

Voltammetric Behavior of Amorphous Pd-Si Alloys in Acid and Alkaline Solutions

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Ligas metálicas amorfas de Pd-Si foram preparadas na forma de fitas por resfriamento rápido de fundidos e suas amorficidades foram estabelecidas por difração de raios-X. Após a determinação das temperaturas de cristalização por calorimetria de varredura diferencial, algumas amostras foram tratadas termicamente e apresentaram padrões de difração característicos de materiais cristalinos.

Estudos destas ligas por voltametria cíclica mostraram, em contraste com o comportamento do Pd policristalino, características típicas dos processos de adsorção/dessorção de hidrogênio. Estas características tornam-se mais definidas com o aumento da concentração de silício e com o tratamento térmico. Na região de formação de óxidos, as ligas cristalizadas apresentaram cargas maiores que as correspondentes amostras amorfas. Análises da carga de redução dos óxidos em função do potencial de inversão da varredura mostrou que a formação de monocamadas de PdOH e PdO não está bem definida como no Pd puro, provavelmente devido aos efeitos eletrônicos e estruturais superficiais decorrentes da presença do Si.

Amorphous Pd-Si alloys prepared by the roller quenching method were characterized for amorphicity by x-ray diffraction. After determination of crystallization temperatures by differential scanning calorimetry, samples were heat-treated and presented diffraction patterns typical of crystalline materials.

Cyclic voltammetry experiments of the Pd-Si alloys showed, in contrast to polycrystalline Pd, characteristics of hydrogen adsorption, which become more pronounced as the Si content is increased and even more pronounced as the Si the oxygen region, the charges involved in the oxide reduction peak of the crystallized alloys were always higher than the corresponding amorphous values. Analyses of the oxide reduction charge as a function of potential did not permit to distinguish the formation of PdOH or PdO monolayers, as easily observed on metallic Pd. This might be a consequence of electronic and structural surface effects due to the presence of silicon.

Key words: *amorphous alloys; glassy metals; palladium-silicon.*

Introduction

Amorphous metallic alloys, also often referred to as glassy metals, can be produced by rapid quenching of certain metal-metalloid or metal-metal melts or, in some cases, by electrodeposition¹. The remarkable physical and chemical properties of these materials¹ has prompted a number of research groups, including ours to investigate possible applications as catalysts or electrocatalysts for technologically important processes. The electrochemical properties of amorphous metallic alloys have been reviewed by Archer *et al.*².

This work is part of a project devoted to the production and characterization of amorphous alloys and examination of their electrochemical properties. Amorphous Pd-Si alloys were produced as ribbons by the roller quenching

method^{3,4}. The amorphous nature of the ribbons were confirmed by x-ray diffraction. The electrochemical behavior of the amorphous and the crystallized alloys was studied in acid and alkaline solutions by cyclic voltammetry.

Experimental

Amorphous alloys with nominal atomic percentage compositions Pd₈₅Si₁₅, Pd₈₂Si₁₈ and Pd₈₀Si₂₀ were produced as ribbons by rolling and quenching ingot melts at ≈ 3500 rpm under purified argon atmosphere. The ingots had been previously prepared in a quartz tube by melting appropriate amounts of Pd (99.99%, Degussa) and Si (99.99%, Wacker). The twin rollers were made from special hard steel covered with a ≈ 2 mm layer of electrodeposited hard chromium. Based on the twin roller dimensions and in

Ref. 5, the quench rate derived was of $\cong 4 \times 10^5$ K/s. The ribbons produced were approximately 3 mm wide and about 30-40 μm thick.

The ribbons were characterized for amorphicity by a Rigaku-Rotaflex RU-200B diffractometer using $\text{CuK}\alpha$ radiation and the crystallization temperatures determined with a DuPont 9900 DSC-V2. 2A differential scanning calorimeter. The dot map for the distribution of Pd and Si in the amorphous alloys were obtained using a Noran Z-Max-30 electron microprobe with x-ray emission detection by means of a Jeol T330A electron microscope operating at 20kV.

Heat treatments of the amorphous alloys were conducted under a flowing Ar atmosphere at 470°C for 1 hour in quartz tube fitted into a horizontal furnace. The temperature in the immediate neighborhood of the samples was regulated by means of a control unit coupled to a chromel-alumel thermocouple junction. The Ar (White Martins) was purified by interposing a multistage train between the cylinder and the quartz tube inlet, consisting of silica gel to remove water, Alfa De-Ox catalyst (Alfa Ventron Corp.) and copper turnings to eliminate O_2 , and molecular sieves 3Å and 12Å to remove water and organic contaminants, respectively. A water trap was installed at the outflow of the tube to prevent back diffusion of gases from the atmosphere.

A conventional three electrode cell with a Luggin capillary was used in the electrochemical experiments. An external reversible hydrogen electrode (RHE) and a Pt foil ($A \cong 2\text{cm}^2$) were used as the reference and auxiliary electrodes, respectively. The working electrodes ($A \cong 0.1-0.3\text{cm}^2$) were prepared by sealing one extreme of the ribbons into pyrex glass tubing with epoxy resin. Silver emulsion was used to make the electrical junction between the ribbons and the Cu wires. The working electrodes were cleaned with acetone, isopropanol and 0.1M HClO_4 , rinsed with water and immediately introduced in the electrochemical cell. Each electrode was further cleaned by using slow anodic sweeps until a steady-state cyclic voltammogram was obtained. The electrode areas were evaluated from the oxide reduction peak charges involved in the cyclic voltammograms recorded up to 1.5V vs RHE at 100 mV/s in 0.1M HClO_4 and assuming a value of $420\mu\text{C}/\text{cm}^2$ for a PdO monolayer⁶. For comparison, experiments were also carried out on polycrystalline Pd electrodes ($A \cong 1.4\text{cm}^2$).

The electrochemical measurements were conducted with a PARC Model 273 potentiostat coupled with a HP-7046B recorder. The solutions used were prepared from 65% HClO_4 (Suprapur Merck) or pre-electrolyzed 6M NaOH (Merck, p.a.) and Milli-Q water (17 $\text{M}\Omega\text{ cm}$). Before starting an experiment, the electrolyte was saturated with purified nitrogen. During the experiments, a steady stream of nitrogen was passed over the solution. The voltammetric response of a Pt electrode was always used as a criterion to assure that the electrolyte was free from contaminants. The Pt electrode was cleaned using the flaming and quenching method⁷.

Results and Discussion

The x-ray diffraction patterns for the $\text{Pd}_{85}\text{Si}_{15}$, $\text{Pd}_{82}\text{Si}_{18}$ and $\text{Pd}_{80}\text{Si}_{20}$ amorphous alloys are shown in Fig. 1a, 2a and 3a, respectively. The features observed at $2\theta < 30^\circ$ are due to the glass slide used to hold the samples. The presence of

broad peaks and total absence of sharp lines demonstrated the amorphicity of these materials.

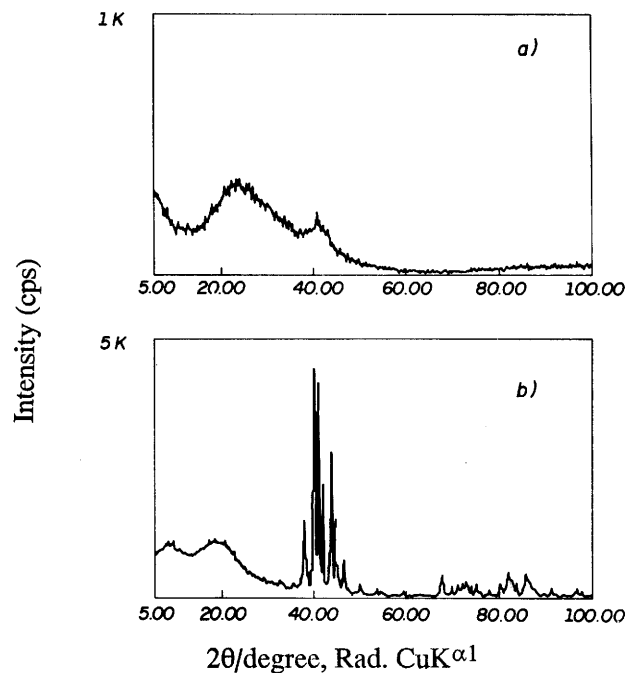


Figure 1. X-ray diffraction data for the amorphous $\text{Pd}_{85}\text{Si}_{15}$ alloy a) before and b) after heat treatment at 470 °C for 1 h under Ar atmosphere.

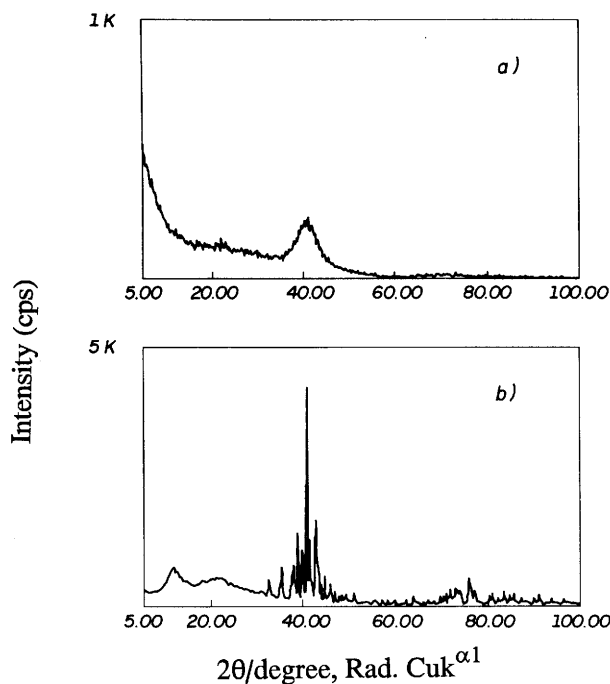


Figure 2. X-ray diffraction data for the amorphous $\text{Pd}_{82}\text{Si}_{18}$ alloy a) before and b) after heat treatment at 470 °C for 1 h under Ar atmosphere.

The morphology of the ribbon surfaces were examined using scanning electron microscopy (SEM). One side of the ribbon always resulted to be smoother and shinier than the

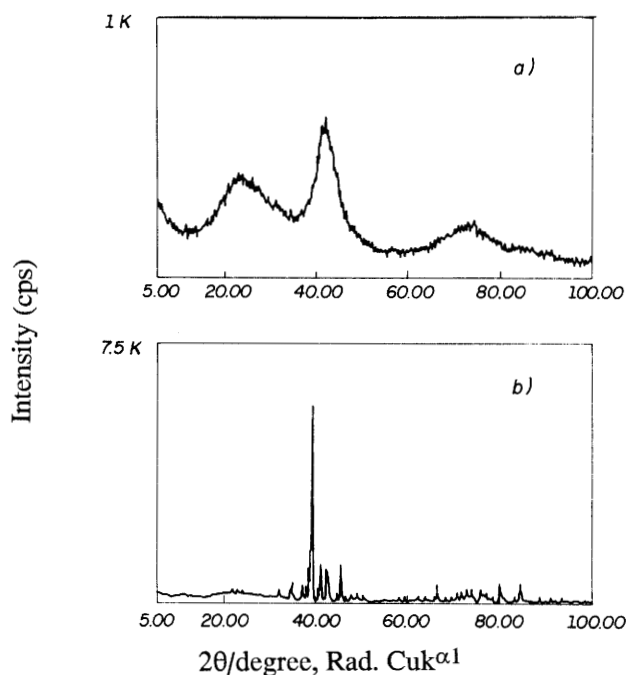


Figure 3. X-ray diffraction data for the amorphous $Pd_{80}Si_{20}$ alloy a) before and b) after heat treatment at 470 °C for 1 h under Ar atmosphere.

other side that was quite rough and presented randomly distributed bubble-like defects, as illustrated in Fig. 4 for the $Pd_{85}Si_{15}$ ribbon. This may be due to the roller-quenching method in which one wheel is attached to a motor and the other wheel turns when in contact with the stream of the molten alloy and therefore physical inhomogeneities can be produced by turbulence during the rapid quenching of the melt. Another possible explanation is the trapping of bubbles of inert gas, as observed on amorphous alloys produced by melt spinning² and known as gas entrapment furrows on the wheel side of the ribbon.

Examination of the ribbon compositions using electron microprobe analysis with x-ray emission detection demonstrated that the ribbons have excellent homogeneity, as shown in Fig. 5 by the dot map for the distribution of Pd and Si atoms across the scanned sample.

Differential scanning calorimeter (DSC) measurements conducted with Pd-Si amorphous samples (Fig.6) demonstrated that the temperature and the energy of crystallization increases as the Si content in the alloy is increased (see Table 1). Based on these data, a temperature of 470°C was established for the heat treatment of the ribbons for 1 h under Ar atmosphere. Such heat-treated materials presented diffraction patterns with sharp and well defined peaks, as shown in Fig. 1b, 2b and 3b for the $Pd_{85}Si_{15}$, $Pd_{82}Si_{18}$ and $Pd_{80}Si_{20}$ alloys, respectively. Peak position analyses^{8,9} indicated the presence of metallic Pd and Pd_3Si , Pd_4Si , and Pd_5Si phases¹⁰.

The electrochemical properties of the amorphous Pd-Si alloys were investigated in 0.1M $HClO_4$ and 0.1M NaOH solutions by cyclic voltammetry. The voltammograms obtained in 0.1M $HClO_4$ for the ribbons as produced and after the heat treatment are presented in Fig. 7. This figure also contains the curve obtained on a polycrystalline Pd

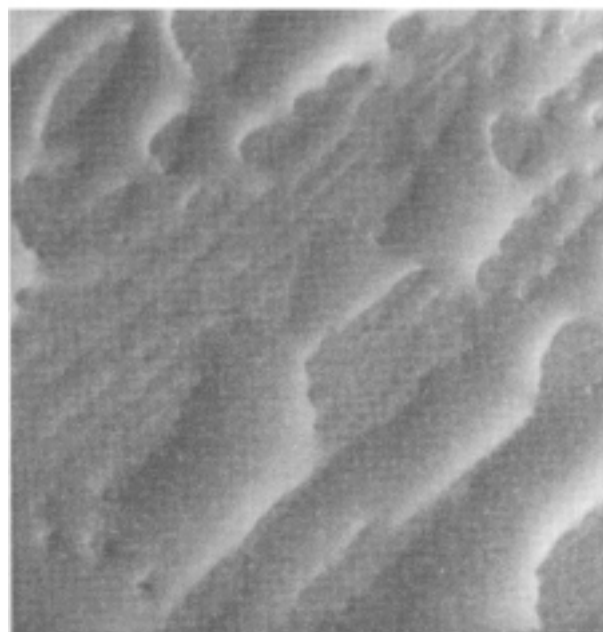
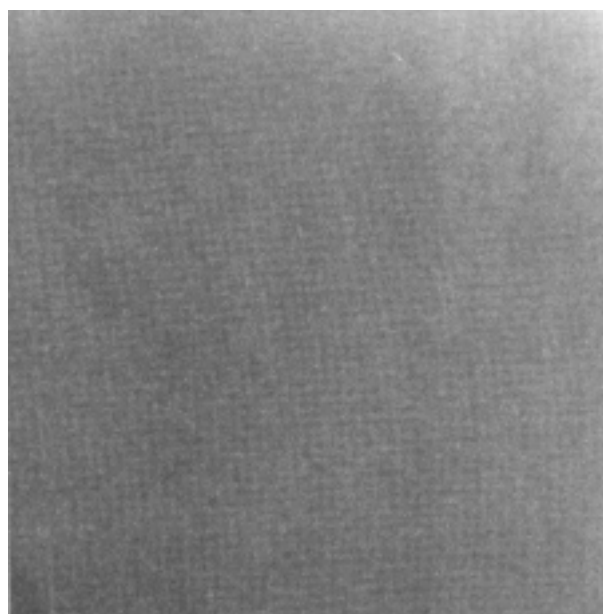


Figure 4. Scanning electron micrographs for the ribbon sides of the amorphous $Pd_{85}Si_{15}$ alloy. Top: smooth side.

Table 1. Temperatures and energies of crystallization of the amorphous Pd-Si alloys.

Alloy	Temperature (°C)	Energy (cal/g)
$Pd_{85}Si_{15}$	386	8.3
$Pd_{82}Si_{18}$	406	9.3
$Pd_{80}Si_{20}$	413	9.9

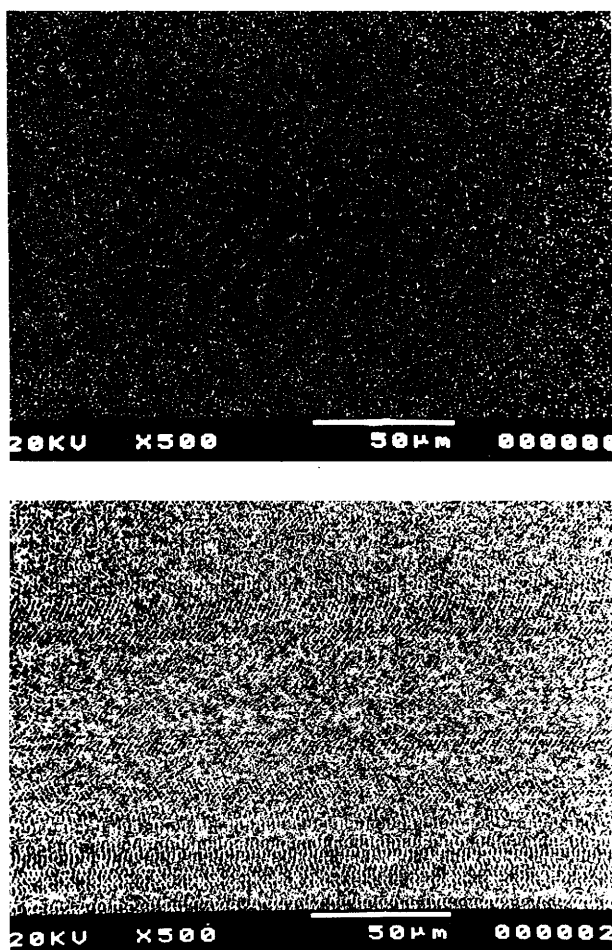


Figure 5. Dot map determined by the scanning electron microprobe for the distribution of Si (top) and Pd (bottom) in the amorphous $Pd_{85}Si_{15}$ alloy.

electrode for comparison. It can be noted that Pd-Si alloys, on contrary of polycrystalline Pd, present characteristics of hydrogen adsorption. Furthermore, such characteristics increase with the increase in the Si content and become more pronounced after heat treatment. These observations may be associated with the diffusion coefficients of hydrogen and the concentration of dissolved hydrogen in the alloys, since according to Petrii *et al.*¹¹, the diffusion coefficients of hydrogen on $Pd_{84.5}Si_{15.5}(\text{heat-treated})$ were evaluated to be about 1.4-1.7 higher than on $Pd_{84.5}Si_{15.5}(\text{amorphous})$, however both are approximately one order of magnitude lower than those obtained for metallic Pd. On the other hand, the atomic ratios H/Pd calculated from charging curves resulted to be 0.66, 0.045, and 0.012 for Pd, $Pd_{84.5}Si_{15.5}(\text{amorphous})$, and $Pd_{84.5}Si_{15.5}(\text{heat-treated})$, respectively. Therefore, the voltammetric behavior of the Pd-Si alloys in the hydrogen region may reflect a balance between the hydrogen sorption and diffusion properties. More specific experiments are necessary to provide a better understanding of such observations.

In the oxygen region, although the shape of the curves in Fig. 7 did not reveal any significant difference, the charges involved in the reduction of the Pd oxides formed in the anodic potential scan for the heat-treated alloys are higher, with a factor of $\approx 1.2-1.4$, than those corresponding to the amorphous state. This suggests that the heat treatment promotes an increase in the roughness factor of the electrode surfaces as well as a possible diffusion of Pd atoms from the bulk to the surface since Auger spectroscopic measurements on Pd-Zr and Pd-Si alloys¹² have shown an increase in the Pd content after the heat treatments of the alloys.

Further experiments in the anodic region were conducted in acid and alkaline solutions. In these experiments, the anodic limit for the reverse of the potential scan direction was increased stepwise by 50 mV from the value cor-

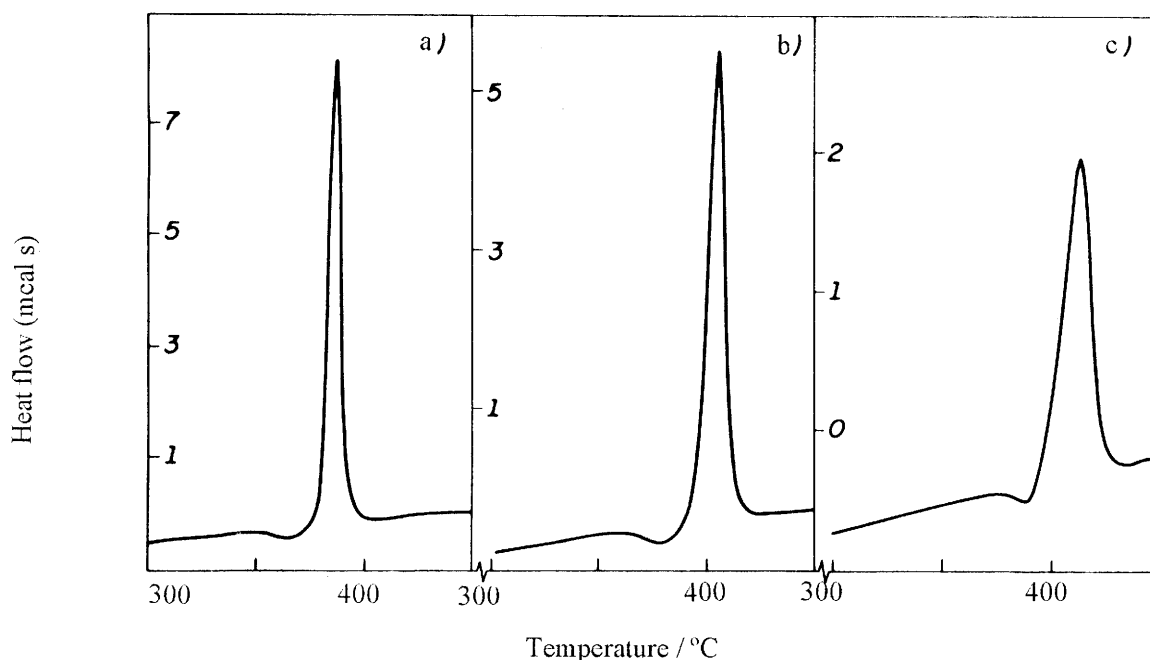


Figure 6. Differential scanning calorimetry analyses for the amorphous a) $Pd_{85}Si_{15}$, b) $Pd_{82}Si_{12}$, and c) $Pd_{80}Si_{20}$ alloys. Scan rate: $40^\circ/\text{min}$.

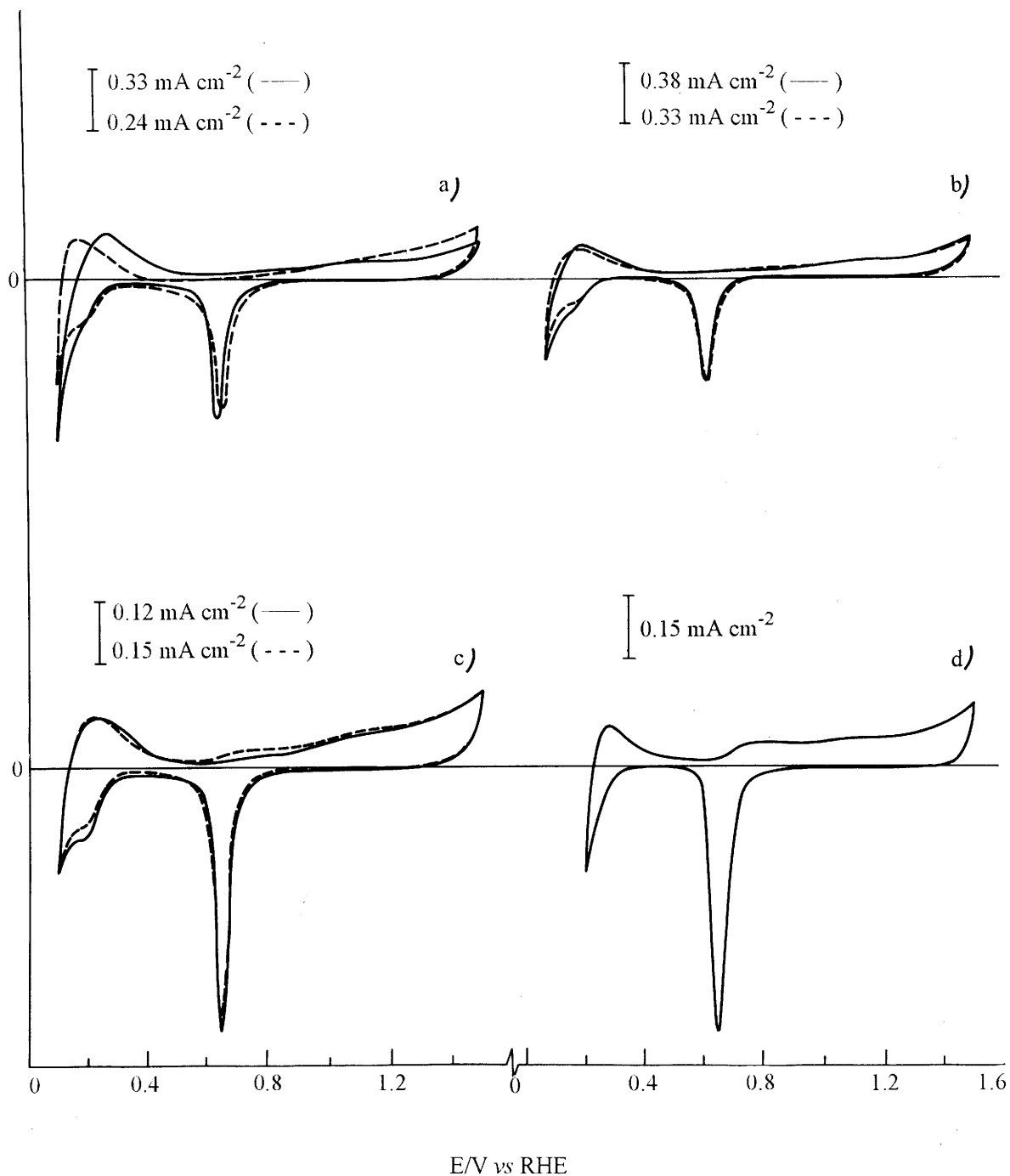


Figure 7. Cyclic voltammograms of a) $Pd_{85}Si_{15}$, b) $Pd_{82}Si_{18}$, c) $Pd_{80}Si_{20}$ amorphous (—) and crystallized (---) alloys, and d) polycrystalline Pd in 0.1M $HClO_4$ solution saturated with N_2 at 25 °C, $v=100V/s$.

responding to the beginning of the oxide formation, i.e. $\approx 0.75V$, up to 1.40V. Thus, the charges related to the oxide reduction peak ($Q_{p,r}$) were plotted against the anodic potential limits (E_a), as shown in Fig.8. It can be noted that polycrystalline Pd presented a linear relation but with changes in the slope lines at $\approx 210 \mu C cm^{-2}$ and $\approx 420 \mu C cm^{-2}$, which correspond to the formations of PdOH and PdO monolayers¹³, respectively. On the other hand, this linear relation was only observed on the Pd-Si alloys for changes higher than $\approx 200 \mu C cm^{-2}$ while the formation of the first

monolayer is anodically shifted by approximately 300 mV, revealing a strong inhibition of the oxidation process. Such behaviour, as well as that observed in the hydrogen region, suggest a modification in the chemisorptive properties of Pd in the alloys in comparison of Pd in the pure form and that silicon in the alloy is not behaving only as an inert filler for the dispersion of Pd.

Investigations of the chemisorptive properties of an electrode material are important to the elucidation of catalytic and electrocatalytic processes. In alloys, changes

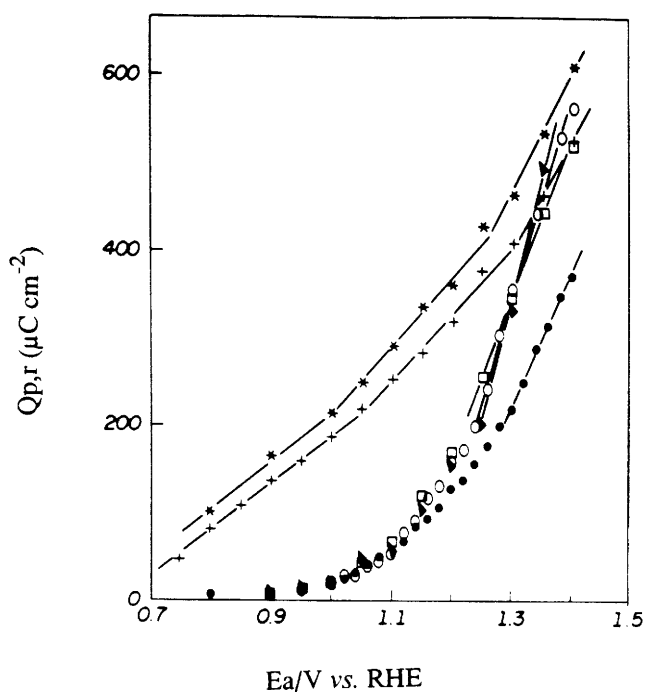


Figure 8. Oxide reduction charges as a function of anodic potential limits for Pd in 0.1M HClO₄ (+) and 0.1M NaOH (*), amorphous (O) and crystallized (●) Pd₈₅Si₁₅, amorphous Pd₈₂Si₁₈ (▲) and Pd₈₀Si₂₀ (□) alloys in 0.1M NaOH. $t \approx 25$ °C and N₂-saturated solutions (see text for details).

in the chemisorptive properties can be related to 1) geometrical effects due to change in number and nature of specific adsorption sites and 2) electronic effects through formation of intermetallic bonds⁶. The first one is difficult to be assessed on amorphous alloys because the lack of structural informations. The second one can be investigated by using appropriate techniques or proposing models. In this context, additional experiments for the determination of surface compositions of the Pd-Si alloys, as well as investigations of their electrocatalytic activities, are in progress for a better characterization of their electrochemical properties.

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