

# Tensile behaviour of as deposited and heat-treated electroless Ni-P deposits

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Electroless Ni-P coatings were deposited on mild steel substrates and the effect of heat-treatment on their structure and tensile behaviour was studied, with the following conclusions. The as-deposited electroless Ni-P coating is amorphous and it remains amorphous up to 300 °C. At 400 °C the coating becomes crystalline and consists of a Ni<sub>3</sub>P matrix containing areas of metallic nickel. For the selected coating/substrate thickness ratio, the contribution of the coating in the tensile properties of the coating-substrate system is negligible as expressed by the values of yield strength, ultimate tensile strength and fracture strain in mild steel substrates and coated as-deposited and heat-treated specimens. Extensive cracking of the coating accompanied by spalling was occurred during the tensile tests. The density of cracks was found to increase close to the fracture surface of the tensile specimen and with increasing heat-treatment temperature. The cracks observed on the surface of the coatings are believed to form due to the inability of the brittle coating to accommodate the strain generated in the ductile substrate. Their orientation to the tensile axis is in close relation to the structure of the coating and the failure mechanism that is dictated by this structure. The first cracks on the surface of the coatings were found to form after the yield strength of the tensile specimen has been reached and plastic deformation of the substrate takes place. Their density increases with the accumulation of strain up to fracture. © 1999 Kluwer Academic Publishers

## 1. Introduction

Electroless nickel coatings on various ferrous alloys are mainly used for the protection of those alloys against corrosion. However, the mechanical properties of coated ferrous metallic materials are thought to be an important parameter under technological conditions in which chemical and mechanical factors play a basic role. The most recent publications dealing with various aspects of nickel coated ferrous alloys are given below.

Keyse and Hammond [1] studied the structure and morphology of electroless Ni-P coatings with high voltage electron microscopy. These investigators mainly observed that the low content in phosphorous coatings (1–3%) are crystalline whereas the coatings with higher phosphorous content (8–14%) are amorphous. Erming *et al.* [2] used transmission electron microscopy in order to study the crystallization of amorphous Ni-P coatings. Weil *et al.* [3] studied the mechanical behaviour and corrosion of electroless and electrodeposited Ni-P coatings. These investigators found that the coatings have low ductility whereas the electrodeposited nickel coatings have higher Young modulus and ultimate tensile strength in comparison with the electroless nickel coatings. Tomlinson and Girardi [4] performed cavitation erosion tests on electroless Ni-P coatings in distilled water and 3% NaCl solution. Heat-treatment of the coatings reduced the mass loss due to cavitation in salt water, while in distilled water the behaviour was

irregular. Das *et al.* [5] found that the corrosion resistance of electroless Ni-P coatings on ferrous substrates is affected by the coating porosity.

In the present work the tensile behaviour of as-deposited and heat-treated Ni-P electroless coatings on mild steel is examined.

## 2. Experimental

Mild steel sheet 0.5 mm thick was used as substrate. The carbon content was 0.07%. Two groups of samples were cut from this sheet, one group with dimensions 30 mm × 10 mm and another group with dimensions 100 mm × 10 mm. The samples of the first group were used in the study of surface morphology, phosphorous content, structure and thickness of the electroless Ni-P deposits, while the second group of samples was used in the tensile tests. Cutting of the samples was followed by a stress-relief annealing process for 2 h at 550 °C.

Prior to the nickel deposition the steel substrates were cleaned in a 0.2 M NaOH solution at 70 °C for 20 min, rinsed with cold distilled water and then immersed in a pickling solution (its trade name is Dreca), consisting of HCl and various retardants, rinsed again and kept in a desiccator. Just before the deposition, the substrates were mechanically polished with 800, 1000 and 1200 grit SiC paper and, afterwards, were washed in methanol and distilled water.

Deposition of the electroless Ni-P coating on the mild steel substrates was made by immersing them in a hypophosphate bath with the following composition:

NiSO <sub>4</sub> ·6H <sub>2</sub> O	21 g/l
NaH <sub>2</sub> PO <sub>2</sub> ·H <sub>2</sub> O	24 g/l
C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	28 g/l
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	2.2 g/l
Pb	9 ppm

The solution had a pH between 4 and 4.5 that was controlled using NH<sub>4</sub>OH and its temperature was kept at 89 ± 2 °C.

Surface morphology of the as-deposited and heat-treated coatings was studied with the aid of a Jenavert optical microscope and a JSM 6100 Jeol scanning electron microscope (SEM) equipped with an EDAX facility. EDAX was used in cross-sections of the Ni-P deposits to determine their average composition. Cross-sections of the deposits were also used in the determination of the coating thickness.

The structural characterization and phase identification of the as-deposited and heat-treated electroless Ni-P coatings was carried out with the aid of a SIEMENS D-5000 X-ray diffractometer (XRD).

Heat-treatment of the deposits was done in a Thermawatt furnace, in an argon inert atmosphere with a constant heating rate of 10 °C/min from room temperature. The specimens were placed into the furnace from the beginning of the heating procedure and when the annealing temperature was reached they stayed at that temperature for 1 hour. After the end of this period the argon flow was used for cooling down the specimens with a relatively fast rate (in a few minutes). When the temperature in the furnace reached

250 °C the specimens were removed from the furnace and left to cool down freely in the air. The annealing temperatures ranged from 100 to 600 °C with 100 °C steps.

Tensile tests of the as-deposited and heat-treated electroless Ni-P coated mild steel substrates were performed, parallel to their rolling lines, with an Instron Series IX automated materials testing system 1.04. The gauge section was 50 mm in length and 10 mm in width. The strain rate for all the tests carried out up to the fracture of the specimens or terminated before their fracture, was  $1.7 \times 10^{-3} \text{ s}^{-1}$ . All the tensile tests were performed in laboratory air at 290 K.

### 3. Results and discussion

Surface morphology and structure of the as-deposited electroless Ni-P coatings were examined prior to the heat-treatment process and tensile tests. In Fig. 1a scanning electron micrograph of the surface of an electroless Ni-P deposit is shown. It can be seen that its surface has a grainy morphology consisting of parallel strings of grains aligned with the direction of gravity in the deposition bath. The size of the grains in the strings is not uniform but there is rather a distribution of sizes. Microcracks were not observed at the surface of the deposits. Cross-sections examined at the optical microscope and the SEM did not show the presence of cracks in the interior of the coatings as well. The lack of microcracks in the deposits is of paramount importance since it is related with the validity of the results of the tensile tests and the subsequent observation of the surface of the deposits.

The thickness of the studied deposits was measured on cross-sections and it was found to be 10 μm

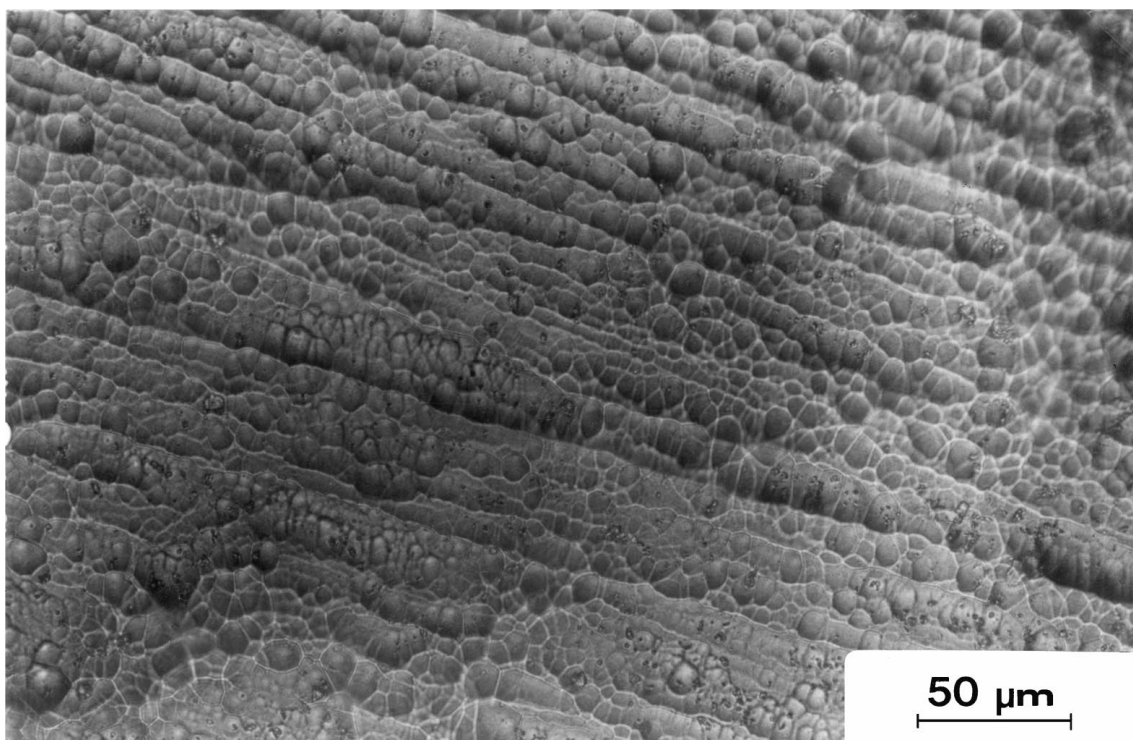


Figure 1 Scanning electron micrograph of the surface morphology of an as-deposited electroless Ni-P deposit.

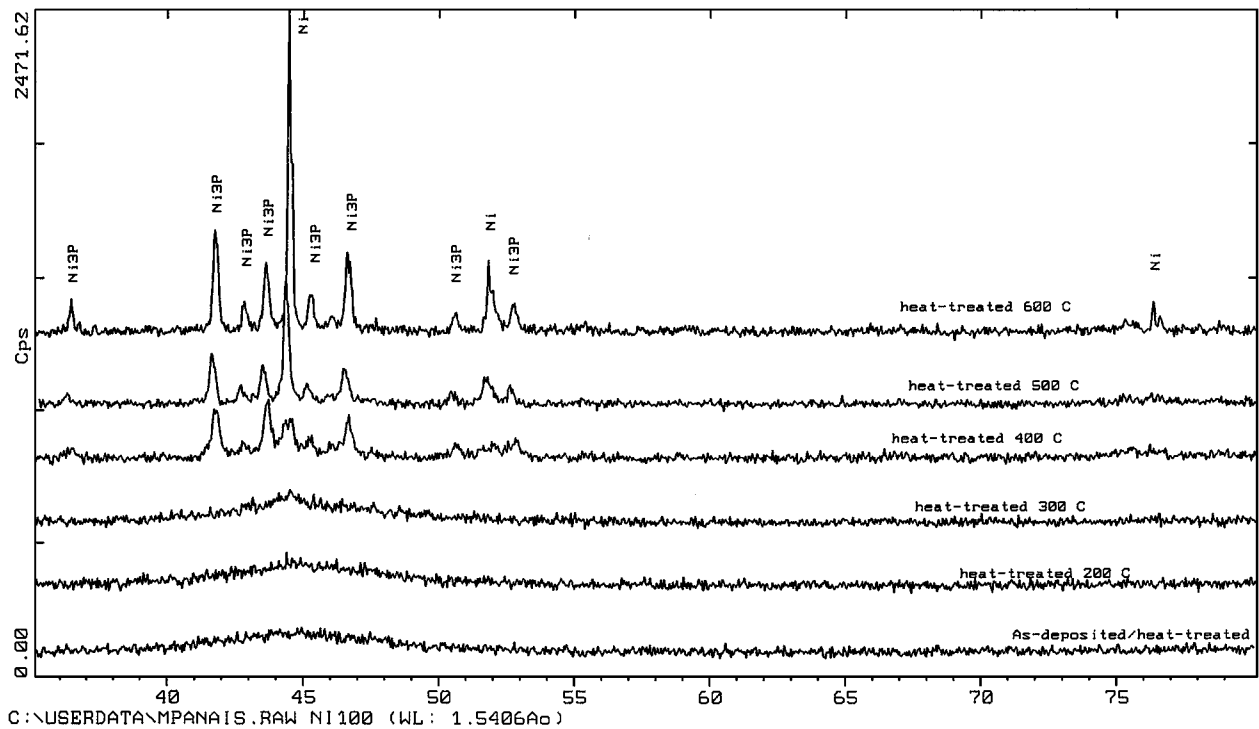


Figure 2 X-ray diffraction spectra of the as-deposited and heat-treated electroless Ni-P deposits.

approximately. EDAX measurements also on cross-sections, yielded an average composition of 11–12% P in weight for the Ni-P alloy the balance being Ni.

In Fig. 2 the X-ray diffraction spectra of the as-deposited and heat-treated electroless Ni-P deposits are shown. The presence of a broad peak close to the Ni (111) peak shows that the as-deposited coating is an amorphous supersaturated solution of phosphorous in a nickel matrix. The above result is in full agreement with previous studies on the structure of electroless Ni-P deposits performed by high voltage electron microscopy (HVEM) [1] and transmission electron microscopy (TEM) [2] which showed that for the above phosphorous content the deposit has an amorphous structure. The threshold phosphorous content for an electroless Ni-P deposit to be amorphous is believed to be 7–8% P in weight [6, 7]. From the XRD spectra of the heat-treated coatings it is observed that up to 300 °C the amorphous deposit is stable since no changes are observed in the XRD patterns. At 400 °C peaks due to Ni<sub>3</sub>P and Ni appear which manifest the crystallisation of the deposit. The phases that appear at 400 °C still exist at the highest annealing temperature (600 °C) without the appearance of new phases. This result shows that at 400 °C the heat-treated deposit has obtained a stability regarding the nature of the formed phases. According to previous studies [1, 2, 6] the microstructure of the crystalline deposit consists of a Ni<sub>3</sub>P matrix containing areas of metallic nickel, for the studied phosphorous content.

In an effort to examine the effect of the coating on the tensile properties of the electroless Ni-P coated mild steel substrates and the effect of heat-treatment on these properties, tensile tests were performed on mild steel substrates, as-deposited electroless Ni-P

coated substrates and heat-treated coated specimens. In Fig. 3 the ultimate tensile strength (UTS) and the yield strength (for plastic strain of 0.2%) for the mild steel substrate, the as-deposited electroless Ni-P coated mild steel and the heat-treated coated specimens are shown. It is observed that both the ultimate tensile strength and the yield strength of the as-deposited and heat-treated specimens do not vary significantly when compared with the same quantities of the mild steel substrate. The above result shows that the tensile properties of the coated specimens are determined mainly by the mild steel substrate and not by the coating. The insignificant effect of the coating on the tensile properties of the coating-substrate system may be attributed to the relatively small (10 μm) thickness of the coating. Due to its small thickness, the coating consists only a tiny volume fraction of the load carrying cross-section of the tensile specimen, thus having a minor role in the determination of the tensile properties of the coating-substrate system, according to the formula (1) giving the tensile properties of composite lamellar materials under isostrain conditions [8]:

$$P_t = P_s V_s + P_c V_c \quad (1)$$

where  $P_t$  is a tensile property (stress or elastic modulus) of the whole system,  $P_s$  and  $P_c$  the same tensile properties of the substrate and the coating respectively and  $V_s$  and  $V_c$  the volume fractions of substrate and coating respectively.

In Fig. 4 the fracture strains ( $\epsilon_f$ ) of the mild steel substrate, the as-deposited electroless Ni-P coated mild steel and the heat-treated coated specimens are given. Although the values of  $\epsilon_f$  show some fluctuation, they

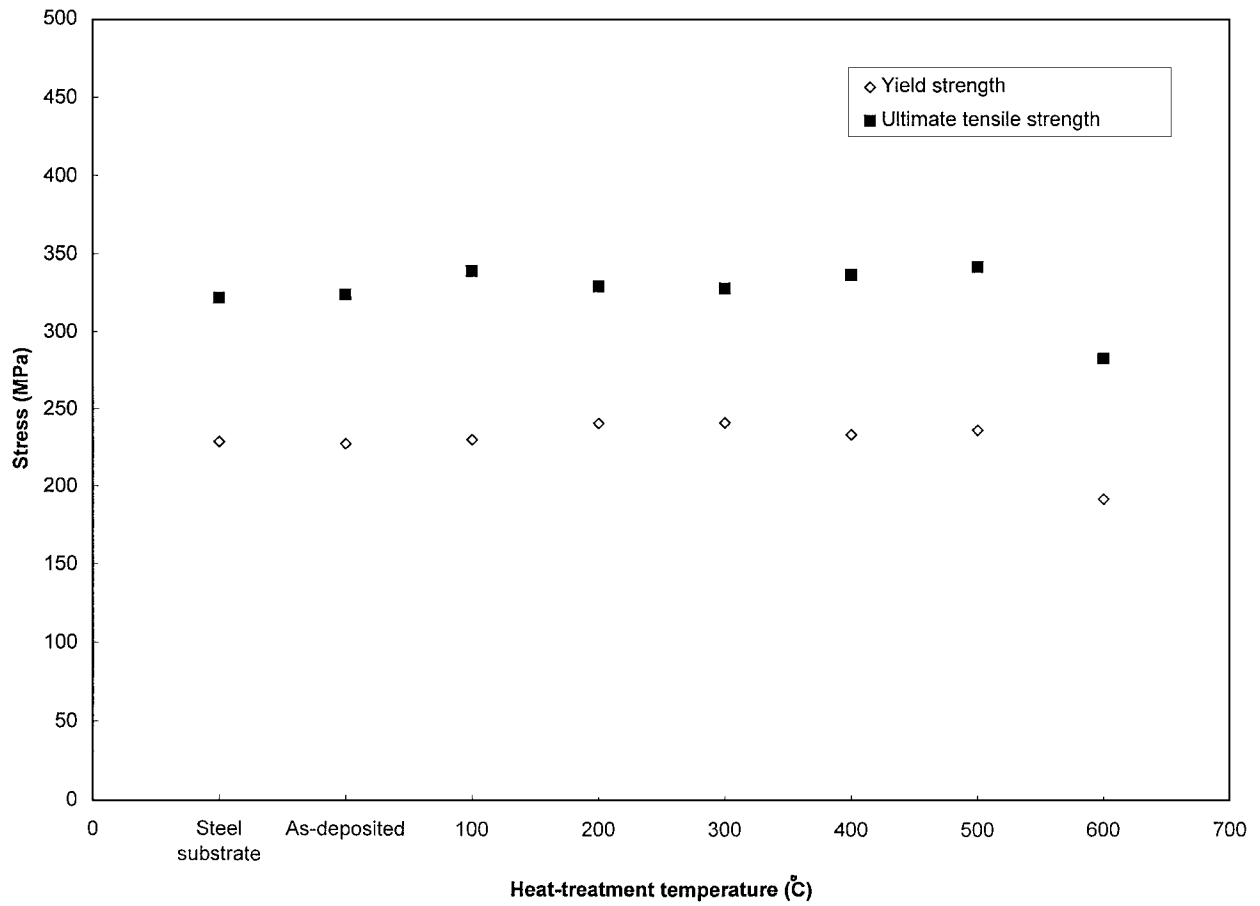


Figure 3 Ultimate tensile strength (UTS) and yield strength of the mild steel substrate and the as-deposited and heat-treated Ni-P electroless deposits.

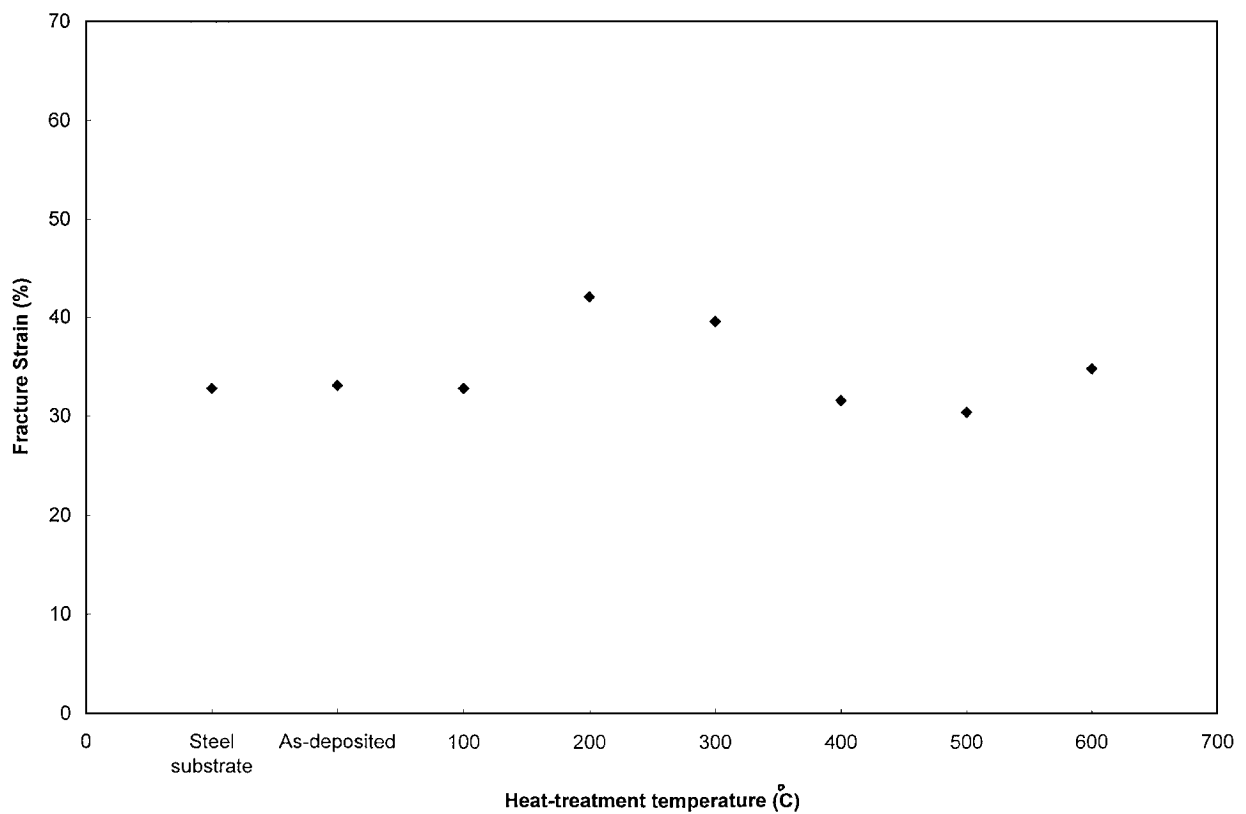
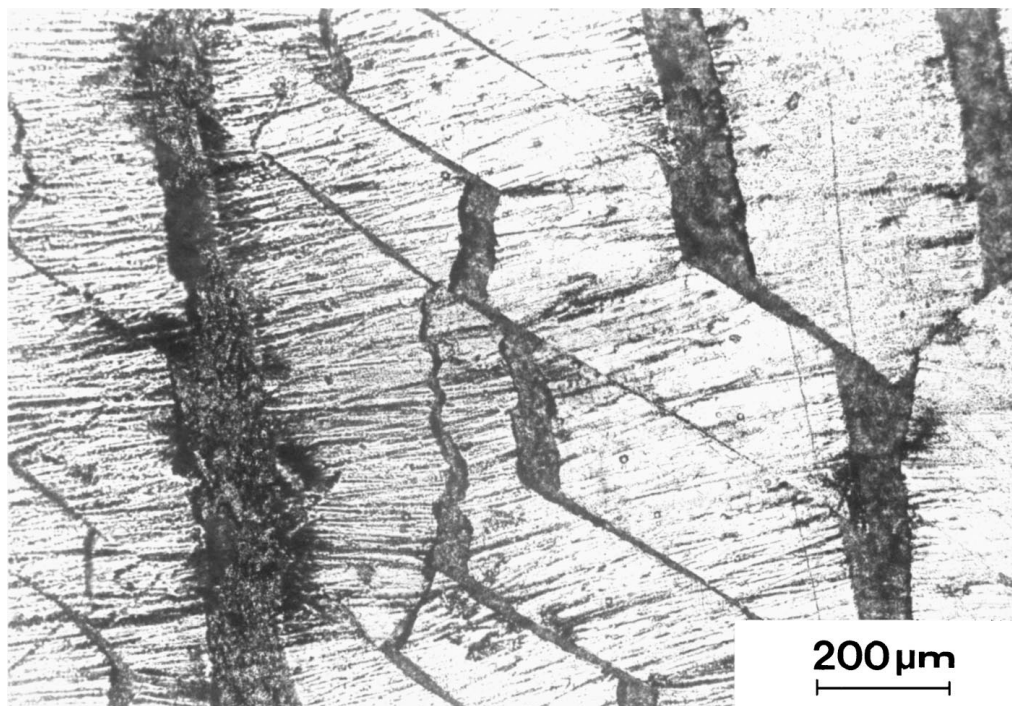


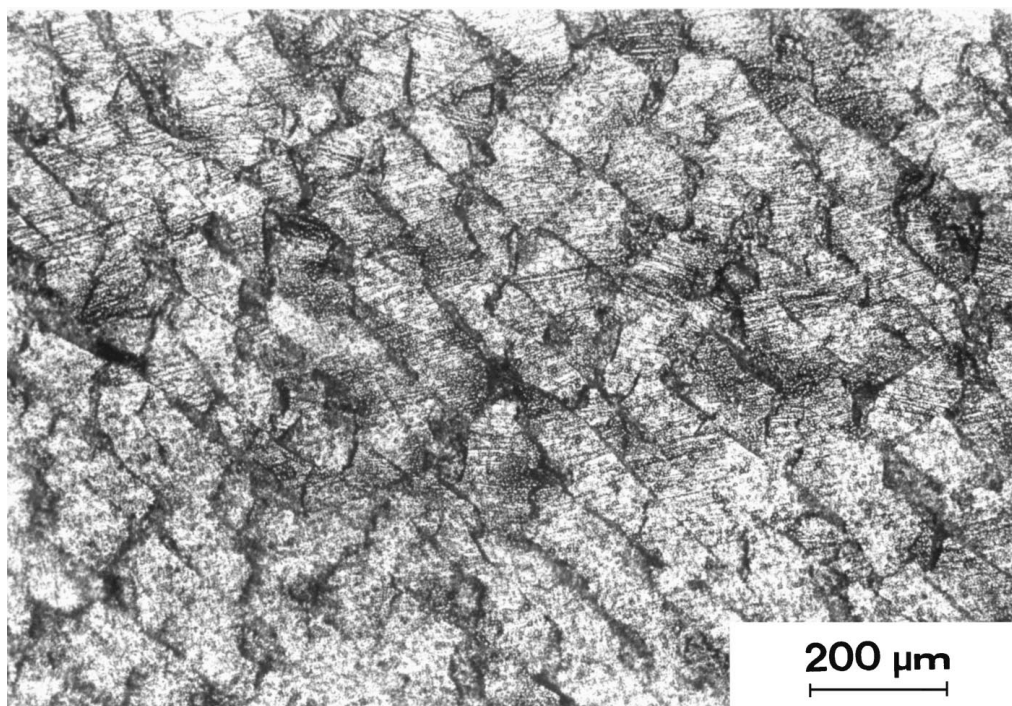
Figure 4 Fracture strain of the mild steel substrate and the as-deposited and heat-treated Ni-P electroless deposits.

cannot be attributed to a coating effect since no definite trend is established. Again the coating does not seem to have a significant role in the determination of the ductility of the coating-substrate system.

From the above discussion it is clearly shown that the contribution of the coating in the tensile properties of the coating-substrate system is negligible for the thickness ratio selected (coating thickness/substrate



(a)



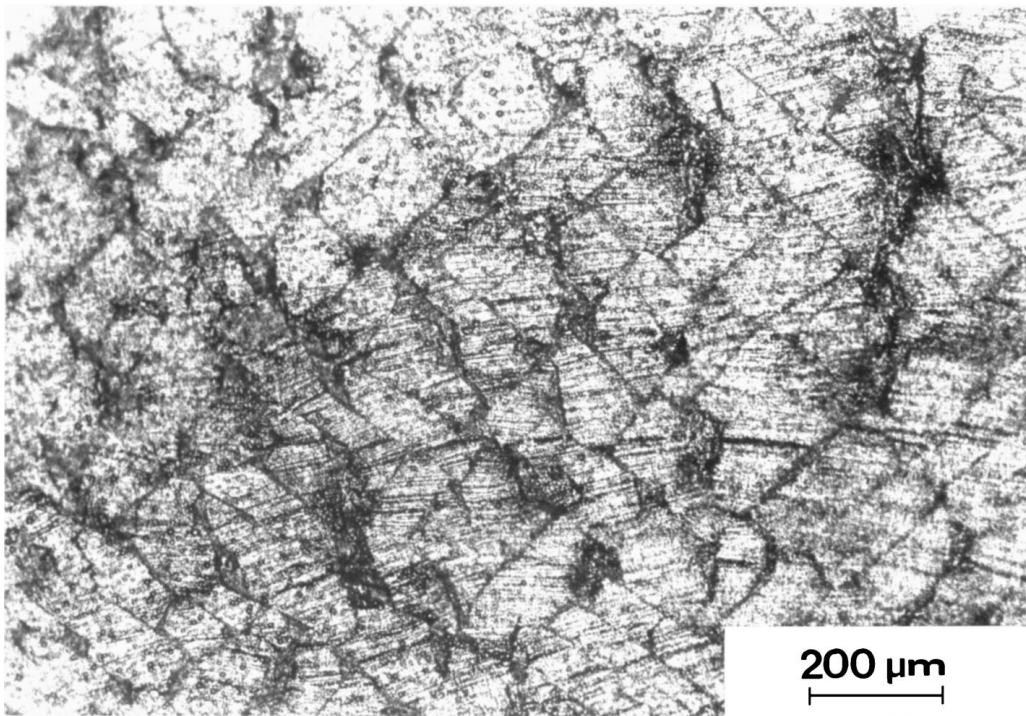
(b)

*Figure 5* Optical micrographs of the surfaces of all the heat-treated coatings, adjacent to the fracture surface of the tensile specimen: (a) coating heat-treated at 100 °C, (b) coating heat-treated at 200 °C, (c) coating heat-treated at 300 °C, (d) coating heat-treated at 400 °C, (e) coating heat-treated at 500 °C, (f) coating heat-treated at 600 °C. Time of heat-treatment was 1 hour. In all micrographs the tensile axis is parallel to the longer side of the photograph. (*Continued.*)

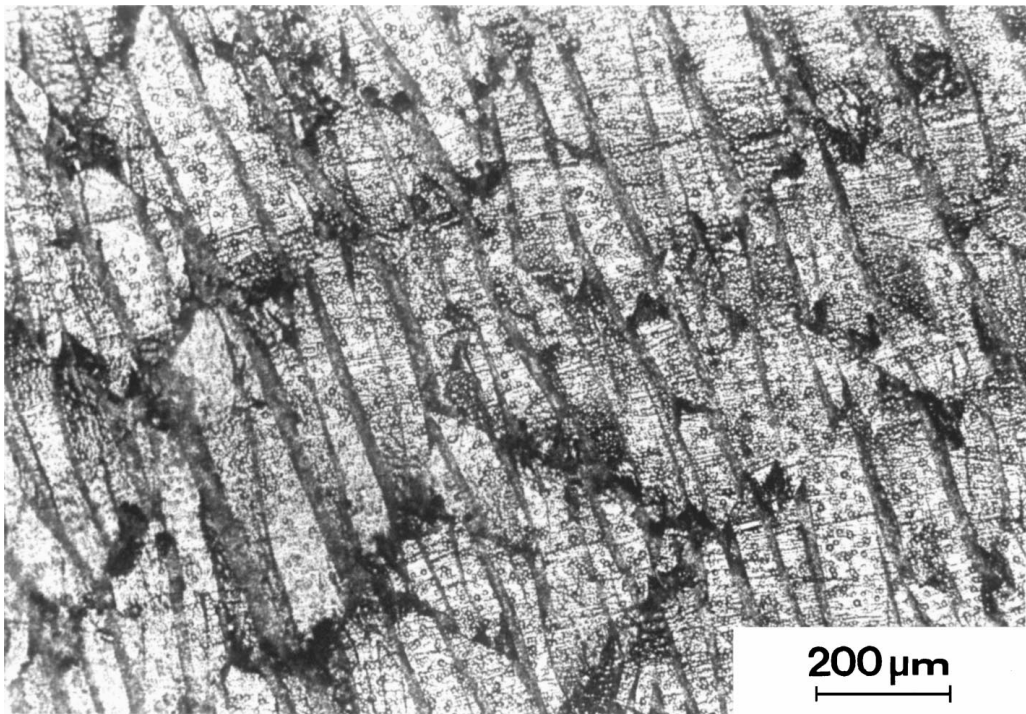
thickness: 1/50). However, the study of the behaviour of the coating during the tensile tests in terms of adhesion to the substrate, continuity and failure mechanism is of great importance since the above parameters will define the performance of the coating in applications where stress is involved. In an effort to derive some qualitative conclusions regarding the above, the surface of the electroless Ni-P coating was examined at different applied strains during the deformation of the coating-substrate system from the elastic region up to the fracture.

In Fig. 5a–f the surfaces of the heat-treated coatings for all heat-treatment conditions are shown, adjacent to the fracture surface of the tensile specimens, while in Fig. 6a–f the same surfaces are shown 1 cm away from the fracture surface of the tensile specimen. The surface of the as-deposited electroless Ni-P coating has the same appearance as the surface of the coating heat-treated at 100 °C, so it is omitted.

From Fig. 5a–f a general observation is that next to the fracture surface of the tensile specimen, the coating is heavily cracked while some pieces of the coating have



(c)



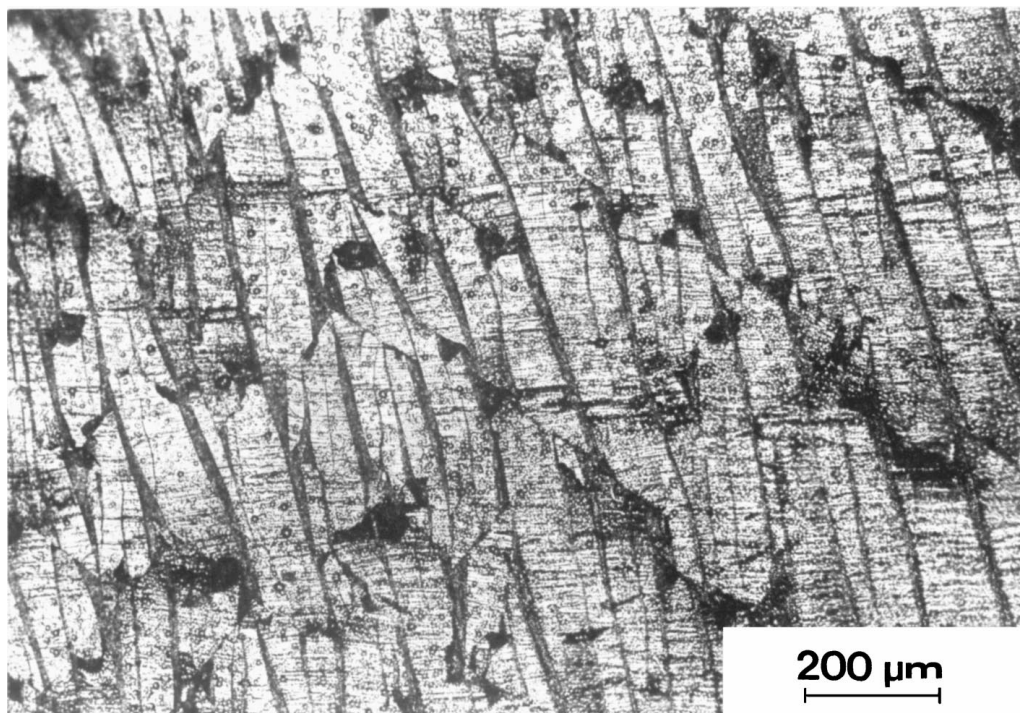
(d)

Figure 5 (Continued.)

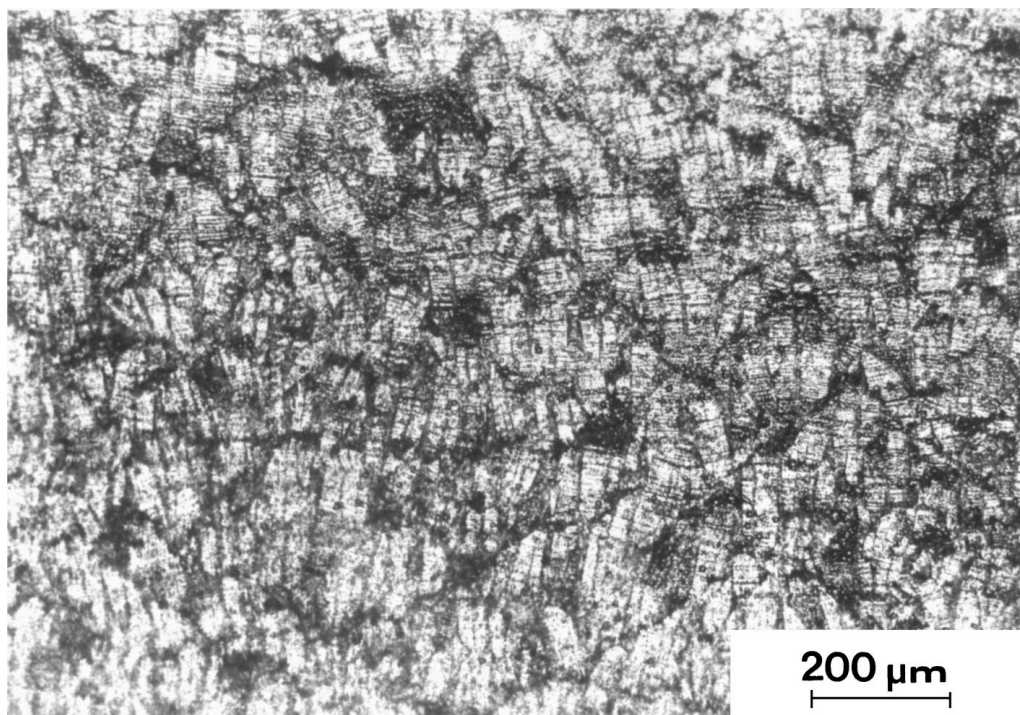
been detached from the substrate. The density of the cracks is smaller for the coating heat-treated at 100 °C (also for the as-deposited) but they are wider and deeper (Fig. 5a) and large pieces of the coating have been detached from the substrate. The cracks form an angle of 45–50° with the tensile axis and they also tend to form kinks and branches. For the coatings heat-treated at 200 and 300 °C (Fig. 5b and c respectively), the density of the cracks has increased substantially but the cracks are narrower and smaller pieces of the coating have been detached from the substrate. Although there is some

irregular cracking the majority of the cracks also form an angle of 45–50° with the tensile axis. For the coatings heat-treated at 400, 500 and 600 °C (Fig. 5d, e and f respectively) the cracks are nearly perpendicular to the tensile axis. This is more evident for the coatings heat-treated at 400 and 500 °C where the cracks are wider and deeper comparing to the narrower and rather irregular shaped cracks of the coating heat-treated at 600 °C. For the coatings heat-treated at 400 and 500 °C the detached pieces are mainly wedge-shaped due to the network of parallel cracks while for the coating





(e)



(f)

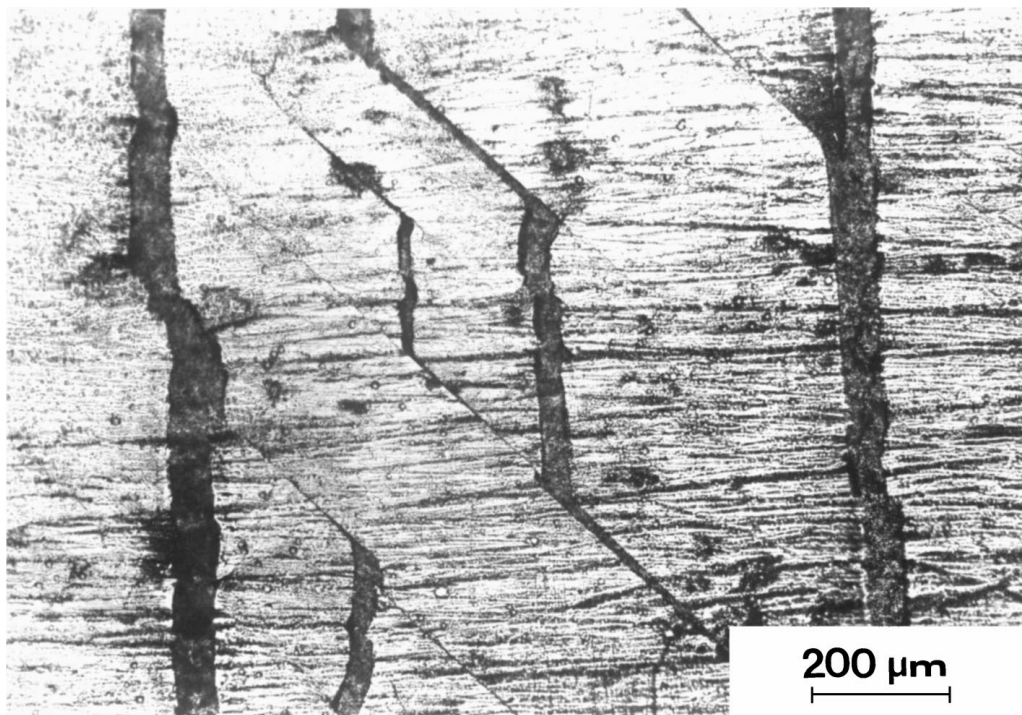
Figure 5 (Continued.)

heat-treated at 600°C the detached pieces are smaller and they have less regular shapes.

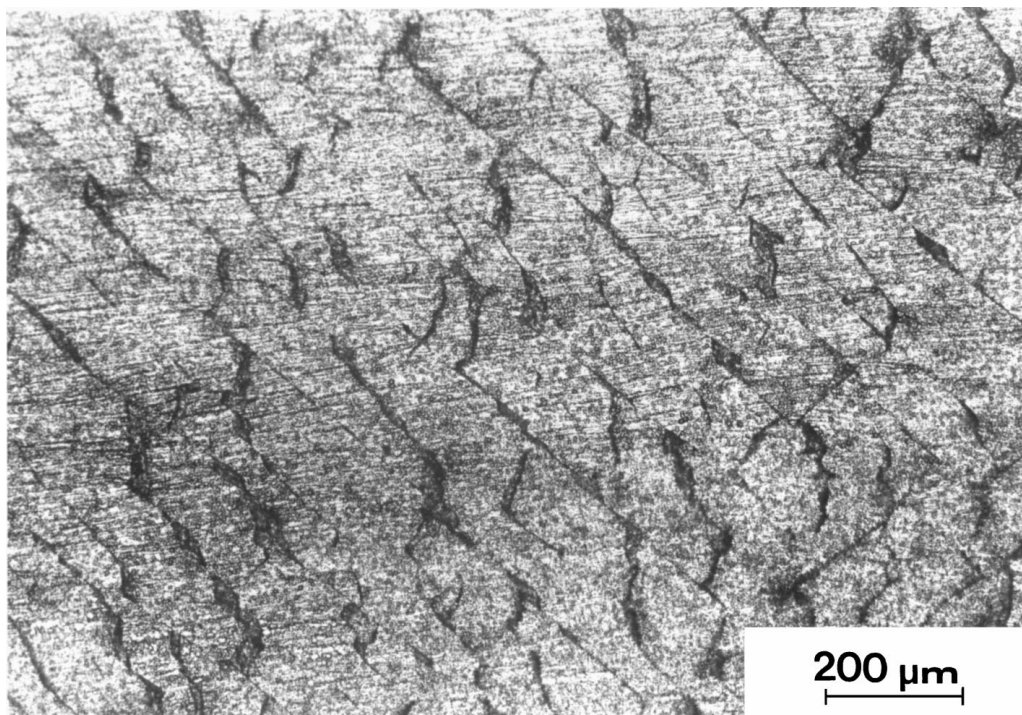
In Fig. 6a–f it is observed that 1 cm away from the fracture surface of the tensile specimens the crack density and the spalling of the coatings have been reduced significantly. Observing the surface of the coatings at the optical microscope, it was found that the crack density reduced gradually from the section next to the fracture surface to a distance about 1 cm from the fracture surface and then took a constant value for the rest of the gauge length. The orientation of the cracks in relation to the tensile axis can be seen more clearly now

and it is found that our previous observations concerning their orientation still hold. Another observation is that as the heat-treating temperature increases the crack density increases as well.

The change in the orientation of the crack as the heat-treating temperature increases, corresponds with the structural changes that take place in the coating with the rise of temperature. Up to 300°C the coating is mainly amorphous as the X-ray diffraction patterns show. At 400°C the coating becomes crystalline and consists of a Ni<sub>3</sub>P matrix containing areas of metallic nickel. As a result, the change in the orientation of the



(a)



(b)

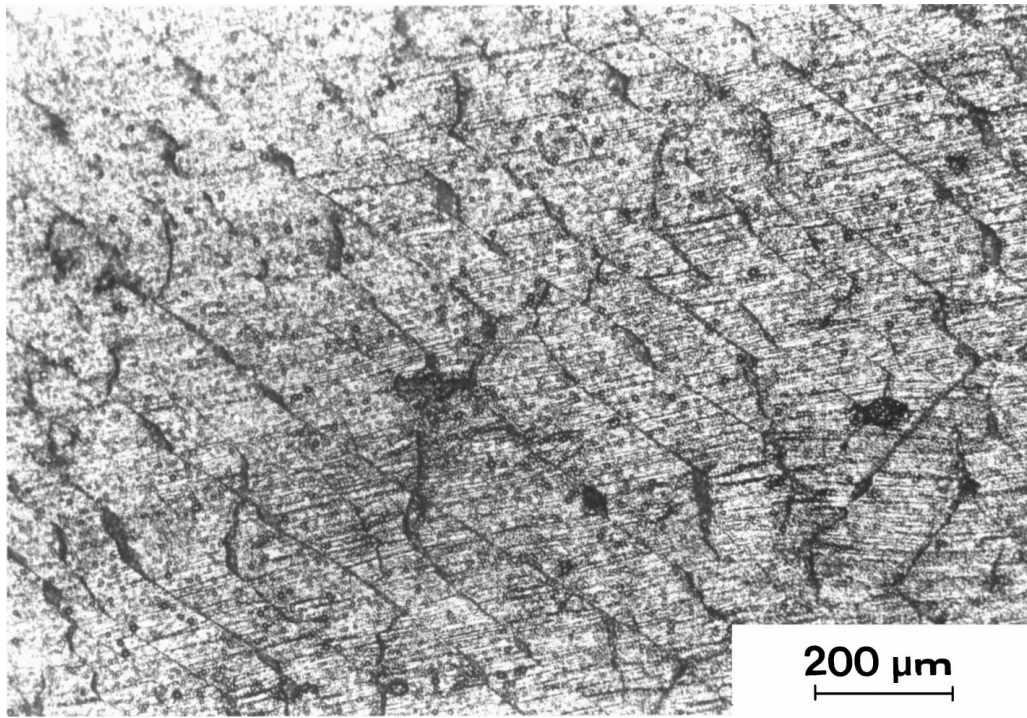
*Figure 6* Optical micrographs of the surfaces of all the heat-treated coatings, 1 cm away from the fracture surface of the tensile specimen: (a) coating heat-treated at 100 °C, (b) coating heat-treated at 200 °C, (c) coating heat-treated at 300 °C, (d) coating heat-treated at 400 °C, (e) coating heat-treated at 500 °C, (f) coating heat-treated at 600 °C. Time of heat-treatment was 1 hour. In all micrographs the tensile axis is parallel to the longer side of the photograph. (*Continued.*)

cracks may reflect a change in the failure mechanism of the coating as the structure of the coating transforms from amorphous to crystalline.

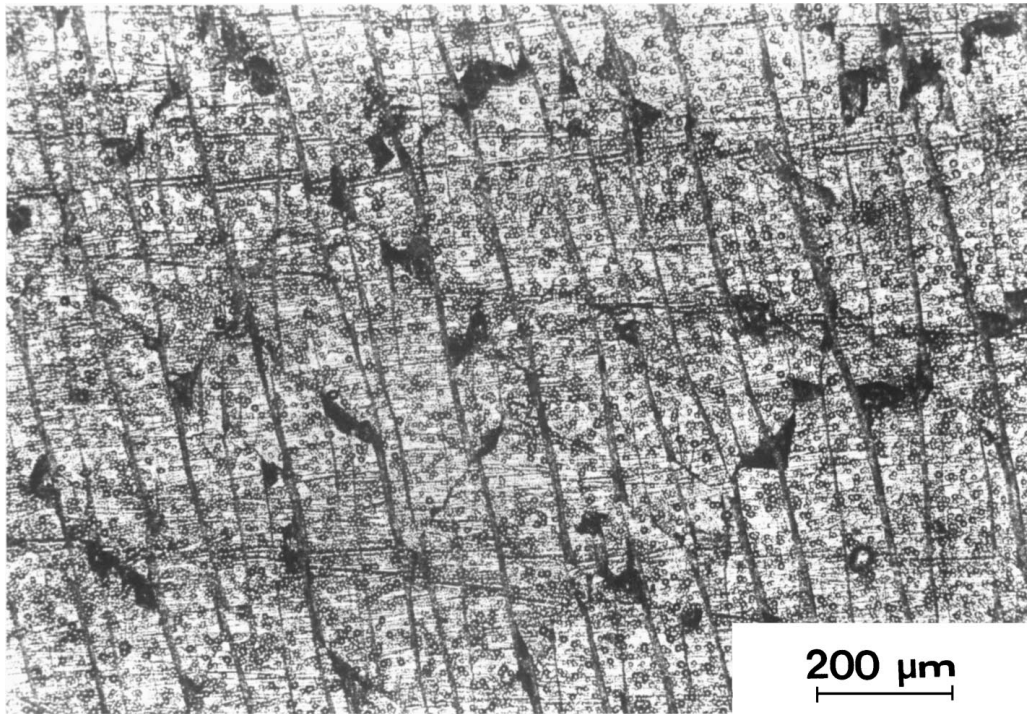
Cracking of the coating during the tensile tests seems to originate from its failure to accommodate the strain generated by the ductile substrate. The as-deposited coating has an amorphous structure with limited ductility, while the crystalline structure that is formed by heat-treating consists of an intermetallic compound

matrix ( $\text{Ni}_3\text{P}$ ) which contains areas of metallic nickel. Although nickel areas are ductile they are dispersed discontinuously [1, 2, 6] in the brittle matrix of the intermetallic compound and as a result the whole structure is brittle. Such brittle structures can accommodate strains much smaller than those accommodated by the ductile mild steel substrate which has a fracture strain of the order of 30%. During the tensile tests, the large difference in the ability for deformation between the





(c)



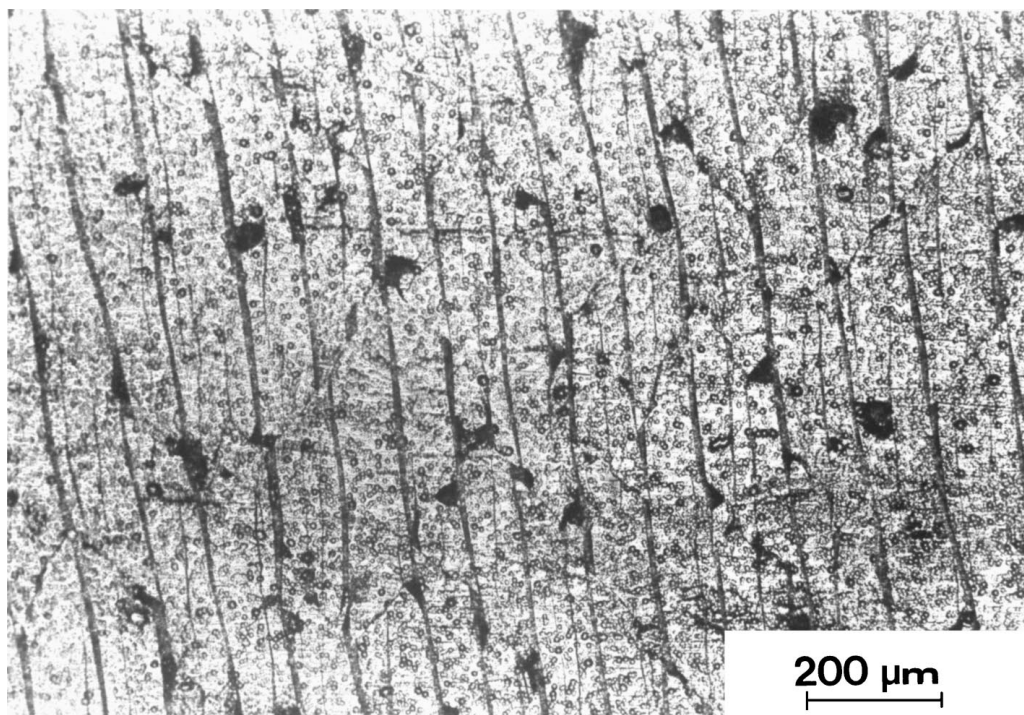
(d)

Figure 6 (Continued.)

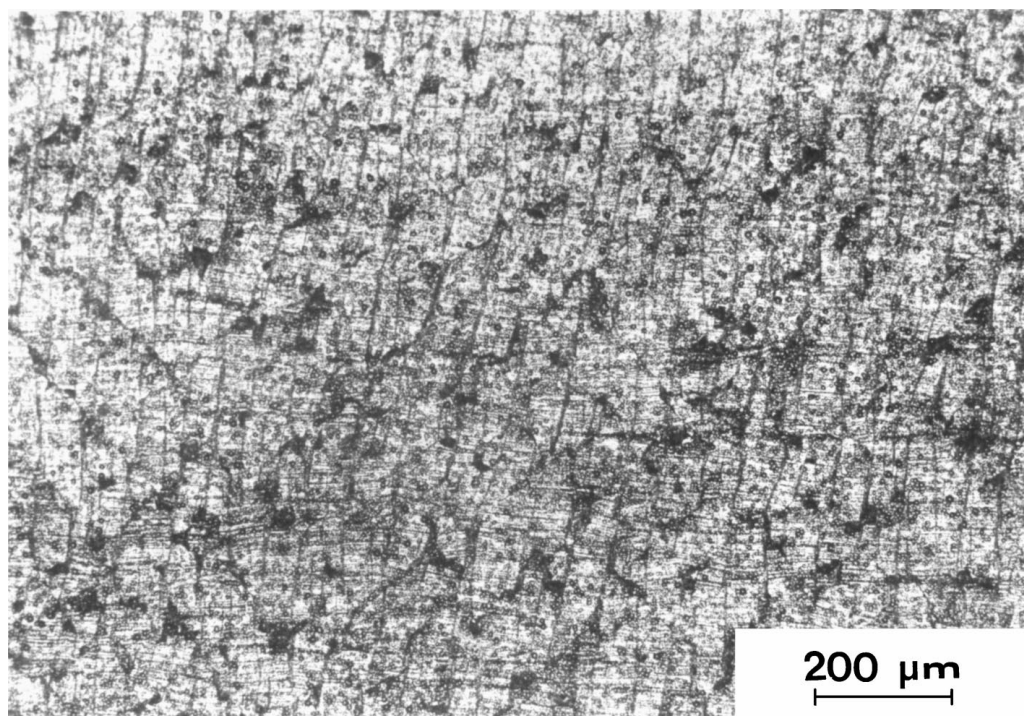
substrate and the coating leads to the generation of stresses which in turn may cause cracking of the coating as a stress relief means. Although the origin of coating cracking may be the same (stresses), the failure mechanism that is followed seems to vary, in close relation to the structure of the coating.

The cracks in the coatings that have an amorphous structure (the as-deposited and those heat-treated up to 300 °C as shown by X-ray diffraction), form an angle 45–50° with the tensile axis as discussed above. The array and orientation of the cracks in these coatings may

be a result of the typical failure mechanism of metallic amorphous materials as will be described below. For metallic amorphous materials it is known [9] that for temperatures not close to their glass transition temperature ( $T_g$ ) the deformation is inhomogeneous and almost entirely confined in a set of intense shear bands. The shear bands are usually formed in planes inclined 45–50° to the tensile axis, where the maximum shear stress acts and where a shear relaxation takes place, initially at regions with less density (or higher free volume) than the rest of the material. As the stress increases the



(e)



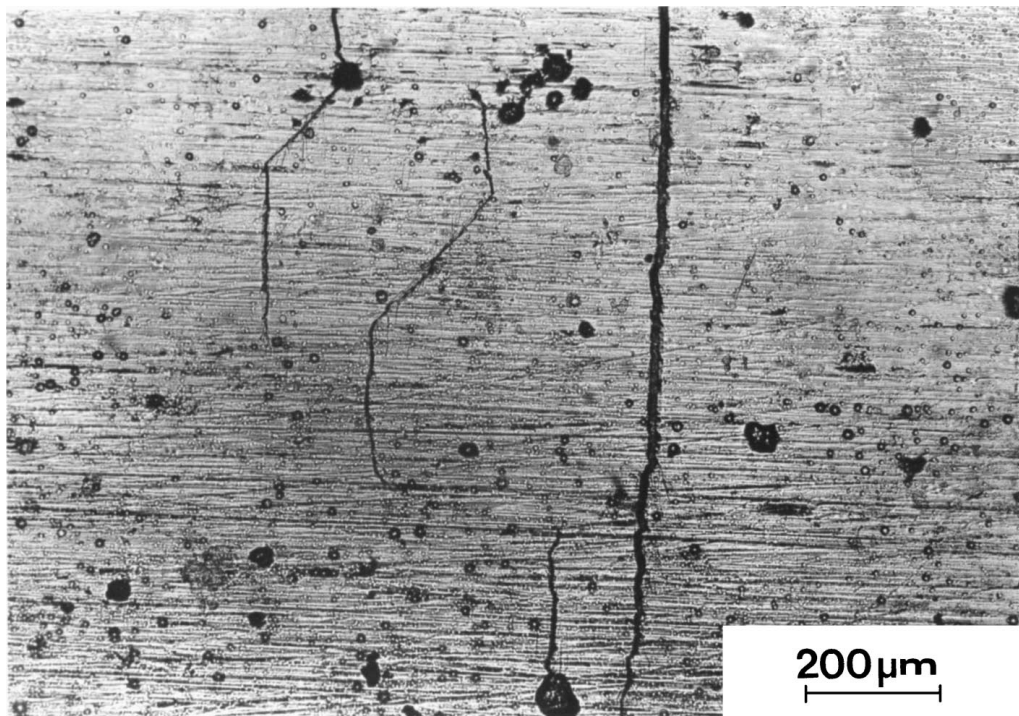
(f)

Figure 6 (Continued.)

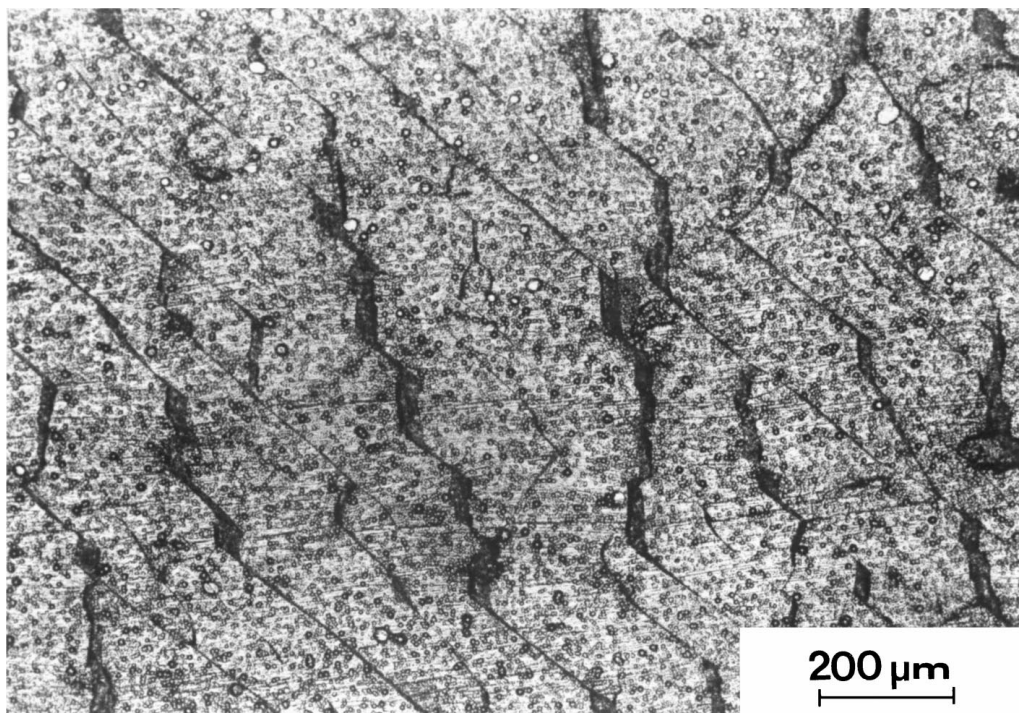
above sheared areas are being linked since other areas with higher threshold stresses can be transformed into sheared states and as a result shear bands are formed. Due to a strain induced softening into the shear bands at low temperatures [10], the resistance to plastic deformation in the shear bands drops, which in turn, concentrates the deformation further to form intense shear bands. Deep surface offsets at these intense shear bands act as initiating sites from which cracks propagate inward usually along the shear bands and finally fracture inside the shear bands occurs according to the “menis-

cus instability” mechanism [11]. In the coatings examined in this study the described fracture mechanism manifests itself by the inclined cracks that are observed at their surface.

The cracks in the coatings that have a crystalline structure (those heat-treated from 400 to 600 °C as shown by X-ray diffraction), are nearly perpendicular to the tensile axis. The brittle crystalline coating probably fails by the propagation of cracks into the brittle intermetallic compound matrix. The cracks nucleate at sites where there is a stress concentration (e.g. surface



(a)



(b)

Figure 7 Optical micrographs of the surface of a Ni-P electroless coating heat-treated at 200 °C at different strain levels: (a)  $\varepsilon = 4\%$ , (b)  $\varepsilon = 24.8\%$ , (c)  $\varepsilon = 33.5\%$ . In all micrographs the tensile axis is parallel to the longer side of the photograph. (Continued.)

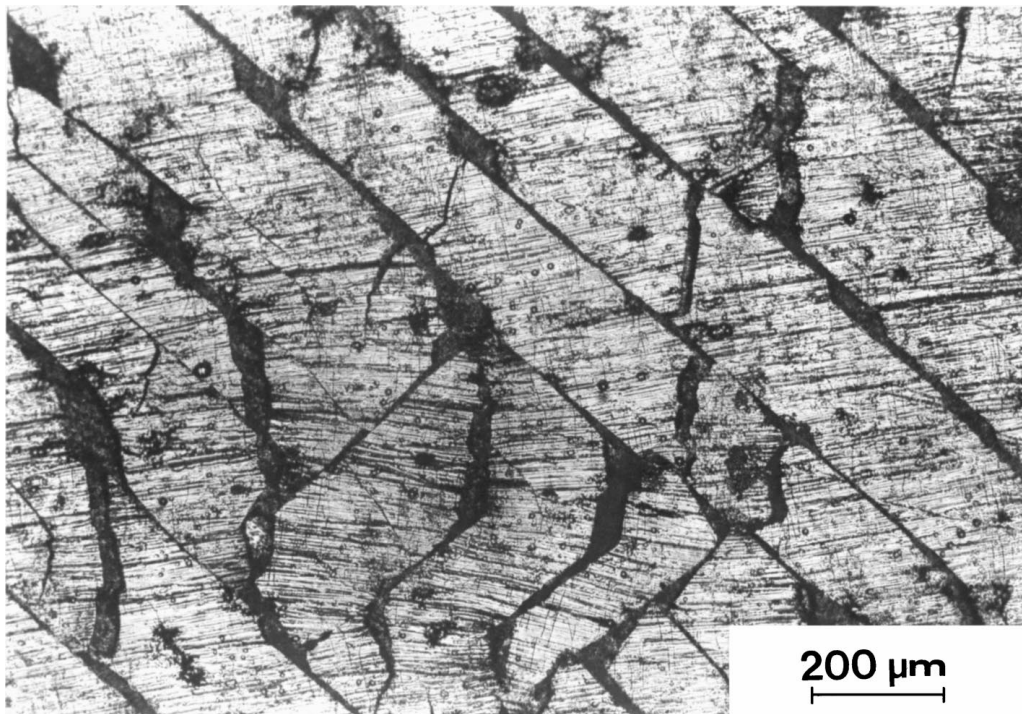
roughness or microvoids) and then they propagate normal to the tensile axis in a mode I fracture mechanism resulting in the array of cracks perpendicular to the tensile axis which are observed by the optical microscope.

The increase in the crack density and spalling of the coatings near the fracture surface of the tensile specimens can be attributed to the increased amount of deformation in this area due to the necking of the substrate. Larger local strains are generated which are more difficult for the coating to accommodate, causing its exten-

sive cracking. The increase in crack density with the rise of heat-treatment temperature as observed in Fig. 6a–f (especially for higher temperatures), may be a result of the increased constraint of the coating as the onset of limited diffusion at the coating-substrate interface with the rise of temperature increases the metallurgical bonding between the coating and the substrate.

A number of the performed tensile tests, were terminated at different strain levels before fracture, in an effort to study the evolution of surface cracks with the



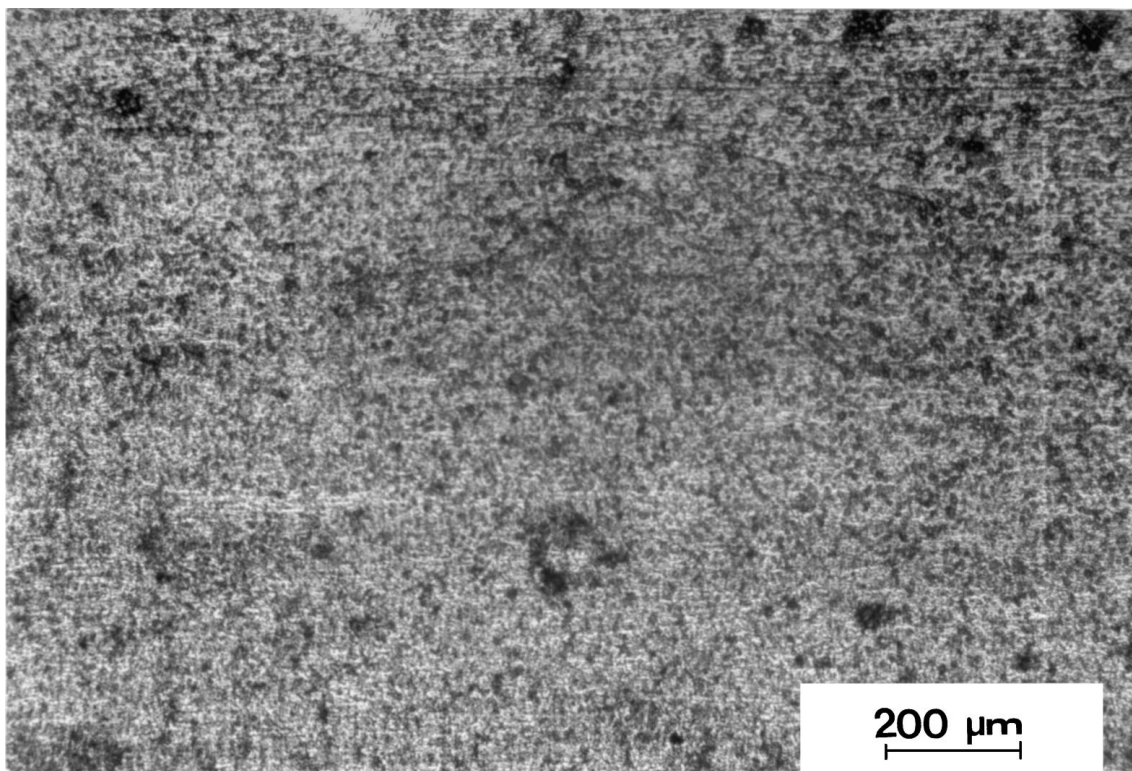


(c)

Figure 7 (Continued.)

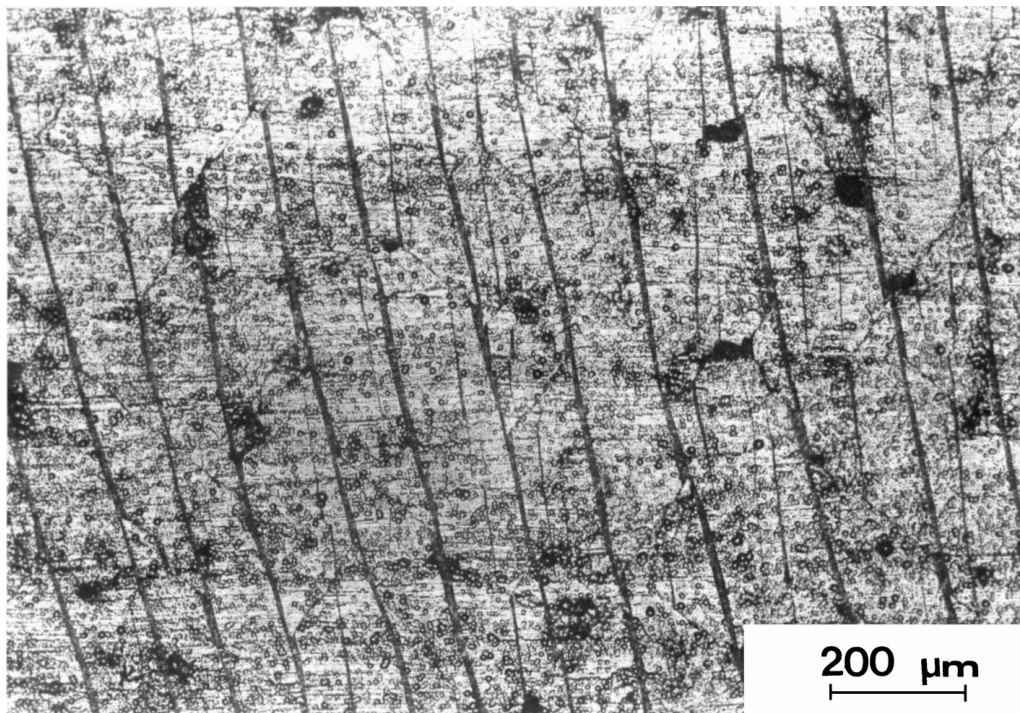
accumulation of strain. In Figs 7a–c and 8a–c the surfaces of two coatings heat-treated at 200 and 600 °C respectively are shown at different strain levels. From the above figures it is seen that for both amorphous and crystalline coatings the cracks form after the yield stress of the tensile specimen has been reached and

plastic deformation has taken place at the substrate (in Fig. 8a the strain is 0.5% and the specimen is still in the elastic region—no cracks are observed along the length of the specimen). When the yield strength of the specimen has been exceeded the first cracks are formed. For the amorphous coatings these cracks are

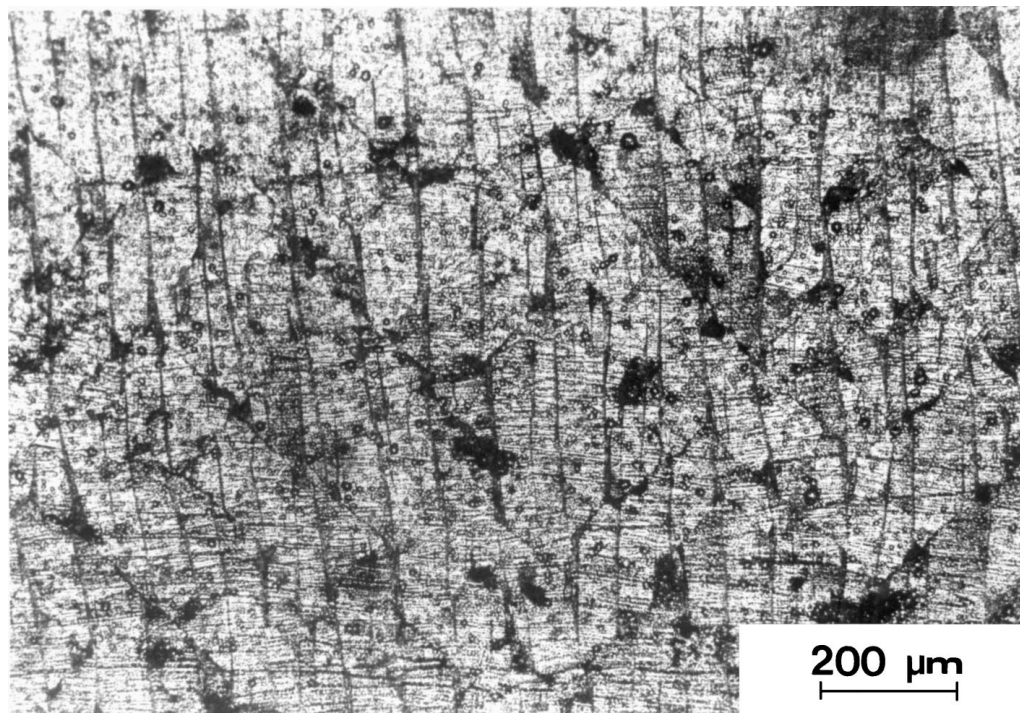


(a)

Figure 8 Optical micrographs of the surface of a Ni-P electroless coating heat-treated at 600 °C at different strain levels: (a)  $\epsilon = 0.5\%$ , (b)  $\epsilon = 26.9\%$ , (c)  $\epsilon = 37.2\%$ . In all micrographs the tensile axis is parallel to the longer side of the photograph. (Continued.)



(b)



(c)

Figure 8 (Continued.)

kinky and some of their segments are inclined to the tensile axis while others lie normal to it. Very few big cracks normal to the tensile axis also exist (Fig. 7a). As the strain is increased the inclined cracks originating at shear bands predominate. Their density and the spalling of the coating increases as the strain increases (Fig. 7b and c). For the crystalline coatings the cracks that form after yielding of the tensile specimen lie nearly normal to the tensile axis and their density also increases with the accumulation of strain (Fig. 8b and c).

#### 4. Conclusions

The study of the effect of heat-treatment on the structure and tensile behaviour of electroless Ni-P deposits on mild steel has come to the following conclusions:

- The as-deposited electroless Ni-P coating is amorphous and it remains amorphous up to 300 °C. At 400 °C the coating becomes crystalline and consists of a Ni<sub>3</sub>P matrix containing areas of metallic nickel.



- For the selected coating/substrate thickness ratio, the contribution of the coating in the tensile properties of the coating-substrate system is negligible as expressed by the values of yield strength, ultimate tensile strength and fracture strain in mild steel substrates and coated as-deposited and heat-treated specimens.
- Extensive cracking of the coating accompanied by spalling was occurred during the tensile tests. The density of cracks was found to increase close to the fracture surface of the tensile specimen and with increasing heat-treatment temperature.
- The cracks observed on the surface of the coatings are believed to form due to the inability of the brittle coating to accommodate the strain generated in the ductile substrate. Their orientation to the tensile axis is in close relation to the structure of the coating and the failure mechanism that is dictated by this structure.
- The first cracks on the surface of the coatings were found to form after the yield strength of the tensile specimen has been reached and plastic deformation of the substrate takes place. Their density increases with the accumulation of strain up to fracture.

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