supplied by Goodfellow (bath 3). Bath 1 is decomposed after about 7 s and metallic nickel precipitates. In bath 2 a chemical reaction with vigorous hydrogen evolution is immediately observed on the palladium grains. This corresponds to Ni^{2+} reduction on contact with palladium particles, which become covered with the Ni–P alloy and whose size progressively increases. In this case, the bath spontaneously decomposes after 90 min. Finally, in bath 3 vigorous gas evolution (H_2) takes place immediately on the palladium foil, which also becomes covered with the Ni–P alloy. However, the deposition proceeds without any bath decomposition. In conclusion, contrary to de Minjer's assertions, palladium in the metallic form behaves as a good catalyst on condition that its surface is not contaminated. Indeed, nickel reduction, identified by hydrogen evolution, occurs as soon as the palladium foil contacts the plating bath. On the other hand, in the case of bath (1), palladium catalyses the reaction after a few seconds, during which Pd^{2+} ions are reduced to $Pd(0)$. Indeed, every Pd^{2+} ion is immediately reduced by the $H_2PO_2^-$ ions and is, therefore, present in the solution in atomic form. With each atom playing the role of a nucleation centre, the Ni^{2+} reduction is very rapid, which explains the rapid solution decomposition.

Compared to the very rapid reduction of Pd^{2+} ions added to the metallization bath, the reduction during the initiation time of Pd^{2+} species chemisorbed onto the sample surface is slower. As mentioned above, a part of the palladium reduced on

contact with the solution could oxidize before being analysed by XPS. It should also be noted that a dynamic equilibrium may exist between the dissolution of Pd^{2+} species chemisorbed on the surface, their reduction to Pd(0) and partial physisorption on the substrate, which would explain the palladium loss during prolonged immersion in the reducing solution (Table 2). After a stay in the hypophosphite solution, corresponding to the initiation time, a new delay is necessary for initiating the Ni^{2+} reduction when the sample, still wetted by a film of the reducing solution, is immersed immediately in the plating bath. As the substrate is protected by the film of reducing solution, palladium reoxidation is uncertain. On the other hand, it may be thought that the new initiation time observed corresponds to the migration of Ni^{2+} ions towards the substrate surface across the reducing aqueous film, the Ni^{2+} ion reduction taking place in the solution on contact with Pd(0) species physisorbed on the surface. It is interesting to note that the particularly short initiation time observed while using the two step process could be due to the participation of the Sn^{2+} ions in the reduction of the Pd^{2+} ions, the reaction taking place in the solution, probably by a mechanism of dissolution/reduction/physisorption.

This mechanism explains why, after the initiation of a few deposits, the plating bath decomposes spontaneously. It has been shown that the instability of the plating bath is only slightly dependent on its working duration and, therefore, on the amount of nickel deposited on each sample, but that it mainly depends on the number of deposition reactions which are initiated in the same solution, that is to say of the area initially treated. Indeed, during this initiation step, some palladium atoms are dragged to the solution.

Furthermore, the plating bath is less stable when used after the simplified one step process proposed by the authors (12 s of initiation time), process which physisorbs more palladium than when it is used after the conventional two step process (2 s of initiation time). This supports the dissolution/physisorption reaction mechanism proposed for the initiation of the reaction. To solve the major drawback due to palladium dissolution in the plating bath we have sought to eliminate the weakly chemisorbed palladium species capable of being dragged by the acidic plating bath but not capable of being removed by a mere water rinse. The problem was solved by immersing the samples, activated by PdCl_2 , in a 0.06 M HCl solution for 1 min, which reduced the Pd concentration on the sample surface and considerably improved the plating bath stability.

4. Conclusion

This work has shown that, during the electroless metallization of polymers, an initiation time is always observed before the reduction of the metallic ions (Ni^{2+} for example) takes place effectively. It was shown that this time depends on the process used to make the substrate surface catalytic and that it can vary between 2 and 40 s in the experimental conditions of this work. The initiation mechanism of the electroless process is very complex and still controversial, but in the light of this work it can be stated that Pd^{2+} reduction to the atomic state is a necessary step. It appears that the reaction initiates in the solution, level with the solid/solution interfacial zone. A reaction mechanism based on a dynamic equilibrium dissolution/reduction/deposition is proposed. Pd^{2+} ions adsorbed on the substrate would drag through the acidic plating bath where they would be reduced to Pd(0). In this atomic state, they could either physisorb on the substrate or remain in the solution and catalyse the reduction of the Ni^{2+} ions. Such a process accelerates the decomposition of the solution. The further catalysis of Ni^{2+} ion reduction would proceed in solution at the solid/solution interface and would be followed by the physisorption of the resulting nickel atoms onto the solid surface.

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