Corrosion resistance of the Dhar iron pillar

R. Balasubramaniam [a,*], A.V. Ramesh Kumar [b]

[a] *Department of Materials and Metallurgical Engineering, Indian Institute of Technology, Kanpur 208 016, India*
[b] *Electrochemistry and Corrosion Division, Defense Materials and Stores Research and Development Establishment, Kanpur 208 013, India*

Abstract

The corrosion resistance of the 950-year old Dhar iron pillar has been addressed. The microstructure of a Dhar pillar iron sample exhibited characteristics typical of ancient Indian iron. Intergranular cracking indicated P segregation to the grain boundaries. The potentiodynamic polarization behaviour of the Dhar pillar iron and mild steel, evaluated in solutions of pH 1 and 7.6, indicate that the pillar iron is inferior to mild steel under complete immersion conditions. However, the excellent atmospheric corrosion resistance of the phosphoric Dhar pillar iron is due to the formation of a protective passive film on the surface. Rust analysis revealed the presence of crystalline magnetite ($Fe_{3-x}O_4$), α-Fe_2O_3 (hematite), goethite (α-FeOOH), lepidocrocite (γ-FeOOH), akaganeite (β-FeOOH) and phosphates, and amorphous δ-FeOOH phases. The rust cross-section revealed a layered structure at some locations.
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1. Introduction

The attention of scientists and archaeometallurgists has not been focused significantly on the Dhar iron pillar, although this pillar, in its original condition, was larger than the Delhi iron pillar. Smith [1] rightly remarked that "while we marvel at the skill shown by the ancient artificers in forging a great mass of the Delhi pillar, we must give a still greater measure of admiration to the forgotten craftsmen who dealt

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Fig. 1. The three pieces of the 950-year old Dhar iron pillar lying horizontally on concrete supports, outside the Lat Masjid at Dhar, Madhya Pradesh, India.

so successfully in producing the still more ponderous iron mass of the Dhar pillar monument with its total length of 42 feet''. It is currently lying in three broken pieces in front of the Lat Masjid at Dhar in Central India (Fig. 1). The history of the pillar has been described in detail elsewhere [2] and briefly summarized below.

Dhar, situated near Indore in Madhya Pradesh, was founded as capital of Malwa by Bhoja (1010–1053 AD). Local tradition holds that Bhoja constructed the pillar. The achievements of the iron industry in Malwa during Raja Bhoja's reign have been well documented [3]. Bhoja was well versed in iron metallurgy as he, in his *Yukti-kalpataru*, discusses the manufacture of iron weapons and refers to earlier texts on iron metallurgy like *Louharnava*, *Louhadspa* and *Louhapradipa* [4]. Dhar first came into Muslim hands around 1300 AD when Allaudin Khilji subdued Malwa as far as Dhar. In its original condition, the pillar, topped with a *trishul* (trident) capital, was located in front of a Shiva temple. This temple was located at the very site where the present Lat Masjid stands. The masonry basement topped with stone boulders, in front of the Lat Masjid, was the original erection site of the Dhar iron pillar.

After being thrown down, its shaft was broken into *at least* two pieces, which lay about for a hundred years. One smaller piece (most probably without the currently missing fourth piece of the pillar) was planted at the Dilawar Khan's mosque in Mandu (in a position similar to that of the Delhi iron pillar in the Quwwat-ul-Islam mosque). The greater length was erected before the Lat Masjid mosque built by Dilawar Khan at Dhar in 1405 AD out of the remains of Hindu and Jain temples. Bahadur Shah of Gujarat, in 1531 AD, captured the area and wished to carry the pillar to Gujarat. In attempting to do so, the pillar fell down and broke into two pieces of lengths 22′ and 13′. The largest broken piece remained in the same sloping position against the masonry terrace in front of the mosque from the time of its fall in 1531 AD till the time it was removed by the Archaeological Survey of India (ASI) around 1980 AD and placed horizontally on a platform adjoining the mosque. In-terestingly, the kids in the nearby areas were utilizing this piece as a slide (before the

ASI set it up on the platform) and therefore, three surfaces of the largest piece appear smoothly polished.

As regards the second piece that was broken during the time of Bahadur Shah, Cousens, in February 1903, saw the same at the Anand High School, where a museum had been established sometime in 1902. This museum was shifted to another location within Dhar sometime between 1922 and 1942. The second pillar piece was not shifted to the museum at the new location but was placed horizontally on the ground, without any support, near the masonry basement where the longest piece lay. This piece was removed from this position by ASI, around 1980 AD, and placed horizontally on concrete supports on a platform near the mosque (Fig. 1).

The original broken piece that was erected in the Dilawar Khan mosque in Mandu, was also moved from this location and brought down to Dhar during the British period [6]. Führer [5] states that the smallest piece was in the garden of the Maharaja's Guest House at Dhar in 1893 (which was later called the Agency House and currently a heritage hotel), while Cousens reports, that in February 1902, this was fixed in a masonry basement in the public gardens known as *Lal Bagh*, quite close to the Anand High School. Cousens had this pillar piece removed from the masonry basement in order to determine its accurate dimensions. It was then placed in the museum at Anand High School and, similar to the second piece, was shifted to its current location. Therefore, this piece has also been shifted from one location to another in Dhar, after being brought down from Mandu.

The three pieces of the Dhar iron pillar are currently lying horizontally on concrete supports on a platform beside the Lat Masjid (Fig. 1). It must be realized from the above discussion that the pillar pieces have been moved around several times during their history and therefore, the handling of the pillar pieces must be taken into account while understanding the corrosion product analysis. The main aim of the present paper is to obtain insights on the corrosion resistance of the Dhar pillar iron.

2. Experimental

A small flat piece of iron from the bottom surface of the second largest Dhar iron pillar piece was obtained with the permission of the Archaeological Survey of India. As the Dhar iron pillar is a product of forge welding [2], there was one location where a small piece of metal in the form of a thin sheet, about 2 mm thick, was protruding out of the surface. A chisel was used to gently ease out this flat piece of metal without damaging the surface of the pillar. This piece of Dhar pillar iron was used in all further studies reported in this paper.

Small samples were cut from the piece and metallographically mounted in order to study the longitudinal and transverse microstructures. The transverse mounted sample further provided cross-sectional microstructural details about the nature of the atmospheric rust. The samples for microstructural observation were prepared by standard metallographic methods. The microstructures were observed in optical and scanning electron microscopes. The composition of the metal from several local

regions and also of some of the entrapped slag inclusions in the iron were determined in a JEOL 8600MXA electron probe microanalyzer. The carbon and phosphorus contents were determined by wet chemical analysis to be 0.17% and 0.25%, respectively.

The sample used for determining the longitudinal microstructure was remounted after providing an electrical connection on its backside and this sample was used for all electrochemical studies. A 0.05% C mild steel sample was also similarly mounted and studied, for comparison purposes. The potentiodynamic polarization behaviour of these specimens was determined using a EG&G PAR 273 potentiostat, at a scan rate of 1 mV/s, in freely aerated 0.05 mol/l H_2SO_4 (pH 1) and borate buffered (pH 7.6) solutions. In all the polarization studies, the experiments were begun after stabilization of the free corrosion potentials.

While observing the fracture surface of the piece that was removed from the Dhar iron pillar, the characteristic features of rust formed on this fresh surface was also recorded in a SEM. The rusts on both the faces of the sample that was removed, was characterized in situ by X-ray diffraction in a Rich-Seifert 2000D X-ray diffractometer using CuK_α radiation. Some atmospheric rust was also scrapped from the pillar surface at a nearby location from where the sample was taken and this rust was utilized for characterization using Fourier infrared spectroscopy (FTIR) and transmission Mössbauer spectroscopy (TMS). The procedures for FTIR and TMS analysis were similar to that described earlier [7].

3. Results and discussion

3.1. Iron microstructure

There is only one published composition of the Dhar pillar iron. According to Tylecote [8], with a quotation of Hadfield [9] and Graves [10], the chemical composition of Dhar pillar iron is 0.02% C and 0.28% P. The carbon and phosphorus contents were determined in the present investigation by wet chemical analysis to be 0.17% and 0.25%, respectively. Local compositions were also determined on the longitudinal section of the Dhar pillar iron piece using an 8600JXA JEOL electron probe microanalyzer (EPMA). The composition varied from one location to another, depending on the microstructure. The composition from one region (containing pearlite) was (in weight percent) 0.683% C, 0.693% P, 0.013% Mn and no sulphur, while from another location (containing both ferrite and pearlite), the composition was 0.276% C, 0.851% P and 0.075% Ag. The carbon content was determined by chemical analysis to be 0.17%. The relatively higher amount of P in Dhar pillar iron must also be noted. Interestingly, the Ag content was insignificant in all the locations analyzed. Cousens [6] commented that the local people believed that the pillar was made of *pancharasa* or *astadhatu*, an alloy of five or eight metals, respectively. He speculated that some bright appearing regions on the surface was silver, imperfectly mixed with iron from the silver-mounted weapons that were supposed to be have been used to construct the pillar [6]. The present compositional

analysis discounts Cousens' hypothesis. The relatively higher amount of P in Dhar pillar iron must also be noted. The entrapped slags were also analyzed and it was found that they were essentially fayalitic. A typical composition obtained was 55.8% Fe, 27.8% Si, 0.1% Mn and 16.3% P.

Microstructural analysis indicated that there were some regions devoid of carbon (Fig. 2a); while at other locations there was a significant amount of carbon as revealed by the presence of a higher volume fraction of pearlite (Fig. 2b). The entrapped slag inclusions were generally surrounded by a higher volume fraction of pearlite (Fig. 3). This aspect has been discussed in detail, elsewhere [11]. The presence of a significant amount of P was also revealed by the characteristic ''ghosting'' effect following nital etching (Fig. 4), which is typical of iron containing phosphorus [12]. The ''ghosting'' phase is a differential etching effect resulting from local phosphorus enrichment and this phase is commonly observed in phosphorus-rich ancient Indian iron. Interestingly, the fracture surface of the iron piece indicated brittle intergranular
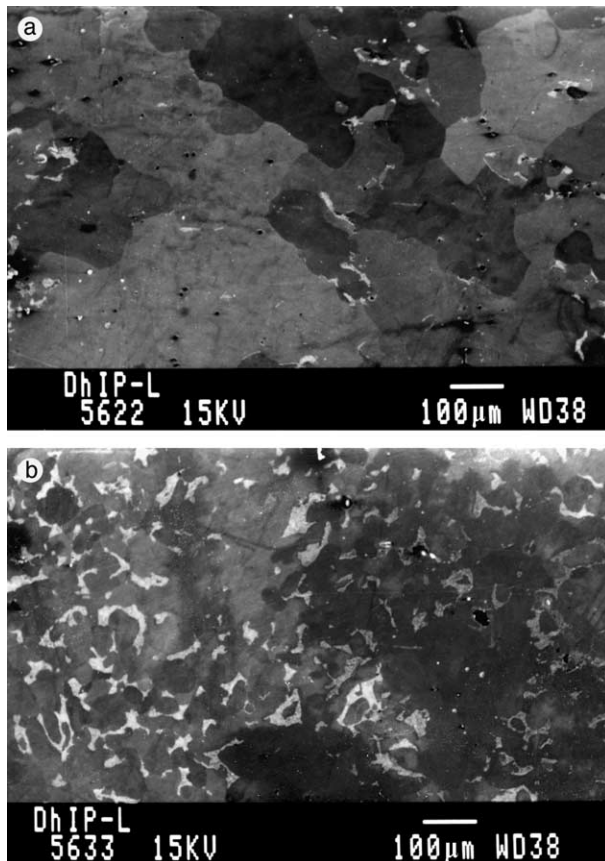

Fig. 2. Scanning electron micrograph of Dhar pillar iron showing a typical region (a) devoid of carbon, and (b) containing significant amount of carbon.
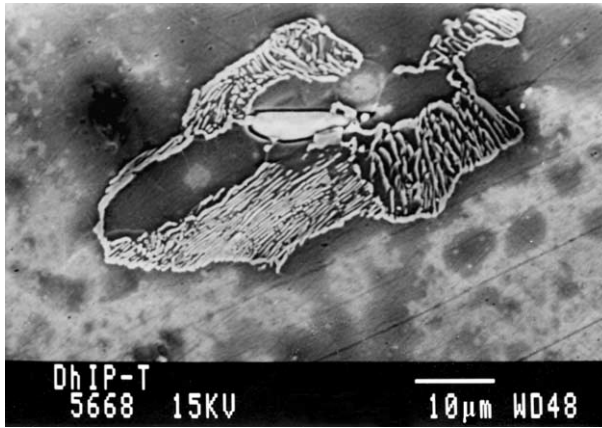
Fig. 3. Microstructure of the Dhar pillar iron showing the presence of a larger fraction of pearlite near some slag particles.
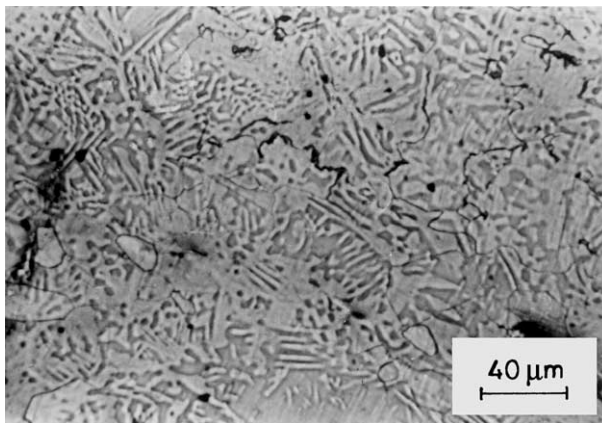

Fig. 4. Optical micrograph after nital etch reveals ''ghosting'' effect that is typical of phosphorus containing iron.

failure at several locations (Fig. 5), which is suggestive of P segregation to the grain boundaries and their subsequent embrittlement. The tendency for P to make iron cold-short (i.e. susceptible to brittle fracture during cold working) is well known [12,13].

3.2. Potentiodynamic polarization

Potentiodynamic polarization studies indicated that the materials (i.e. Dhar pillar iron and mild steel) exhibited active behaviour in the acidic solution and stable passive behaviour in the borate buffered solution (Fig. 6). The passive current density
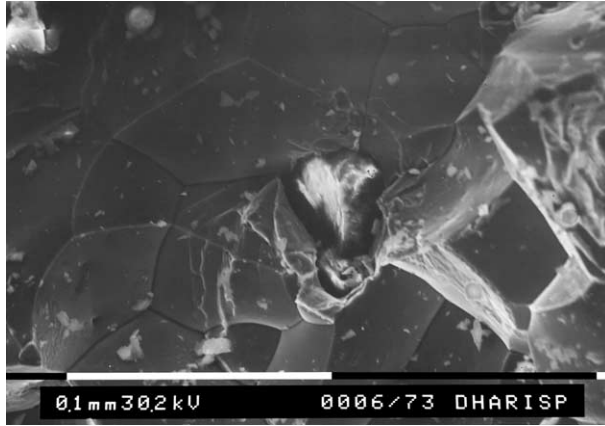
Fig. 5. Fracture surface of the Dhar pillar iron piece showing intergranular embrittlement due to phosphorus segregation to the grain boundaries.
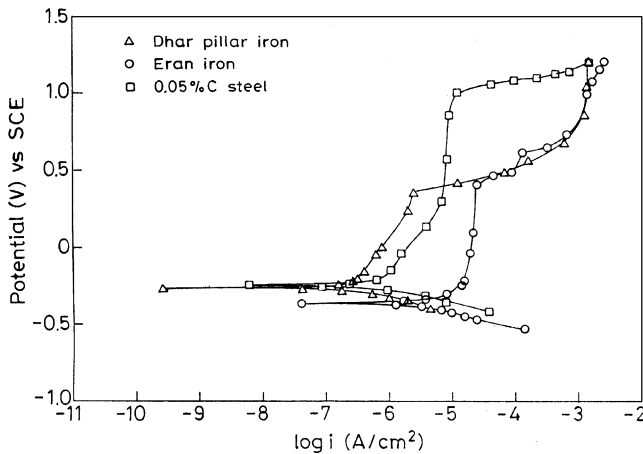

Fig. 6. Experimental potentiodynamic polarization diagrams for Dhar pillar iron, Eran iron and 0.05% C steel in borate buffered solution of pH 7.6.

and the passive range were lower in the case of the Dhar pillar iron in the borate buffered solution. These observations co-relates well with earlier studies on ancient Indian iron [14]. Although complete immersion testing is much more severe compared to atmospheric corrosion, it, nevertheless, provides ideas about relative corrosion rates. The higher corrosion rate for the Dhar pillar iron in the acidic solution is due to the presence of slag inclusions in the material. The slag particles would be cathodic with respect to the iron matrix because they are generally surrounded by a high volume fraction of pearlite (Fig. 3). Therefore, this results in higher corrosion rates for the iron matrix in immersion testing. The pitting potential of the Dhar pillar

iron was more active compared to that of mild steel, indicating the increased susceptibility to localized attack in the case of the Dhar pillar iron for complete immersion conditions. Interestingly, the pitting potential of the Dhar pillar iron was similar to Eran iron, an ancient Gupta-period Indian iron dated to the 6th century AD. This indicates the deleterious effect of the slag inclusions on passivity breakdown in both the ancient Indian irons under complete immersion conditions. The interfaces between the iron matrix and slag inclusions provide ideal initiation sites for pitting corrosion and hence the passive ranges in both Dhar pillar iron and Eran iron are lower compared to mild steel [14]. The polarization characteristics of the Dhar pillar iron can, therefore, be correlated with microstructural features.

The polarization studies indicate that the Dhar pillar iron would be inferior to mild steel under complete immersion conditions. However, under atmospheric corrosion conditions (with its associated wetting and drying cycles), the development of a protective passive film on the phosphoric iron (i.e. Dhar pillar iron) is indicated. If atmospheric corrosion initiates pitting faster than protective film formation, then localized corrosion of the surface would be a major problem. On the other hand, if the protective passive film covers the surface faster than the initiation of pitting, then there would be no pitting of the surface. The latter situation appears to apply in the case of atmospheric corrosion of Dhar iron pillar. The high degree of surface passivity must be the reason for the persistence of the Dhar iron pillar over many centuries. The nature of the atmospheric protective passive film will, therefore, be analyzed to understand the pillar's excellent atmospheric corrosion resistance.

3.3. Rust analysis

X-ray diffraction patterns were obtained at several different locations on the flat specimen from both the sides—the side exposed to the atmosphere and the inner side. The diffraction patterns obtained from the side that was exposed to the atmosphere will be presented and discussed. The patterns taken at different locations were reproducible, thereby indicating the uniform nature of the atmospheric rust. The crystalline phases identified were goethite, lepidocrocite, magnetite, akaganeite and phosphate phases. The akaganeite phase could have formed due to the presence of chloride ions during storage of the iron piece. It was not possible to unambiguously identify the nature of the phosphate, unlike in the case of the Delhi iron pillar rust [6].

The FTIR spectrum from another rust sample collected from the surface of the pillar (Fig. 7) indicated the presence of α-Fe_2O_3 (peak appearing at 572 cm^{-1}), γ-FeOOH (peak appearing at 1023 cm^{-1} and its shoulder at 791 cm^{-1}), α-FeOOH (peak appearing at 884 cm^{-1}) and δ-FeOOH (peak appearing at 465 cm^{-1}). The broad band seen in the region 3000–3500 cm^{-1} is due to hydration of the rust. It is known that O–H stretching leads to strong peak between 3000 and 3700 cm^{-1} while O–H bending to a medium band between 1200 and 1500 cm^{-1} [15,16]. Therefore, this implies hydration of corrosion product(s) in the Dhar iron pillar rust. Misawa et al. [17,18] attributed the following peaks as key absorption bands: 890 cm^{-1} for α-FeOOH, 1020 cm^{-1} for γ-FeOOH, and 470 cm^{-1} for δ-FeOOH. Ishii and Nakahira [19]
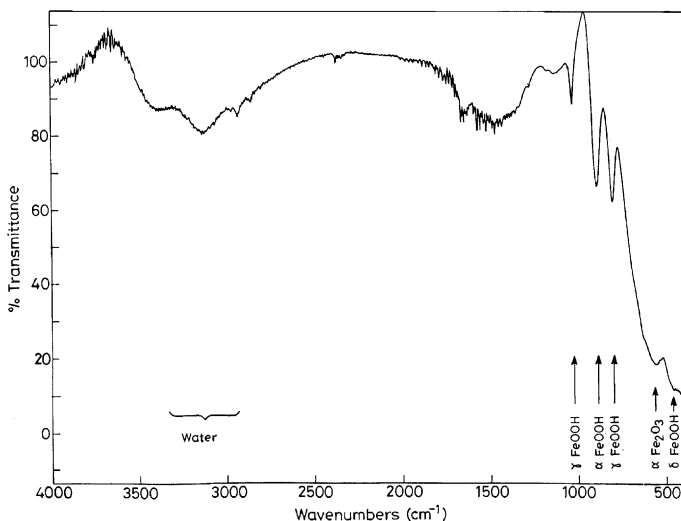
Fig. 7. Fourier transform infrared spectrum from Dhar iron pillar rust.

confirmed that the Fe–O stretching vibration in iron oxides corresponds to a wave number 570 cm^{-1}. The peak appearing at 572 cm^{-1} is indicative of Fe–O vibration in the oxide of iron. The exact nature of this oxide cannot be determined from the FTIR spectrum. However, the exact nature of this was oxide was revealed by Mössbauer spectroscopy and therefore, it is possible to precisely attribute the Fe–O vibration to α-Fe$_2$O$_3$. A shoulder in FTIR spectrum (Fig. 7) corresponding to phosphate ions could be discerned (1030–1120 cm^{-1}) indicating that ionic phosphates were present in the rust that was studied. The wave numbers for ionic phosphate is 1030–1120 cm^{-1}, while for covalent phosphate the band should occur at 920–1050 cm^{-1} and for P=O bonds, the spectra occurs at 1200–1250 cm^{-1} [15,16]. It is difficult to conclude whether the ionic phosphate, that provided the signal in the spectra, was H$_3$PO$_4$ or FePO$_4$. Nevertheless, FTIR spectroscopy proves the existence of phosphates in the Dhar iron pillar rust.

The Mössbauer spectrum (Fig. 8) from the second rust sample, that was used for the FTIR spectroscopic analysis, is composed of two sextets and one central doublet. The experimental data points have been computer fitted to the line shown in Fig. 8. The sextets correspond to hematite (α-Fe$_2$O$_3$) and goethite as the hyperfine magnetic fields from the two sextets (518 and 367 kOe) correspond precisely to the room temperature magnetic fields for these two phases [20,21], respectively. The central doublet is indicative of the presence of γ-FeOOH, δ-FeOOH and maybe some superparamagetic α-FeOOH. The IS (isomer shift) for the central doublet is 0.468 mm/s and this is similar to that for γ-FeOOH while the QS (quadrupole splitting) for the doublet is 0.744 mm/s which is a little high and arises due to the water of hydration. The presence of phosphate could not be precisely verified in the Mössbauer spectrum. However, the significant broadening in the central region
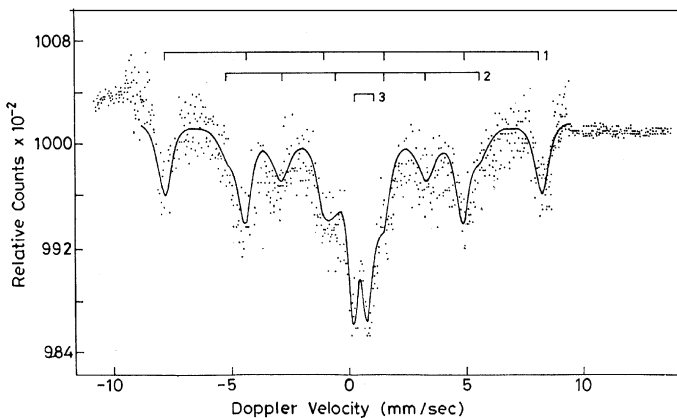
Fig. 8. Mössbauer spectrum from Dhar iron pillar rust.

of the spectrum (i.e. near the doublet) indirectly indicates the possible presence of a doublet due to iron phosphate.

The FTIR spectroscopy and TMS analyses of the second rust revealed that it contained hematite (α-Fe_2O_3), a relatively stable end product [20]. Hematite was not present in the first rust sample analyzed by XRD. Therefore, the presence of hematite in the rust needs to be understood. The δ-FeOOH phase forms due to catalytic action of elements like Cu, P, and Ni that are added for weathering resistance [17,18].

3.4. Rust structure

The growing rust on the surface of the specimen fracture surface was observed after a period of 12 months. The rust on the fracture surface was observed while primarily studying the nature of fracture of the Dhar pillar iron piece.

The rust characteristics were studied by scanning electron microscopy. There were relatively few regions where rusting was not significant (Fig. 5), and the intergranular nature of fracture could be observed. The nature of the growing rust at another location on the fracture surface has been shown in Fig. 9, from which it can be observed that the rust was heterogeneous in nature. At some locations, the external scale had cracked, revealing the rust structure underneath, while at other locations, protrusions (globular nodules) were observed on the surface. On closer examination, these nodular structures, at higher magnifications, were composed of flowery needle-like rust (Fig. 10a and b) growing on top of a cracked rust layer (Fig. 11). Analysis of the needle-like structures in the EDAX indicated the presence of Fe and O. Structural information could not be obtained from the SEM. The growth of the needle-like rust flower was evident in areas where considerable cracking was observed in the outer layer. This indicated that the flowery needle-like rust grew at locations where the outer oxide rust layer was cracked. The nature of observed rusting on the Dhar pillar iron sample was comparable to rust characteristics on weathering steels [22,23].
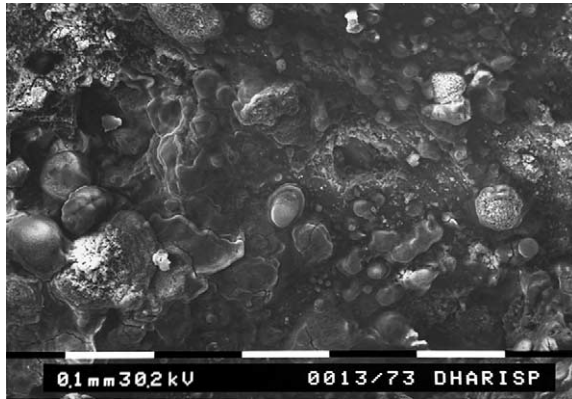
Fig. 9. Nature of the growing rust on the fracture surface of the Dhar pillar iron. Notice the heterogeneous nature of rust.
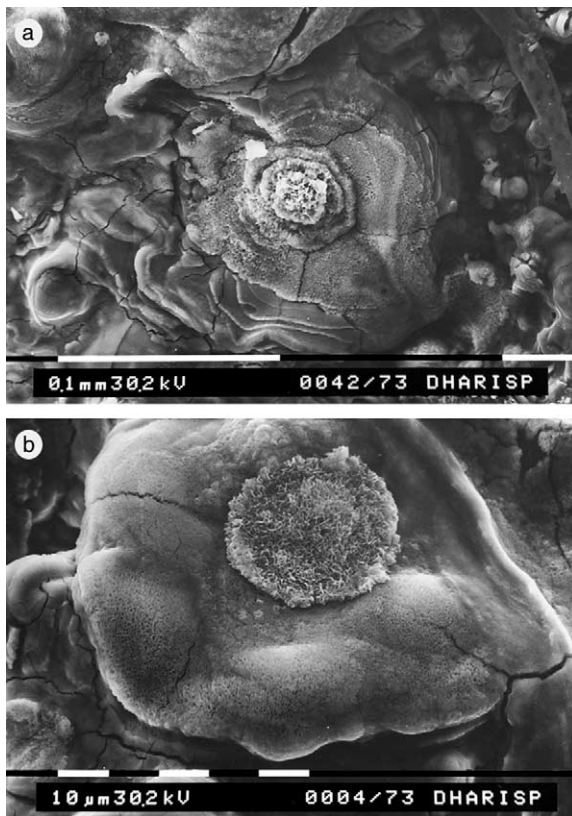

Fig. 10. Several of the nodular features noticed in Fig. 9 were composed of flowery needle-like rust. Two such features from two different locations are shown in (a) and (b).
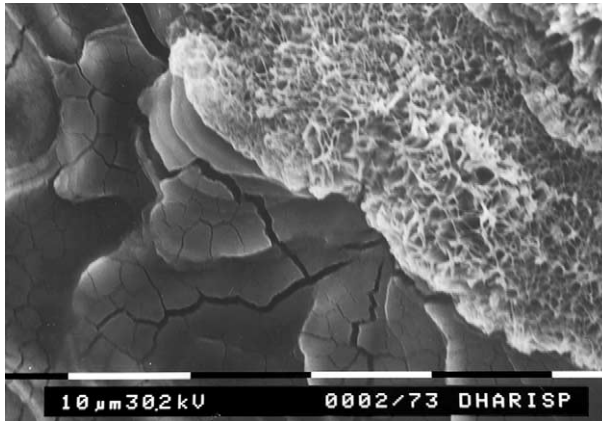
Fig. 11. The external rust layer on the fracture surface of the Dhar pillar iron was heavily cracked. The flowery needle-like rust can also be seen in the upper right portion of the figure.

In the case of weathering steel of composition 0.08C–0.35Si–0.40Mn–0.09P–0.008S–0.32Cu–0.32Ni–0.59Cr–0.04Nb [22], it was noted that in the regions where the outer layer had flaked off, the initial corrosion product had formed. This aggregate was shaped like mushrooms and was composed of fine crystals. After extended periods of time, the corrosion products were interconnected and were converted to characteristics typical of the outer layer [22]. In the case of weathering steel of composition 0.12C–0.49Si–0.50Mn–0.149P–0.02S–0.57Cu–1.19Cr–0.49Ni [23], the component particles of the outer layer were loosely aggregated whereas the inner layer was composed of densely packed fine particles. Similar to these studies, the inner rust that formed on atmospheric corrosion of the Dhar pillar iron sample extruded out of the outer rust layer in the areas where the outer rust layer was heavily cracked, and later spreads on the surface (Figs. 10 and 11).

3.5. Rust cross-section

Cross-sectional microscopy of the transversely mounted iron sample indicated that the atmospheric rust at several locations consisted of two layers, an optically dull inner thin layer and an optically bright thick outer layer (Fig. 12). The layered structure of the protective rust in the case of weathering steels is well established [17,18,22–25]. Regarding the optical nature of the layers on weathering steels, it has been pointed out that the inner optically isotropic layer of the surface rust is composed of X-ray amorphous spinel type iron oxide which can protect the steel matrix [24,25]. Yamashita et al. [23] also observed that the rust layer present on a weathering steel exposed for 26 years could be divided into two parts: an outer layer which was optically active (i.e. illuminated) and an inner layer which was optically isotropic (darkened). On the other hand, the surface rust formed on mild steels consisted of the mottled structure consisting of the optically active and isotropic corrosion products [23]. It is also established that weathering steels obtain their protection due
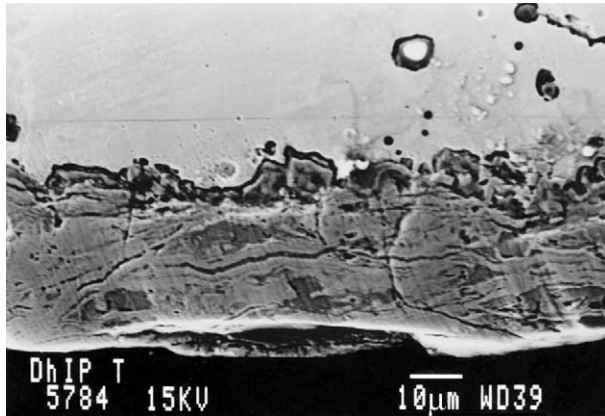
Fig. 12. Cross-section of the atmospheric rust of the Dhar pillar iron showing an optically dull thin inner layer and an optically bright thick outer layer.

to the presence of the dark inner layer [23]. Therefore, based on the above studies, it is reasonable to state that the inner optically dull layer seen in the Dhar iron pillar rust microstructure must be amorphous in nature while the outer layer must be crystalline in nature. The innermost thin layer seen next to the metal surface may be enriched with phosphorus or may contain crystalline phosphates, as has been found in corrosion-resistant ancient Indian iron [7,26]. The outer layer must consist of the usual corrosion products expected on atmospheric corrosion of iron (i.e. magnetite, goethite and lepidocrocite) and can also be enriched in phosphorus or contain phosphates. As the Dhar pillar iron contains a relatively significant amount of phosphorus, the formation of phosphates is expected. The golden reddish brown color of the surface of the pillar also indicates that phosphates must be present in the atmospheric rust. A detailed study of the rust from several locations of the three pillar pieces must be undertaken to elucidate the nature of the protective passive film and mechanism of its formation. This is all the more important in the case of Dhar pillar iron because, as noted earlier, the three pillar pieces have been handled and shifted around several times during their history.

4. Conclusions

Some aspects of the corrosion resistance of the Dhar iron pillar have been studied. The history of the pillar has been briefly reviewed. The microstructure of Dhar pillar iron is characteristic of ancient Indian iron, in that it contains entrapped fayalitic slag inclusions and a relatively high amount of phosphorus. Intergranular fracture surface proved the presence of relatively higher amount of P and its segregation to the grain boundaries. The polarization behaviour of Dhar pillar iron has been compared with 0.05% C mild steel in solutions of pH 1 and 7.6. The Dhar pillar iron is inferior to mild steel under complete immersion conditions. However, a

high degree of surface passivity on the pillar iron upon atmospheric exposure is responsible for its excellent atmospheric corrosion resistance. Samples of atmospheric rust from the Dhar iron pillar have been characterized by XRD, FTIR and Mössbauer spectroscopy. The existence of crystalline magnetite ($Fe_{3-x}O_4$), hematite (α-Fe_2O_3), goethite (α-FeOOH), lepidocrocite (γ-FeOOH), akaganeite (β-FeOOH) and phosphates, and amorphous δ-FeOOH phases in the rust has been detected. Cross-sectional analysis of the atmospheric rust indicated an optically dull thin layer next to the metal–scale interface and an optically bright thick layer above the inner layer at some locations.

References

[1] V.A. Smith, Dhar iron pillar, J. Roy. Asiatic Soc. Great Britain Ireland (1898) 143.
[2] R. Balasubramaniam, A new study of the Dhar iron pillar, Indian J. History Sci. 37 (2002) 115.
[3] S.V. Sohoni, Historical background of iron industry in Malwa of Bhoja's period, Soc. Sci. 10 (1990) 104.
[4] A.K. Biswas, Minerals and Metals in Ancient India, vol. II, D.K. Printworld, New Delhi, 1996.
[5] A. Führer, Annual Report of the Archaeological Survey Circle, North-Western Provinces and Oudh for the Year ending 30th June 1893, Thomson College Press, Rourkee, 1893, p. 21.
[6] H. Cousens, The iron pillar at Dhar, Archaeological Survey of India Annual Reports (1902–03) 205.
[7] R. Balasubramaniam, A.V. Ramesh Kumar, Characterization of Delhi iron pillar rust by X-ray diffraction, Fourier infrared spectroscopy and Mössbauer spectroscopy, Corros. Sci. 42 (2000) 2085.
[8] R.F. Tylecote, A History of Metallurgy, The Metals Society, London, 1979, p. 4.
[9] R. Hadfield, Sinhalese iron and steel of ancient origin, J. Iron Steel Inst. 85 (1912) 134.
[10] H.G. Graves, Further notes on the early use of iron in India, J. Iron Steel Inst. 85 (1912) 187.
[11] R. Balasubramaniam, On the corrosion resistance of the Delhi iron pillar, Corros. Sci. 42 (2000) 2103.
[12] J.E. Stead, Iron, carbon and phosphorus, J. Iron Steel Inst. 91 (1915) 141.
[13] S. Suzuki, M. Obata, K. Abiko, H. Kimura, Effect of carbon on the grain boundary segregation of phosphorus in alpha-iron, Scripta Metall. 17 (1983) 1325.
[14] V. Puri, R. Balasubramaniam, A.V. Ramesh Kumar, Corrosion behaviour of ancient 1500-year old Gupta iron, Bull. Metals. Museum 28-II (1997) 1.
[15] D.A. Skoog, J.J. Leary, Principles of Instrumental Analysis, fourth ed., Harcourt Brace College Publishers, New York, 1992, pp. 252–309.
[16] R.A. Nyquist, R.A. Kagel, IR Spectra of Inorganic Compounds, Academic Press, New York, 1971.
[17] T. Misawa, T. Kyuno, W. Suetaka, S. Shimodaira, The mechanism of atmospheric rusting and the effect of Cu and P on the rust formation of low alloy steels, Corros. Sci. 11 (1971) 35.
[18] T. Misawa, K. Asami, K. Hashimoto, S. Shimodaira, The mechanism of atmospheric rusting and the protective amorphous rust on low alloy steel, Corros. Sci. 14 (1974) 279.
[19] M. Ishii, M. Nakahira, Infrared absorption spectra and cation distributions in $(Mn,Fe)_3O_4$, Solid State Commun. 11 (1972) 209.

[20] J.M. Daniels, A. Rosenewaig, Mössbauer spectroscopy of stoichiometric and non-stoichiometric magnetite, J. Phys. Chem. Solids 30 (1969) 1561.

[21] A. Vertes, I. Czako-Nagy, Mössbauer spectroscopy and its application to corrosion studies, Electrochim. Acta 34 (1989) 721.

[22] I. Suzuki, Y. Hisamatsu, N. Masuko, Nature of atmospheric rust on iron, J. Electrochem. Soc. 127 (1980) 2210.

[23] M. Yamashita, H. Miyuki, Y. Matsuda, H. Nagano, T. Misawa, The long term growth of the protective rust layer formed on weathering steel by atmospheric corrosion during a quarter of a century, Corros. Sci. 36 (1994) 283.

[24] H. Okada, Atmospheric corrosion of steels, J. Soc. Mater. Sci. Jpn. 17 (1968) 705.

[25] H. Okada, Y. Hosoi, K. Yukawa, H. Naito, Structure of the rust formed on low alloy steels in atmospheric corrosion, J. Iron Steel Inst. Jpn. 55 (1969) 355.

[26] A.V. Ramesh Kumar, R. Balasubramaniam, Corrosion product analysis of ancient corrosion resistant indian iron, Corros. Sci. 40 (1998) 1169.