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Transmission microscopy of the corrosion scale formed on a stainless steel exposed to liquid sodium

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The scale, formed on 304 stainless steel during exposure to sodium for 85 days, was removed electrolytically, examined in transmission in the Hitachi high voltage microscope and found to consist of hexagonal close packed crystallites, typically 0.3 to 1 μm in diameter. Approximately 90% of the crystallites were of basal (0001) orientation and the others either of $\{4, \bar{1}, \bar{3}, 15\}$ or $\{\bar{2}110\}$ orientations. Lattice parameters $a = 2.96$ Å and $c = 13.89$ Å were determined by analysing electron diffraction patterns derived from the scale. Confirmatory evidence was obtained by examining the scale formed after a shorter exposure of 29 days, in the Philips EM 200 microscope. Previous studies [1, 2] have indicated that the scale may be sodium chromite (with lattice parameters $a = 2.96$ Å and $c = 15.95$ Å). The results of the present study are in apparent conflict with this suggestion unless a contraction parallel to the c-axis $\sim$ 13% is assumed.

1. Introduction

Hooper *et al.* [1] and Hooper and Fisher [2] have used a combination of instrumental techniques such as X-ray diffraction, microanalysis and scanning electron microscopy (SEM), to examine the scale formed on many steels during exposure to sodium. They suggest that the scale consists mainly of sodium chromite. In the present study such scales are removed from exposed 304 steels and examined in transmission in the electron microscope. The results show the scale to be polycrystalline in nature and yield information concerning the orientation relationships between scale crystallites and the underlying steel, the crystallite size and the lattice parameters of the material.

2. Experimental

Samples of cold worked 304 steel were exposed to flowing sodium at 650°C in the well of a flowing sodium loop at REML, Culcheth (see Hooper *et al.* [1]). The concentration of dissolved oxygen in the sodium was maintained at 25 ppm by cold trapping. After an 85 day exposure, the samples were removed, cleaned and dried. Each sample was then placed as the anode into an electrolytic cell at room temperature. The cathode used was Inconel 625 and the electrolyte a 10:1 solution of specially dried methanol and perchloric acid. The current and voltage conditions of the cell were chosen such that oxygen evolution occurred at the anode causing the undamaged corrosion layer, i.e. the scale, to peel away from the scale/steel interface. This scale was collected on nickel microscope grids rapidly washed and dried, and then transferred to the Hitachi high voltage electron microscope for examination. Another specimen which had received a shorter exposure of 29 days was also prepared in the same way and examined in the Philips electron microscope operating at 100 keV.

The lattice parameters of the corrosion scale were determined from an analysis of the spot spacings observed in selected-area diffraction patterns derived from the scale. These were compared with spacings obtained, under identical operating conditions, from a specimen standard of known crystallographic structure and orientation, and with known lattice parameters as determined by X-ray measurements. In all cases the diffraction patterns were enlarged photographically to a known magnification and the spot spacings measured with the use of. a travelling microscope. To reduce

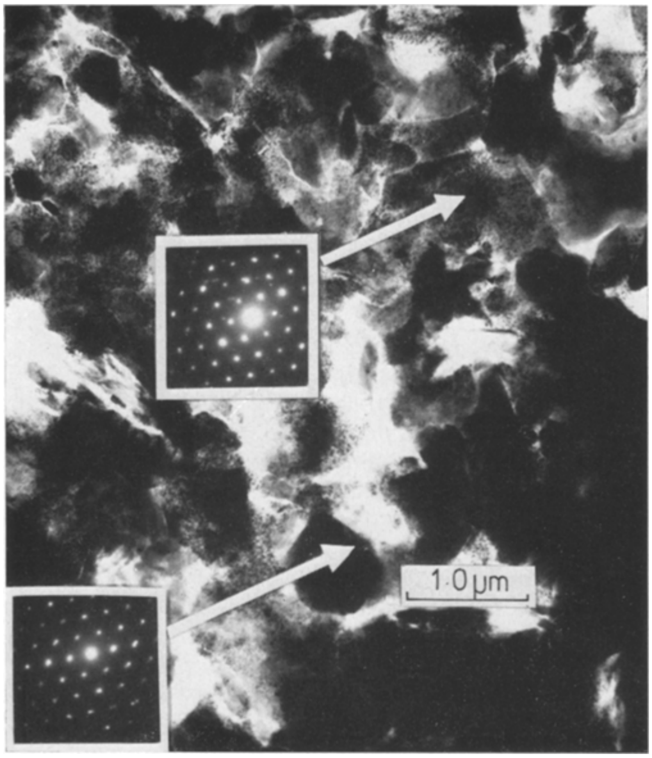

Figure 1 The general appearance of the corrosion scale observed in the Hitachi HVM operating at 1 MeV. Examples of selected-area diffraction patterns with six-fold symmetry derived from individual crystallites are inset.

errors further, the spot spacings were determined by measuring the distance between many spots along systematic rows in the diffraction patterns, or in the case of the ring patterns, by measuring the diameters of the rings.

3. Results

3.1. 85 day sample examined in the HVEM

A representative micrograph of the polycrystalline scale is shown in Fig. 1. The individual crystallites are typically 0.3 to 1 μm in diameter and overlap between them is frequently observed. Approximately 90% of the grains examined in a given area give rise to diffraction patterns exhibiting six-fold symmetry. Often the patterns obtained from any two particular grains are rotated with respect to each other (Fig. 1).

In addition to these diffraction patterns with six-fold symmetry, two other typical types of pattern were obtained from the scale, e.g. the diffraction patterns derived from regions A and B in Fig. 2. The crystallites giving rise to the latter type of pattern are invariably striated in appearance (see also Fig. 3).

First, the patterns with six-fold symmetry were analysed. It is possible that they arise from (111) orientation cubic structures of the face centred, body centred or diamond types, or from a hexagonal close packed (0001) basal orientation structure. The spot spacings in the diffractions patterns of Fig. 1 were measured and the corresponding interplanar spacings determined to be $n_1 = 2.56 \pm 0.01$ Å and $n_2 = 1.48 \pm 0.01$ Å. From these values the lattice parameter of the scale was calculated for each structure in turn. In the cubic system the interplanar spacing n_{hkl} corresponding to a reflection (hkl) is given by the relationship [3]:

$$n_{hkl} = a(h^2 + k^2 + l^2)^{-\frac{1}{2}} \qquad (1)$$

where a is the lattice parameter.

Bearing in mind the selection rules governing allowed reflections, lattice parameters of 7.24, 3.62 and 14.48 Å were calculated from the measured spacings, assuming face centred, body centred and diamond cubic structures, respectively. The other possibility, i.e. crystallites with a hexagonal close packed structure, requires

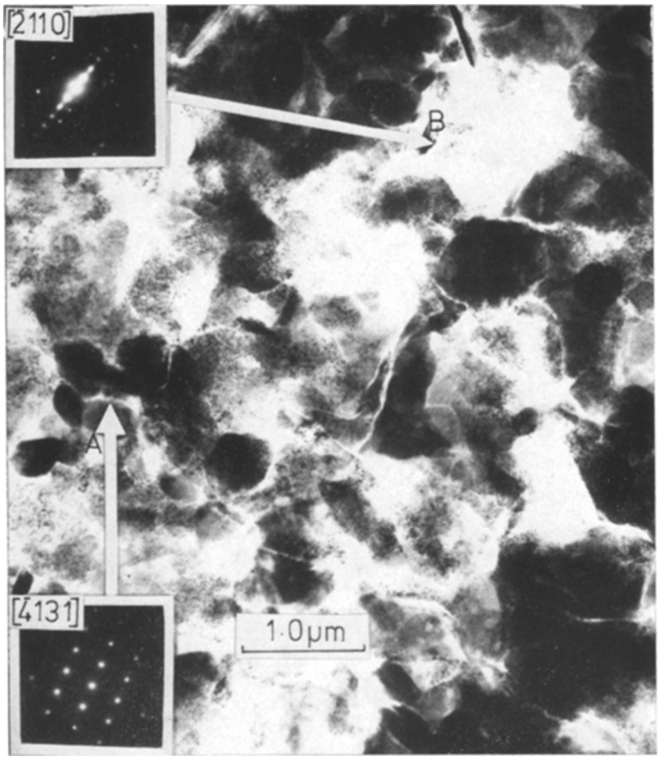

Figure 2 The two other possible types of selected-area diffraction pattern, obtained from regions A and B of the scale.

that the orientation of each crystallite is basal since this is the only orientation which will produce a diffraction pattern with the observed six-fold symmetry. The interplanar spacing n corresponding to a particular reflection $(hkil)$* is given by the relationship [4]:

$$n = a_0\{\tfrac{4}{3}(h^2 + hk + k^2)\}^{-\frac{1}{2}} \text{ since } 1 = 0 \qquad (2)$$

where a_0 is the lattice parameter in the basal plane.

The two values of n given above, i.e. $n_1 = 2.56$ Å and $n_2 = 1.48$ Å corresponding to reflections of the type $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ respectively, were substituted into Equation 2 yielding values of 2.98 and 2.96 T for a_0. Thus $a_0 = 2.97 \pm 0.01$ Å which is in good agreement with the value of $a_0 = 2.96$ Å in the hexagonal sodium chromite structure suggested by previous results [2]. However, at this stage the scale could not be identified positively as sodium chromite because no information about the c lattice parameter had been obtained. The cubic possibilities could not be completely eliminated either.

The spot spacings in the diffraction pattern derived from region A in Fig. 2 were measured and the corresponding interplanar spacings determined to be $n_3 = 2.42 \pm 0.01$ Å and $n_4 = 1.88 \pm 0.01$ Å. If the structure giving rise to these spots is cubic then by Equation 1 above.

$$\left(\frac{a}{n_{hkl}}\right) = h^2 + k^2 + l^2 = \text{integer} \qquad (3)$$

where h, k and l may only correspond to allowed reflections. The measured interplanar spacings n_3 and n_4 were substituted into Equation 3 for each of the lattice parameters of 7.24, 3.62 and 14.48 Å, i.e. the values for face centred, body centred and diamond cubic structures, respectively. In every case it was found that Equation 3 was not satisfied and thus the cubic possibilities were eliminated. Thus, we feel that these particles, which do not produce patterns with six-fold symmetry, are very unlikely to be unattacked particles from the parent material since the parent material itself has cubic fcc symmetry. In the light of X-ray evidence [1, 2], it

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*See Appendix.

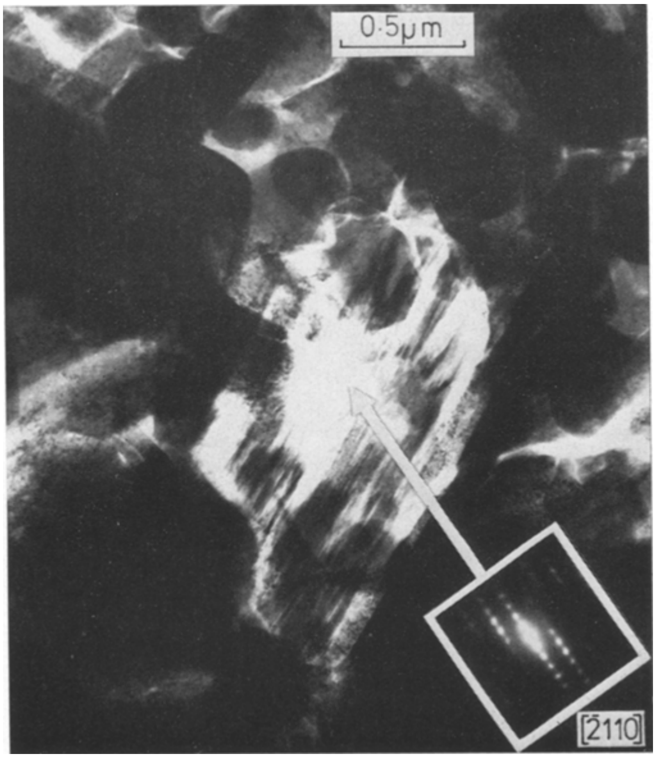

Figure 3 Crystallite with its typical striated appearance and the corresponding diffraction pattern.

seemed reasonable to assume that all the diffraction patterns were derived from hexagonal sodium chromite, i.e. the patterns with and without six-fold symmetry were derived from crystallites with basal and non-basal orientations, respectively. The analysis was continued on the basis of testing this hypothesis.

The interplanar spacings for different $\{hkil\}$ planes were computed for a wide range of h, k and l using the relationship given by Otte and Crocker [4], i.e.

$$n = a_0\{\tfrac{4}{3}(h^2 + hk + k^2) + \gamma^{-2}l^2\}^{-\frac{1}{2}} \qquad (4)$$

where $\gamma = c/a_0 = 15.95/2.96$ for sodium chromite [5].

The measured interplanar spacings, i.e. $n_3 = 2.42 \pm 0.01$ Å and $n_4 = 1.88 \pm 0.01$ Å, showed best agreement with the values of 2.44 and 1.99 Å computed for planes of the type $\{01\bar{1}2\}$ and $\{01\bar{1}5\}$, respectively. In order to check these possible planes and thence to assign consistent indices to them, the angles between all the $\{01\bar{1}2\}$ and $\{01\bar{1}5\}$ type planes were computed using the relationship [4]:

$$\cos\phi = \tfrac{4}{3}\, n_1 n_2\, a_0{}^{-2}\{h_1h_2 + \tfrac{1}{2}\,(h_1k_2 + h_2k_1) + k_1k_2 + \tfrac{3}{4}\,\gamma^{-2}\, l_1l_2\} \qquad (5)$$

(where ϕ is the angle between the normals to the planes $(h_1k_1i_1l_1)$ and $(h_2k_2i_2l_2)$; n_1 and n_2 are the corresponding interplanar spacings in real space; $\gamma = c/a$).

It is found that the planes $(01\bar{1}2)$ and $(\bar{1}10\bar{5})$ are inclined at an angle of 79.66° in "reasonable agreement" with the experimentally observed value of 84 ± 1°. Having thus determined the indices of these reflecting planes, the zone axis $[u, v, t, w]$ of the crystallite was determined using the following relationships [6]:

$$\left.\begin{aligned} u &= l_1(h_2 + 2k_2) - l_2(h_1 + 2k_1) \\ v &= l_2(2h_1 + k_1) - l_1(2h_2 + k_2) \\ w &= 3(k_1h_2 - k_2h_1) \end{aligned}\right\}. \qquad (6)$$

The zone axis, which is a direction in real space unlike the plane normals which are directions in reciprocal space, was found to be $[\bar{4}131]$. The results of the above analysis are summarized in Fig. 4.

The orientation of the crystallite in region A of

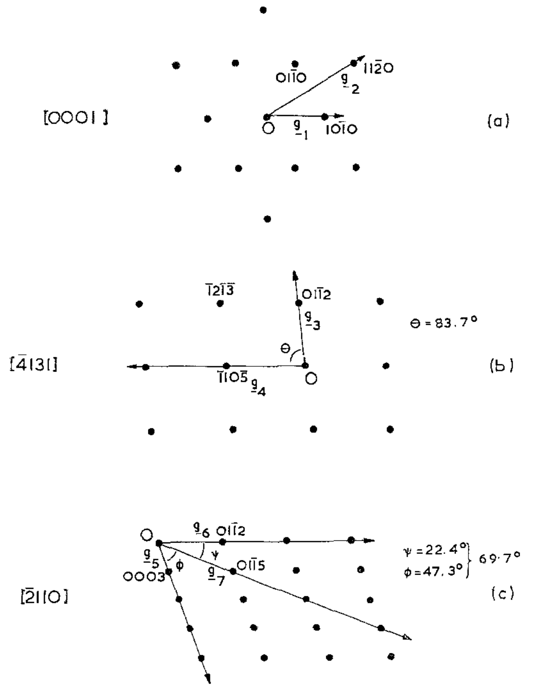

Figure 4 The analysis of the selected-area diffraction patterns derived from (a) a crystallite with basal orientation; (b) a crystallite with a $[\bar{4}131]$ zone axis; (c) a crystallite with a $[\bar{2}110]$ zone axis; θ, ψ and ϕ are angles which were measured on the diffraction patterns.

Fig. 2, i.e. the orientation of the planes in the crystallite perpendicular to the $[\bar{4}131]$ zone axis, was determined using the following transformations given by Frank [7]:

(1) the direction symbolized as $[u, v, t, w]$ is that of a Cartesian 4-vector $[u, v, t, \lambda w]$;

(2) the normal to the plane crystallographically indexed (h, k, i, l) is the Cartesian 4-vector $[h, k, i, l/\lambda]$.

The factor $\lambda = (2/3)^{\frac{1}{2}}\, c/a$ arises because except in the special instance when $c/a = (3/2)^{\frac{1}{2}}$ plane normals and directions characterized by the same indices are not parallel in the hexagonal system.

Thus a $[\bar{4}131]$ zone axis is found to correspond to a $(\bar{4}, 1, 3, 2c^2/3a^2)$ or $(\bar{4}, 1, 3, 19)$ crystallite orientation.

The spot spacings in the pattern derived from the crystallite characterized by a striated appearance (region B of Figs. 2 and 3) were measured and the corresponding interplanar spacings determined to be $n_5 = 4.63$ Å, $n_6 = 2.42$ Å and $n_7 = 1.88$ Å. The computed interplanar spacings of the sodium chromite structure contain no value at 4.63 Å. The closest values of 5.32 and 3.99 Å correspond to the (0003) and (0004) planes respectively. However, the interplanar spacings n_6 and n_7 have already been identified as those corresponding to reflections of the $\{01\bar{1}2\}$ and $\{01\bar{1}5\}$ types (cf. $n_3 = 2.42$ Å and $n_4 = 1.88$ Å). Thus it seemed likely that n_5 could arise from the (0003) planes with a corresponding crystallite orientation of $\{\bar{2}110\}$, since

$$\mathbf{g}_{0003} = (\mathbf{g}_{01\bar{1}5}) - (\mathbf{g}_{01\bar{1}2}) \text{ (see Fig. 4c)}$$

where $\mathbf{g}_{hkil}$ = reciprocal lattice vector associated with the $(hkil)$ plane. This in turn implies that the value of the c parameter is 13.89 Å and not 15.95 Å as in the sodium chromite structure, and that the crystallite orientation is $(\bar{4}, 1, 3, 15)$

TABLE I Analysis of the electron diffraction patterns derived from the 15 day scale

Computed and measured interplanar spacings

Plane	n (computed assuming $c = 15.95$ Å) (Å)	n (computed assuming $c = 13.89$ Å) (Å)	n (measured) (Å)
{0003}	5.32	4.63	4.63 ± 0.01
$\{10\bar{1}0\}$	2.56	2.56	2.56 ± 0.01
$\{01\bar{1}2\}$	2.44	2.41	2.42 ± 0.01
$\{\bar{1}105\}$	1.99	1.88	1.88 ± 0.01
$\{11\bar{2}0\}$	1.48	1.48	1.48 ± 0.01

Computed and measured angles between planes

Planes	Angle (assuming $c = 15.95$ Å) (degrees)	Angle (assuming $c = 13.89$ Å) (degrees)	Angle (measured) (degrees)
$(01\bar{1}2, (\bar{1}10\bar{5})$	79.7	83.7	84.0 ± 0.5
$(01\bar{1}2), (0003)$	72.2	69.7	69.5 ± 0.5
$(01\bar{1}5), (0003)$	51.2	47.3	46.0 ± 0.5
$(01\bar{1}2), (01\bar{1}5)$	20.9	22.4	23.5 ± 0.5

TABLE II Analysis of the polycrystalline diffraction pattern derived from the 29 day scale

Measured interplanar spacings (Å)	Computed interplanar spacings			
	(i) assuming $c = 13.89$ Å		(ii) assuming $c = 15.95$ Å	
	Plane	Spacing (Å)	Plane	Spacing (Å)
1.24 ± 0.01	$\{02\bar{2}3\}$	1.235	$\{02\bar{2}4\}$	1.220
	$\{11\bar{2}6\}$	1.247	$\{02\bar{2}3\}$	1.246
	$\{02\bar{2}2\}$	1.260	$\{02\bar{2}2\}$	1.265
1.48 ± 0.01	$\{11\bar{2}1\}$	1.472	$\{11\bar{2}1\}$	1.474
	$\{11\bar{2}0\}$	1.480	$\{11\bar{2}0\}$	1.480
1.87 ± 0.01	$\{01\bar{1}5\}$	1.884	$\{01\bar{1}5\}$	1.998
2.25 ± 0.01	$\{01\bar{1}3\}$	2.243	$\{01\bar{1}3\}$	2.310
2.57 ± 0.01	$\{01\bar{1}0\}$	2.563	$\{01\bar{1}0\}$	2.563
2.74 ± 0.01	$\{0005\}$	2.770	—	—
3.74 ± 0.01	—	—	—	—

rather than ($\bar{4}$, 1, 3, 19). Assuming this modified value, the interplanar spacings for different $\{hkil\}$ planes over a wide range of h, k and l were again computed using Equation 4. In general, the calculated spacings were insensitive to this change in c except in those cases where the Miller index l was significantly greater than the indices h and k as in for example the $\{01\bar{1}5\}$ planes. Table I compares the measured interplanar spacings and angles for the diffraction patterns in Figs. 2 and 3, with those calculated using the sodium chromite c value and the proposed $c = 13.9$ value. Best agreement is obtained in the latter case. Thus the results indicate that in the non-basal crystallites at least, the structure is not identical with the suspected sodium chromite structure.

3.2. 29 day sample examined in the Philips EM 200

In an attempt to determine whether or not this reduction in the c parameter exists in basal and non-basal orientation crystallites alike, further investigations were carried out in the Philips EM 200 electron microscope. This microscope, in which the specimen may be tilted by up to ± 45°, provided the possibility of obtaining non-basal reflections from the basal crystallites and thus of determining the c lattice parameter in these crystallites. Polycrystalline ring type diffraction patterns were derived from a scale which had been formed during a 29 day exposure to sodium (see Fig. 5). Even with zero tilting it was apparent that the crystallites in this scale did not have the same basal preference as those present in the scale resulting from the longer exposure of 89 days, because of the presence of many strong non-basal reflections. The ring diameters were measured and the corresponding interplanar spacings determined. Table II shows that although some rings may not be accounted for there is generally better agreement between measured and computed spacings when a lattice parameter $c = 13.89$ Å is assumed. Analysis of these diffraction patterns was complex because of double diffraction effects between overlapping crystallites. At first sight spots A, B and C in Fig. 5 appear to be systematic reflections arising from a particular crystallite. The inner spot corresponding to an interplanar spacing of 3.74 Å cannot be matched with any of the computed values, while spots B and C agree well with $\{01\bar{1}5\}$ and $\{02\bar{2}3\}$ reflections. However, spot A may be generated if a type C reflection from one crystallite is diffracted into a type B reflection in an underlying crystallite, which requires that the $\{01\bar{1}5\}$ planes of the first crystallite are aligned parallel to the $\{02\bar{2}3\}$ planes of the second.

4. Discussion

The results of the present study indicate that the structure of the scale, formed during the exposure of 304 stainless steel to sodium although hexagonal, does not correspond exactly with the suspected sodium chromite structure. The a lattice parameter, i.e. the one measured in the basal plane, agrees well with the chromite value but the observed c parameter indicates that the scale, if chemically equivalent to sodium chromite, has undergone a 13% contraction parallel to the c-axis, i.e. normal to the basal planes.

The presence of the 0003 reflection (Fig. 4c)

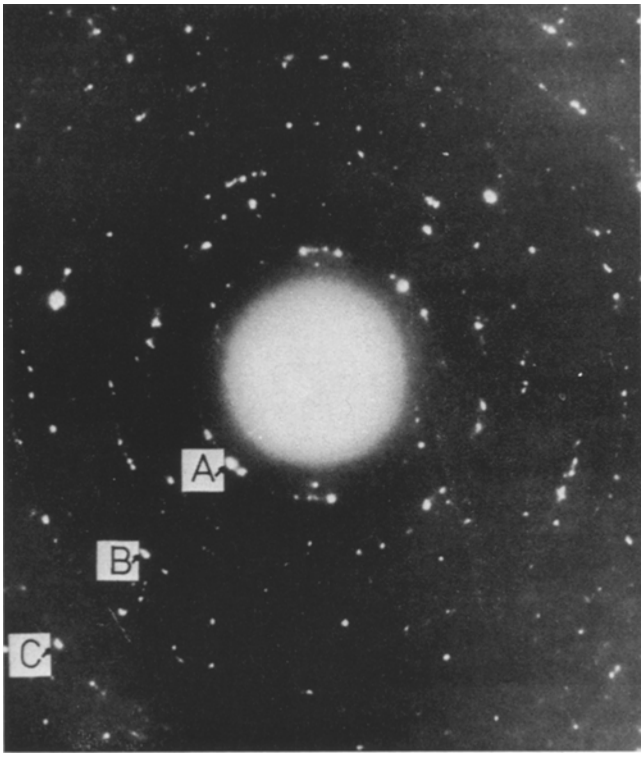

Figure 5 Diffraction pattern from a scale formed during a 29 day exposure to sodium.

is of extreme importance since this reflection is normally forbidden by the selection rules relevant to hexagonal structures [8]. Double diffraction between allowed reflections of the $01\bar{1}5$ and $0\bar{1}1\bar{2}$ types may at first sight provide a possible explanation. However, this hypothesis may be dismissed after careful consideration of the diffraction pattern derived from region B of Fig. 2. Here a systematic row of the forbidden 0003 reflections is strongly excited while the allowed $01\bar{1}5$ and $0\bar{1}1\bar{2}$ type reflections are very weakly excited, if at all. Supposing the $01\bar{1}5$ reflections are strongly excited, then in order that only "0003" spots may appear in the diffraction pattern, we must assume that the $01\bar{1}5$ diffracted beams are totally diffracted again by the $0\bar{1}1\bar{2}$ planes according to a $(01\bar{1}5) + (0\bar{1}12)$ double diffraction mechanism, otherwise $01\bar{1}5$ spots are to be expected in the resultant diffraction pattern. Now when using 1 MeV electrons, the Bragg angle for these reflections is $\simeq 0.2°$ and so if the $0\bar{1}1\bar{2}$ planes are oriented correctly for double diffraction effects, they must be sufficiently close to the Bragg condition for primary diffraction also to occur. Thus some weaker (relative to the "0003" spots) $0\bar{1}1\bar{2}$ spots are to be expected. This argument is valid because of the very small Bragg angles involved. Thus a double diffraction mechanism cannot explain the observation of only "0003" strongly excited spots without $01\bar{1}5$ and $0\bar{1}1\bar{2}$ spots. Now it turns out that the sodium chromite system is not simple hexagonal, but instead it is that of the more complex caesium dichloroiodide hexagonal type. A basal plane projection of this structure [5] shows that the atomic arrangement is such that a three layer stacking sequence exists parallel to the *c*-axis in a manner similar to the familiar ABCABC stacking sequence of (111) planes in a face centred cubic structure. Thus the 0003 reflection is expected to be an allowed reflection in this particular type of hexagonal crystal and has, in fact, been observed in X-ray studies of, for example, sodium chromite [9]. Consequently, the results of the present study are consistent with the scale structure being a distorted version of the suspected sodium chromite structure.

Approximately 90% of the crystallites formed during the growth of the corrosion scale were observed to have a basal (0001) orientation as might be expected. The remaining 10% were divided equally between {4, $\bar{1}$, $\bar{3}$, 15} and {$\bar{2}$110} orientations. An analysis of diffraction patterns derived from these non-basal crystallites showed that in both cases planes of the {01$\bar{1}$5} type exist perpendicular to the scale surface. The spacing of these planes is very similar to that of the {002} planes in the underlying steel, being 1.88 and 1.79 Å respectively. Other work of Fisher *et al.* [10] has shown the steel to be polycrystalline, the individual crystallites having a preferred {110} orientation. Thus {002} planes are often perpendicular to the surface. It seems probable that the non-basal hexagonal scale crystallites grow onto the steel surface by some epitaxial process such that the {01$\bar{1}$5} planes of the scale line up with the {002} planes of the steel. Unfortunately, this proposal could not be checked in the present study since the scale was examined after removal from the steel substrate.

An X-ray investigation of the scale, still in contact with the steel substrate, has been performed by Hooper [11]. His data in contrast to the results of the present analysis, indicate that there is no distortion of the sodium chromite structure. It is thus essential that further X-ray experiments are performed on the scale alone, to establish whether this distortion is in some way related to the removal of the scale from the steel surface.

5. Conclusion

It has been possible using electrolytic techniques to remove, undamaged, the corrosion scale from samples of sodium exposed stainless steel. Subsequent examination of the scale in the high voltage electron microscope led to the following observations and conclusions:

(1) The layer is composed of irregularly sized and shaped crystallites in the diameter range 0.3 and 1.0 μm.

(2) Overlap between neighbouring grains frequently occurs.

(3) Electron diffraction patterns derived from ~ 50 crystallites show that the scale formed during an 89 day sodium exposure, contains crystallites with three types of hexagonal orientation with respect to the underlying steel surface. Approximately 90% are of basal (0001) orientation. The remaining crystallites are either of {4, $\bar{1}$, 3, 15} or {$\bar{2}$110} type orientations. A schematic summary of the corresponding electron diffraction patterns is given in Fig. 4.

(4) The lattice parameters were determined to be $a = 2.96 \pm 0.01$ Å and $c = 13.89 \pm 0.02$ Å.

(5) The presence of the 0003 reflection, normally forbidden in hexagonal structures, indicated that the scale structure is consistent with that of the caesium dichloroiodide hexagonal type (sodium chromite also has this structure).

(6) The results obtained indicate that the scale is a distorted form of sodium chromite such that there is a reduction of ~ 13% in the "*c*" lattice parameter.

(7) The non-basal crystallites contain planar spacings similar to the underlying steel spacings and thus are likely to form by some epitaxial growth process.

Additional information was obtained from an examination in the Philips EM 200 of a scale formed during a 29 day sodium exposure, namely:

(8) The crystallites formed in this shorter exposure scale did not exhibit the same basal orientation preference.

(9) An analysis of the electron diffraction pattern derived from the scale indicated that the same reduction of ~ 13% in the "*c*" lattice parameter existed as in the scale formed during the longer 89 day sodium exposure.

6. Appendix

Throughout this work, the 4-axis (4 index) system is used in the description of crystallographic planes, plane normals and directions, while the 4-axis (3 index) system is used in the computations. The differences between the three principle systems which may be used to describe the hexagonal system, i.e. 3-axis, 4-axis (4 index) 4-axis (3 index), have been described by Otte and Crocker [4]. In their Table 2, these authors present a convenient list of most of the crystallographic relationships required by workers in the field. However, as noted by Nicholas [6], three errors are made in this Table 2, one of which is relevant to the 4-axis (3 index) system, i.e. a factor of $\frac{1}{3}$ should be included before the term $\gamma^2 w_1 w_2$ in the expression for $\cos \rho$.

The relationships of Otte and Crocker [4] may be checked conveniently, because the usual rules of vector algebra concerning dot products are valid in the 4-axis hexagonal system, providing the vector transformations of Frank [7] described in Section 3 of the present work are used.

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