Vanadic Hot Corrosion – Creep Interaction of Superni – C 276 in the Temperature Range 650 - 750°C

J. Swaminathan and S. Raghavan

Department of Metallurgical Engineering
Indian Institute of Technology, Madras - 600 036, India

ABSTRACT

Molten vanadic deposit induced hot corrosion is a serious problem in power plants using residual fuel oil. Hot corrosion in addition to surface degradation reduces the mechanical strength properties like creep and fatigue strength. In order to study the effect of vanadic deposits on the creep rupture properties of a nickel base superalloy, creep rupture tests have been performed on a molybdenum containing nickel base superalloy, Superni - C 276 (equivalent to Hastelloy C 276), with and without corrosive deposit coating of sodium metavanadate (NaVO₃) and sodium metavanadate + 15 wt.% sodium sulphate (Na₂SO₄) (eutectic composition) in a temperature range of 650 to 750°C. The effect of corrosives on creep rupture properties are: enhanced steady state creep rate and reduction in rupture life. The eutectic NaVO₃ + 15 wt.% Na₂SO₄ mixture is more severe in degrading the creep rupture properties. The corrosives were found to reduce the rupture life through enhanced creep deformation and their effects on creep fracture processes are less severe. Though the surface crack formation is enhanced in presence of corrosive deposits, the fracture morphologies are unchanged in the uncoated and corrosive deposit coated conditions. The presence of molybdenum, a known element increasing the acidic fluxing character of oxy-anionic salts like Na₂SO₄, is found to increase the overall corrosion attack through the formation of molten mixture of Na₂MoO₄-MoO₃. A fluxing mechanism is proposed for the NaVO₃ induced attack and in the NaVO₃ + 15 wt.% Na₂SO₄ mixture coated condition early formation of Ni₃S₂ facilitated by fluxing of protective oxides by NaVO₃ melt induces a self-sustaining hot corrosion attack through Ni-Ni₃S₂ eutectic.

1. INTRODUCTION

Vanadium bearing residual fuels have been used in power generating systems like gas turbines and boilers. Their use, however, has a serious drawback in terms of severe material degradation caused by the presence of molten deposits of vanadium pentoxide (V₂O₅) and alkali vanadates like sodium metavanadate (NaVO₃), sodium vanadyl vanadate (NaO₂V₂O₄.5V₂O₃ and 5Na₂O.V₂O₄.11V₂O₅) /1-3/. The vanadic corrosive deposits increase the oxide ion content of the melt and induce acidic fluxing of the protective oxide scales present on the surface of the metal /4/. Residual fuels, in addition to vanadium, contain sulphur as one of the impurities which results in formation of alkali vanadate – alkali sulphate as deposits /1/. The alkali vanadate/sulphate mixture in the deposits is in the molten condition at the operating temperatures of the power generating systems and induces accelerated oxidation generally known as "hot corrosion" /4/.

Nickel base superalloys used in power plant components have their life limited by the hot corrosive attack of the molten deposits /2/. These deposits degrade the protective oxides and affect the mechanical
properties too /5-7/. Hot corrosion attack resulting in intergranular damage which is often alloy specific is undesirable and corrosive; alloy systems showing this type of damage have to be identified to study and improve the knowledge of hot corrosion-mechanical property interaction /8/.

Much of the available literature on creep-corrosion interaction deals with alkali sulphate-alkali chloride effects /9-15/. Studies on residual fuel impurity effects on creep strength properties of nickel base superalloys are few. Jones and Williams /16/ investigated the hot corrosion of Co-Cr-Al-Y alloys by molten Na₂SO₄-NaVO₃ deposits at 700°C in the absence of mechanical stress. Seierstein and Kofstad /17/ reported thermogravimetric studies under the conditions of simultaneous sulphate- and vanadate-induced corrosion at 650 to 800°C for NiCrAlY coatings on Inconel 600. Sidky and Hocking /18/ reported electrochemical investigations of nickel base superalloys in vanadate-sulphate melts of different compositions in the temperature range 680-900°C. Except for that of the present authors /19/, no investigation has been reported in the literature on the hot corrosion-creep interaction of nickel base superalloys in the presence of NaVO₃-Na₂SO₄ deposits. Decreasing high quality oil resources necessitates the use of residual fuel oil and systematic research on their attack by hot corrosion is needed for their better usage.

Molybdenum is an important alloying element used in superalloys as a solid solution strengthenner when chromium level is reduced /20,21/. Oxides of molybdenum like MoO₃ and MoO₂ are known to induce hot corrosive attack similar to V₂O₅ and their effects on alkali sulphate induced hot corrosion are well reported /22-28/. The effect of molybdenum oxides on alkali vanadate induced hot corrosion is not known. In the recent work on creep-vanadic corrosion interaction studies on Superni-600 (equivalent to Inconel-600) by the present authors /19/, synergistic interaction of creep-corrosion was found to reduce the rupture life.

The present work on Superni C-276 (equivalent to Hastelloy C-276), a molybdenum containing alloy, has been carried out by applying sodium meta vanadate and sodium sulphate as corrosive deposits. These deposits simulate the residual fuel oil impurity environment.

### 2. EXPERIMENTAL

The chemical composition of the alloy Superni C-276 is given in Table 1. The alloy in the form of cold rolled sheet 1 mm thick was solution annealed at 1150°C for 1 hour and air cooled. Creep samples of dimensions 110 mm in length, 4 mm width at the gauge section and 1 mm thick were made. Creep rupture studies were carried out in a constant load creep testing machine. The gauge section over which the creep strain was measured was 40 mm in length. The test temperatures were 650, 700 and 750°C. The salt deposits used to simulate residual fuel impurity environment were sodium metavanadate (NaVO₃) with a m. pt. 630°C, a major component of the deposit in this environment /29/, and sodium metavanadate - 15 wt.% sodium sulphate (eutectic composition) with m. pt. 615 ± 5°C /30/. The salt was coated on the alloy surface by spraying the aqueous solution of the salt on the samples kept in an oven. A uniform coating of the deposit of about 2 mg/cm² was applied. Creep-rupture experiments at each test temperature were made at stress levels so chosen as to have a life in the range 100 - 1000 hours in the uncoated condition. The creep strain and the rupture time were noted for the uncoated and salt coated conditions at the test stress levels. Thermogravimetric studies were carried out for the unstressed coupons in the uncoated and salt coated conditions to identify the corrosion kinetics at the test

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<th>Cr</th>
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<td>15.49</td>
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The following table shows the chemical composition of the alloy Superni C-276 (in wt.%)
temperatures used for the creep study. The corrosion products present on the stressed and unstressed samples were identified by X-ray diffraction. The fractured sample surface was analysed by optical microscopy and the fracture morphology was analysed by Scanning Electron Microscopy (SEM). SEM - EDAX (energy dispersive X-ray analysis) analysis of the surface feature on the metavanadate-sulphate mixture corroded sample was also made.

3. RESULTS

3.1. Creep rupture properties

Typical creep curves of the alloy Superni C-276 tested in air in salt coated and uncoated conditions are shown in Fig. 1. The creep curves for the uncoated condition show higher rupture life and lower steady state creep rate compared to the salt coated condition at all the test temperatures. The sodium metavanadate-sodium sulphate eutectic mixture coated samples

Fig. 1: Typical creep rupture curves for alloy Superni - C-276 at (a) 650°C, (b) 700°C and (c) 750°C.
showed lowest rupture life and enhanced steady state creep rate among the salt coated conditions at all the test temperatures. The creep curves for the corrosive deposit applied samples show early onset of accelerated creep stage.

The relation between applied stress (σ) and steady state creep rate (\(\dot{e}_s\)) for the uncoated and salt coated condition at the test temperatures are presented in Fig. 2. A straight line relation of the type \(\dot{e}_s = A\sigma^n \exp (-Q/kT)\) is obtained, where A is a constant, "n" is the creep exponent, Q is the activation energy in kJ mol\(^{-1}\) and kT has its usual meaning. For all the test stress levels at the test temperatures the steady state creep rate for the corrosive salt coated condition shows higher values compared to the uncoated condition indicating that the corrosives have influenced the creep rate. In Fig. 3 the relation between rupture life time \(t_r\) and the applied stress (σ) under the test conditions is shown. Straight lines obtained indicate that a power function of the form \(t_r = A\sigma^k \exp (Q/kT)\) governs the relation. The reduction in rupture life under the corrosive coated condition is significant at all the stress levels and at all the test temperatures. Among the corrosive deposits the eutectic mixture of sodium metavanadate-sodium sulphate shows higher severity towards reduction in rupture life. This trend is consistent with that observed for steady state creep rate versus applied stress. The reduction in rupture life in the longer life region (low stress levels) is slightly more, indicating a normal behaviour of pronounced degradation as the corrosion proceeds for a longer duration.

3.2. Effect of corrosives on the creep processes

The effect of hot corrosion on the creep deformation and creep fracture processes can be ascertained from the steady state creep rate /11/. The relation between steady state creep rate and rupture life time (Monkmon-Grant relation) under the test conditions is shown in Fig. 4. This relation of the form \(t_r = A\dot{e}_s^k /3^1/\), where "A" and "k" are constants and the value of k = -1, holds good even for the corrosive coated condition within a reasonable scatter of data. Yoshiba et al. /11/ note that a hot corrosive environment can affect (i) the creep deformation process through a general corrosion induced loss in load carrying cross sectional area resulting in increased steady state creep rate, (ii) the creep fracture process through enhanced initiation and propagation of creep cracks which has a direct effect on the fracture process. The observed fact of data points in the present investigation for the uncoated and corrosive coated conditions lying around the same straight line implies that at a given \(\dot{e}_s\) the corrosive environment too gives the same rupture life as that of the uncoated condition. The corrosive environment affected the creep deformation processes rather than the creep fracture processes. A separate straight line for the corrosive coated condition with a significant gap from the line for
Fig. 2: Relation between applied stress ($\sigma$) and steady state creep rate ($\dot{\varepsilon}_s$) at a) 650°C, (b) 700°C and (c) 750°C.
Fig. 3: Relation between applied stress (σ) and rupture life (t_r) at (a) 650°C, (b) 700°C and (c) 750°C.
the uncoated condition would be obtained had there been a dominant effect of corrosive on the creep fracture processes. For the present alloy Superni C-276 in the sodium metavanadate and sodium metavanadate/sodium sulphate coated conditions the corrosives have pronounced influence on the creep deformation processes.

The temperature dependence of rupture life under the test conditions is shown in Fig. 5, for a stress level of 200 MPa. The slope of the straight line gives the activation energy for the rupture process. The values obtained show that hot corrosive environment did not affect the rupture processes in a dominating way. The temperature dependence of steady state creep rate under the test conditions at a stress level of 200 MPa is shown in Fig. 6. The activation energy obtained indicates that essentially the same creep mechanism is operating in the corrosive environment.

3.3. Thermogravimetric studies

The weight change versus time curves for the corrosive coated and uncoated conditions are shown in Fig. 7. The magnitude of weight change for the corrosive coated conditions is higher compared to the uncoated one. The increase in weight gain is rapid in the initial period and slows down in the end. The corrosion rate is approximately parabolic indicating that a diffusion process governs the corrosion rate. There is not much difference in the magnitude of weight change among the corrosives during the initial period although the overall weight change was increased for the sodium metavanadate/sulphate coated condition. The magnitude of weight change increased with increase in temperature.

3.4. Metallography

Visual examination of corroded specimens showed loose and porous scales on the surface with an adherent inner oxide scale. The deposits were liquid at the test temperatures and the presence of liquid is confirmed by the visual appearance of the surface. The chemical composition of the corrosion products present on the surface of the specimens was identified by X-ray diffraction and presented in Table 2. There is no difference in the type of corrosion product formed on the stressed and unstressed specimens. From the composition of the corrosion products it is seen that nickel reacted preferentially with the metavanadate component and formation of the nickel sulphide (Ni₅S₂) occurred in the metavanadate-sulphate condition. The presence of molybdenum compounds was noted for the corrosive coated condition which
shows the severity of the environment in degrading the alloy. For the unstressed samples at 750°C visible pits were noted on the alloy surface (Fig. 8) in the metavanadate/sulphate coated condition and at the lower temperatures the pits were very small to be noticed visually and often limited to the oxide layer near the alloy surface. The stressed samples also show pits shallow in nature, unlike the unstressed ones. SEM-EDAX spectrum identification of one such pit area after carefully removing the outer layer shows the presence of Ni$_3$S$_2$ inside the pit and nickel oxide (NiO) on the edges of the pit region (Fig. 9).

The macrophotographs of the fractured samples shown in Fig. 10 reveals surface cracks perpendicular to the stress axis and the size of the crack is larger in the corrosive coated condition. Optical metallographs of the fractured samples show intergranular corrosive attack and the intergranular cracks were seen
The corrosive coated samples show a large number of cracks near the fractured tip signifying the role of stress in aggravating the intergranular corrosion. The creep fracture morphologies for the coated and uncoated samples are shown in Figs. 14, 15 and 16. Similar fracture morphology in the corrosive and uncoated condition confirms that the same fracture process has occurred in the corrosive environment too. The creep fracture has occurred via the nucleation and growth of surface and internal creep cracks. These cracks were formed by the coalescence of creep voids. Floreen and Kane /32/ note that intergranular attack resulting from environmental factors often does not cause a different type of fracture but accelerates the inherent cracking process that occurs independent of the environment. The enhancement of cracking is due to the stress assisted diffusion of the impurities to the grain boundaries. The fracture morphology would have been different from that of the uncoated condition, had
Fig. 7: Weight change curves for alloy Superni - C-276 (a) uncoated, (b) NaVO₃ coated, (c) NaVO₃ + 15% Na₂SO₄ coated coupons.
Fig. 8: Macrophotograph of the NaVO$_3$ + 15% Na$_2$SO$_4$ coated sample after hot corrosion at 750°C for 100 hours.

Fig. 9: a  

Fig. 9: Corrosion products in the pit formed beneath the globular growth (a) SEM microphotograph of the coupon surface corroded by NaVO$_3$ + 15% Na$_2$SO$_4$ at 750°C, (b) EDAX profile of the pit interior, (c) EDAX profile of the pit edge.
Fig. 10: Macrophotographs of the crept samples at (a) 650°C, (b) 700°C and (c) 750°C.

Fig. 11: Optical metallographs of the crept samples at 650°C (a) uncoated, (b) NaVO$_3$ coated, (c) NaVO$_3$ + 15% Na$_2$SO$_4$ coated.
Fig. 12: Optical metallographs of the crept samples at 700°C (a) uncoated, (b) NaVO₃ coated, (c) NaVO₃ + 15% Na₂SO₄ coated.

Fig. 13: Optical metallographs of the crept samples at 750°C (a) uncoated, (b) NaVO₃ coated, (c) NaVO₃ + 15% Na₂SO₄ coated.
Fig. 14: SEM fractographs of the crept samples at 650°C (a) uncoated, (b) NaVO₃ coated, (c) NaVO₃ + 15% Na₂SO₄ coated.

Fig. 15: SEM fractographs of the crept samples at 700°C (a) uncoated, (b) NaVO₃ coated, (c) NaVO₃ + 15% Na₂SO₄ coated.
the corrosives been able to initiate and propagate an intergranular crack even before a creep induced damage occurs. The unchanged fracture morphology indicates that for the alloy Supenni C-276 the corrosives reduces the rupture life by accelerating the inherent creep damage and not by initiation and propagation of corrosion dominated intergranular crack. The longitudinal section of the crept samples showed intergranular penetration and the corrosive coated samples showed deeper and larger cracks. Typical longitudinal section of the metavanadate/sulphate coated sample, crept at 750°C representing the most corrosive condition, is presented in Fig. 17. The intergranular crack is not sharp.

4. DISCUSSION

4.1. General discussion

Weight change curves for the corrosive coated condition confirm the significant effect of corrosives in accelerating the oxidation attack. However, the observed reduction in rupture life cannot be explained by the sole factor of general corrosion induced loss in load bearing cross-sectional area. Appreciable loss in rupture life has been noticed in the corrosive coated
conditions and among the corrosives the metavanadate/sulphate eutectic mixture reduces the life time to a higher degree. The rupture life degradation is brought about by the increase in creep rate and early onset of accelerated creep stage in the corrosive environments. The presence of intergranular cracking perpendicular to the stress axis near the fracture tip (region of higher strain rate) implies that the stress also played a significant role in reducing the rupture life time through a synergistic action /7,33/. The region of higher strain rate will undergo a higher degree of corrosion and the corroded grain boundaries can easily undergo enhanced creep damage /33,34/. In the presence of liquid corrosive deposits, initiation and growth of creep voids are much easier as the cohesive strength of the grain boundaries is reduced /6,7,14,35/. Preferential cracking in the direction perpendicular to the stress axis has been explained by Stroosnijder et al. /34,35/ in their study on corrosion creep behaviour of alloy 800H in sulphidizing/oxidizing/carburizing environment at 700°C by the general mechanisms of (i) premature oxide cracking above grain boundary/oxide scale intercepts due to inhomogeneous deformation in these regions, (ii) higher diffusion at grain boundaries leading to faster attack of this region than the matrix and by (iii) an additional mechanism when corrosion takes place under stress. In this additional mechanism it is proposed that the excess vacancies generated on grain boundaries perpendicular to the tensile stress axis will diffuse to the crack surface and a counter diffusion of crack surface atoms (in the presence of corrosives it is the corrodent species) to the crack tip occurs. Under this condition the corrosive action at the crack tip may enhance the crack propagation or the corrosive may reduce the cohesive strength of the grain boundaries /35/. When the corrosives are in the molten condition an active crack propagation could occur at the crack tip similar to stress corrosion cracking /13/ in which case one can notice sharp intergranular cracks. In the present study even for the most corrosive condition of metavanadate/sulphate deposit coating at 750°C, the longitudinal section of the crept sample shows blunted cracks (Fig. 17). In the absence of active crack propagation, the enhanced degradation may be caused by the decrease in cohesive strength of the grain boundary by the corrosive. Molten corrosives and corrosion products can also contribute towards reduction in cohesive strength of the grain boundaries.
The creep rupture behaviour in the hot corrosive environment is determined by the competitive processes of /11/: (i) initiation and propagation of creep induced grain boundary cracks, (ii) preferential intergranular cracks characteristic of the hot corrosive environments. The absence of any significant effect on the ductility and similar fracture morphology in the corrosive coated and uncoated condition confirms that the corrosives for this alloy, Superni C-276, did not induce a predominant intergranular crack initiation and propagation ahead of the creep damage. The presence of molten deposits at the grain boundaries has resulted in reduction of cohesive strength and initiation of creep damage, i.e. nucleation of cavities, microcracks, and their growth has been promoted. Observed higher overall weight gain in the corrosion environments has been the result of fluxing action of the metavanadate and combined sulphide-induced self-sustaining hot corrosion in the metavanadate/sulphate mixture. The presence of molybdenum compounds in the corrosion products, namely sodium molybdate and molybdenum trioxide, suggests that they too would have contributed towards the accelerated attack. The effect of molybdenum is discussed later in this section.

The degradation of the alloy in the corrosive coated condition is attributed to the fluxing action of the metavanadate melt /17,36-40/ and early onset of self-sustaining hot corrosion through Ni - Ni$_3$S$_2$ eutectic (m. pt. 645°C) in the presence of sulphate in the mixture. Sodium metavanadate can help in the formation of nickel sulphide by fluxing of the protective scales and the sulphate anion can have easy access to the bare metal under these conditions /36/. The formation of liquid corrosion products also contributes to enhanced corrosion. Kerby and Wilson /40/ observed low melting eutectics with melting points in the temperature range of 500 - 650°C for the Na$_2$O - V$_2$O$_5$ - Cr$_2$O$_3$ and Na$_2$O - V$_2$O$_5$ - Fe$_2$O$_3$ mixtures. Nickel base superalloys containing molybdenum and coated with Na$_2$SO$_4$ undergo catastrophic hot corrosion in the presence of molten Na$_2$MoO$_4$-MoO$_3$ mixture in the temperature range 750 - 900°C /28/. Oxides of nickel, chromium and iron form low melting constituents in the presence of molybdenum oxides with melting points in the range of 650 - 750°C and Na$_2$O/MoO$_3$ constituent has a m. pt. of 550°C /2/. Liquid corrosion deposits/corrosion products reduce the cohesive strength of the grain boundaries and reduction in cohesive strength can lead to enhancement of creep crack nucleation and its growth /6/. The presence of molybdenum compounds and the possibility of formation of low melting eutectics among the corrosion products and the molten nature of the corrosive deposits at the test temperatures favour the enhanced degradation.

The double attack of metavanadate (VO$_3^-$) and Na$_2$MoO$_4$ - MoO$_3$ melt in the sodium metavanadate coated condition and the additional contribution of Ni-Ni$_3$S$_2$ eutectic induced corrosion in the presence of sulphate melts are responsible for the alloy degradation. The schematic diagram of alloy degradation in corrosive environments is shown in Fig. 18 (a) and (b). The presence of surface cracks can alter the corrosion attack as the cracks filled with corrosive/corrosion products provide different environmental conditions /7,10/. Oxygen supply to the crack tip can be hampered by the presence of the corrosion products inside a crack and healing of a cracked protective scale formed beneath is not possible in time and in the presence of sulphate, the reduced oxygen partial pressures inside the crack favour the sulphide attack. Slower corrosion kinetics after longer time of exposure is expected from the formation of a solid nickel vanadate, change in melt chemistry and consumption of the corrosive for the metavanadate coating /39/ and MoO$_3$ saturation of Na$_2$MoO$_4$-MoO$_3$ melt causing solid NiMoO$_4$ formation /28/. In the present case of hot corrosion - creep interaction for the alloy Superni C-276, it seems that synergistic action of corrosion and stress has taken place and the corrosion is enhanced by the stress assisted diffusion and the creep damage is enhanced by the corrosives.

4.2. Reactions during hot salt corrosion by NaVO$_3$

The corrosion mechanism in the presence of sodium metavanadate is as given by Seierstein and Kofstad /39/. Simultaneous growth and dissolution of the oxide layer in the melt governs the corrosion process. The rapid attack of the metavanadate on the surface oxides leaves the metal surface enriched in molybdenum which oxidises easily. The molybdenum compounds
were identified for corrosive coated condition only.

4.2.1. Effect of molybdenum

Molybdenum present in the alloy can alter the hot corrosion process and its effects on sodium sulphate induced hot corrosion are well reported /22-28/. Effect of molybdenum on sodium metavanadate induced hot corrosion is not reported. But, being an oxy-anionic salt like sodium sulphate, the hot corrosion mechanisms proposed from the study with sodium sulphate can be extended to the sodium metavanadate-sodium sulphate melt /44-46/. Misra /28/ explained the enhanced effect of molybdenum on the hot corrosion attack of sodium sulphate on molybdenum containing nickel base superalloys in the temperature range 750-900°C as that due to the formation of Na₂MoO₄-MoO₃ melt. The enhanced attack was explained by a mechanism different from the fluxing mechanism proposed earlier /22,25,41-43/. According to this mechanism, the Rapp-Goto criterion of negative solubility gradient for the fluxing of the oxides cannot be satisfied in a melt containing MoO₃ and a dissolution of the base metal nickel as Ni²⁺ at alloy/oxide interface and formation of oxide above the melt at the melt-gas interface takes place. The transport of the nickel ion is assumed to be coupled with electronic conduction in the MoO₃ containing melts. Sodium molybdate was found /28/ to reduce the evaporation rate of MoO₃ by dissolution. Reduction of corrosion rate was observed with the formation of nickel molybdate (NiMoO₄), a solid, at higher MoO₃ content in the melt. Because of the presence of sodium molybdate and molybdenum trioxide in the corrosion products in the present study a similar effect can be envisaged. But the metavanadate melt can accelerate the corrosion on its own since the metavanadate melt is an excellent flux for many of the oxides /3,4/ and the rapid reaction (as shown by the weight gain) from the initial period itself suggests that it is independent of the molybdenum compound induced effects. The molybdenum compounds can add to the fluxing action of the metavanadate towards increasing the degradation. Formation of nickel molybdate has been observed only at the higher test temperature of 750°C in the present work. Thus the saturation of the Na₂MoO₄-MoO₃ melt by MoO₃ occurred at this temperature because of higher rate of oxidation of the surface by the corrosives. A rapid conversion of molybdenum oxide to molybdate ion can be expected in a metavanadate melt similar to its reaction with sulphate anion (SO₄²⁻) as /26/,

\[
\begin{align*}
\text{SO}_4^{2-} + \text{MoO}_3 & \rightarrow \text{MoO}_4^{2-} + \text{SO}_2 + 1/2 \text{O}_2 \\
\text{MoO}_3 + 2\text{VO}_3^- & \rightarrow \text{MoO}_4^{2-} + \text{V}_2\text{O}_5
\end{align*}
\]

The molybdate in the presence of MoO₃ is molten and the Na₂SO₄-Na₂MoO₄-MoO₃ melt can form a porous scale /28/. Similarly a NaVO₃-Na₂MoO₄-MoO₃ melt is expected to form porous scales which increases the corrosion attack. Peters et al. /27/ in their studies on oxidation/hot corrosion of Ni-Cr-Mo alloys at 900°C note that static oxygen atmosphere favours accumulation of the otherwise volatile molybdenum trioxide (volatile above 600°C /26/), and his observation is significant to the present study which was conducted in static air only. The reactions that take place in the NaVO₃ induced hot corrosion are /18/:

\[
\begin{align*}
2 \text{NaVO}_3 + 2 \text{NiO} & \rightarrow \text{Ni}_2\text{V}_2\text{O}_7 + \text{Na}_2\text{O} \\
\text{Ni}_2\text{V}_2\text{O}_7 + \text{NiO} & \rightarrow \text{Ni}_3\text{V}_2\text{O}_8 \\
2 \text{NaVO}_3 + 3 \text{NiO} & \rightarrow \text{Ni}_3\text{V}_2\text{O}_8 + \text{Na}_2\text{O} \\
2 \text{NaVO}_3 + \text{NiO} & \rightarrow \text{Ni}(\text{VO}_3)_2 + \text{Na}_2\text{O} \\
4 \text{NaVO}_3 + \text{Cr}_2\text{O}_3 & \rightarrow 2\text{Na}_2\text{CrO}_4 + \text{V}_2\text{O}_5 + \text{O}_2 \\
\text{Cr}_2\text{O}_3 + 2 \text{Na}_2\text{O} + 3/2 \text{O}_2 & \rightarrow 2 \text{Na}_2\text{CrO}_4 \\
\text{NaVO}_3 + \text{MoO}_3 & \rightarrow \text{Na}_2\text{MoO}_4 + \text{V}_2\text{O}_5
\end{align*}
\]

Sodium chromate can also form sodium molybdate as /48/:

\[
\begin{align*}
2 \text{Na}_2\text{CrO}_4 + 2 \text{MoO}_3 & \rightarrow \text{Cr}_2\text{O}_3 + \\
2 \text{Na}_2\text{MoO}_4 + 3/2 \text{O}_2 & \rightarrow \text{Na}_2\text{MoO}_4 + \text{V}_2\text{O}_5
\end{align*}
\]

The formation of the nickel molybdate in the melt is as follows /26/:

\[
\text{NiO} + \text{MoO}_3 \rightarrow \text{NiMoO}_4
\]

The underline symbolises the dissolved species in the melt.

4.3. Reactions during hot salt corrosion by NaVO₃ + 15% Na₂SO₄:
In the metavanadate/sulphate mixture in addition to
the fluxing action of the metavanadate, sulphate ion provides an additional attack by the formation of Ni-Ni\textsubscript{3}S\textsubscript{2} eutectic (m. pt. 645°C). Reduction in melting point of the sodium vanadate from 630°C to 615°C when 15 wt.% sodium sulphate is added helps in easier attack by the sulphate in the melt. Formation of nickel sulphide is as follows:

\[ \frac{9}{2} \text{Ni} + \text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2 \text{O} /49/ + 3 \text{NiO} + \frac{1}{2} \text{Ni}_3\text{S}_2 \] (12)

4.3.1. Effect of molybdenum:

Effects of molybdenum on sodium sulphate induced corrosion are interpreted by different mechanisms like enhanced sulphidation /41-43,50,51/, fluxing by the Na\textsubscript{2}MoO\textsubscript{4}-MoO\textsubscript{3} melt /24,25,48/, formation of porous scales in the presence of NiMoO\textsubscript{4} /26/, a direct dissolution of the base metal nickel as nickel ions in the Na\textsubscript{2}MoO\textsubscript{4}-MoO\textsubscript{3} molten mixture /28/. The mechanisms differ as the experimental conditions are different. Kameswari /50/ observed enhanced sulphidation in molybdenum containing nickel base superalloys for sodium sulphate coated condition in the temperature range of 700 - 800°C. In a metavanadate/sulphate mixture sulphidation is aided through the fluxing action of metavanadate /19,36/. It is likely that the formation of nickel sulphide in the present case may further be enhanced by the presence of molybdenum compounds which act as catalysts for sulphide formation /50,51/. The presence of molybdenum compounds provides additional enhancement of corrosion through the formation of a Na\textsubscript{2}MoO\textsubscript{4}-MoO\textsubscript{3} mixture by a mechanism proposed by Misra /28/ (explained in Section 4.2.1).

5. CONCLUSIONS

1. Superni C-276 shows reduction in rupture life through enhanced creep damage in the presence of molten corrosives of NaVO\textsubscript{3} and NaVO\textsubscript{3} - 15 wt.% Na\textsubscript{2}SO\textsubscript{4} at all test temperatures of 650, 700 and 750°C. The corrosives did not induce a rapid intergranular crack nucleation and growth ahead of the creep damage.

2. Synergistic interaction of corrosion and creep can explain the observed reduction in rupture life.

3. In sodium metavanadate melt the degradation is due to the cracking of the protective scales under the influence of the applied stress and the fluxing action of the melt. The additional presence of molybdenum compounds Na\textsubscript{2}MoO\textsubscript{4} - MoO\textsubscript{3} causes enhanced degradation. The presence of a liquid deposit and corrosion products including molten molybdenum compounds helps in easier creep crack nucleation and growth at the grain boundaries.

4. The addition of sodium sulphate to sodium metavanadate increased the corrosivity of the deposit by lowering the melting point and by the formation of molten Ni-Ni\textsubscript{3}S\textsubscript{2} eutectic which initiates a self-sustaining hot corrosion. The combined action of the molten deposits including the metavanadate-sulphate, Ni-Ni\textsubscript{3}S\textsubscript{2} eutectic and molybdenum compounds is suggested for the greater effect of the metavanadate-sulphate mixture than the metavanadate alone in reducing the rupture life at all test temperatures.

REFERENCES


34. J.R. Nicholls, J. Samuel, R.C. Hurst and P. Hancock, ibid., Ref. 5, pp. 911-926.


42. J.R. Nicholls, J. Samuel, R.C. Hurst and P. Hancock, ibid., Ref. 5, pp. 911-926.

43. J.R. Nicholls, J. Samuel, R.C. Hurst and P. Hancock, ibid., Ref. 5, pp. 911-926.

44. J.R. Nicholls, J. Samuel, R.C. Hurst and P. Hancock, ibid., Ref. 5, pp. 911-926.

45. J.R. Nicholls, J. Samuel, R.C. Hurst and P. Hancock, ibid., Ref. 5, pp. 911-926.


