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► **To cite this version:**

Alexandre Freulon, Anh Truc Trinh, Jacques Lacaze, Benoît Malard, Ke Oanh Vu. Effect of cast iron microstructure on adherence of an epoxy protection. International Journal of Cast Metals Research, The, In press. hal-03054007v1

HAL Id: hal-03054007

<https://hal.science/hal-03054007v1>

Submitted on 9 Jun 2020 (v1), last revised 11 Dec 2020 (v2)

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Effect of cast iron microstructure on adherence of an epoxy protection

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Abstract

To study the influence of the microstructure of cast iron on the adhesion of an epoxy coating, ferritic, pearlitic and austempered samples were prepared in as-received, polished and oxidized states.

A pull-off test (dry adhesion) was performed before immersing in water while the cross-cut test was made after 24 days of exposition in distilled water (wet adhesion). X-rays were combined with optical microscopy (LOM) and scanning electron microscopy (SEM) for surface analysis.

The adhesion of the epoxy coating on the cast iron surface firstly depends on the roughness of the surface; polished samples showed high adherence by comparison with as-received samples. On the oxidized samples, the surface oxide significantly improves the adhesion of the coating in both dry and wet states for all three sample microstructure. The presence of carbide in the structure was observed to decrease adherence.

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Introduction

Usual unalloyed cast irons have the same corrosion resistance or are more resistant than usual steels in many applications [1]. Amongst the several possible coatings for improving long-lasting corrosion resistance of cast iron components, epoxies appear as highly versatile ones and give a scratch-resistant finish [1]. In most conditions, graphite shape (lamellar vs. nodular) was reported to have little effect on corrosion resistance of cast irons [2]. In recent literature, a few works have been devoted to corrosion experiments in NaCl solutions [3, 4, 5, 6, 7] but only one was dealing with polymer protection of cast iron [8]. The present work was thus intended to investigate the possible effect of surface preparation and cast-iron microstructure on adherence of an epoxy protective layer. The investigation used both pull-off and adherence testing.

Materials and experimental details

Experiments were performed on an industrial nodular cast iron that has been processed to give ferritic, pearlitic and austempered grades. The material was received as three plates 2·80·80 mm³ of each grade. Three types of surface treatment were studied in this work: 1) as received; 2) polished with SiC papers from 80 to 1200 grades; 3) thermal treated at 600°C for 3 hours.

Micrographs of the material in the as-received state are presented in figure 1 for the ferritic and pearlitic grades. It is seen that the so-called ferritic alloy contains some pearlite while the pearlitic one shows some ferrite. The heat-treatment at 600°C did not lead to any noticeable change of the microstructure of the ferritic and pearlitic grades. In the case of the austempered material, the heat treatment led to limited evolution as can be seen in figure 2 where are compared the microstructures before (a) and after (b) treatment.

Before coating, all surfaces were initially alkaline degreased at 80°C for 15 min and washed with distilled water and then ethanol, and finally properly dried. The selected coating was a solvent-free epoxy resin, i.e. without solvent or water as diluent. The epoxy resin was diglycidylbisphenol-A (Epon 828, from Hexion) with an equivalent weight of about 185-192 g/eq. The hardener was a low viscosity modified cycloaliphatic polyamine (Ancamine 2735, from Air Products and Chemicals) with an equivalent weight per active H of 95 g/eq. The deposition of the epoxy coating was performed on the whole samples and processed so that

its final thickness was about 60 μm which was afterwards controlled with a Minitest FN2 600 from Erichsen. The variation in coating thickness from place to place on any of the samples was found to be $\pm 1 \mu\text{m}$.

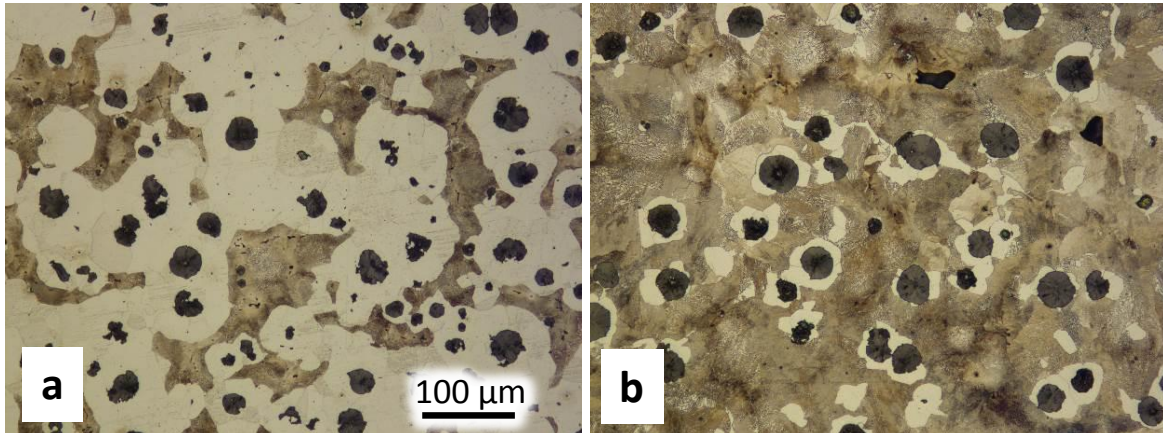


Figure 1 – Microstructure after Nital etching of the as-received ferritic (a) and pearlitic (b) materials. The scale is the same for both micrographs.

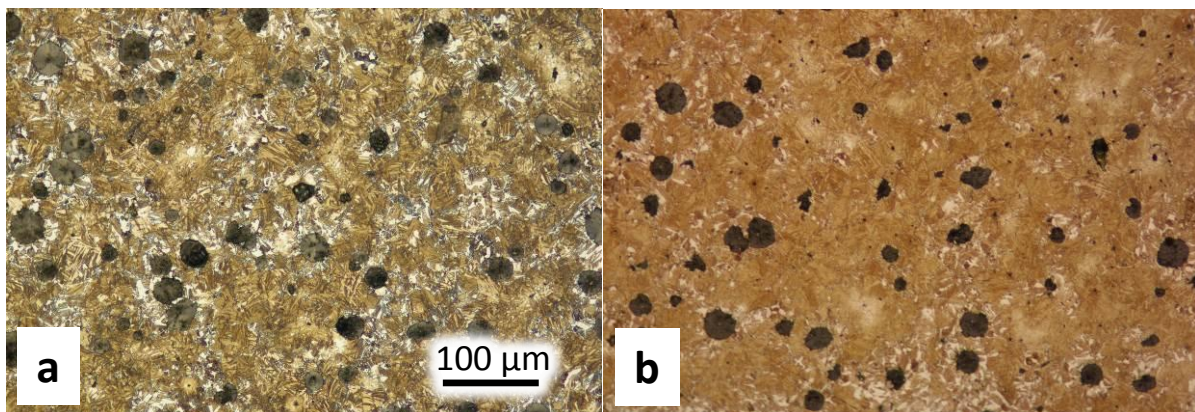


Figure 2 - Microstructure after Nital etching of the austempered material, respectively as-received (a) and after heat-treatment (b). The scale is the same for both micrographs.

The obtained coating is characterized by high density and adherence that make it highly suitable as a primer for subsequent protective or finish surface treatments. For checking the quality of the coating, the conventional adhesion pull-off test was first performed on one of the large surfaces of the samples. This was carried out using Positest Automatic Adhesion Tester following ASTM D-4541 standard. Though only one test was performed on each sample in the present study, the standard deviation of individual measurement may be set at 0.3 MPa on the basis of more extended results obtained on steels [9].

On the other large surface of each sample, the cross-cut adherence test was performed according to ASTM D-3359 standard (method B) to evaluate the adherence of the coatings after ageing in distilled water. Firstly, cross-hatch cuts with 6 blades spaced by 2 mm between cutting edges were performed. The samples were then immersed in water for 24 days, a duration which appeared necessary by preliminary tests for differentiating the samples. After this exposure, the samples were dried with a clean tissue paper to remove the surface water, and then kept at room temperature for 10 min to be sure of surface dryness. An adhesive tape 50 mm wide with adhesive strength of 9.5 N per 25 mm (ISO 2409) was then applied to the cross-cut coating surface. The tape was removed by a quick pull and the coating removal content was determined. The adhesive strength was evaluated by expressing the adhesive loss as $100 \cdot x/25$, where x is the number of squares of the coating that have been detached by the tape, with 25 being the total number of squares on the intact coating.

X-rays were performed in conditions allowing getting information from the surface and the substrate. Measurements were carried out with a X-rays beam from a copper anti-cathode (1.5406 Å) which is parallelized by a Gobel mirror. A constant low incidence angle of 10° was set while a Lynexeye XR-T detector was scanned from 10 to 120°.

Small samples were then cut and mounted, and finally prepared for observation by standard metallographic methods. Optical microscopy (LOM) and scanning electron microscopy (SEM) were used to observe the microstructure, the coating and the interface between them.

Results

Pull-off test results in table 1 showed a very good adherence of the epoxy layer, with effects of the substrate microstructure and of the surface preparation. The pull-off stress was seen to decrease from ferritic to pearlitic, and from pearlitic to austempered matrix structure for all three initial surface states. It should be stressed this applies as well for oxidized samples where it has been seen that the heat-treatment does not significantly modify the matrix structure as compared to the original ausferritized one. X-rays reported later suggest this decrease relates to the increased amount of carbides in the substrate.

For all matrix microstructures, table 1 showed also that polishing improved adherence and that oxidation did improve it further. It may mean that the surface roughness was too large in

the as-received state and that polishing and oxidation did decrease it. The suggested change in surface roughness is illustrated with the micrographs in figure 3.

Table 1: Pull-off test results (MPa)

Sample	As-received	Polished	Oxidized
Ferritic	7.7	8.8	12.8
Pearlitic	7.3	8.0	9.6
Austempered	6.8	7.1	8.2

After exposure to water during 24 days, adherence results listed in Table 2 showed again a significant effect of surface treatment for the as-received and polished states. It is noteworthy that the as-received material had better properties than the polished one, and also that the ferritic material showed an excellent adherence in both states while the ausferritized one showed deteriorated properties. However, an excellent adherence was obtained for all substrates after pre-oxidation of the material. Though it is generally admitted that roughness may improve adhesion [10], it is also known that stresses are generated at surface protrusions which may be decreased with a thin and regular oxide layer.

Table 2: Adhesive loss (%) after 24 days of exposure in distilled water

Sample	As-received	Polished	Oxidized
Ferritic	0	0	0
Pearlitic	0	26	0
Austempered	46	100	0

It appeared of interest to observe more specifically the ferritic samples as all of them are reported as having no loss (table 2). Figure 4 shows LOM images of the ferritic samples after the adhesive loss test using dark-field conditions to image differently the substrate, the epoxy layer and the mounting. It is seen that only the oxidized sample showed that all of the epoxy remained effectively attached to the surface. For the other two samples, as-received and polished, the cut area is marked by large gaps in the epoxy layer. In the case of the polished sample (Figure 4-b), it is seen that these gaps originate from a separation appearing between the epoxy layer and the substrate, which leads or not to a partial breaking-off of the epoxy layer. This improved adherence of the epoxy on the oxidized materials as compared to the

other two is in line with results by Wielant [11]. It is thought to relate to the high polarity of epoxy resins which supports the adhesion by favouring the interaction between hydroxyl group or oxirane ring with active hydrogens on the oxide surface.

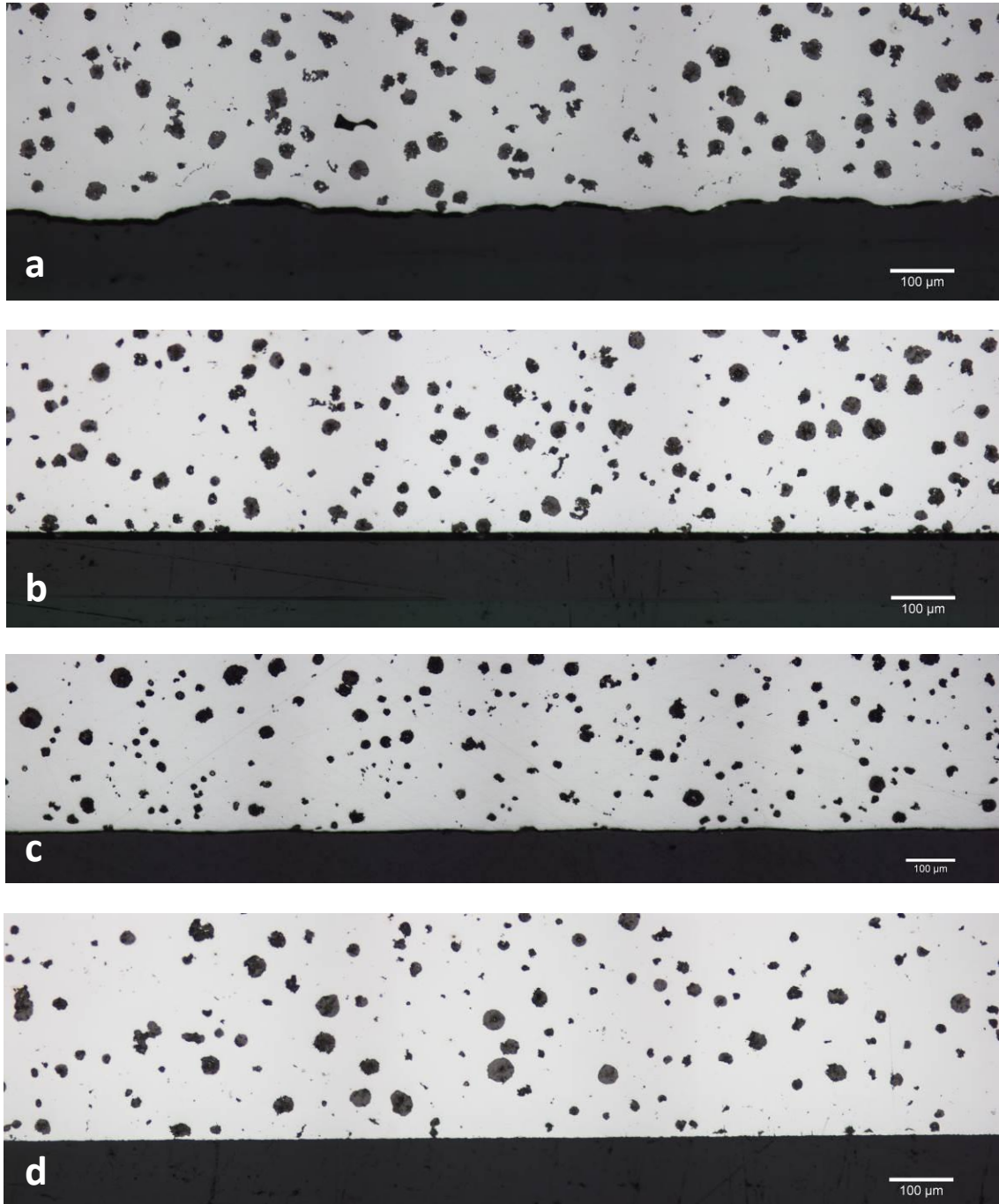


Figure 3 - Micrographs showing the surface of ferritic (a and b) and ausferritized (c and d) materials in as received condition (a and c) and after polishing (b and d). The dark area at the bottom of each micrograph is the mounting; the epoxy layer in between the mounting and the material surface can hardly be noticed.

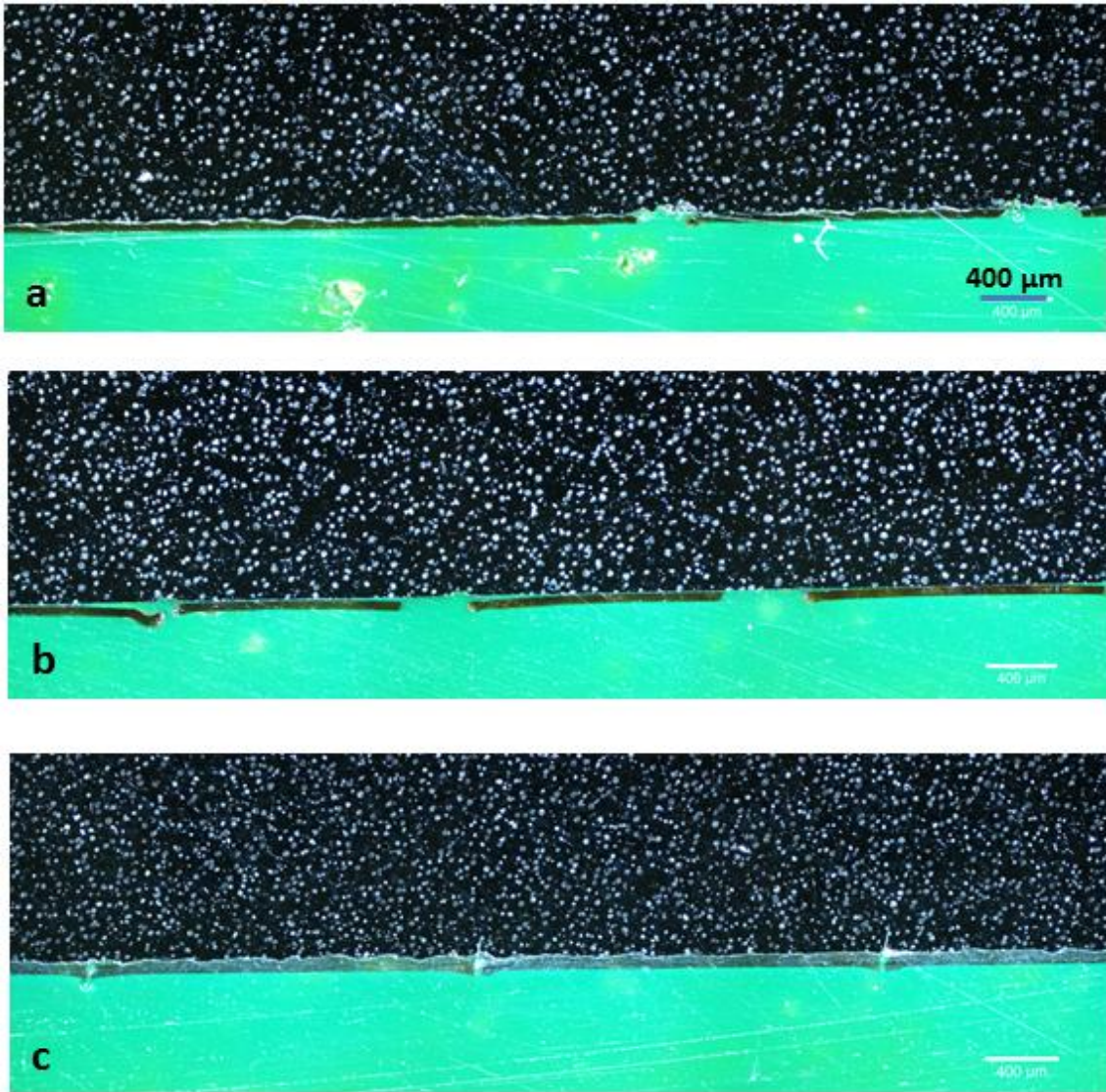


Figure 4 - Dark field LOM micrographs of the ferritic samples in the as-received (a), polished (b) and oxidized (c) states. The scale is the same for all three micrographs.

SEM observations were also performed on all samples which did not allow a clear visualization of the epoxy layer as no contrast developed between it and the resin used for mounting the samples. As an example, figure 5 shows a section of the oxidized ferritic alloy where a uniform oxide layer appears at the surface of the substrate. It is clear that this oxide layer has smoothed the small surface irregularities.

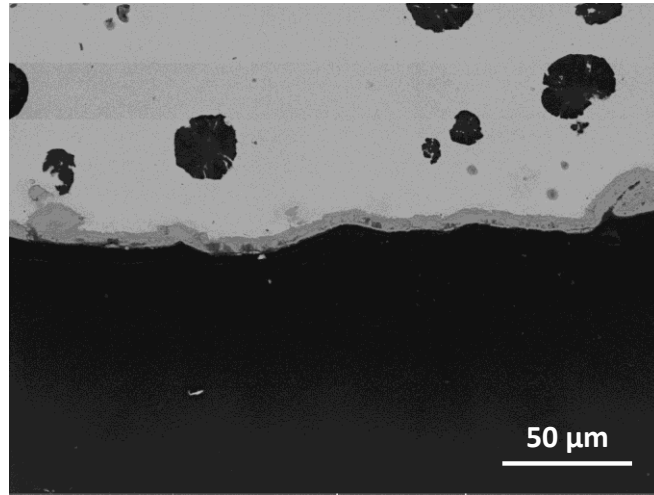


Figure 5 - SEM micrograph of the oxidized ferritic alloy

X-rays were acquired on all nine samples which are illustrated in figure 6 with the records acquired on the three oxidized samples. Diffusion due to the polymer is clearly observed for angles in between 10° and 60° . For easing the analysis, this contribution was withdrawn giving records as illustrated in figure 7 for the same samples.

Table 3 lists the phases observed for all samples using PDF-2 database [12]. The phases corresponding to the cast iron matrix that have been detected are ferrite F (cubic, $a=2.86 \text{ \AA}$), cementite C (orthorhombic, $a = 5.08 \text{ \AA}$, $b = 6.76 \text{ \AA}$, $c = 4.52 \text{ \AA}$), austenite A (cubic, $a=3.62 \text{ \AA}$) and Hägg's carbide H (monoclinic, $a = 11.56 \text{ \AA}$, $b = 4.56 \text{ \AA}$, $c = 5.03 \text{ \AA}$). Note that graphite was not detected as very few nodules are expected to be cut by the metallographic section. Hägg's carbide has been sometimes reported in the literature [13,14], it appears when high carbon austenite formed during the first stage of austempering starts decomposing. It is noted in table 3 that polishing of the austempered sample allowed the low fractions of austenite and Hägg carbide to be detected when they were not with the as-received sample.

Table 3: Phases detected by X-rays. Only the oxides are reported for the oxidised samples for which only the ferrite peak of the matrix was identified.

Sample	As-received	Polished	Oxidized
Ferritic	F+C	F	$\text{FeO} + \text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$
Pearlitic	F+C	F+C	$\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$
Austempered	F	F+A+H	$\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$

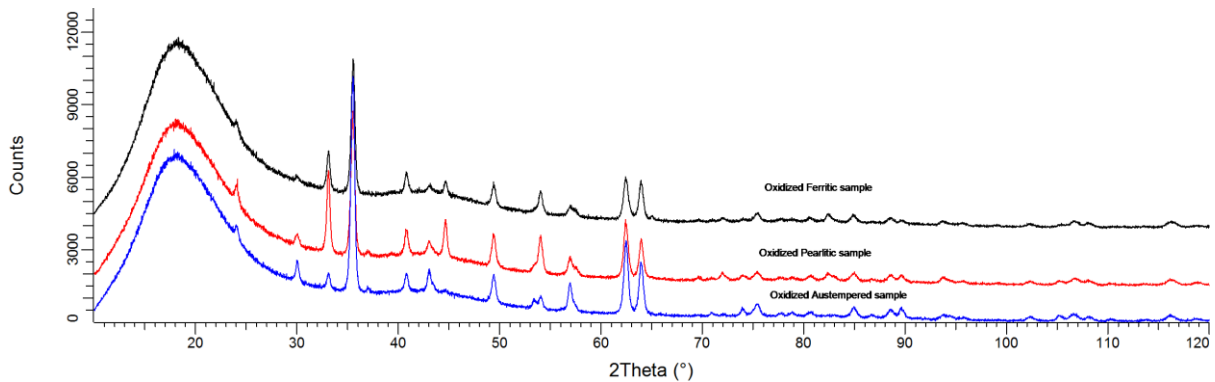


Figure 6 - X-ray records for the three oxidized samples. The records have been arbitrarily shifted along the Y axis for clarity.

On the oxidised samples, see figure 7, the only peaks from the matrix that were identified are those of ferrite though their microstructure should be the same as for as-received and polished samples. The peak for ferrite at 44.65° (see the insert to the right in figure 7) allowed estimating the thickness of the oxide layer which appeared to be slightly thicker on the austempered alloy and thinner on the pearlitic one. These thicknesses were estimated of the order of $2\ \mu\text{m}$ which is a bit smaller than what could be evaluated from figure 5.

Analysis of the X-rays records in figure 7 allowed identifying only iron oxides on the oxidized samples. All three oxides, hematite Fe_2O_3 (rhombohedral, $a = 5.04\ \text{\AA}$, $c = 13.75\ \text{\AA}$), magnetite Fe_3O_4 (cubic, $a = 8.39\ \text{\AA}$) and wustite FeO (cubic, $a = 4.29\ \text{\AA}$), could be observed depending on the samples as listed in table 3. Hematite and magnetite could be identified in all oxidized samples, while a small amount of wustite was only observed on the ferritic sample (see the insert to the left in figure 7).

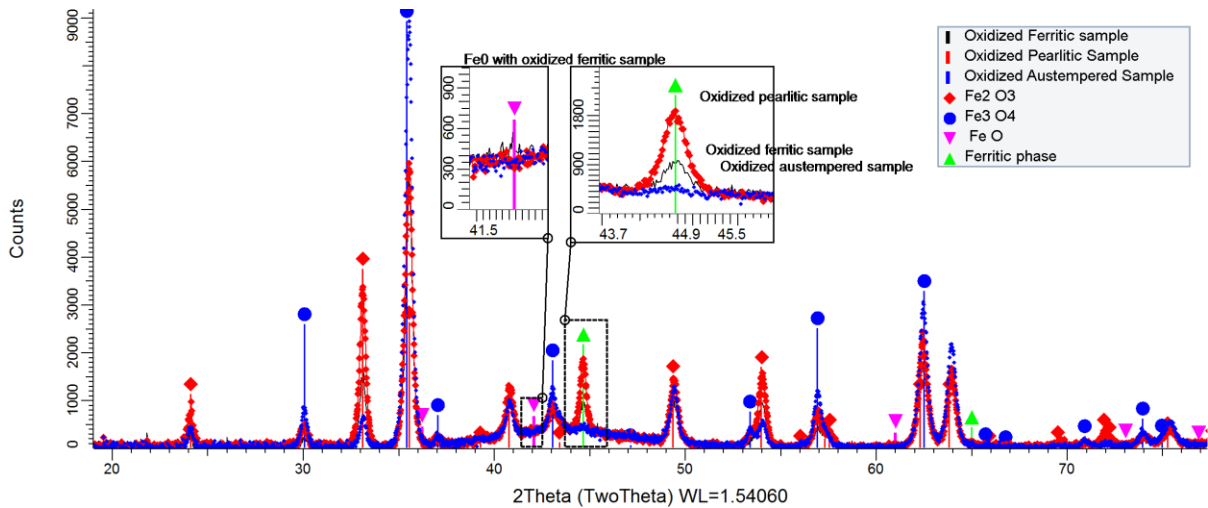


Figure 7 – X-ray records for the three oxidized samples after withdrawing of the background due to diffusion of the polymer layer. The insert to the right shows an enlargement of the peak associated to ferrite at 44.65° , and that to the left demonstrates that wustite appeared only on the ferritic sample.

Conclusion

Decreasing initial surface roughness improves the adherence strength of the primer as measured with the pull-off test, and this improvement is enhanced after limited oxidation of the surface. On the contrary, increasing the amount of carbides in the microstructure decreases this strength, and this may well be related with the low polarity of carbides. After exposure to water, excellent adherence of the primer may be ensured by a limited pre-oxidation of the surface.

Acknowledgment

This work was prepared in the framework of the associated international laboratory “Functional Composite Materials (FOCOMAT)” between France and Vietnam.

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