Hydrogen embrittlement resistance of ultrahigh strength cupronickel alloy: effects of exposure to gaseous hydrogen environment on fatigue resistance

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The ultrahigh strength cupronickel alloy Marinel and the nickel alloy Monel K-500* were saturated with gaseous hydrogen at 450°C and their fatigue behaviour was measured and compared with that of hydrogen free material. The presence of hydrogen was found to reduce the fatigue properties of Monel K-500, but did not affect the performance of Marinel alloy. No evidence of obvious microstructural change induced by hydrogen was apparent, but use of hydrogen diffusivity data was made in calculations relating to the diffusivity and trapping of hydrogen in the two materials. It was demonstrated that the solubility of hydrogen, the degree of dislocation–hydrogen interaction, and the ease of hydrogen trap formation (as a precursor to crack initiation) were lower in Marinel alloy than in Monel K-500, thus contributing to an explanation of the resistance of Marinel alloy to the debilitating effects of hydrogen.*

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INTRODUCTION

It is generally accepted that many engineering materials suffer a reduction in their mechanical properties through interaction with hydrogen[1–3] and it has become apparent that metal–hydrogen reactions can take several forms.[4] These include the formation of internal hydrides within the metal, the formation of compounds of hydrogen with impurities in the material, and the retention of hydrogen at internal discontinuities within the structure.[5] These effects can be exhibited when the hydrogen involved in the reaction is in the gaseous form or when it is produced by a cathodic corrosion reaction. Many stress corrosion cracking mechanisms are dependent on the presence of electrochemically generated hydrogen.[6,7]

The entry of hydrogen into a metal is assisted by dislocation transport[5,8] and this effect has been experimentally demonstrated by the measurement of hydrogen permeation rates through nickel while it is undergoing plastic deformation.[9] Dislocation sweep in of hydrogen from the surface, in the case of several different metals, has been found to be consistent with the calculated energy of activation of hydrogen induced cracking.[10] During dislocation transport, the hydrogen can be deposited at various 'trap sites' or internal discontinuities such as grain boundaries or precipitates.[5] These can take the form of 'reversible' traps, which the hydrogen can subsequently leave, or 'irreversible' traps, which the hydrogen can not leave and which tend to encourage local fracture through a lowering of the surface energy of the material.[3] The effectiveness of the traps in promoting hydrogen embrittlement is related to the degree of strengthening present in the material matrix, as it is well established that materials in a higher strength state (i.e. cold worked or age hardened) are more susceptible to hydrogen embrittlement than the same materials in a lower strength condition.[3,11] Thus, measurement of both the hydrogen entry kinetics of a metal (or alloy) and the ability of the metal to trap hydrogen would give an indication of its hydrogen embrittlement susceptibility.[12]

Nickel is known to display hydrogen embrittlement[13] and the nickel alloy Monel K-500 has been shown to suffer stress corrosion cracking through reaction with hydrogen produced by cathodic potentiostatic charging.[11] However, the ultrahigh strength cupronickel alloy Marinel, which possesses mechanical properties similar to Monel K-500, shows resistance to hydrogen embrittlement under cathodic charging conditions.[14] The comparative mechanical behaviour of these two alloys after hydrogen charging from the gas phase has previously been investigated by slow strain rate testing,[15] but the results have proved to be inconclusive. Thus, the present work describes fatigue testing of the materials after exposure to gaseous hydrogen in order to determine whether this method is able to detect any effects of gaseous hydrogen exposure on this aspect of the mechanical behaviour of the two materials.

EXPERIMENTAL

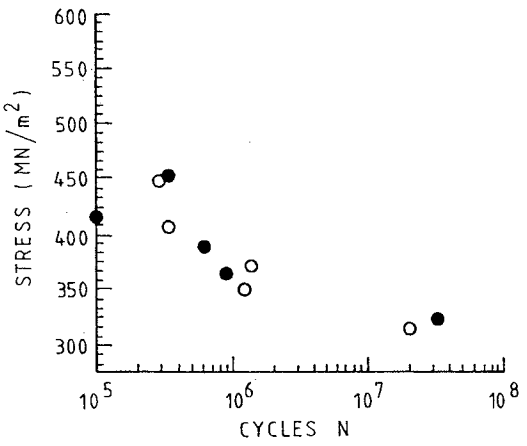
The experimental method was designed to compare samples of Marinel and Monel K-500 (both in the aged condition) with and without occluded hydrogen. The compositions and typical mechanical properties of both alloys used in this investigation are given in Tables 1 and 2. Samples of 6 mm diameter and 600 mm length were machined from rod and heated in a silica tube under a slowly flowing atmosphere of hydrogen or nitrogen.

The temperature was recorded via a thermocouple on the specimen and the temperature used was 450 ± 2°C. At this temperature, any further precipitation reactions which

*The products 'Marinel' and 'Monel' are both registered trade marks: 'Marinel' of Langley Alloys Ltd and 'Monel' of International Nickel, Huntingdon Alloy Products.

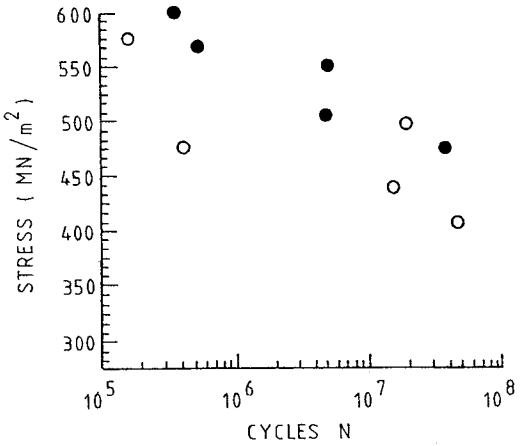
Table 1 Composition of alloys used in investigation, wt-%

	Ni	Cu	Fe	Mn	Si	C	Co	Al	Ti	Cr	Nb
Marinel	14·9	77·0	0·95	4·32	0·05	...	...	1·59	...	0·39	0·64
Monel K-500	64·9	33·0	0·80	0·66	0·08	0·13	0·01	2·93	0·46	...	...



● sample exposed to nitrogen at 450°C for 15 h before testing;
○ sample exposed to hydrogen at 450°C for 15 h before testing

1 *Fatigue resistance curves of Marinel*



● sample exposed to nitrogen at 450°C for 15 h before testing;
○ sample exposed to hydrogen at 450°C for 15 h before testing

2 *Fatigue resistance curves of Monel K-500*

would occur in these alloys would be very slow. The control samples were heated in nitrogen under identical conditions, ensuring that the thermal history during exposure was the same as that for hydrogen exposure. As gas absorption in the metals is diffusion controlled, the time for saturation of hydrogen was calculated from the diffusion equation[16]

$$\frac{Q_t}{Q_\infty} = 1 - \sum_n^\infty \frac{4}{\alpha_n^2} \exp\left(\frac{-D\alpha_n^2}{a^2}\right) \quad \ldots\ldots (1)$$

where Q_t and Q_∞ are the quantities of gas diffused in time t and ∞, a is the specimen radius, D is the diffusion coefficient at the temperature concerned, and α_n is the nth root of the Bessel equation $J(\alpha) = 0$. For this experimental method, the α_n values were only taken for the first four Bessel equation roots, the values being 2·405, 5·522, 8·654, and 11·792. A time of 15 h was determined to give near 100% saturation of the alloys with hydrogen and therefore this time was adopted as the experimental exposure time for both hydrogen and nitrogen.

Optical microscopy was carried out after etching polished sections of the materials which had been exposed to either hydrogen or nitrogen. X-ray diffraction of filings from the same specimens was also undertaken.

The major part of the experimental work involved fatigue testing of the alloys and comparing results obtained from specimens exposed to hydrogen with those obtained from specimens exposed to nitrogen. The fatigue tests were carried out according to BS 3518, which describes the rotating bend (Wöhler) method, yielding *S–N* curves. Miniature Wöhler machines of the Rolls-Royce pattern were used. These consisted of a motor running at 50 Hz carrying a chuck in which one end of the specimen was gripped. The other end of the specimen was secured in a second chuck connected, via a loading arm, to a jockey weight which applied the bending stress. The motor and timer were switched off automatically when the testpiece fractured and the maximum number of cycles used was $3·9 \times 10^7$.

Table 2 Typical mechanical properties of alloys used in investigation

	0·2% proof stress, MN m^{-2}	UTS, MN m^{-2}	Elongation, %
Marinel	700	870	18
Monel K-500	600	1070	24

RESULTS

Figures 1 and 2 show the *S–N* curves produced by Marinel and Monel K-500 respectively. Table 3 gives the endurance limits derived from these graphs at 10^7 cycles and, although test duplication was not carried out, the results indicated that no effect of hydrogen exposure on the endurance limit of Marinel was apparent. However, although the results were subject to a degree of scatter, there was an apparent deterioration in the endurance limit of Monel K-500 which had been exposed to hydrogen. In this case, a decrease of approximately 16% for the endurance limit was recorded at 10^7 cycles.

Optical microscopy of the alloys after exposure to hydrogen revealed no apparent differences between samples exposed to hydrogen and those exposed to nitrogen. The grain size in all cases was in the range 15–20 μm. There was also no evidence of the presence of internal voids produced by molecular hydrogen or additional phases formed as a result of internal hydrogen reactions, for instance the production of hydrides.

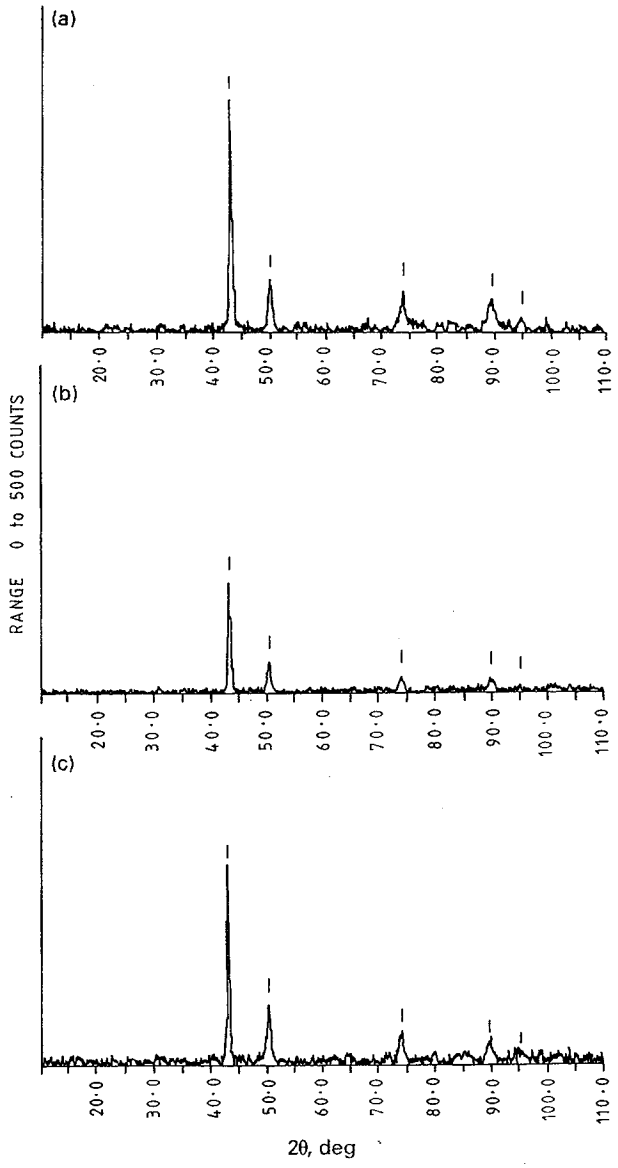
The X-ray diffraction patterns for Marinel are shown in Fig. 3, with interplanar spacing d given in Table 4. Comparison of the pattern obtained from Marinel which had not been exposed to hydrogen and nitrogen with the patterns obtained from Marinel exposed to either hydrogen or nitrogen shows no significant differences in the number or intensity of the lines present. Similar results were obtained in the case of Monel K-500, again showing no apparent structural differences between exposed material and material which had not been reacted with hydrogen or nitrogen.

DISCUSSION

The results of fatigue testing aged Marinel and aged Monel K-500 which had been exposed to hydrogen at 450°C showed that there was a deterioration of the fatigue life and fatigue endurance limit of hydrogen saturated Monel

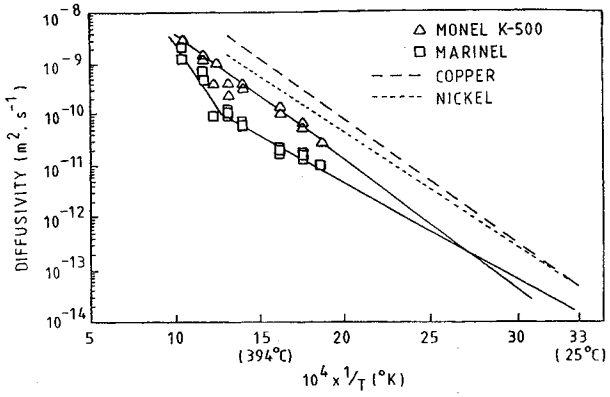
Table 3 Fatigue endurance limits derived from *S–N* curves, MN m^{-2}

	Atmosphere (450°C, 15 h)	Endurance limit (10^7 cycles)
Marinel	Nitrogen	315
	Hydrogen	312
Monel K-500	Nitrogen	480
	Hydrogen	404



a unexposed sample in as received condition; *b* sample exposed to nitrogen at 450°C for 15 h; *c* sample exposed to hydrogen at 450°C for 15 h

3 *X-ray diffraction patterns for Marinel produced from metal filings*



4 *Graph showing diffusivity of hydrogen in Marinel and Monel K-500 compared to that of pure copper and pure nickel*

K-500. Such a fall off in fatigue properties was not evident in the case of hydrogen saturated Marinel. Thus the effect of gaseous hydrogen on the fatigue properties of the two alloys demonstrates a debilitating effect on Monel K-500 somewhat reminiscent of the exposure effect of electrolytically generated hydrogen on this alloy.[11]

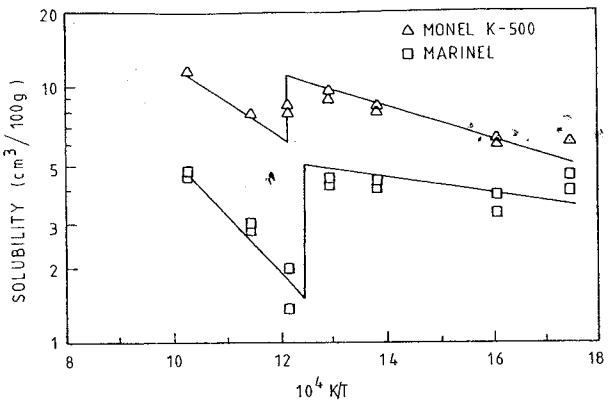
In order to further discuss these observations and give possible explanations, differences in hydrogen solubility and hydrogen diffusion rates between the two alloys will be considered. Previous experimental work by Talbot *et al.*[15] under similar experimental conditions yielded the diffusion data and solubility data shown graphically in Figs. 4 and 5 respectively. The data shown in Fig. 4 suggest that diffusivity of hydrogen in Monel K-500 is approximately the same as that of hydrogen in Marinel at temperatures below approximately 100°C although it is less than the diffusivity of hydrogen in either copper or nickel. From Fig. 5, the hydrogen solubility of Marinel at 450°C was found to be $4{\cdot}5 \times 10^{-2}$ L kg^{-1} and that of Monel K-500 was determined to be $9{\cdot}5 \times 10^{-2}$ L kg^{-1}. The diffusivity of hydrogen in Monel K-500 is approximately 7 times that of Marinel at 450°C. Thus, hydrogen would diffuse into Monel K-500 more readily than into Marinel at the temperature used for hydrogen charging. However, it should diffuse out from both materials at approximately the same rate at the temperature used for the fatigue studies.

There appears to be no evidence from the metallographic examination of the specimens or from their X-ray diffraction patterns that the hydrogen has produced second phases in the materials. The Marinel diffraction patterns (Fig. 3) can readily be explained purely in terms of an fcc copper–nickel solid solution alloy, although it is likely that other metallographic phases are present, these being produced by reactions between various alloying elements. X-ray diffraction can rarely show the presence of phases if they are less than 5% by volume, thus any intermetallic compounds present in Marinel must be at a concentration lower than 5%.

Table 5 gives the results of duplicated slow strain rate testing (10^{-6} s^{-1}) of Marinel and Monel K-500 before and after hydrogen exposure obtained by Talbot *et al.*[15]. In this case, the hydrogen gas was charged at 700°C, but the solubilities of hydrogen for the two materials at this temperature are not dissimilar to the values at 450°C, the temperature used in the present work. It is apparent from Table 4 that there is no conclusive evidence of changes in ductility (elongation and reduction of area) produced by the presence of hydrogen, but that the 0·1% proof

Table 4 Interplanar spacing *d* from diffraction lines of X-ray diffraction patterns for Marinel alloy filings

Peak number	Angle 2θ, deg	*d*, Å	Relative intensity
Unexposed sample in as received condition			
1	43·28	2·090	100
2	50·42	1·810	21
3	74·15	1·279	18
4	89·76	1·093	12
5	95·20	1·044	5
Sample exposed to nitrogen at 450°C for 15 h			
1	43·26	2·091	100
2	50·40	1·810	30
3	74·13	1·279	14
4	89·86	1·092	8
5	95·05	1·045	3
Sample exposed to hydrogen at 450°C for 15 h			
1	43·38	2·086	100
2	50·50	1·807	27
3	74·18	1·278	15
4	89·85	1·092	12
5	95·13	1·045	8



5 *Graph showing solubility of hydrogen in Marinel and Monel K-500*

stress/UTS ratio is affected in the case of Monel K-500. This increase in the effective yield strength of Monel K-500 indicates that the hydrogen present in the alloy inhibits dislocation movement.[17] As the same effect is not apparent in Marinel, this demonstrates that there is less hydrogen–dislocation interaction in this alloy. This could be due either to the hydrogen not being present in the matrix of Marinel or to its having a lower binding energy with dislocations in Marinel. The latter seems likely, even if a proportion of the hydrogen in Marinel were located at internal discontinuities, as there should be a fraction of the occluded hydrogen which would be subjected to dislocation transport.

In addition to possessing dislocations which bind more strongly to hydrogen than those of Marinel, Monel K-500 undergoes a more massive aging reaction than Marinel. If it is assumed that about 1%Al remains in solution after aging of both Monel K-500 and Marinel and that the precipitate in both alloys is of the type $Ni_3(Al,Ti,Nb)$, then the volume of precipitate in Monel K-500 can be calculated to be approximately 2·5 times that in aged Marinel. Thus there would probably be a much greater opportunity for hydrogen to become irreversibly trapped at the matrix/precipitate interfaces in the case of Monel K-500.

Recent work by Pound[18,19] has enabled a mathematical analysis of the lattice diffusion and trapping of hydrogen in both Monel K-500 and Marinel to be carried out. This analysis involves a model which has been used to evaluate the hydrogen ingress kinetics of Monel K-500 and Marinel under electrochemical hydrogen charging conditions.[19] Under such conditions, with the approximation that the rate of hydrogen ingress in an alloy is controlled by diffusion whereas the entry flux across the interface is restricted, the total charge passed results in the determination of an apparent hydrogen trapping constant k_a, measured for irreversible traps in the presence of reversible traps. It is found that

$$k_a = k(D_a/D_l) \quad \ldots\ldots\ldots\ldots \quad (2)$$

where k is the irreversible trapping constant, D_a is the apparent diffusivity of hydrogen, and D_l is the lattice diffusivity. Pound[19] found that the value of k_a for aged Monel K-500 was $0{\cdot}021\ s^{-1}$ and k_a for Marinel was $0{\cdot}034\ s^{-1}$. However, for the work of Pound, no data were available for diffusivity of hydrogen in the two alloys at ambient temperatures D_a, so the author could only speculate as to the values of the irreversible trapping constants k.

The data on hydrogen presented in Fig. 4 are assumed to be valid in discussing comparison of the present work with the work of Pound, as generally the same type of effects on mechanical properties is observed for gaseous hydrogen charging as for cathodic hydrogen charging.[1] From Fig. 4, values of diffusivity for aged Monel K-500 and aged Marinel can be estimated at 25°C. These values appear to be almost equivalent at $1 \times 10^{-14}\ m^2\ s^{-1}$. D_l values for similar materials are available in the literature[20] as $3 \times 10^{-14}\ m^2\ s^{-1}$ (30Cu–70Ni) for Monel K-500 and $1{\cdot}6 \times 10^{-15}\ m^2\ s^{-1}$ (77Cu–23Ni) for Marinel. With these figures and the data of Pound for k_a, irreversible trapping constants can be calculated from equation (2) as k (Monel K-500) $= 6{\cdot}3 \times 10^{-2}\ s^{-1}$ and k (Marinel) $= 5{\cdot}4 \times 10^{-3}\ s^{-1}$. Thus the irreversible trapping constant of Marinel is approximately 10 times lower than that of Monel K-500. This would mean that hydrogen would be much more likely to be present within Monel K-500 in a form which would encourage the initiation of cracks. Pound's value of k (Monel K-500) was $4{\cdot}2 \times 10^{-2}\ s^{-1}$, which would again indicate an approximate order of magnitude difference in the irreversible hydrogen trapping constants of Marinel and Monel K-500, with Marinel possessing the lower figure.

CONCLUSIONS

Marinel alloy does not display a debilitation in its fatigue properties after exposure to hydrogen, unlike Monel K-500. This is likely to be due to the following factors:

1. The solubility of hydrogen in Marinel is lower by approximately 50% than the solubility of hydrogen in Monel K-500.
2. The diffusivity of hydrogen in Monel K-500 is 7 times higher than the diffusivity of hydrogen in Marinel at 450°C. At ambient temperature, the diffusivity of hydrogen in Marinel is approximately the same as that in Monel K-500.
3. The binding of hydrogen to dislocations in Marinel is not as effective as the binding of hydrogen to dislocations in Monel K-500. Also, the mass of aging precipitates per unit volume is 2·5 times greater in Monel K-500 than Marinel. Thus hydrogen can be transported more readily to a larger number of potential irreversible hydrogen traps in Monel K-500.

Table 5 Mechanical properties of Marinel and Monel K-500 before and after exposure to hydrogen gas at 700°C obtained by slow strain rate testing[15] (duplicate test results are given)

Alloy	Condition	UTS, MN m^{-2}	0·1% proof stress, MN m^{-2}	Elongation, %	Reduction in area, %	Ratio PS/UTS
Marinel	Hydrogen saturated	833	512	73	49	0·61
		849	518	74	45	0·61
Marinel	Hydrogen free	808	499	66	51	0·61
		745	465	...	58	0·62
Monel K-500	Hydrogen saturated	830	428	61	49	0·52
		845	440	60	53	0·52
Monel K-500	Hydrogen free	614	217	46	61	0·35
		630	241	82	49	0·38

4. The rate of irreversible trap formation in Monel K-500 is approximately one order of magnitude higher than that in Marinel alloy, thus allowing greater opportunity for crack initiation in hydrogen charged Monel K-500.

ACKNOWLEDGEMENTS

The authors would like to thank Langley Alloys Ltd and Brunel University for permission to publish the results of this paper. They would also like to acknowledge the helpful comments made by Dr C. A. Clark and thank him for his assistance in the discussion of the results.

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