Surface Characteristics of Structural Steel Processed Using Electro-Plasma Techniques

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Electro-plasma cleaning and deposition (EPCAD) is a recently developed electrolytic process for cleaning mill scale and other impurities from newly manufactured steel. The process offers reduced costs, improved coating adhesion, and increased corrosion resistance as potential benefits. Test samples of A-36 mild steel were cleaned using the EPCAD process and an industrial wheelabrator unit. Surface profile measurements and scanning electron microscopy were performed on both sets of samples to investigate the respective surface morphologies. Cleaned samples were then coated with an inorganic ceramic-based zinc primer. Tensile adhesion tests were performed and showed comparable adhesion properties for the EPCAD-cleaned and shot-blasted samples. The favorable adhesion properties are attributed to the microroughness and unique surface morphology produced by the EPCAD process.

Keywords A-36 steel, corrosion resistance, electro-plasma cleaning and deposition (EPCAD), tensile adhesion

1. Introduction

Most of the approximately 90 million metric tons of steel manufactured in the United States each year must be cleaned and protected from further oxidation (by applying organic or metallic coatings) before it can be further processed. The primary cleaning processes currently used for the removal of mill scale include acid pickling and grit- or shot-blasting, each of which has advantages and disadvantages in terms of cost, performance, and environmental effects. There remains a need for cost-effective cleaning and coating processes that can produce long-lasting corrosion resistance and are environmentally friendly.

One promising process is electro-plasma cleaning and deposition (EPCAD), a recently developed electrolytic process for cleaning mill scale and other impurities from newly manufactured steel and from steel to be refurbished, as well as applying metal coatings to the cleaned steel surface.[1-3] The process may offer benefits such as reduced processing costs, improved coating adhesion, and increased corrosion resistance. It is being investigated for its potential application to processing of structural steel and steel plate, particularly in the shipbuilding industry. The current study concentrates on the unique surface morphology generated by the electro-plasma technique, and its effect on the adhesive properties of the treated surface. The surface profile, morphology, and adhesive properties of the electro-plasma-cleaned surface are compared to those of steel cleaned by conventional shot-blasting.

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2. Background

Because EPCAD is a recently developed and relatively unknown process, a brief description is presented. Electro-plasma cleaning and deposition is a novel electrolytic process developed by Steblianko and Riabkov.[1-3] It can be used to clean the surface of a workpiece, or to clean the surface and simultaneously deposit a metal coating. In the process, an electrolytic cell is established in which the workpiece (the object or structure to be cleaned/coated) serves as the cathode, and an anode is introduced in close proximity (on the order of 10's of millimeters) to the workpiece surface. An electrolyte flows under pressure through holes in the anode, and is introduced into the space between the anode and the cathode (workpiece). The process is conducted at voltages that lie within a regime in which the electrical current decreases, or remains approximately constant, with an increase in the applied voltage between the anode and the workpiece. This corresponds to a condition where discrete bubbles of gas are present on the workpiece surface (rather than a continuous gas film or layer). Establishment of this state depends on the proper combination of several variables, including the voltage, inter-electrode working distance, electrolyte conductivity, electrolyte flow rate, and electrolyte temperature.

Metal cations, present in the electrolyte film, begin to migrate toward the steel surface, but the large majority of these ions attach to the gas bubbles. As the ions concentrate on the gas bubble surface, the bubble is converted into a small capacitor. The electrical field between the positive ions at the bubble surface and the negatively charged steel surface ionizes the gas in the bubble, forming a high-temperature plasma. This all occurs quickly and the life span of the average bubble is <1 ms and the plasma exists for 1 to 10 μs. The plasma is continuously forming at this high rate over the entire surface and results in fine sparks that produce local surface melting, and also creates forceful pressure disruptions at the surface associated with bubble collapsing and shock wave production. The net effect of these processes in the case of steel with mill-scale is removal and/or reduction (to iron) of the scale at the surface, and formation of circular wavelets and spheroids. For cleaning and coating applications, this process is accompanied by the simultaneous deposition of the anode material (or metal ions from the electrolyte).

Electrolytic cleaning is an established technique for cleaning metal surfaces, whereas plasma-based techniques conducted under vacuum conditions have been demonstrated for surface treatment of materials, including both cleaning and coating applications. The EPCAD process can in some ways be viewed as a combination of these techniques. In direct current, or cathodic electrocleaning, a negative bias is applied to the workpiece in a manner analogous to the EPCAD process.[4] The main aspect that distinguishes the EPCAD process from traditional electrocleaning is the operating voltage. Electrocleaning is conducted at voltages in the 1 to 12 V range, whereas EPCAD operates at higher voltages, somewhere in the range of 10 to 250 V, depending on the process parameters.

Although electrocleaning is a familiar technique in the steel industry, plasma processing is a more novel technique under consideration for industrial steel processing. Low-temperature plasma generation in low-pressure electrical discharges is an accepted technique for cleaning material surfaces, formation of thin-film structures and coatings, and surface modification, particularly in the electronics industry.[5-10] Hydrogen discharge cleaning is a well-known technique for the removal of light impurities from stainless steel in vacuum vessels.[12-17] In cleaning applications, such plasma processes have been demonstrated to remove lubricant layers from metal surfaces and to improve adhesive properties of the surface.[18,19] Bertrand et al. demonstrated that H_2 plasma treatment could produce almost complete reduction of the native oxide coating on stainless steel, along with cleaning of hydrocarbon surface contamination.[20] Plasma cleaning in argon and hydrogen atmospheres has been studied for the decontamination of steel, and its effect on the covering ratio and adhesion of protective plasma-deposited polymer coatings.[21-23] Oxygen plasmas have been shown to be effective for removing residual carbon contamination from annealed and cold-rolled aluminum surfaces.[24] A major consideration is that industrial application of these techniques requires feeding stock through several pressurized stages with load-lock systems, and such systems have been investigated by Lucas et al.[12] Belkind et al. reported the design and operation of a linear hollow cathode plasma source, with gas flow passing through holes in the cathode into the vacuum chamber, for cleaning metal surfaces in in-line systems.[25] Thus, progress toward industrial applications is being made. Since the EPCAD process involves the generation of a near-surface plasma, and if this can be controlled, there is potential to utilize the unique advantages demonstrated for plasma treatment, without the restriction of vacuum conditions.

3. Experimental

Coupons of structural grade A-36 mild steel (cold rolled; <0.25% C, <0.04% P, <0.05% S, <0.4% Si) with mill scale (<2% red dust) were used as the starting material for testing. One set of coupons was cleaned using the EPCAD process operating with a 14% $NaHCO_3$ electrolyte solution at 220 V. Another set of coupons was cleaned with an industrial wheelabrator unit using SAE size no. S-170 steel shot to produce an SSPC-10 near white, NACE-2 surface. Sets of each type of cleaned sample were coated with an inorganic ceramic-based zinc primer at a thickness of 20 μm.

The surface profile of the cleaned samples was measured using (1) an Elcometer (Elcometer, Manchester, U.K.) 225 digital surface profile gauge (as used in field measurements) and (2) a stylus-based profilometer. Scanning electron microscopy (SEM) was performed using a Hitachi (Tokyo, Japan) S-4500II field emission SEM. Photomicrographs were obtained from cross sections of the cleaned samples and the samples coated with the preconstruction primer and surface views of the cleaned samples. Tensile adhesion tests were performed in accordance with ASTM D-4541. Dollies with a 1.27-cm diameter were glued to the coated samples using an epoxy adhesive. The force to remove the dollies was measured using an Elcometer 106-2 adhesion tester.

4. Results and Discussion

The first set of surface profile measurements of the EPCAD-cleaned and shot-blasted surfaces were performed using the Elcometer 225 digital surface profile gauge. This instrument measures peak-to-valley height with a range of 0 to 1 mm and a resolution of 0.001 mm. More than 30 individual measurements were made for each type of sample. The measurements of the EPCAD samples gave a mean peak-to-valley value of 22 μm and a maximum peak-to-valley reading of 38 μm. The measurements of the shot-blasted samples gave a mean peak-to-valley value of 49 μm and a maximum peak-to-valley reading of 153 μm. The maximum roughness height (R_y) within a sample length of 2 mm was measured using a stylus profilometer, producing values of 13 and 21 μm for the EPCAD-cleaned samples and 50 and 55 μm for the shot-blasted samples. These results are consistent with the mean values obtained using the digital surface profile gauge. In addition to the peak-to-valley values, stylus profilometers were used to obtain values of the average roughness (R_a) and root mean square roughness (R_q) for the surface profiles. The results of the profilometer scans are summarized in Table 1.

These parameters indicate a higher surface roughness, or superior profile, for the shot-blasted samples. This is very significant. The surface profile is a critical parameter used to assess the quality of surface preparation for coating, because the surface roughness can be correlated to the adhesive properties of the surface. In industrial applications, a required pro-

Table 1 Surface Profile Parameters

Sample		R_a (μm)	R_q (μm)	R_y (μm)
EPCAD cleaned	EP-1	2.3	—	13
	EP-2	2.0	—	21
	EP-3	1.88	3.09	—
Shot blasted	SP-1	7.9	—	55
	SP-2	7.7	—	50
	SP-3	5.58	7.04	—
	SP-4	6.49	8.31	—
	SP-5	6.78	8.39	—

file is defined, e.g., 28 μm. On the basis of such criteria, the surface profile produced using the EPCAD process would be considered inadequate, and poor adhesion characteristics would be expected. Producing an adequate surface profile for adhesion of the preconstruction primer is critical for industrial application of the EPCAD process as an alternative to shot-blasting.

SEM was performed on cross sections to reveal the surface profiles of the cleaned steel surfaces. Photomicrographs of an EPCAD-cleaned surface profile are shown in Fig. 1, and reveal a high degree of microroughness, with features on a scale of <10 μm. In contrast, photomicrographs at the same magnification taken from a shot-blasted sample do not exhibit this microroughness (Fig. 2). The shot-blasted surface profile has features on a larger scale—10's of micrometers—as can be seen at lower magnification in Fig. 3. The EPCAD-cleaned surface is relatively smooth on this larger scale. The difference in morphology between the two surfaces is further illustrated in Fig. 4 and 5. In Fig. 4, photomicrographs of EPCAD-cleaned and shot-blasted surfaces are shown at a lower magnification (approximately equal to that in Fig. 3). At this magnification, the surface roughness of the shot-blasted surface is evident, but the EPCAD surface looks relatively flat. However, when these same surfaces are viewed at higher magnification (Fig. 5), the microroughness and the unique surface morphology of the EPCAD-cleaned surface are evident. In addition, the sources of the two types of profiles are reflected in their respective surface morphologies. In the shot-blasted material (Fig. 5b), individual indentions made by the shot can be distinguished, and the scale of features is correlated to the shot size (<0.850 mm for S-170 shot) and the energy at impact or depth of indention. In contrast, the EPCAD-cleaned surface morphology reflects the history of local surface melting, with a porous surface profile in which the scale results from the size of the hydrogen bubbles formed in the plasma region. The size of the hydrogen bubbles is determined by processing parameters such as the gap be-

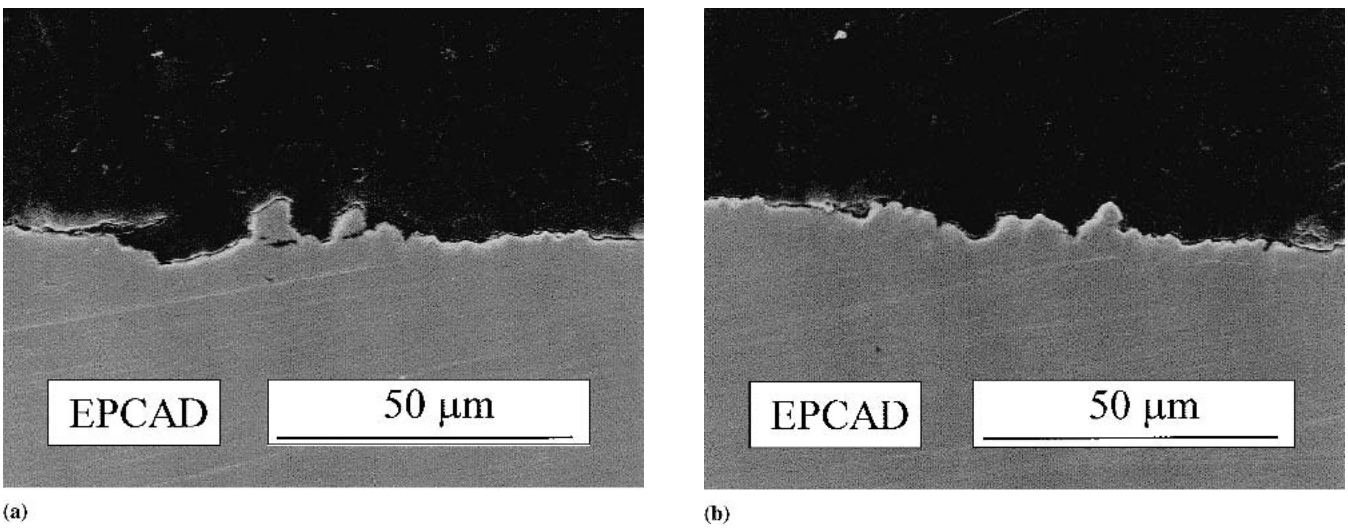


Fig. 1 SEM photomicrographs of an EPCAD-cleaned surface profile

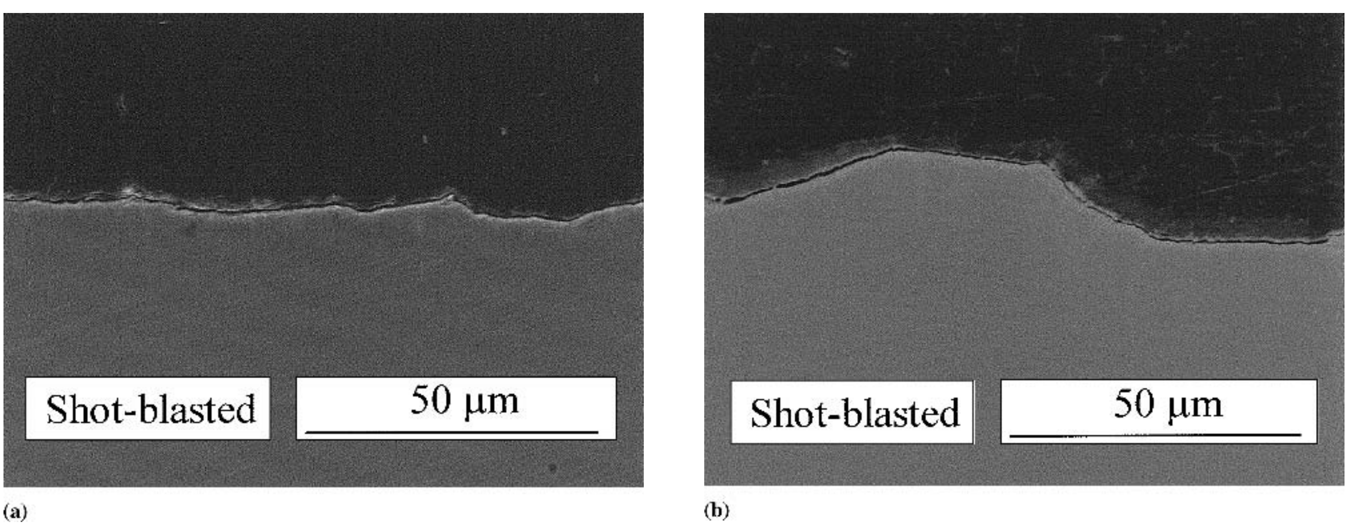


Fig. 2 SEM photomicrographs of shot-blasted surface profile (same magnification as Fig. 1)

tween the workpiece and anode, current, electrolyte concentration, flow rate, and pressure.

The SEM results are consistent with the surface profile measurements, that is, values of roughness parameters R_y, R_a, and R_q approximated from the SEM images are consistent with the values in Table 1. However, these images give a much different view with regard to the surface profile. The fact that these are two completely different types of profiles becomes evident upon viewing the SEM results.

Tensile adhesion tests were performed in accordance with ASTM-D 4541 as a measure of the adhesive properties of the EPCAD-cleaned and shot-blasted surfaces. The preconstruction primer was applied in an identical fashion for all samples. The results are summarized in Table 2. The EPCAD-cleaned surfaces and shot-blasted surfaces exhibited similar adhesive properties. At loadings above ~28 MPa, the failure was generally 100% adhesive; i.e., the dolly was removed due to failure of the epoxy adhesive, with no indication of debonding be-

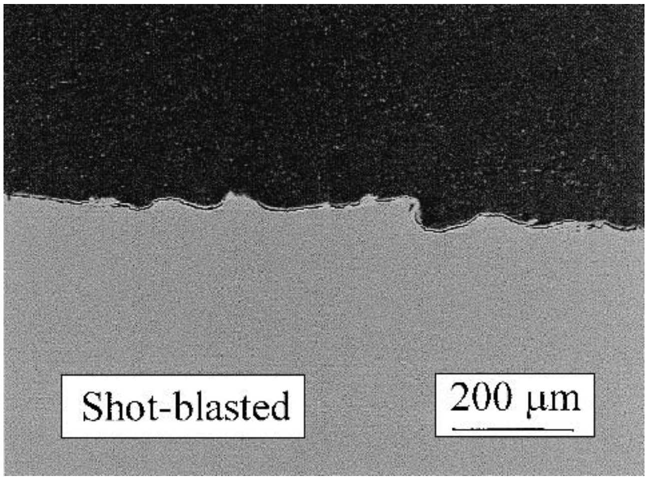
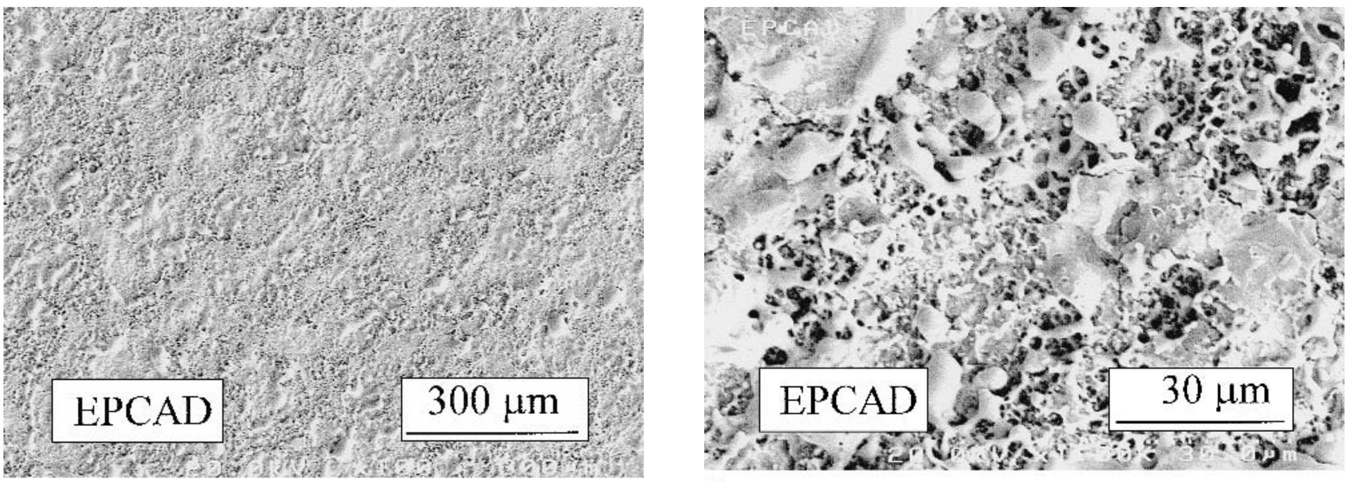
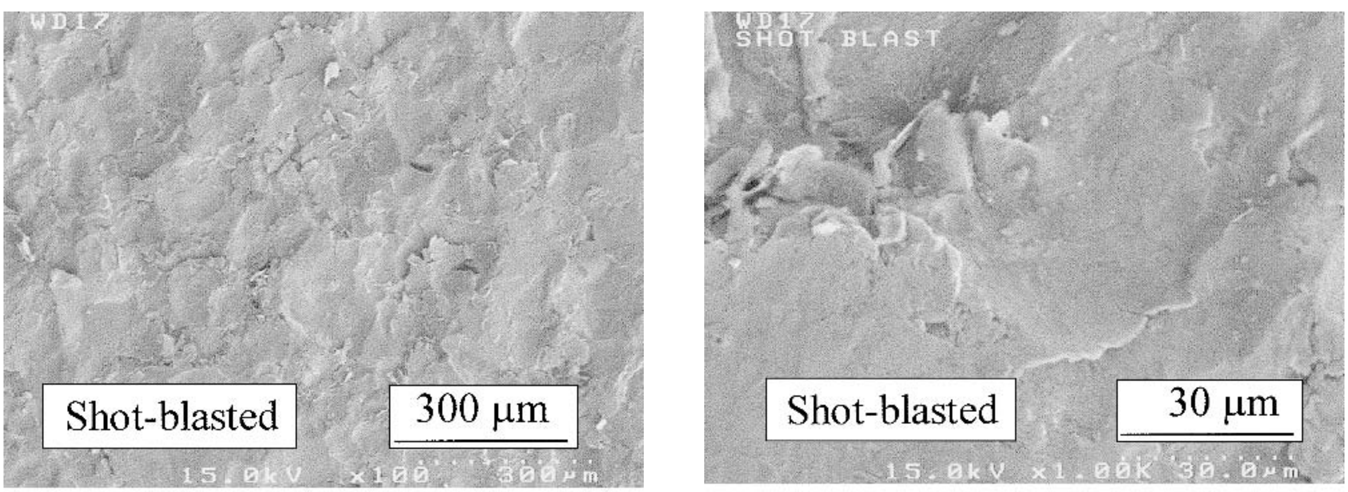


Fig. 3 SEM photomicrographs of shot-blasted surface profile (lower magnification than Fig. 2)



(a) **(b)**

Fig. 4 SEM photomicrographs EPCAD-cleaned and shot-blasted surfaces at (relatively) low magnification (similar to the profile view in Fig. 3)



(a) **(b)**

Fig. 5 SEM photomicrographs EPCAD-cleaned and shot-blasted surfaces at (relatively) higher magnification (similar to the magnification in the profile view of Fig. 1 and 2) tween the coating and the steel surface. For both EPCAD-cleaned and shot-blasted samples, two of five tests showed some cohesive failure (debonding between the coating and the steel), with the shot-blasted samples failing at slightly lower average loading. The results can be taken as evidence that the EPCAD-cleaned samples are a viable alternative from the standpoint of adhesive properties.

Table 2 Results of Tensile Adhesion Tests

Sample		Cohesive Failure	Adhesive Failure	MPa (psi)
EPCAD cleaned/	EP-1	90%	10%	3.5 (500)
NippeCeramo	EP-2	95%	5%	2.1 (300)
primer	EP-3	0%	100%	>7.0 (>1000)
	EP-4	0%	100%	>7.0 (>1000)
	EP-5	0%	100%	3.5 (500)
Shot blasted/	SP-1	50%	50%	1.4 (200)
NippeCeramo	SP-2	75%	25%	2.1 (300)
primer	SP-3	0%	100%	2.8 (400)
	SP-4	0%	100%	2.8 (400)
	SP-5	0%	100%	4.1 (600)

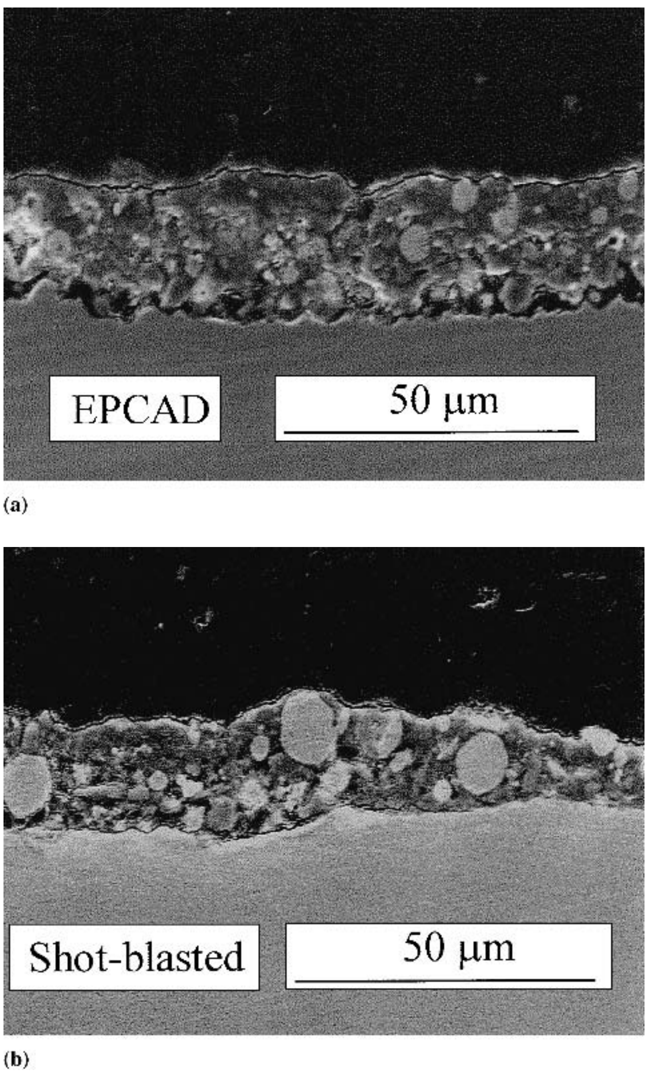


Fig. 6 SEM photomicrographs of samples coated with preconstruction primer: (a) EPCAD-cleaned surface; (b) shot-blasted steel surface

It is interesting that the EPCAD-cleaned and shot-blasted samples have similar adhesive properties, although the physicomechanical component of the coating adhesion is drawn from surface profiles with roughness features on very different scales. It is concluded that the microroughness observed in the SEM photographs (Fig. 1 and 5) is responsible for the adhesive properties of the EPCAD-coated samples. This effect can be seen in Fig. 6, which presents SEM photomicrographs of coated samples. The microroughness of the EPCAD-cleaned samples is observed, with the coating penetrating the valleys of the profile, wetting the entire surface. It is significant that the EPCAD-cleaned surface exhibits excellent adhesive properties, despite falling well below the profile of 28 μm required for many industrial coating applications. The correlation between the surface profile and the adhesive properties of a surface used in these applications is based on the type of surface profile produced by abrasive methods. As the SEM results clearly indicate, because the EPCAD process produces a completely different surface morphology, these correlations are not valid. If a simple surface roughness parameter is to be used to predict the adhesive properties of steel surfaces cleaned using the EPCAD process, a complete new set of standards (or an experimentally proven calibration to the current standards) must be established.

5. Conclusions

Test samples of A-36 mild steel were cleaned using the EPCAD process and an industrial wheelabrator unit. Surface profile measurements and SEM were performed on both sets of samples to investigate the respective surface morphologies. Cleaned samples were then coated with an inorganic ceramic-based zinc primer. To investigate the effectiveness of the resulting surface profiles to retain the coating, adhesion tests were performed.

Tensile adhesion tests showed comparable adhesion properties of the EPCAD-cleaned and shot-blasted samples. This was an unexpected result because the surface roughness produced by the EPCAD process, as indicated by values of R_y, R_a, and R_q, is much lower than that of the shot-blasted samples in the study. The adhesion properties are attributed to the microroughness and unique surface morphology produced by the EPCAD process. This indicates that the correlation between roughness parameters and adhesion properties developed for abrasive cleaning may not be applicable for surfaces cleaned using the EPCAD technique, and a new set of standards may be required.

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