Galvanic corrosion of an implant consisting of iron and brass

H. ZITTER and K. PAULUZZI
Institute of Chemistry, University of Mining and Metallurgy, Leoben, and the Hospital for Traumatology, Graz, Austria

Corrosion of an implant consisting of almost equal parts of iron and brass proceeded due to the cathodic protection of the brass, which was attacked only after the iron portion had dissolved. The corrosion of the brass proceeded as dezincification, during which dissolved copper was redeposited on the brass where it acted as a cathode that accelerated the corrosion process. Especially noteworthy was the precipitation of secondary corrosion products from ions originating in the acidified area of the anode during the primary stage of corrosion by neutralization with body fluids. These secondary corrosion products were identical with chemical compounds occurring in nature as minerals. The processes of corrosion, as well as the conversion of the primary to secondary corrosion products, are in accordance with thermodynamics, which states that all metals created from minerals through the expenditure of chemical energy have a tendency to revert to their original state.

1. Introduction

Galvanic corrosion of biomaterials is encountered primarily in the field of dentistry [1], where base metals are still used in combination with precious metals. Only a very few cases of galvanic corrosion of osteosynthetic implants have been reported, but the circumstances surrounding them have tended to be quite spectacular. In such cases the implants were made either entirely of base or precious metals [2] or of base metals with a precious-metal coating [3, 4]. A particularly serious case was the focus for an in-depth study of the consequences of galvanic corrosion of implants.

2. Medical description of the case

At the age of 13 years a patient developed osteomyelitis of the thigh bone without having sustained any injury to the area. Five years later his knee joint was surgically fixed by means of screws. In 1989, 53 years after the joint had been ankylosed, the patient had an accident and broke his lower leg just below the location of the arthrodesis, at a point where pus had been exuding since 1931 from fistulae in a hand-sized defect extending clear to the bone (Fig. 1a). X-ray examination of the region revealed an object in the shape of a screw (Fig. 1b).

When attending to the fractured bone, an attempt was made to treat the myelitis by widening the opening in the medullary space and removing the screw, which was found floating freely in a bed of pus. It is this screw that formed the subject of the investigation reported here. Although the fracture has since healed, it has not been possible to bring the myelitis under control.

3. Macroscopic investigation of the implant

The implant, which was explanted undamaged, was shaped like a screw and was covered with solid corrosion products. A number of lighter-coloured ossifications were found around the head (Fig. 2), where bare metal also showed through in places (Fig. 2b).

Before embedding the screw in synthetic resin, an attempt was made to cut into the protruding edge of the screw head. However, the screw broke apart at the point where the head intersected the shank, revealing that the shank had corroded all the way through. From Fig. 3, which shows the two fracture surfaces, it can be seen that the head of the screw had been hollow and that this space was now completely filled with corrosion products from the broken-off shank.

4. Microscopic investigation of the implant

After putting the two parts into their original position, they were embedded in synthetic resin and ground along their longitudinal axis. (This type of preparation ensures that almost none of the corrosion products are lost.) The resultant longitudinal section showed that the completely corroded shank had consisted of a hollow shaft attached to the head (Fig. 4).

4.1. Microscopic investigation of the cut surface of the implant

4.1.1. Screw head

Fig. 5 shows the surface of the transversal section of the head of the screw, with larger magnifications of parts of the same picture given in Fig. 6. Fig. 7 shows
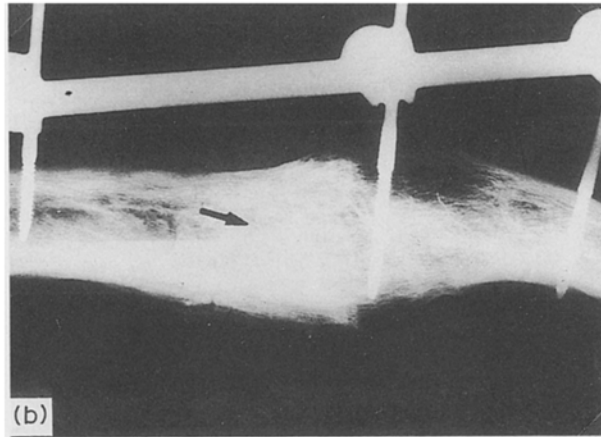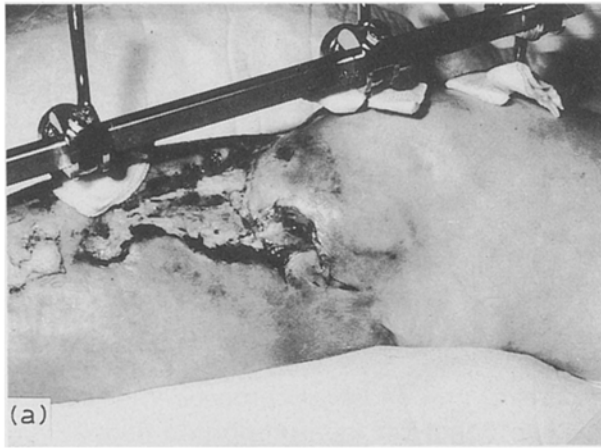
Figure 1 (a) Condition after arthrodesis of the knee joint due to osteomyelitis and (b) location of the screw.
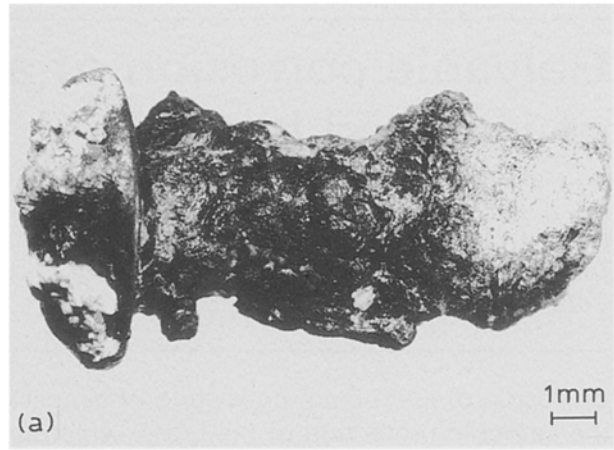

Figure 2 The screw after explantation: (a) total view and (b) screw head

the results of scanning electron microscopy (SEM) of selected areas.

Given its colour, the brightest of the reflecting areas is easily identifiable as brass (Fig. 5), whose underside bears signs of selective corrosion. From the type of corrosion, the metal can be identified as α/β brass, whose low copper content β-phase was selectively corroded while its more copper rich, and thus more resistant, α-phase remained intact (A in Fig. 6). Pictures of the uncorroded part of the metal taken by
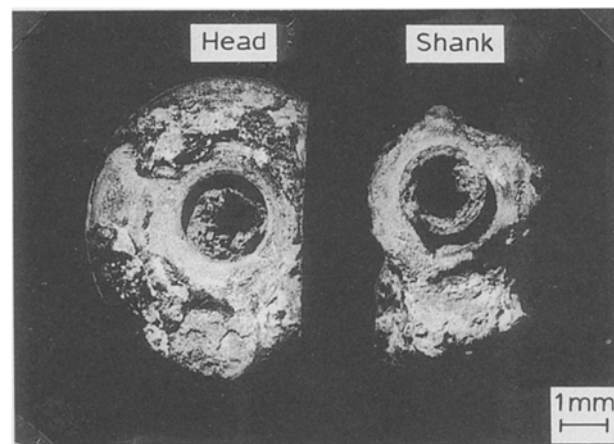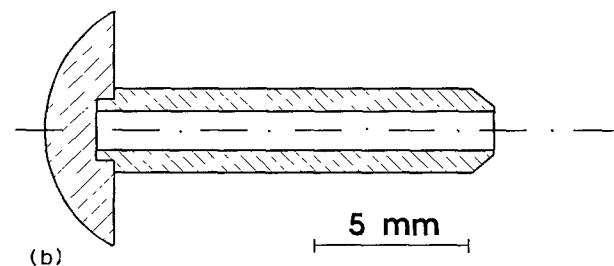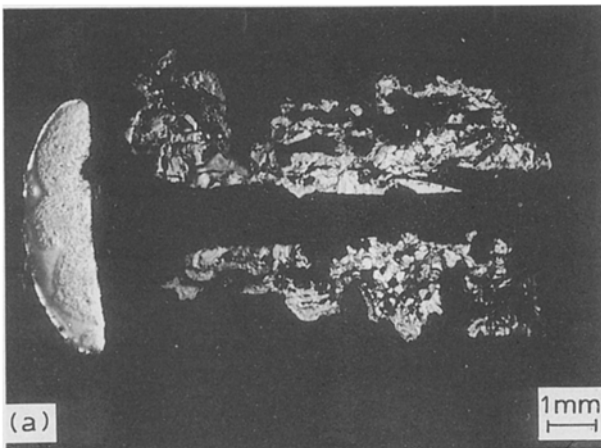

Figure 3 Fracture between head and shank of the screw.

Figure 4 Longitudinal sections of (a) the corroded screw and (b) the presumed original implant.

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scanning electron microscopy (Fig. 7) show tiny inclusions inside the metal that, given their light colour, are likely to consist of an element with a high atomic number (B in Fig. 7). Inside the selectively corroded parts (i.e. what formerly was β-brass) several phases could be observed: the colour of the porous phase (C in Figs 6 and 7) indicated copper, such as might have precipitated in the course of the dezincification from the primary soluble products of corrosion.

A finely precipitated phase appeared blue in the reflection, but red in the internal reflections (D in Figs 6 and 7), similar to the behavior of cuprite (a product of corrosion found in water pipes). Immediately adjacent, a much rarer blue phase was observed (E in Fig. 6) which, under the SEM, appeared considerably lighter than all other phases (E in Fig. 7).

The metal also had a covering of up to 50 μm corrosion products with a zoned structure (bottom of Fig. 6b) which it was not possible to reproduce photomicroscopically. SEM (Fig. 7a) revealed a lighter phase (G) on one side of the metal and a darker phase (F) on the outside.

Figure 5 Head of the screw in longitudinal section

4.1.2. Corrosion products of the hollow shaft

The solid corrosion products found in the hollow shaft of the screw consisted primarily of homogeneous layers that developed cracks (Fig. 8) during the course of preparation. The optical characteristics of these layers, especially their red internal reflexes, point to the presence of a hydrate of ferric oxide [FeO(OH)] [12], better known as rust [13] (H in Fig. 8). SEM uncovered a few areas where an additional phase existed that could not be identified photomicroscopically (J in Fig. 8).
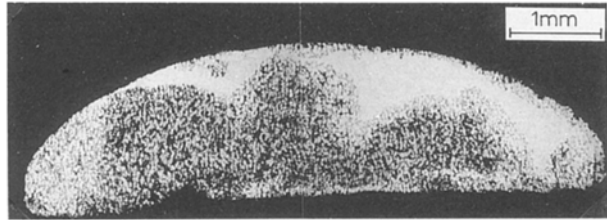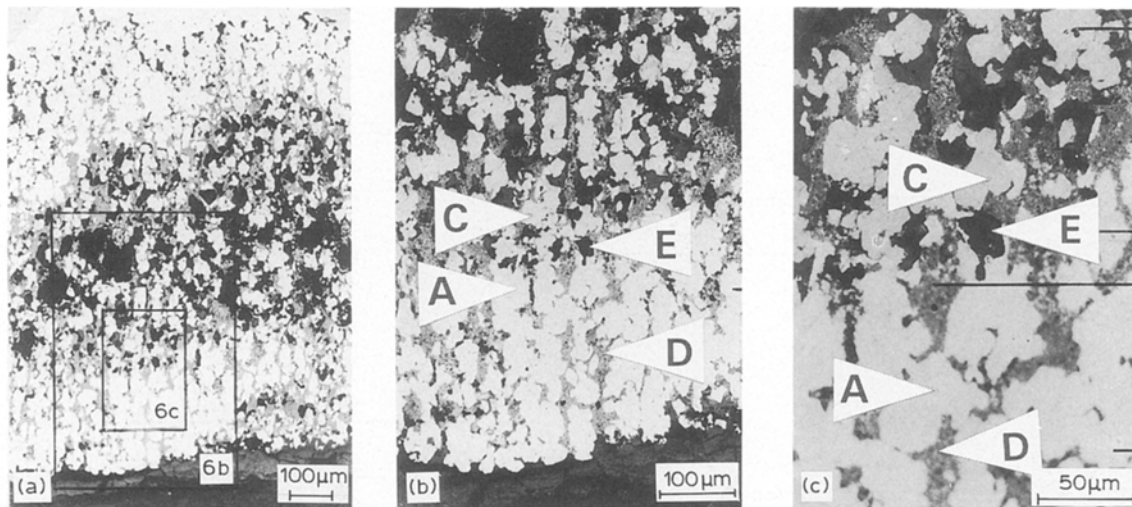

Figure 6 Structure of the locally corroded screw head (photomicroscopic view).
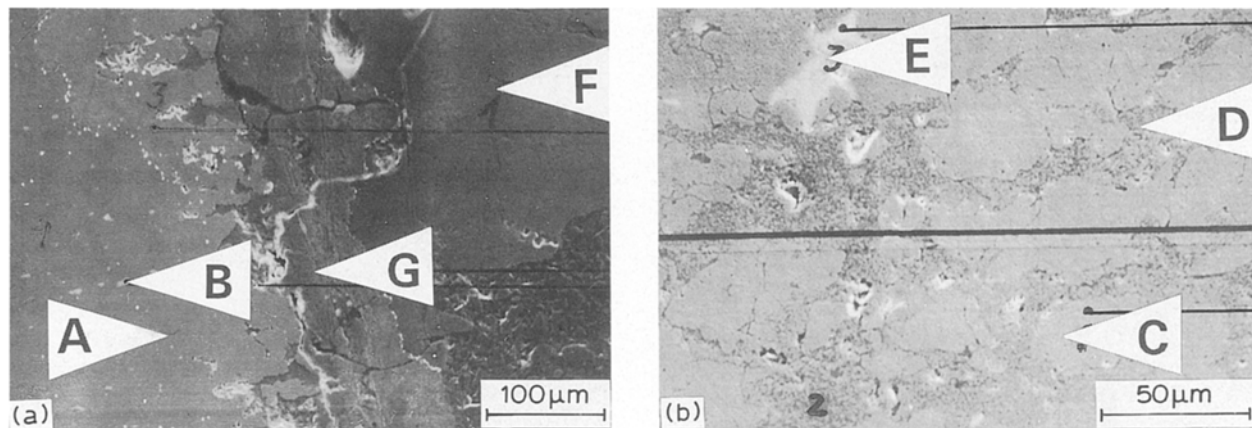

Figure 7 Structure of the locally corroded screw head (SEM micrograph).
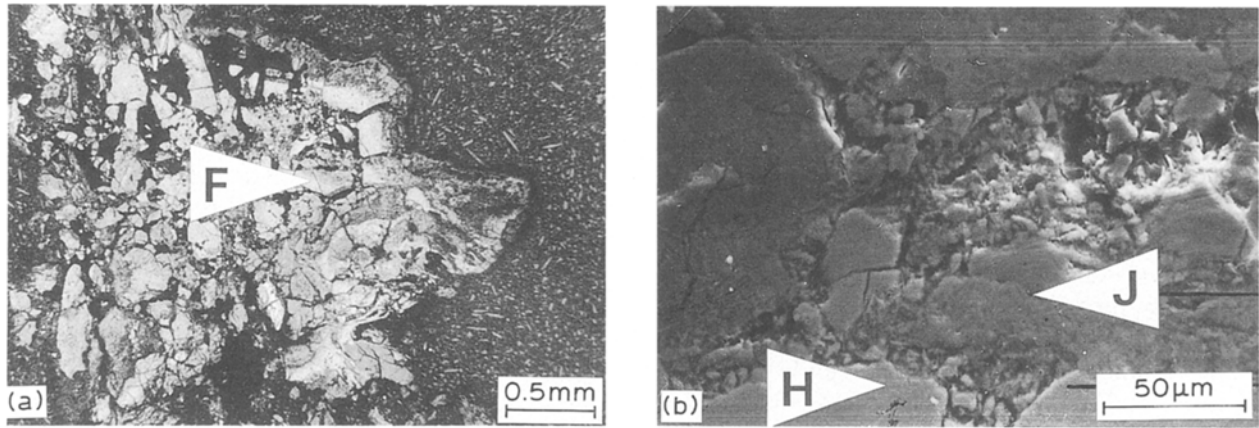
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Figure 8 Corrosion products of the hollow shaft: (a) optical micrograph and (b) SEM micrograph
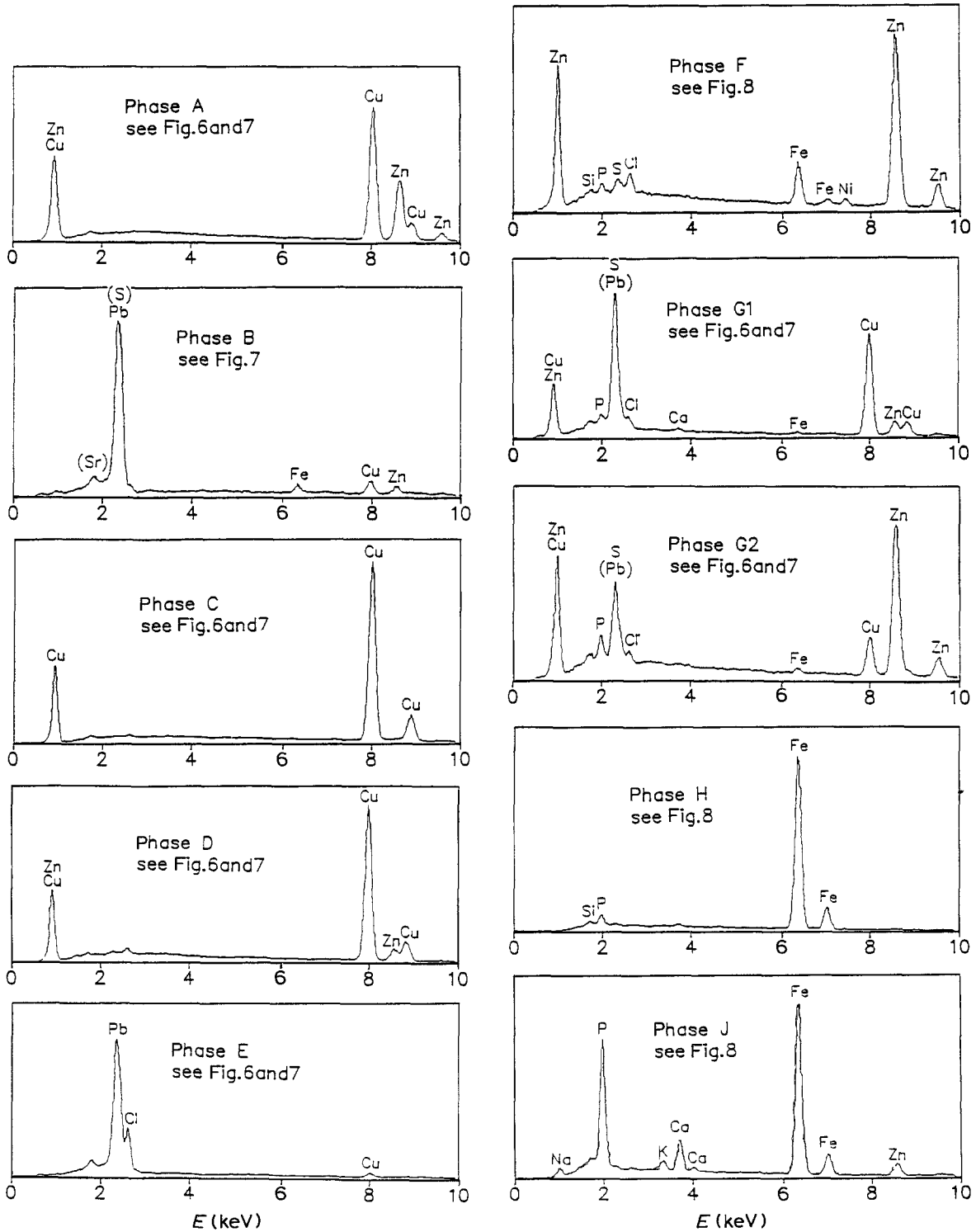

Figure 9 Electron microprobe analysis of different phases.

4.2. Analysis of individual phases by microprobe

In certain selected phases and regions, a microprobe was used both to confirm the photomicroscopic results and to identify phases that it was not possible to identify photomicroscopically. The resultant spectra are shown in Fig. 9 and have been assigned the same letters as used in the photomicroscopic pictures and SEM micrographs.

These spectra prove that the uncorroded matrix consisted of brass (phase A) and, as was to be expected, the red porous matter consisted entirely of copper (phase C in Fig. 6). Inclusions found in the metal (phase B in Fig. 7a) were pure lead. We therefore conclude that what we were dealing with was brass to which lead had been added by alloying in order to improve its machinability. Today such alloys are manufactured with lead contents of up to 3%, an example being CuZn36Pb3, carrying the material number 2,0375 [5]. Apart from copper, phase D (Fig. 7a) showed only minor traces of zinc, evidence that the material was largely pure cuprite [6, 7].

It was particularly surprising to find the elements Pb, Cu and Cl in the analysis of phase E. From among the possible minerals this could indicate, diaboleite mineral phase $2Pb(OH)_2CuCl_2$ [8] seemed the most likely, based on the microprobe analysis and the observed optical characteristics. Subsequent comparative analysis of a sample of diaboleite from the Mamouth Mine in Tiger, Arizona, USA, the crystal structure of which was confirmed by X-ray examination, produced exactly the same intensity ratios of Pb, Cu and Cl as in Fig. 9 (phase E).

Microprobe analysis of corrosion products not visible in the micrograph sections produced the following results. Based on the spectrum shown in Fig. 9, region F in Fig. 7 consisted mainly of zinc. The analysis indicated the presence of white rust [9, 10], known to be a product of the corrosion of zinc, the chemical composition of which was identical to that of the mineral zincite (ZnO) [11]. Again based on the analysis presented in Fig. 9, region G in Fig. 7 probably contained a mixture of zinc oxide and cupric sulphide in various proportions.

Iron was the only element found in the corrosion products of the hollow shaft, confirming the photomicroscopic result of FeO(OH) (Fig. 9, phase J).

The second phase (Fig. 9) that could not be identified photomicroscopically consisted mainly of iron and phosphorous. This analysis pointed to the existence of an iron phosphate, such as vivianite, $Fe_3(PO_4)_2·8H_2O$ [14].

5. Conclusion about the corrosion process

In the case of iron and brass, the corrosion potentials (i.e. those mixed potentials that metals have in ambient electrolytes) of the two metals differ by several hundred mV [15]. This thus provides the first prerequisite for the creation of a galvanic element. The second prerequisite, that of a conductive connection between the two metals, definitely existed, as iron corrosion products were found directly on the surface of the brass (cf. Figs 2 and 3). There can also be no doubt that the third prerequisite, that of the capacity of the ambient medium to conduct ions, was also given. In the case of an open circuit, i.e. with separated electrodes, iron and brass would have corroded with about the same corrosion rate by reduction of oxygen as the cathodic process (Fig. 10). In the short-circuit condition a galvanic element is built up with iron as sacrificial anode, which is preferentially dissolved whereas brass is cathodically protected (Fig. 11). The galvanic current between the two metals is compensated by an equal current of ions with the surrounding electrolyte. This cathodic protection lasted as long as the shaft of iron was in conductive contact with the part of brass. Then the corrosion of brass began with the dissolution of β-grains with lower copper content. With this corrosion process copper ions were precipitated as metallic copper on the surface of the alloy, forming a local cathode which accelerated the anodic dissolution of brass.

Phases identified photomicroscopically or with the electron microprobe were all secondary corrosion products that originated primarily through neutralization of ions released during primary corrosion processes [16]. Precipitations of certain unexpected species, such as diaboleite and vivianite, cannot be explained other than by the same process by which these rather rare minerals occur in nature, i.e. through the conjunction of dissolved species in concentrations likely to promote such precipitations.
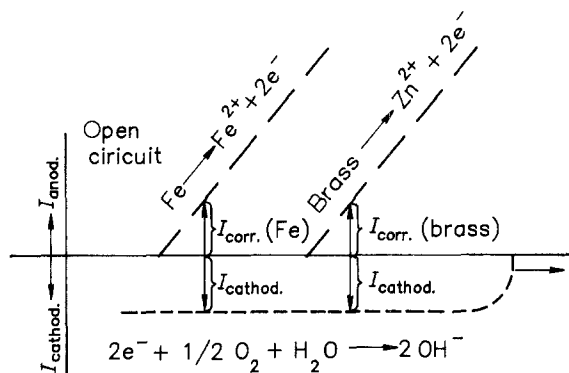

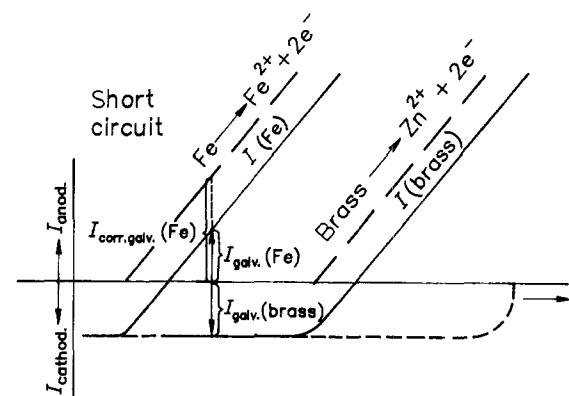Figure 10 Electrochemical processes during corrosion of separated iron and brass.

Figure 11 Electrochemical processes during corrosion of short-circuited iron and brass. (———) Partial currents and (— — —) measurable currents.

Acknowledgements

References

1. U. RHEINWALD. *Dt. Zahn-, Mund- Kieferheilk.* **18** (1953) 881.
2. D. C LUDWIGSON, *J. Metals* (1964) 226.
3. H. J. RUNNE and H. MORITZ, *Zbl. Chir.* **86** (1961) 2341.
4. H ZITTER and D. SCHASCHL-OUTSCHAR, *Werkstoffe Korros.* **32** (1981) 324.
5. INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO 426/2, 2nd Edn (ISO, Geneva, 1983)
6. P. RAMDOHR and H STRUNDZ, in "Klockmanns Lehrbuch der Mineralogie" (Ferdinand Enke Verlag, Stuttgart, 1978) p. 498
7. V F. LUCEY. *Werkstoffe Korros.* **26** (1975) 185.
8. P RAMDOHR and H STRUNDZ, in "Klockmanns Lehrbuch der Mineralogie" (Ferdinand Enke Verlag, Stuttgart, 1978) p. 496.
9. F TÖDT, in "Korrosion und Korrosionsschutz" (Walter de Gruyter, Berlin, 1961) p. 819.
10. K. A VAN OETEREN, in "Korrosionsschutz durch Beschichtungsstoffe" (Carl Hauser Verlag, Munich, 1980) p. 129.
11 P RAMDOHR and H STRUNDZ, in "Klockmanns Lehrbuch der Mineralogie" (Ferdinand Enke Verlag, Stuttgart, 1978) p. 499.
12. P RAMDOHR and H. STRUNDZ, in "Klockmanns Lehrbuch der Mineralogie" (Ferdinand Enke Verlag, Stuttgart, 1978) p. 552.
13. F. TÖDT, in "Korrosion and Korrosionsschutz" (Walter de Gruyter, Berlin, 1961) p. 56.
14 P. RAMDOHR and H. STRUNDZ, in "Klockmanns Lehrbuch der Mineralogie" (Ferdinand Enke Verlag, Stuttgart, 1978) p. 642.
15. J ELZE, G. OELZNER and H KAESCHE, in "Die Korrosion der Metalle" (Springer-Verlag, Berlin, 1966) p. 225.
16. H ZITTER. *Z. Unfallheilk.* **79** (1976) 91.