The controlling effect of 0.05% hydrogen sulfide gaseous atmosphere on the accelerated fatigue failure of coated MM-002 nickel-base superalloy at 650 °C

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A systematic study was carried out aimed at evaluating the environmental effects of H_2S containing environment on the creep–fatigue failure of coated undirectionally solidified MM-002 nickel-base superalloy at high temperature. The cyclic loading conditions were constant and consisted of creep tension and plastic compression following the CP-mode of the strain range partitioning method. The results obtained have shown that although the pack cementation coating used showed adequate resistance under the combination of cyclic loading and oxidizing environments, this resistance was not evident under the H_2S containing atmosphere. In fact, it was found that even an amount as little as 0.05% H_2S had an extremely detrimental effect on the creep–fatigue life of the coated superalloy at 650 °C. The crack initiation and propagation in the H_2S environment was controlled by an aggressive sulphidation attack ahead of the crack tip. This was demonstrated by the formation of low melting eutectic sulfides at the plastic zone ahead of the crack tip, causing an accelerated transdendritic cracking and premature failure.

1. Introduction

Coated MM-002 nickel-base superalloy is one of the structural materials for turbine blades used in the hot section of a jet engine. Under regular service conditions, this material system is exposed to the combined effects of creep–fatigue loading and the environment generated by the combustion products of jet engine fuel, usually under excessive air conditions. However, in the case of jet engine fuel combustion in deficient air conditions, the danger of forming the hostile H_2S gaseous atmosphere is imminent [1]. The aspects concerning the controlling effects of H_2S environment on the failure mechanism of the coated superalloy is the subject of the present investigation.

Owing to the extremely aggressive nature of H_2S-containing environments, the information on the combined effects of this atmosphere with cyclic loading on the failure mechanism of coated superalloy is very limited. However, little research of this nature has been carried out on uncoated superalloys. Floreen and Kane [2] examined the creep–fatigue failure of uncoated IN-800 alloy in H_2S and SO_2 bearing environments. They found that while the SO_2-containing atmospheres played a significant role in shortening the high temperature low cycle fatigue life of the alloy, the H_2S-containing atmosphere played a devastating role, particularly at increased H_2S concentrations and temperatures. For equal stress intensity factors and temperatures, the H_2S-bearing environment produced a far higher crack propagation rate. The authors limited their testing in order to preserve their test apparatus from the extremely destructive corrosion attack of the H_2S species. Aghion *et al.* [3] examined the effect of altering loading and Ar + 5% SO_2 environment on coated MM-002 alloy at 870 °C, and concluded that the protection afforded by the same chrome–aluminide coating was limited, with the coated alloy suffering accelerated fatigue failure compared to air and inert argon environments.

The present paper is aimed in evaluating and demonstrating the detrimental effects of H_2S-containing environment on the failure mechanism of conventionally pack cementation coated MM-002 superalloy, and hence, the potential danger of a premature failure of this material system under deficient air combustion conditions.

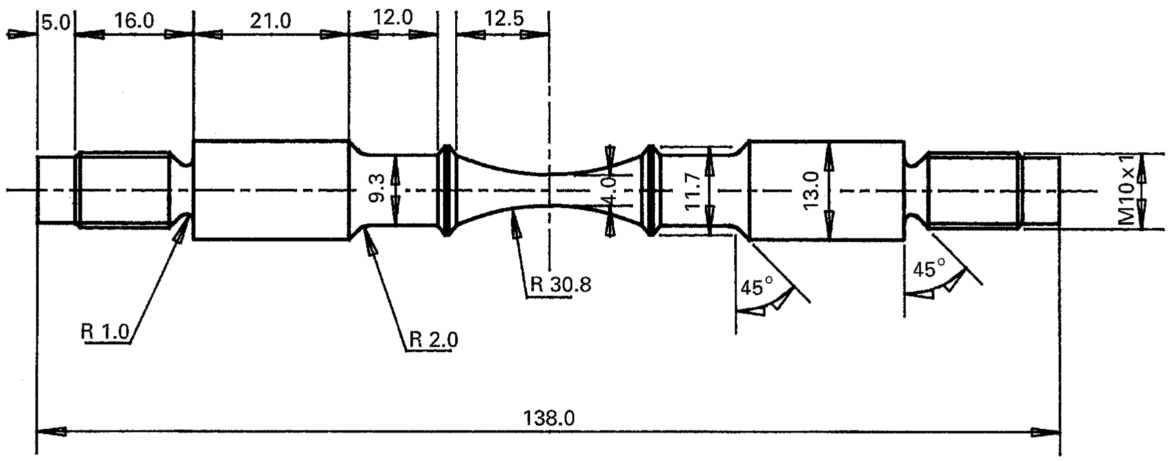


Fig. 1. The fatigue specimen design and dimensions (in mm).

TABLE I The chemical composition in wt % of MM-002 nickel base superalloy

	Ni	Cr	Co	W	Ta	Al	Ti	C	Zr	Hf	Others
Materials as-received	59.41	8.9	10.4	10.2	1.8	5.2	1.35	0.35	0.23	1.9	0.16 Fe, 0.1 Nb
Nominal composition	61	9.0	10.0	10.0	2.5	5.5	1.5	0.14	0.05	1.5	0.015 B

2. Experimental procedures

Test specimens were machined from directionally solidified bars of MM-002, to produce a profile with dimensions as shown in Fig. 1. The chemical composition of the base alloy is given in Table I, and is in accord with the nominal chemical composition of MM-002 nickel-base superalloy [4]. The superalloy fatigue specimens were then coated with a chrome–aluminide coating, using the conventional pack cementation method. This was followed by an age hardening heat treatment at 870 °C, for 16 h.

The testing procedure involved the use of the semi-empiric phenomenological strain range partitioning (SRP) high temperature low cycle fatigue (HTLCF) life prediction method, developed by Manson *et al.* [5]. The basic premise for SRP is that in any hysteresis loop there are combinations of merely two directions of straining (tension and compression) and two types of inelastic strain, (creep and plasticity). By combining the two directions with the two types of inelastic strain, four modes of loading can be obtained, namely, pp, cc, cp and pc (the first letter indicates the tension condition, the second compression, while c stands for creep and p for plasticity). These may be used as basic building blocks for any conceivable hysteresis loop. The four life relationships result from the four combination types, and are used to predict the corresponding HTLCF life.

The present research made use of the cp mode of loading at 650 °C, due to the detrimental effect of tension creep on the fatigue life of MM-002 [6]. Two sets of tests were conducted for comparative purposes, such that the tensile and compressive strain rates for the first load case were 2.8×10^{-4} and $68 \times 10^{-4}\ s^{-1}$, while those for the second were 2.5×10^{-4} and $60 \times 10^{-4}\ s^{-1}$, respectively. This has resulted in producing a strain range of 0.68% for the first set of loading, and 0.60% for the second set.

TABLE II Various combinations of temperatures and H_2S concentrations that were tested with the coated MM-002 superalloy

Environment	Temperature (°C)
Ar + 5% H_2S	870
Ar + 0.5%H_2S	870
Ar + 0.1%H_2S	870
Ar + 0.033% H_2S	870
Ar + 0.033% H_2S	700
Ar + 0.033% H_2S	650
Ar + 0.05% H_2S	650
Ar + 0.05% H_2S	600

The test environments chosen were Ar + 0.05% H_2S, air, and pure inert argon for reference purposes. It should be mentioned that higher temperatures and increased concentrations were tested as shown in Table II, and they resulted in unacceptably high levels of system and specimen environmental attack.

The thermo-mechano-chemical experimental system and method used to conduct the creep–fatigue tests in the controlled atmospheres has been described by Aghion *et al.* [7]. In principle, the specimen neck is enclosed in a metal sleeve through which the specific combination of gases produced by a gas mixing system flow. This is carried out while the specimen is mechanically loaded within a split furnace using a closed-loop MTS electrohydraulic machine. The strain was measured with two strain transfer rods, attached to the specimen collars on either side of the neck. The rods were connected to a linearly variable displacement transducer (LVDT), outside of the furnace, and the signal was conditioned by an amplifier. The gas supplied by piping to the specimen was maintained at a pressure of about 1.52×10^5 Pa.

For X-ray diffraction analysis and pure corrosion tests, unstressed disc samples of coated MM-002 alloy were subject to the test environment and temperature within a specially prepared corrosion chamber. These were obtained from a bar of the superalloy, perpendicular to the direction of solidification.

3. Results

The microstructure of the undirectionally solidified MM-002 alloy was dendritic, with the dendritic grains consisting mainly of cuboidal gamma prime precipitates of $Ni_3(Al,Ti)$, as well as Ni_3Ta and Ni_3Hf. The interdendritic zones contained eutectic like nodular gamma prime phase, as well as carbide phases such as Cr_3C_2 and Cr_7C_3.

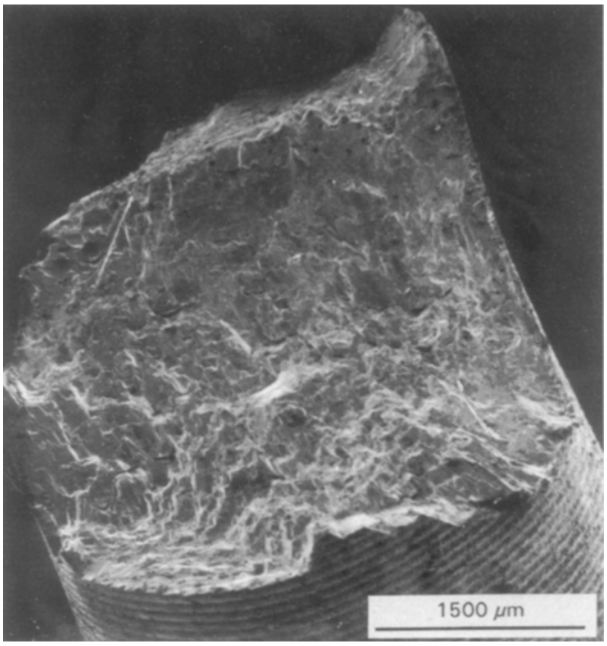


Fig. 2. Fracture surface obtained after HTLCF failure in pure argon environment.

The coating was approximately 60 μm in thickness, with an interdiffusion zone of about 20 μm. The coating matrix consisted mainly of the NiAl intermetallic phase, while Al_2O_3 phases formed the external protective scale.

The average HTLCF life of the coated alloys subject to Ar + 0.05% H_2S environment at 650 °C was less than 40 cycles, for both sets of loading conditions (CP-mode strain ranges 0.68 and 0.60%). By comparison, when coated alloy specimens were subject to pure inert Ar environment, at 650 °C, the average life to failure was 3745 cycles, for the first loading case (0.68% strain range) and 8647 cycles, for the second (0.60% strain range). In air atmosphere the average life to failure at a strain range of 0.68% is 2495 cycles and at 0.60% for 3560 cycles.

Whereas the argon cycled specimens usually displayed failures, as shown in Fig. 2, the specimens tested in the H_2S containing environments, and as depicted in Fig. 3, displayed brittle failures. In addition, the fracture surface obtained in the H_2S atmosphere was covered with dark spongy sulphide corrosion products, that made detailed study quite difficult.

Metallographic examination of the cross-section adjacent to the fracture surface of specimens cycled in the H_2S bearing environment showed that the cracks propagated transdentritically with crack nucleation at the coating as shown in Fig. 4. In order to evaluate the crack growth mechanism and the effect of environment, the microstructure and chemical composition of layers comprising the fatigue crack edges within the substrate alloy were examined. The results obtained for the coated specimen after creep–fatigue loading in Ar + 0.05% H_2S atmosphere is shown in Fig. 5. It is evident that the sulfur content at the edge of the fatigue crack was extremely high (8.45 wt %). This clearly indicates a severe reaction between the material and the environment which in fact controls the accelerated fatigue crack propagation.

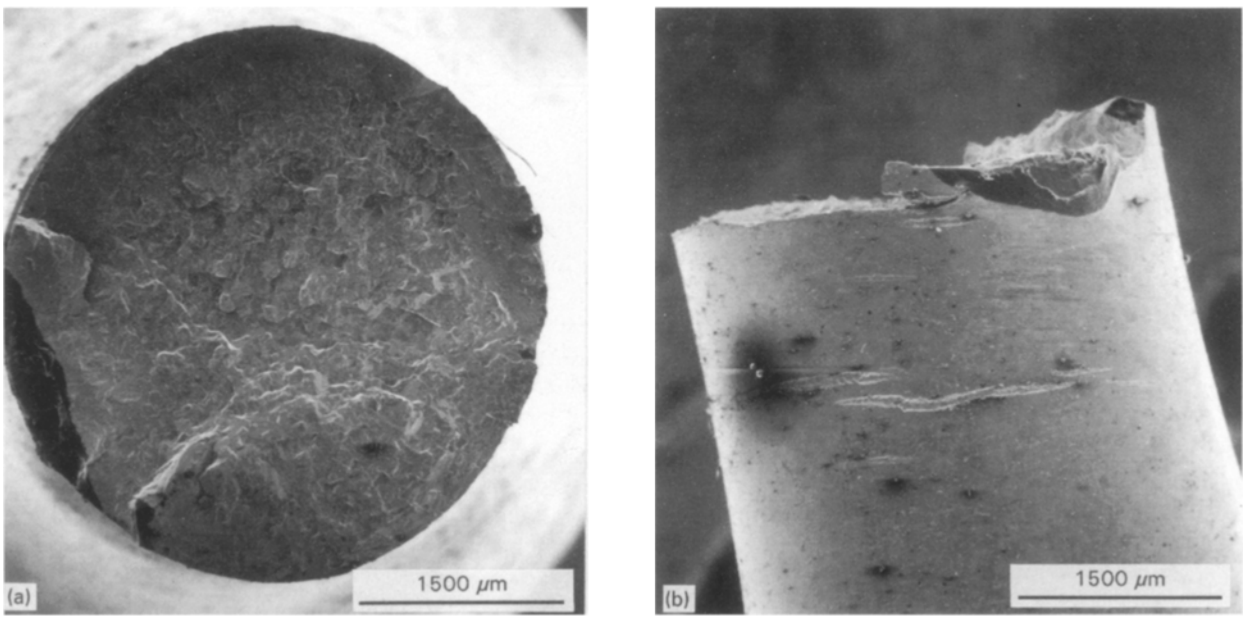


Fig. 3. The fracture surfaces obtained after HTLCF failure in Ar + 0.05% H_2S environment. (a) Coated alloy (top view) and (b) Uncoated alloy (side view).

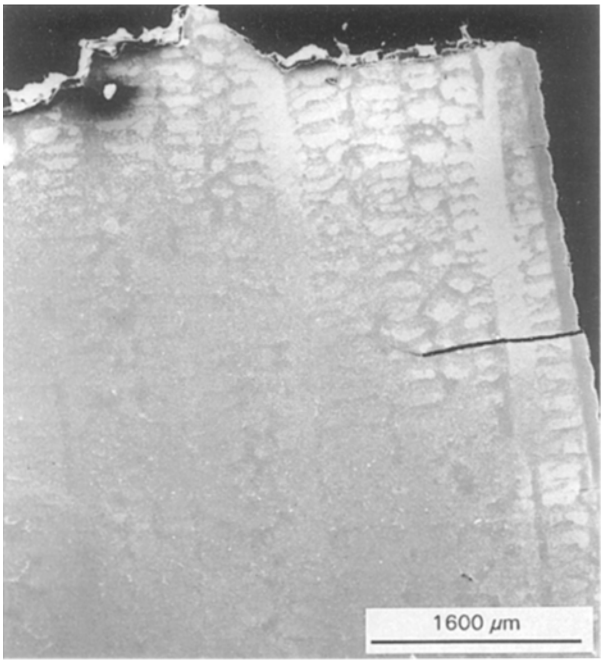


Fig. 4. Cross section view showing transdendritic cracking of coated specimen after HTLC failure in Ar + 0.05% H_2S environment.

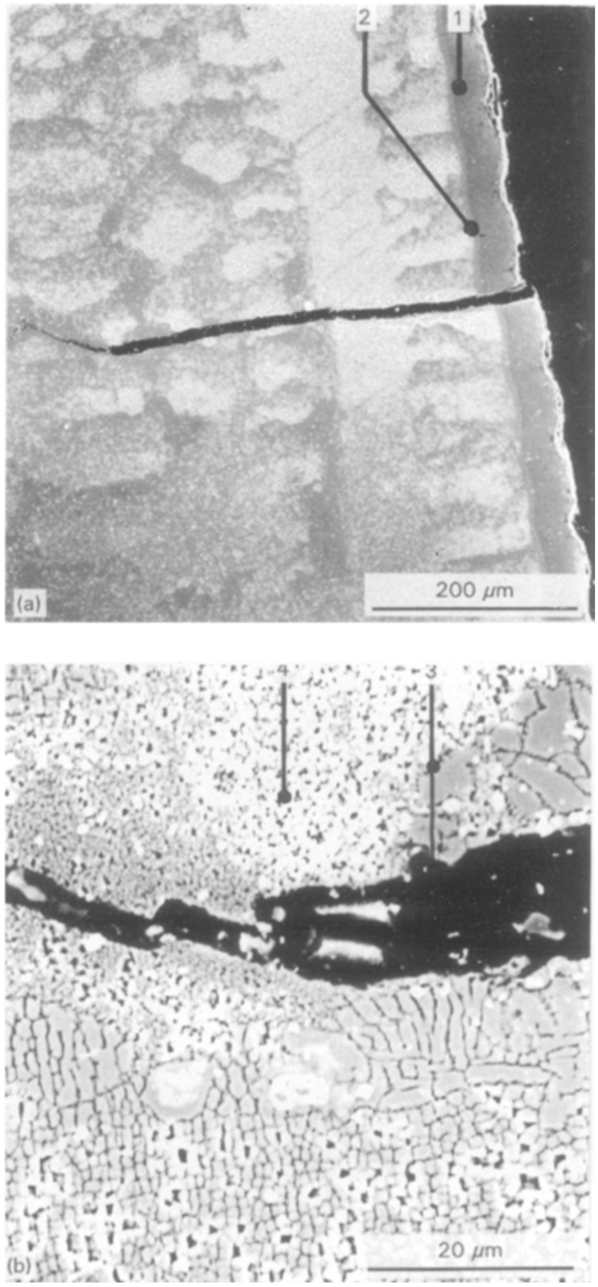
The results of X-ray diffraction analysis carried out on the coated corrosion disc samples which had been subjected to the Ar + 0.05% H_2S environment for five hours at 650 °C are shown in Fig. 6. It is evident that while the characteristic phases that form the coating, namely aluminium oxide, chromium oxide and NiAl, were present, various sulfide phases evolved, such as NiS, Al_2S_3, Cr_2S_3, and CrS.

4. Discussion

The results of the present investigation clearly demonstrated the unacceptable protection provided by the conventional aluminide pack cementation coating under the combined effect of creep–fatigue loading and the H_2S-containing environment. In fact, it was evident that even the very small amount of 0.05% H_2S in an argon atmosphere had an extremely detrimental effect on the creep–fatigue life of the coated system at a relatively low temperature of 650 °C.

The creep–fatigue failure in an argon environment was purely mechanically controlled, while in an H_2S atmosphere, the acceleration failure was controlled by the environmental effects caused by the H_2S-containing atmosphere. In an oxidizing environment (air) the creep–fatigue results were relatively adequate, attributed to the acceptible protection provided by the pack cementation coating in an oxygen controlled atmosphere.

Following the above and in comparison with the previous results obtained in an SO_2 environment under similar creep–fatigue loading conditions [3, 8], it is evident that the nature of the failure mechanism in 5% SO_2 at 870 °C as far as the fatigue life, and the crack growth behaviour are concerned, is quite similar to the one obtained in the present investigation (e.g. 0.05% H_2S at 650 °C). This highlights the relative increase in aggressiveness of the H_2S atmosphere when compared with the SO_2 atmosphere. While the environmental effect of H_2S is manifested by pure sulfidation attack, the environmental effect of SO_2 combines oxidation and sulfidation processes. As the chemical tendency for oxidation is higher than for sulfidation, oxidation can be considered as a retarding



Element	Layer 1 (wt %)	Layer 2 (wt %)	Layer 3 (wt %)	Layer 4 (wt %)
Al	26.29	14.57	10.14	5.64
S	2.87	–	8.45	0.26
Ti	–	2.67	2.79	1.21
Cr	16.72	8.93	11.11	8.90
Co	3.12	11.79	0.79	8.68
Ni	46.32	52.88	66.13	63.91
Ta	2.01	3.21	0.23	1.53
W	2.67	5.95	0.36	9.87

Figure 5 Microstructure and chemical compositions of layers comprising the fatigue crack edges obtained after HTLCF failure of coated MM-002 superalloy in Ar + 0.05% H_2S environment: (a) crack initiation; and (b) crack tip.

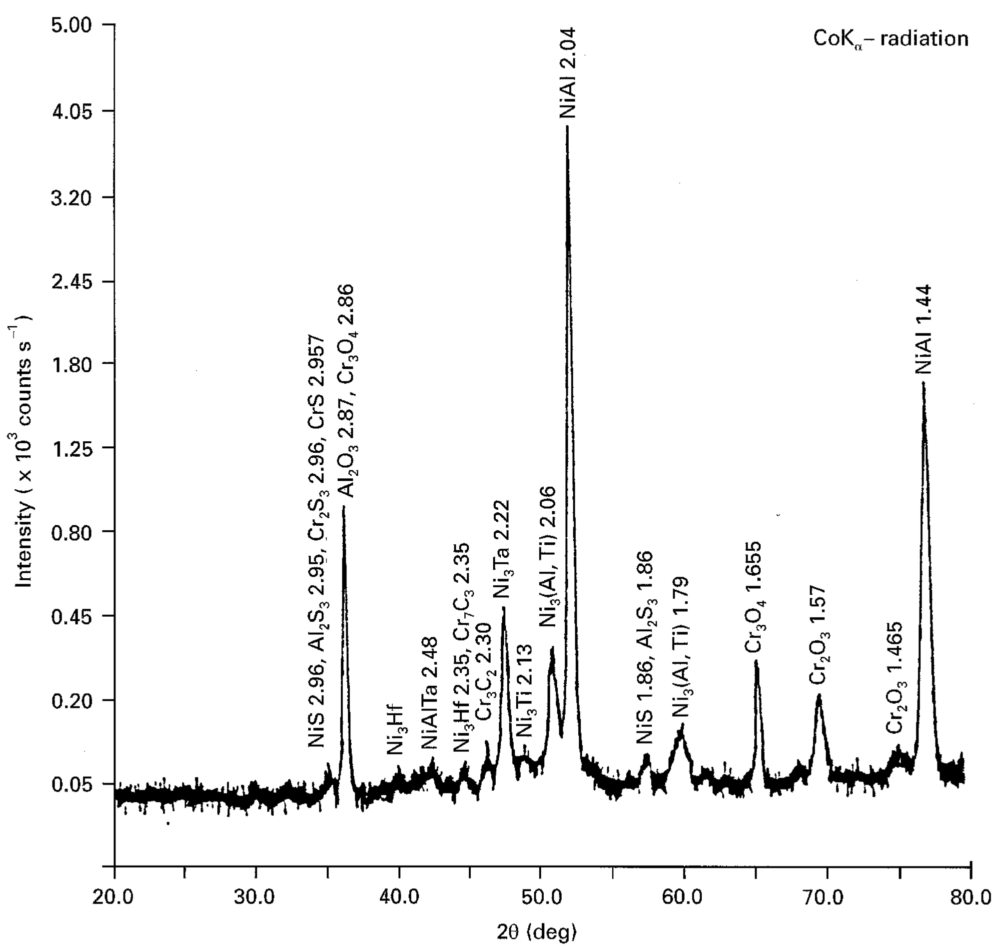


Fig. 6. X-ray diffraction spectrum of coated disc sample subjected to Ar + 0.05% H_2S environment for 5h at 650 °C.

factor for sulfidation, which practically moderates the sulfidation attack. Hence, the abnormal detrimental effect of Ar + 0.05% H_2S environment can be attributed to the fact that this environment does not contain any oxygen which could moderate the sulfidation attack.

In principle, the environmental controlling effect of H_2S may be divided into two stages. The first stage which can be considered as the incubation/initiation stage, refers to the stage where an aggressive environmental attack of the coating occurs, causing a severe deterioration and breakdown of the coating, and exposing the base metal to the environment. The second stage of crack propagation is demonstrated by accelerated transdendritic crack growth behaviour. The accelerated crack propagation is controlled by the direct sulfidation attack ahead of the crack tip. The sulfidation effect at the crack tip is carried out mainly by the development of nickel–nickel sulfide eutectic phases which may have a melting point in the range of 625 to 645 °C, that is lower than the testing temperature of 650 °C. A further contribution to the crack tip brittleness is caused by elemental sulfur diffusion which is generated from the H_2S environment. When both effects recur at the propagating crack tip region, the premature creep–fatigue failure of the material system becomes imminent.

5. Conclusions

The abnormal premature creep–fatigue failure of conventional pack cementation coated unidirectionally solidified MM-002 nickel-base superalloy in H_2S-containing environment clearly demonstrates the aggressiveness of this environment and the potential hazard of partial combustion conditions of jet engine fuel that might introduce this kind of atmosphere. In addition, while the conventional pack cementation coating has provided a relatively adequate protection in oxidizing atmospheres, this protection is not evident in the H_2S-containing environment. Hence, other advanced coating systems should be considered or developed for adequate protection in an H_2S atmosphere, or alternatively, the conditions in which H_2S environment is generated should be strictly eliminated.

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