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Stress corrosion cracking of leaded brass in a sulphuric acid environment

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Free-cutting leaded brass is commonly used as sleeve fittings (also termed clamping ferrules) on polytetrafluoroethylene-lined flexible hoses for the filling and distribution of compressed gases, e.g., oxygen, nitrogen and carbon dioxide, for various industrial and medical applications. Some of the gas-filling and gas distribution facilities are located in the proximity of highly industrialized areas for the convenience of transportation, application and customer service. Therefore, the gas-filling and gas distribution gears are frequently exposed to the environment containing various chemical substances, which in the presence of ambient moisture and under the influence of mechanical and residual stresses in the material can effect an undesirable material degradation reaction. Stress corrosion cracking (SCC) has been identified to occur in C36000 Cu–Zn–Pb leaded brass ferrules under the synergistic reactions of a sulphuric acid production environment in a sustained tensile stress environment. The tensile stress was imparted to the material by the mechanical crimping process applied on the ferrules, and superimposed by cyclical high-pressure gas-cylinder-filling operations. The chemical species responsible for the SCC originated from the gaseous vapours and/or ionic derivatives of S-containing substances emitted from a neighbouring sulphuric acid production plant, which reacted with water and moisture condensates on the brass ferrule surfaces and effected the chemical corrosion reaction(s). SCC of the leaded brass ferrules gave rise to predominantly intergranular failures with fracture surfaces heavily decorated by corrosion products of various configurations. Most corrosion products were found to have embedded on the grain-boundary planes of the fracture surfaces, suggesting that grain-boundary short-circuit diffusion may have served as a viable mechanism for the SCC of C36000 leaded brass under the operating conditions of this case study. © *1998 Kluwer Academic Publishers*

1. Introduction

Stress corrosion cracking (SCC) has been the subject of extensive review in recent years [1–11]. SCC failures were first reported in copper–zinc alloys more than 80 years ago in India, where they occurred to brass cartridge cases under an ammonia vapours environment during the rainy season [5]. This phenomenon was later characterized by the descriptive term "season cracking".

The phenomenon of SCC can be generally defined as the occurrence of macroscopic brittle fracture of a normally ductile metal due to the combined and synergistic interaction of sustained mechanical stresses and some specific corrosive environments [2–4]. The stresses required to effect SCC can be small, i.e., below the macroscopic yield stress, and are tensile in nature. Susceptibility is largely a function of stress magnitude. Generally, the higher the stress, the weaker the corroding medium must be to cause SCC [6]. Environments that can facilitate SCC are generally aqueous and can be present in the form of either condensed layers of moisture or bulk solutions [2]. According to our knowledge accumulated to date, it is generally accepted that SCC is alloy and environment specific, which is a complex function of such parameters as temperature, concentration of ionic species and degree of aeration, state of loading stress, alloy composition and microstructure, and thermal and mechanical treatment. As a result, the list of alloy–environment combinations that can cause SCC is continually expanding [2].

Among many attributes of SCC, two important characteristics are noteworthy: firstly, the environment need not be chemically aggressive to result in high general dissolution rate; secondly, the roles and effects of anodic dissolution and hydrogen absorption on cracking are generally difficult to differentiate. SCC has been identified to occur in a number of material systems, including copper alloys, ferritic steels, stainless steels, high-strength steels, and titanium, magnesium and aluminium alloys. Classic examples of SCC are generally referred to season cracking of copper alloys, due to the presence of ammonia in the environment, and exacerbate cracking of stainless steels and aluminium alloys in chloride ion environments. Despite numerous previous studies performed on the SCC

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of copper alloys, only a few cases can be cited for SCC of leaded brasses in a non-ammoniacal environment [5]. To the best of the present author's knowledge on the basis of literature search, little information is available on the SCC of leaded brasses in acidic environment, e.g., sulphuric acid [12].

The intent of this paper is to present a case study on the failure of Cu–Zn–Pb brass sleeve fittings, effected by SCC, in a sulphuric acid environment. The leaded brass sleeve fittings (also termed brass ferrules) were used as a cramping device on flexible hoses for cylinder filling or transmission of various industrial gases including O_2, N_2, and CO_2. In general, the environment under which gas filling or transmission is conducted varies a great deal, depending upon neighbouring industry, air quality and climatic condition at the perimeter of the facility. In this case study, the gas-filling facility was near a sulphuric acid production plant. The brass sleeve fittings were claimed to have cracked after the flexible hoses have been used for operation over a period of time, which in turn gave rise to gas leakage and hose dislocation, under extreme cases.

2. Material descriptions and experimental procedures

Cracked brass ferrules with polytetrafluoroethylene-lined stainless steel braided flexible hoses were removed from field service and inspected visually as well as by optical microscopy. Samples were then extracted from the cracked brass ferrules and analysed in duplicate for their chemistry by inductively coupled plasma (ICP) optical emission spectrometry and by the X-ray diffraction–fluorescence technique.

The cracked brass ferrules were further examined for their fracture surfaces and metallurgical microstructures. Additionally, intact brass ferrules were obtained from a used flexible hose as well as from a virgin flexible hose and fractured *ex situ* for examination in order to establish baseline information. To differentiate between these materials, they are denoted as "cracked ferrule", "intact ferrule" (from used flexible hose) and "unused ferrule" (from virgin flexible hose) in the contents. The fracture surfaces of and polished cross-section metallurgical samples from the cracked, intact and unused ferrules were examined using scanning electron microscopy. Additionally, X-ray photoelectron microscopy (XPS) and energy-dispersive spectrometry (EDS) X-ray microanalyses with the ZAF (where Z is the atomic number, A the absorption correction factor and F the fluorescence correction factor) correction were performed to determine the chemistry of various reaction products on the fracture surfaces. Limited by its beam size, the XPS has a lateral resolution about 600 μm.

3. Experimental results and discussion

According to the ICP chemical analyses, the nominal composition of the brass ferrules was determined to be as follows: Cu, balance; Zn, 35.26 wt %; Pb, 3.04 wt %; Al, less than 0.01 wt %; Si, less than 0.01 wt %; Fe, 0.1 wt %; Mn, 0.01 wt %; Ni, 0.03 wt %. According to this composition, the ferrule can be classified as a free-cutting leaded brass, i.e., C36000.

A failed flexible hose attached to a cracked brass ferrule and hexagonal-head brass adaptor is presented in Fig. 1. A macroscopic crack extended along the longitudinal direction is clearly visible in Fig. 1a. Additionally, a few longitudinal frills are noted and are indicated by arrows on the surface shown in Fig. 1b. In some cases, localized cracks and/or fissures were noted to have incubated on these frills. Some of these crack-bearing frills were *ex situ* fractured and classified as a "cracked ferrule" sample for fracture surface examination. It is important to point out that most *ex situ* fractures performed on all the ferrules, including the intact and unused ferrules, were cracked along the passages of the longitudinal frills. These frills were generated by mechanical crimping during the fabrication process of a flexible hose in order to seal leakage effectively between the flexible hose and its bullnose adaptor–connector (also made of brass).

Cross-sectional view metallurgical samples were prepared from the cracked, intact and unused ferrules to reveal their microstructures across the radial thickness. Fig. 2a, b and c show scanning electron photomicrographs of the microstructures from the cracked,

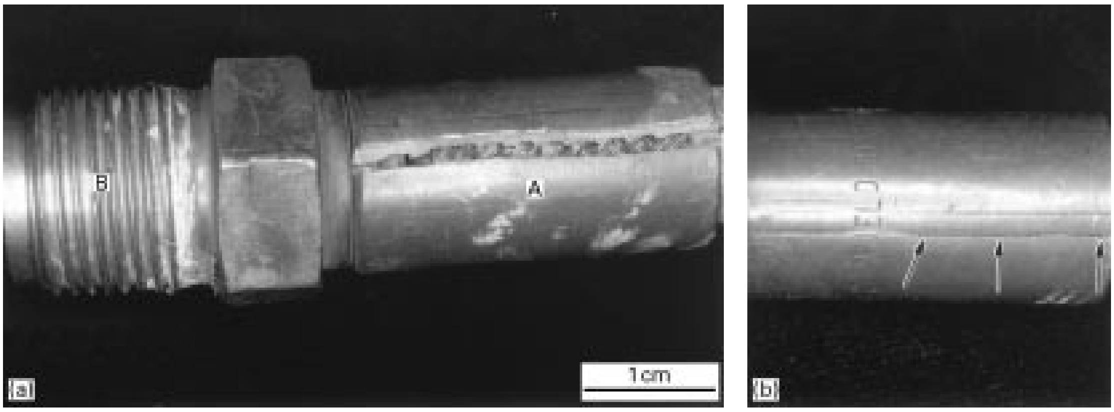

Figure 1 Optical photographs showing (a) the physical characteristics of a cracked brass ferrule in service condition and (b) the presence of longitudinal frills on the surface as a result of a mechanical crimping process. The brass ferrule and brass adaptor–connector are denoted as A and B, respectively, in (a). The formation of localized cracks on the frills is clearly visible and denoted by arrows in (b).

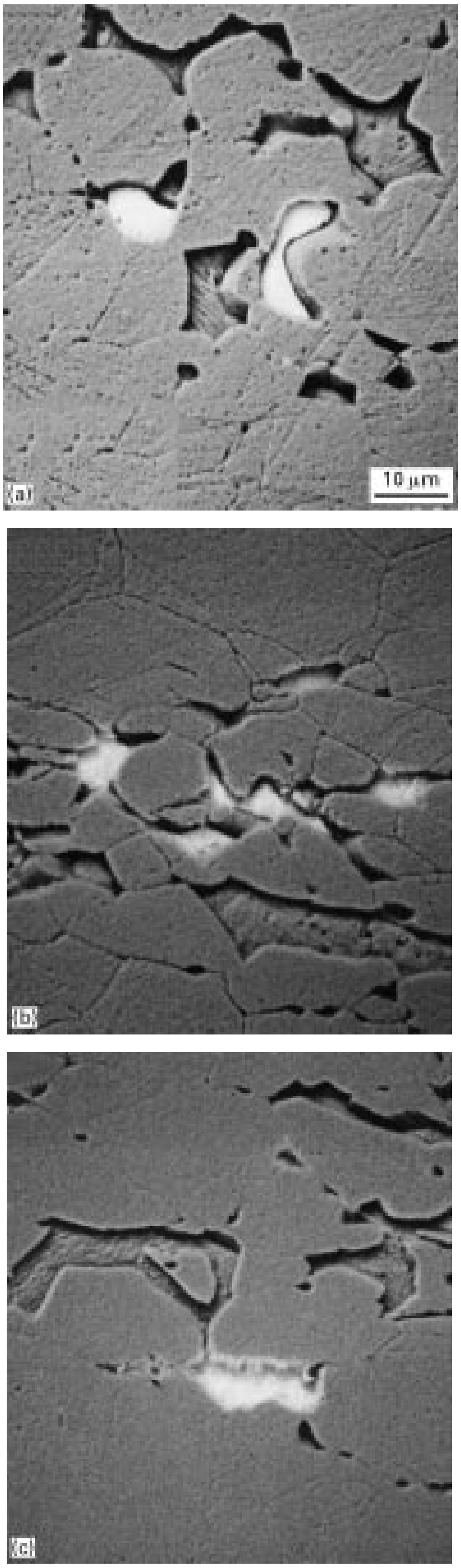

Figure 2 Back-scattered electron micrographs showing the cross-section view microstructures of (a) a cracked ferrule, (b) an intact ferrule and (c) an unused ferrule. The samples were slightly etched using 5 g of FeCl + 100 ml of ethanol + 30 ml of HCl. The white areas feature Pb inclusions.

intact and unused leaded brass ferrules, respectively. All the brass materials exhibited a two-phase microstructure, containing a small quantity of β phase dispersed in an α-phase matrix, with some lead precipitates and inclusions. Because of its low solubility in Cu–Zn alloy, Pb segregated and conglomerated to form inclusions in the $\alpha + \beta$ matrix in order to minimize the total surface free energy of the alloy. The lead inclusions appeared as white areas in the back-scattered electron micrographs shown in Fig. 2, because of its higher atomic density than Cu and Zn. The presence of lead inclusions was also confirmed by X-ray diffraction, in which the (1 1 1), (2 0 0), (2 2 0) and (2 2 2) peaks of Pb were identified.

Examination on the fracture surfaces of cracked ferrules revealed the presence of fascinating microstructures (Fig. 3a), which showed drastically different characteristics from those observed on the *ex situ* fractured surfaces of the intact and unused ferrules, shown in Fig. 3b and c, respectively. The fracture surfaces on the cracked ferrule were noted to have been heavily decorated by particulate-like corrosion–reaction products, compared with dimple-like morphological characteristics exhibited by the *ex situ* fractured surfaces from the intact and unused ferrules. The dimple-like fracture surface morphology is reminiscent and indicative of a ductile failure mode, generally exhibited by aluminium and copper alloys caused by normal mechanical failures.

Close examinations of the fracture surfaces on the cracked ferrule indicated that the reaction–corrosion products exhibited various morphological characteristics, as illustrated in Fig. 4, which included sphere, whisker–flake and rosette. In many cases, they were present in a clustered form and were embedded on the grain-boundary planes, as revealed by intergranular fractures. It appears that the chemical–corrosion reaction in question preferentially attacked the grain boundaries of the brass material and left behind various reaction–corrosion products. According to XPS and EDS X-ray microanalyses, most of the corrosion products contained S, Pb, Cu, Zn and Na. In some cases, small quantities of Cl or F were also detected by XPS. As a comparison, analyses performed on the *ex situ* fractured surfaces, from the intact and unused brass ferrules, revealed the presence of mainly Cu and Zn with various quantities of Pb.

According to the present case study, crack failure of the in-service brass ferrules appeared to have taken place over a period of time. On the basis of fracture surface analyses, numerous corrosion products of various morphological characteristics were identified on the fracture surfaces produced under service conditions. The fracture surfaces were characterized predominantly by an intergranular failure, indicative of a brittle failure mode. Chemical analyses of the clustered corrosion products as well as intergranularly fractured grain-boundary planes revealed the overwhelming presence of S in addition to Pb, Cu and Zn. By contrast, fracture surfaces of intact and unused ferrules produced by *ex situ* fracture revealed the presence of a dimple-like surface morphology, indicating a ductile failure mode. Chemical analyses of the ductile fracture surfaces revealed the presence of Cu, Zn, and Pb.

The detection of S on the fracture surfaces of the cracked ferrules substantiates that S-containing

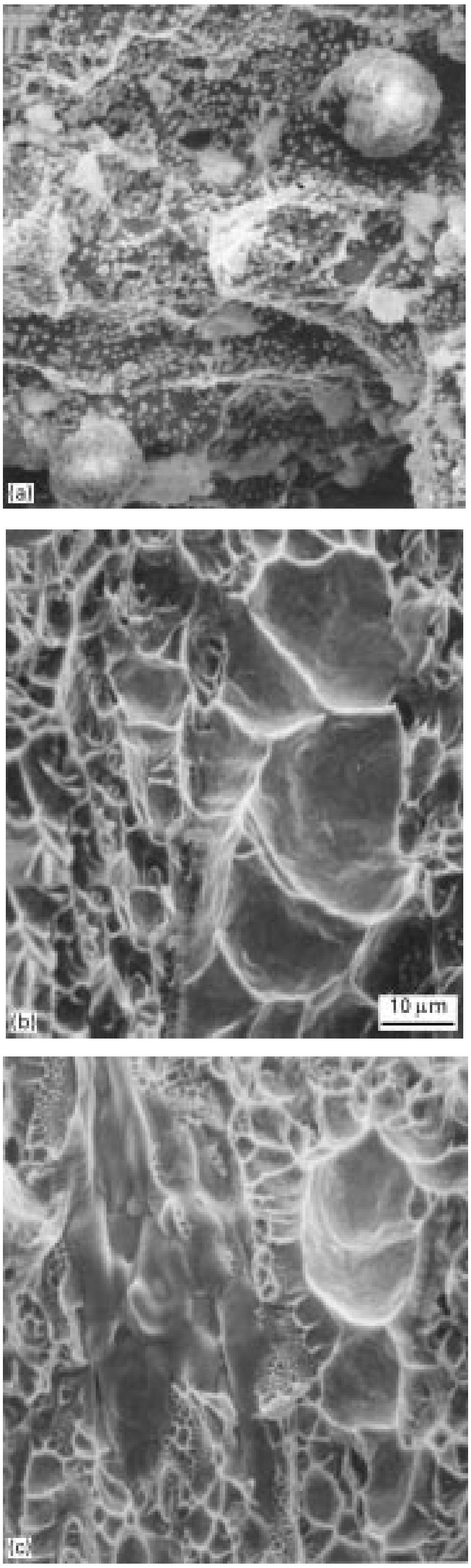

Figure 3 Scanning electron photomicrographs showing the microstructural characteristics of fracture surfaces exhibited by (a) a cracked ferrule, (b) an intact ferrule and (c) an unused ferrule.

derivatives, present via either a solubilized ionic state or a gaseous vapor state, are most probably responsible for the environmentally assisted SCC of the brass ferrules. The source of sulphur is believed to have originated from the neighbouring sulphuric acid production plant, which is about 1 km away from the gas-filling facility. While a limited research on SCC of brass has been carried out in nonammoniacel environments [5], it is now recognized that SCC of copper alloys also occurred in many different environments including cupric ion solutions, chloride solutions, sulphate and sulphide solutions, sulphur dioxide gas, sulphuric acid, sodium nitrite and aqua regia [6, 11]. Furthermore, it has been well established that susceptibility to SCC is significantly affected by zinc content; alloys contain more zinc are more susceptible. Resistance increases substantially as zinc content decreases from 15 to 0% [4, 6, 13]. As far as additives such as Pb, P and Mn are concerned for their influence on SCC, little or no effect was reported [6]. On the basis of the present case study, SCC was found to occur in a leaded brass under sulphuric acid environment, and most corrosion products appeared to have resided on the grain-boundary planes, suggesting that diffusion of the corrosive species took place predominantly along the grain boundaries. Possibly owing to a kinetics reason, grain-boundary diffusion of the corrosive species and its follow-on chemical reactions with the leaded brass alloy were confined to the proximity of the grain–boundary planes.

As far as mechanical stresses are concerned, it is attributable to the mechanical crimping process introduced to the ferrules during fabrication. The ferrules were crimped in an ambient condition, which is analogous to cold work. As a result, sustained tensile stresses were produced and imparted to the ferrules, while the brass adapters received compressive stresses. It is well established that residual stresses introduced into brass components by cold forming can increase susceptibility to SCC [5, 14–16]. The presence of a tensile stress state in the ferrules is further exacerbated by the gas-filling process which usually involves variable filling cycles at high pressures in a temperature range, owing to Joule–Thomson cooling by gas expansion. In the present case, the flexible hoses were used for cylinder filling of industrial oxygen, where the inlet gas pressure from the manifold was greater than 20 MPa (2900 lbf in^{-2} gauge). The implication of Joule–Thompson cooling by isenthalpic gas expansion lies in the formation of icing in the vicinity of the high-pressure end of a filling hose, which would subsequently melt down and form water condensate on the surface. Additionally, natural condensation of moisture from the environment onto brass surface is expected to occur owing to temperature differential. All these attributes would prevail in the occurrence of an aqueous environment which may be required to facilitate the conversion of a S-containing atmosphere into a suitable ionic state of SCC to take effect. As for the reason why cracking occurred predominantly along the longitudinal frills caused by crimping, it is postulated to have resulted from much accelerated reaction–corrosion kinetics facilitated by crimping-introduced mechanical defects which aggregated on the frills. Mechanical crimping is expected to generate defects and to enhance their density in a brass material, in consideration of its relatively low hardness and rather small stacking-fault energy of copper.

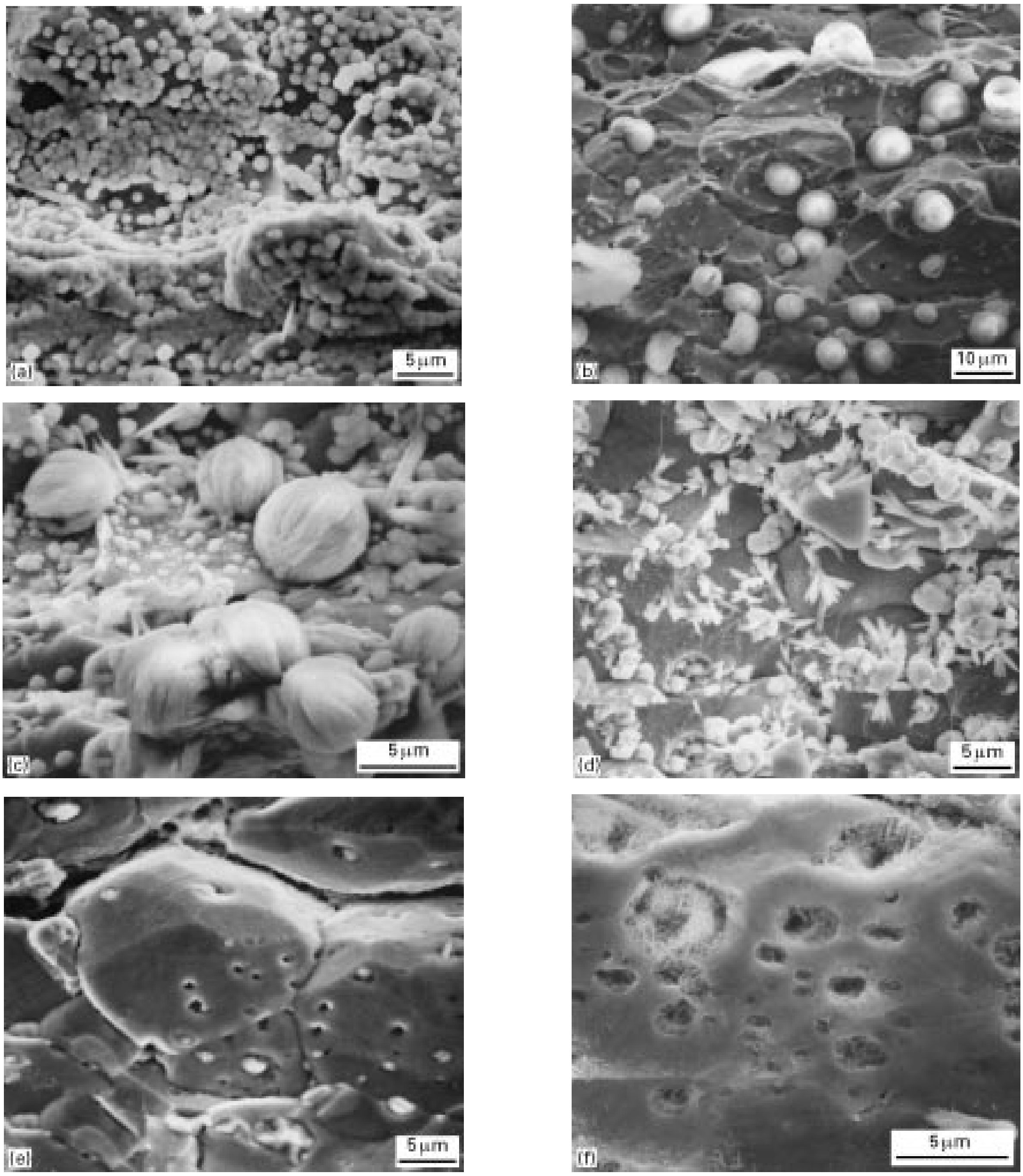

Figure 4 Scanning electron photomicrographs showing the various microstructural characteristics of corrosion products present on the fracture surfaces of the cracked brass ferrules.

4. Summary

According to the present study, C36000 Cu–Zn–Pb leaded brass ferrules are susceptible to SCC under the synergistic reactions of a sulphuric acid production environment in a sustained tensile stress environment. The tensile stress was introduced by the mechanical crimping process applied on the ferrules, superimposed by cyclical high-pressure gas-cylinder-filling operations. The noxious species responsible for the SCC is believed to have originated from the gaseous vapours and/or ionic derivatives of S-containing substances from the neighbouring sulphuric acid production plant. The chemical corrosion reactions may be facilitated or enhanced by the formation of water and moisture condensates on the brass ferrule surfaces, as a result of natural condensation and/or Joule–Thomson cooling, effected by gas expansion during high-pressure gas-filling processes.

SCC of the leaded brass ferrules gave rise to predominantly intergranular failures, compared with ductile failures exhibited by the *ex situ* fractured surfaces of the intact and unused ferrules. The SCC-failed fracture surfaces were heavily decorated by numerous corrosion products, manifested in clustered forms of sphere, whisker–flake, rosette, etc., which were identified to contain primarily S, Pb, Zn and Cu. By contrast, fracture surfaces of the intact and unused ferrules showed no signs of corrosion products. Most corrosion products were found to have embedded on the grain-boundary planes of the fracture surfaces, suggesting that grain-boundary short-circuit diffusion served as a viable mechanism for the SCC of C36000 leaded brass under the operating conditions of this case study.

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