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Creep rupture of Nimonic-90 under salt-induced high temperature corrosion

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Materials used in hot section components of gas and steam turbines, boilers, etc., undergo deterioration and degradation due to simultaneous actions of aggressive salts deposit hot corrosion and mechanical stresses developed at the high operating temperatures. Creep-ruptured properties are reported here at different stress levels at 650, 700 and 750°C on Nimonic-90 specimens in air and coated with ternary salt mixture of Na_2SO_4-$NaVO_3$–NaCl (in 50, 30 and 30 mole %). To assess the extent of hot corrosion, coupons of Nimonic-90 uniformly coated with the ternary salt mixture are exposed into a furnace for 170-180 h at 650, 700 and 750°C. The various corrosion products have been identified by XRD technique. The probable chemical reactions and hot corrosion mechanisms are also discussed.

Materials used in hot section components of gas and steam turbines, boilers, refinery furnaces and heat exchangers are subjected to aggressive environments and mechanical stresses developed at the high operating temperature[1-4]. The aggressive environments cause chemical attack and consequently structural alteration resulting degradation of mechanical properties. Degradation effects essentially are due to: (i) reduction of load bearing cross-section (ii) loss of alloying elements, and (iii) stress associated to the corrosion products[5,6]. The chemical attack is caused by the salts, e.g., sodium sulphate and a series of vanadium compounds arising from the combustion products. Further, if the gas turbine is operated in marine atmosphere, NaCl particles are ingested into the turbines predominantly as an aerosol of sea salt together with the intake air. As a result, the salt deposits comprise of a complex mixture of sodium sulphate-vanadium compounds-sodium chloride[7-9]. Therefore, the high temperature materials being utilised should be evaluated for performance considering high temperature corrosion and their influence on mechanical properties instead of high temperature corrosion alone or mechanical properties separately. Creep-corrosion interaction studies are reported in environments such as sodium sulphate, mixtures of sodium sulphate-sodium vanadate, sodium sulphate-sodium chloride[10-12], and sodium sulphate-sodium vanadate-sodium chloride[13]. The present paper describes the influence of the ternary mixture Na_2SO_4-$NaVO_3$–NaCl (in 50, 30 and 20 mole %) salts deposit hot corrosion on creep rupture properties of Nimonic-90 and possible corrosion reactions.

Experimental Procedure

Composition of Nimonic-90 samples, used in the present studies was: C (0.069%), Cr (20.29%), Co (15.67%), Al (1.84%), Ti (2.62%), Mn (0.40%), Fe and Cu (traces) and Ni (balance). The received plate was rolled to a thickness of approximately 0.8 mm and subjected to desired heat treatment. The adopted heat treatment schedule[14] involved: (i) Solution treating of the specimens at 1080°C for 8 h followed by air cooling, (ii) Age hardening of the solution treated specimens by heating to 780°C and holding for 16 h followed by air cooling. For hot corrosion studies, coupons of dimension 18x15x0.8 mm^3 were cut from the heat-treated plate.

The fusion point of the ternary salt mixture was determined by differential thermal analysis method[15-16]. The DTA curve of this mixture is shown in Fig. 1.

The creep specimens and the coupons for hot corrosion studies, were kept in an oven at 150°C and the corrosive coatings were applied by spraying saturated salt solution of the corrodents. A uniform deposition of approximately 2 mg/cm^2 was made. The creep specimens obtained from the heat treated plate were in the form of sheet 110 mm long, 4 mm wide,

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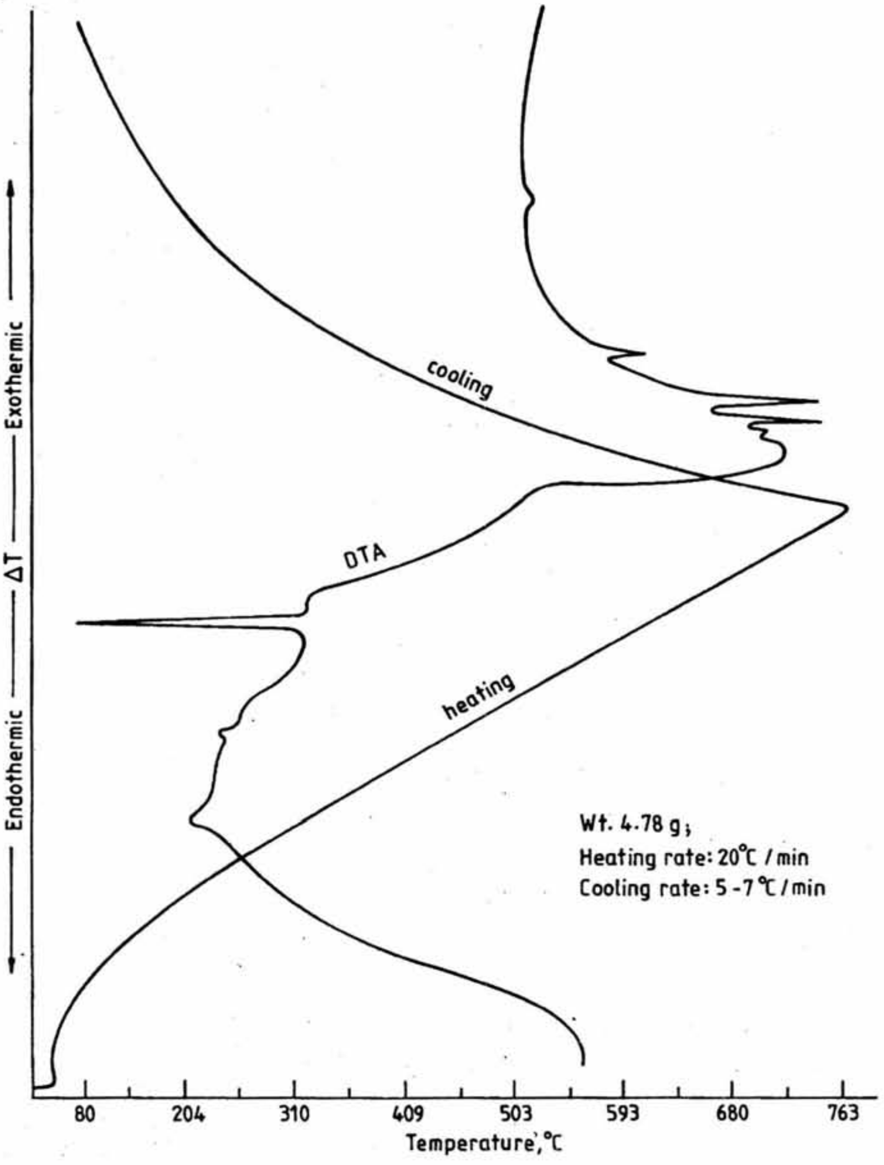


Fig. 1—DTA curve of Na_2SO_4-$NaVO_3$-NaCl (in 50, 30 and 20 mole %)

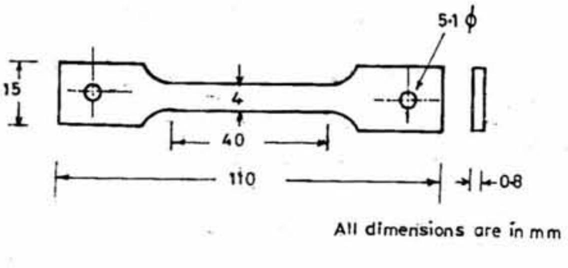


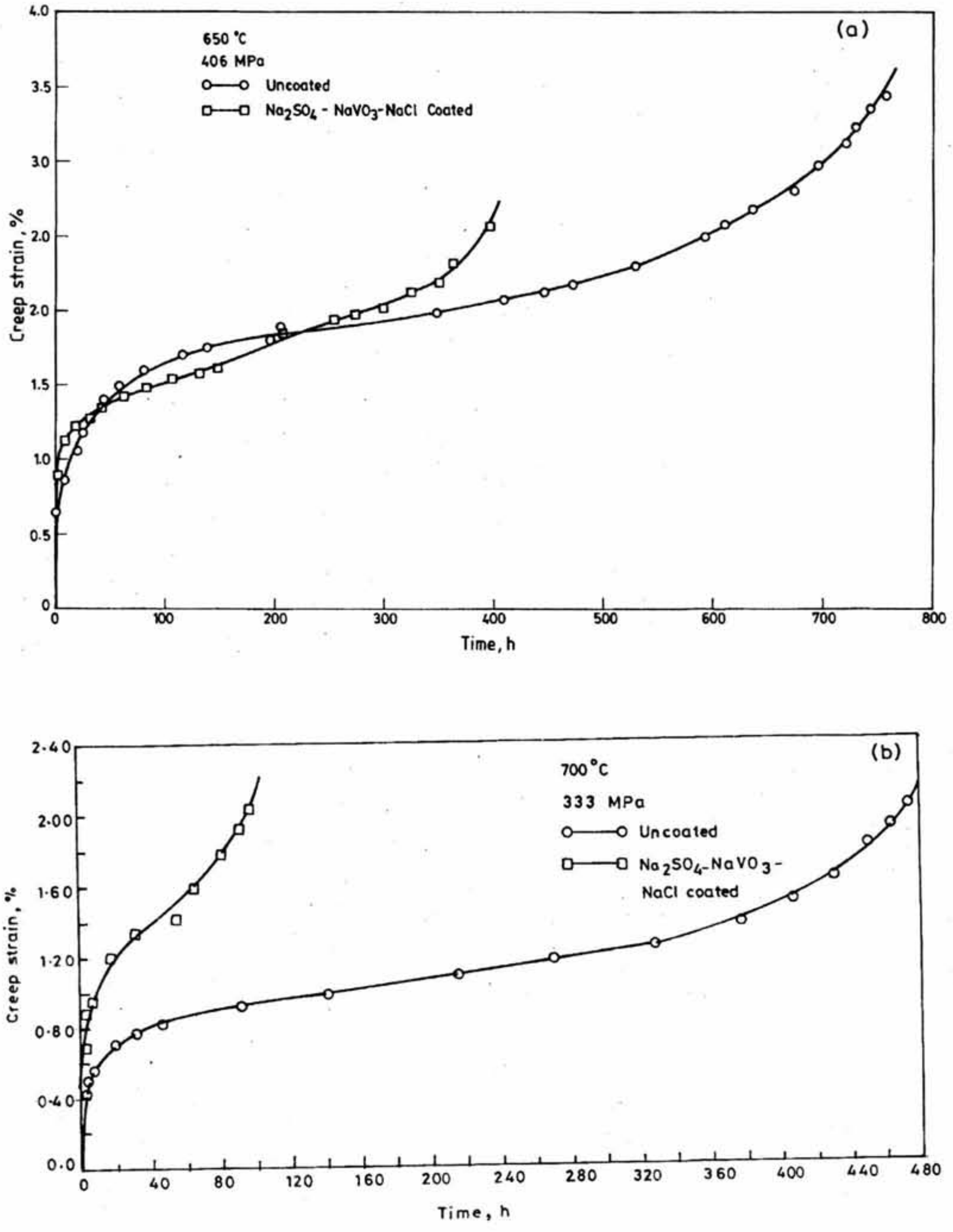
Fig. 2—A sample creep specimen

0.8 mm thick with gauge length 40 mm, as shown in Fig. 2. The creep rupture experiments were carried out in a constant load creep testing machine with a loading arm ratio of 1:10, at different stress levels on the coated and uncoated specimens. The test temperatures were maintained at 650, 700 and 750±3°C, as controlled by a thyristorised temperature controller. The rupture time was noted and elongation measured by means of a dial gauge with sensitivity of 0.01 over the gauge length of the specimen.

To find out the chemical nature of the hot corrosion products of the uncoated and coated specimens, coupons of dimensions 18x15x0.8 mm^3 were kept in a muffle furnace at the desired test temperatures (650, 700 and 750°C). These coupons were removed from the furnace after approximately 170 h. The corrosion products were analysed by fully automatic and computer controlled JEOL, JDX-8030 type X-ray diffractometer with JCPDS search match.

Results and Discussion

Figs 3 show typical creep curves of uncoated and coated samples at the test temperatures 650, 700 and 750°C, respectively. The shapes of the creep curves are essentially similar in air and hot corrosive environments. However, hot corrosion tends to cause enhanced secondary creep rate and drastic reduction in rupture life.



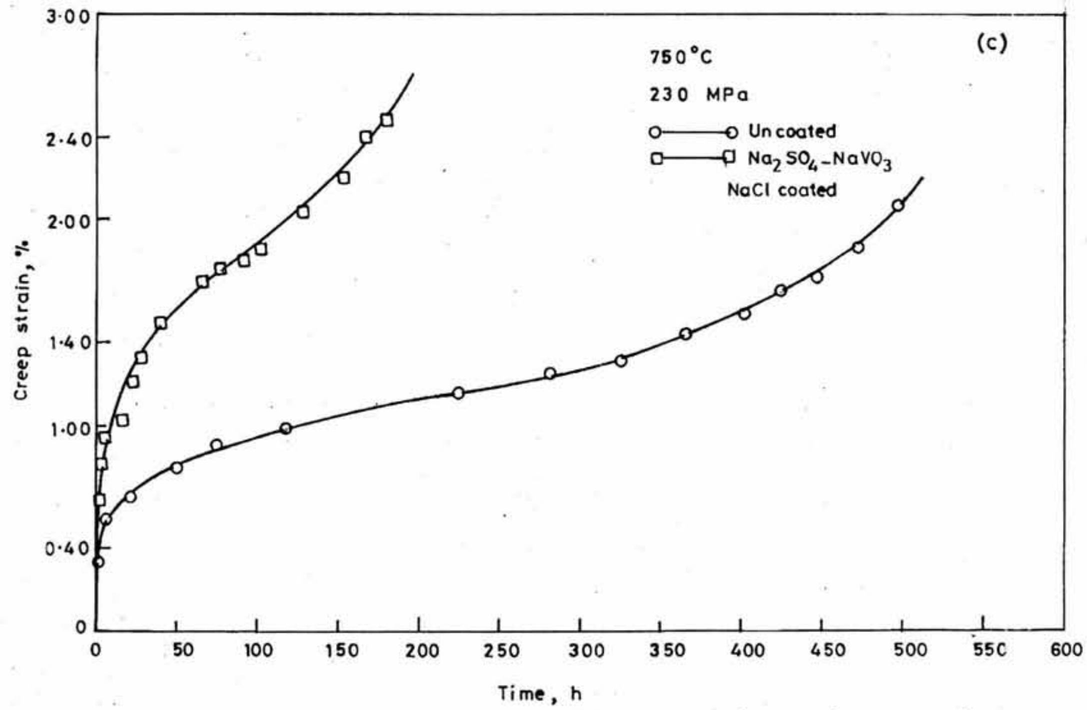
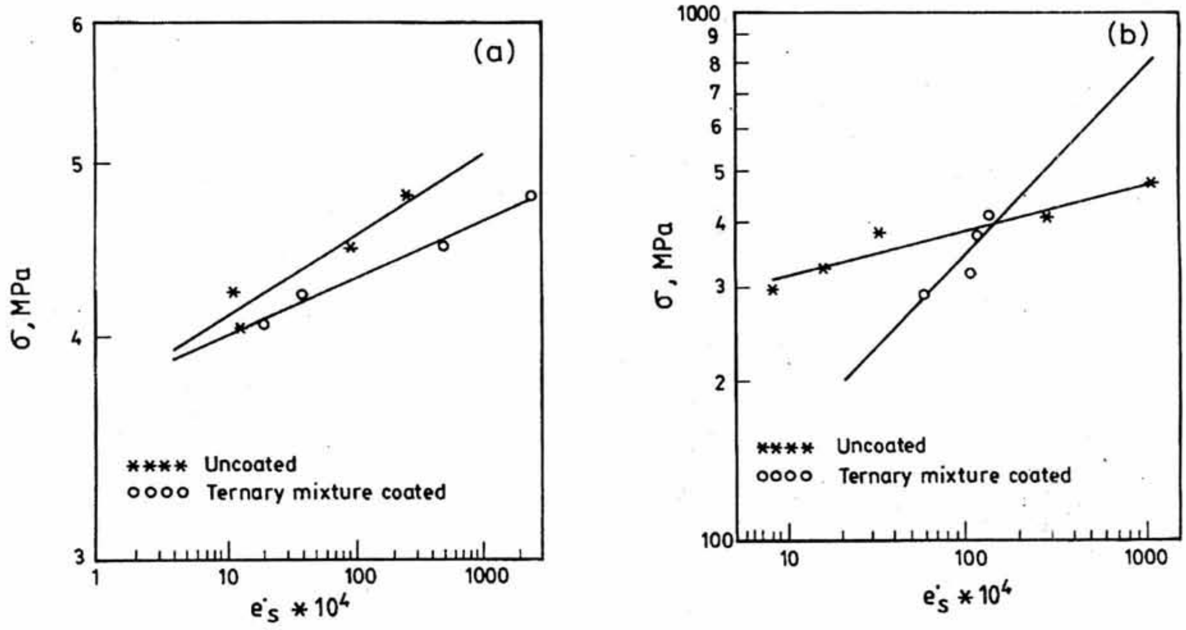


Fig. 3—Creep curves of Nimonic-90 at: (a) 650°C, (b) 700°C, and (c) 750°C



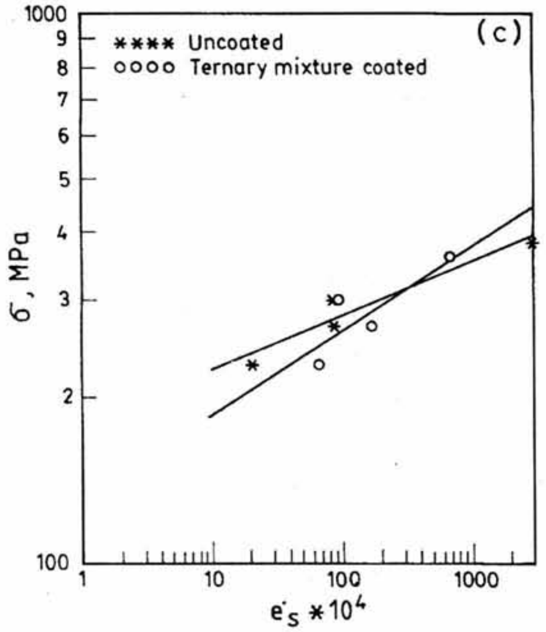


Fig. 4—Relation between applied stress and steady state creep rate of Nimonic-90 at: (a) 650°C, (b) 700°C, and (c) 750°C

The relation between applied stress (σ) and steady state creep rate ($\dot{e}_S$), is shown in Figs 4a-4c at the three test temperatures on log-log scale. The straight line relationship can be expressed by Eq. (1):

$$\dot{e}_S = A_1\, \sigma^{n_1} \quad \ldots (1)$$

where A_1 is the material constant and n_1 is the creep exponent.

Fig. 5 shows the relation between the steady state creep rate ($\dot{e}_S$) and the rupture life (t_r) in uncoated and coated conditions on log-log scale. The straight line yields the following equation well known as Monkmann-Grant (MG) relation which is applicable in uncoated and corrosive coated conditions:

$$t_r = A_2\, \dot{e}_S^{\,k_1} \quad \ldots (2)$$

where A_2 and k_1 are material constants. The value of k_1 is close to unity for uncoated where as the value of k_1 for Na_2SO_4-$NaVO_3$-NaCl coated specimens deviates from unity. The deviation from unity is due to aggressive corrosive nature of the ternary deposits, seriously decreasing the rupture time as compared to that for the same in air.

Combining Eqs (1) and (2), we obtain relation (3) for a given stress and temperature:

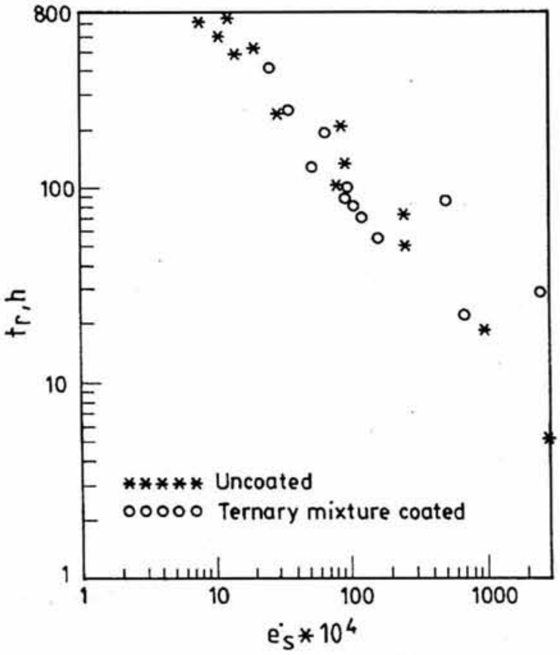


Fig. 5—Monkmann Grant relation

$$t_r = A_3\, \sigma^{n_2} \quad \ldots (3)$$

where A_3 and n_2 are material constants.

Figs 6a to 6c show the relationship between applied stress and rupture time for uncoated and coated condition at the test temperatures on log-log scale. A straight line relation is obtained for uncoated and corrosives coated condition as shown by Eq. (3). Figs 7a and 7b show the diffractograms obtained from the corroded surface of uncoated and coated samples exposed at 750 and 700°C, respectively. The various compounds identified are given in Table 1. The compounds identified are simple and complex oxides, metallic sulphates, stoichiometric and non-stoichiometric sulphides.

Reactions during the hot corrosion

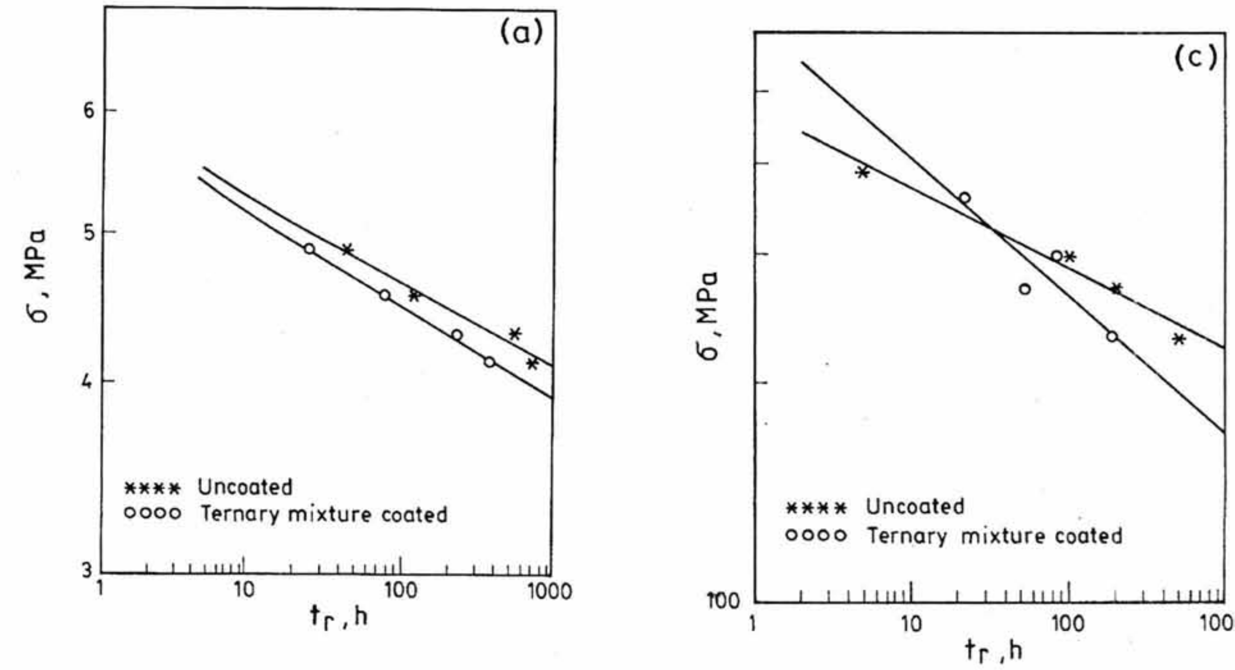
The ternary deposit is in liquid state at test temperatures. When the deposit is in the liquid state, the deposited salts may decompose, according to following reactions[17]:

$$Na_2SO_4 = 1/2O_2 + SO_2 + Na_2O \quad \ldots (4)$$

or

$$Na_2O + SO_3 = Na_2SO_4 \quad \ldots (5)$$

Therefore, a sodium sulphate melt has an oxygen ion or Na_2O activity which can be defined by oxygen or sulphur trioxide potentials.



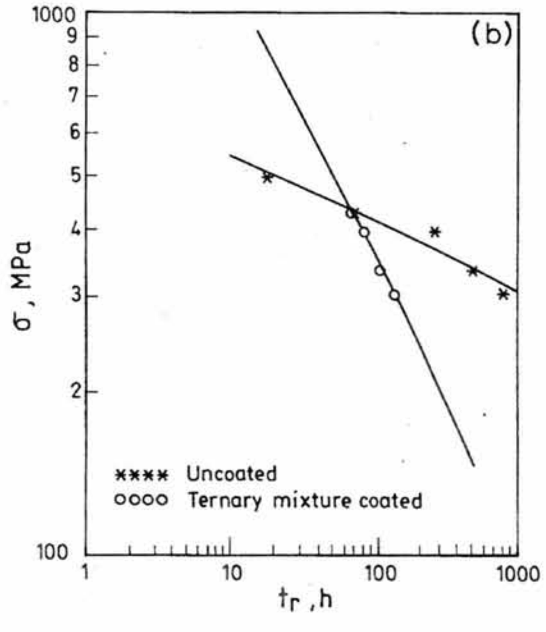


Fig. 6—Relation between applied stress and rupture time of Nimonic-90 at: (a) 650°C, (b) 700°C, and (c) 750°C

Table 1—Various compounds in corroded Nimonic-90 samples, as identified by the X-ray analysis

Uncoated samples	Ternary mixture coated samples
$NiCr_2O_4$, Cr_2O_3, $Ni_3(Al, Ti)$	Na_5NiO_4, NiV_2O_7, $NiCr_2O_4$, CrOCl, $NiCl_2$ $CrCl_3$, Ni_3S_2, Cr_2S_3, Ni-Cr-Co, Ni_3S_4, $Ni_3(Al, Ti)$, Na_2CrO_4, $NiCrO_4$

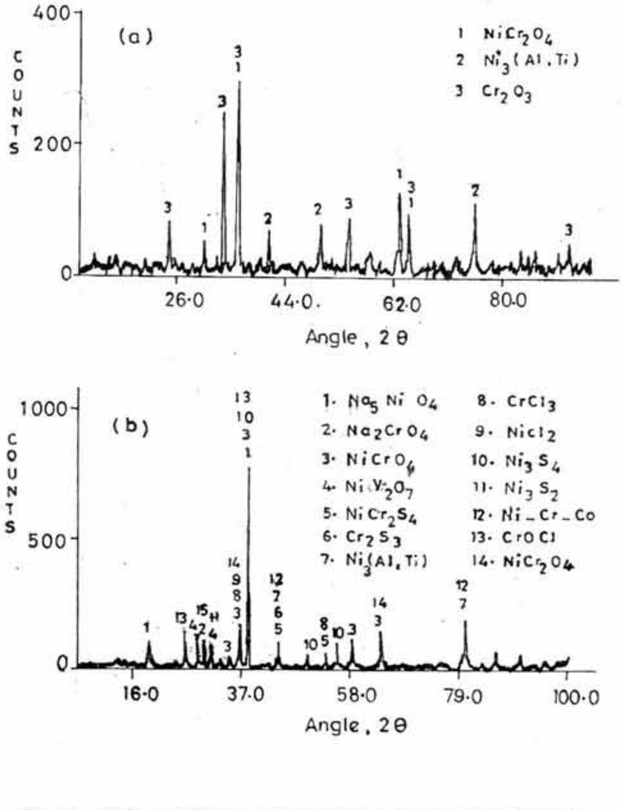


Fig. 7—X-Ray diffractograms of corroded surface for: (a) uncoated sample, (b) coated sample

$$K_5 = \frac{a_{\mathrm{Na_2SO_4}}}{a_{\mathrm{Na_2O}}.p_{\mathrm{SO_3}}} \qquad \dots (6)$$

So, based on the oxygen ion concentration of the melt, acid fluxing or basic fluxing occurs, resulting in dissociation of metal oxides into metal ions and formation of complex ions. Once, the oxygen activity of the Na_2SO_4 has reduced sufficiently, adequate sulphur pressure according to Eq. (6), is achieved at which sulphide phase can be formed in the alloy beneath the oxide layer. The removal of sulphur from the Na_2SO_4 due to sulphides formation will cause an increase in the activity of Na_2O. Hence, such alteration in activity of Na_2O and SO_3 will cause an accelerated oxidation, dissolution of oxides and sulphidation subsequently resulting in enhanced corrosion.

Kofstad and Seierstein[18] suggested that Na_2SO_4, $NaVO_3$ and NaCl will have an independent action. The corrosion product formed with the reaction of Na_2SO_4 present in liquid melt in Na_2SO_4-$NaVO_3$-NaCl can be described[19-22] by Eqs (7) to (9):

$$2Ni+O_2+2Cr_2O_3=2NiCr_2O_4 \qquad \dots (7)$$
$$Na_2SO_4+4Ni=NiS+NiO+Na_2O \qquad \dots (8)$$
$$9/2Ni+Na_2SO_4=Na_2O+3NiO+1/2\ Ni_3S_2 \qquad \dots (9)$$

The presence of $NaVO_3$ in the deposit will act as an additional fluxing agent enhancing the hot corrosion which can be described[23] by Eq. (10)

$$2NaVO_3+2NiO=Ni_2V_2O_7+Na_2O \qquad \dots (10)$$

The presence of NaCl in the deposit modifies the initiation stage of hot corrosion by virtue of its rapid disruptive effect on protective scales by producing cracking and spalling and the chloride ions play an important role in impoverishing the alloying elements such as Cr, Fe and Ni by the formation of volatile compounds[24-26] by Eqs (11) to (13):

$$2Cr_2O_3+5O_2+8NaCl_2=4Na_2CrO_4+4Cl_2 \qquad \dots (11)$$
$$2Cr_2O_3+6Cl_2=4CrCl_3+3O_2 \qquad \dots (12)$$
$$NiO+Cl_2=NiCl_2+1/2O_2 \qquad \dots (13)$$

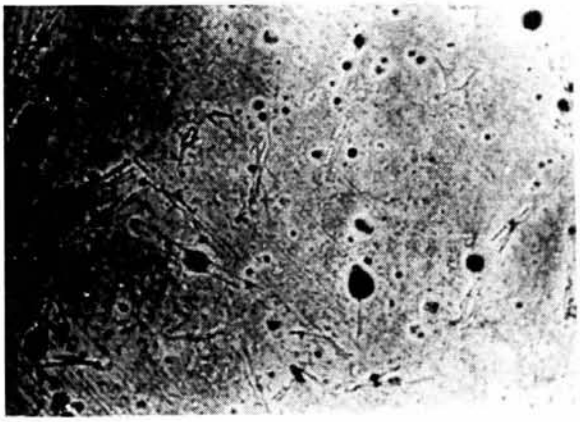


Fig. 8—Microphotograph of ternary coated samples showing numerous pits and voids

Such volatile products tend to migrate outwards from the metal, which leads to the formation of voids or pits [27]. The microphotograph (Fig. 8) of ternary coated sample, exhibits numerous pits and voids. The outward migration continues until they reach the zones of higher oxygen potentials where the displacement reaction may be favoured according to Eq. (14):

$$2MCl+½O_2=2MO+Cl_2 \qquad \dots (14)$$

So, the chlorination and subsequent oxidation leaves behind highly porous and non-adherent oxide scale. Therefore, in the presence of $NaVO_3$–$Na_2\ SO_4$–NaCl, the hot corrosion occurs due to oxidation and dissolution of oxides by fluxing action with both $NaVO_3$ and Na_2SO_4, sulphidation and chlorination, simultaneously.

Conclusions

There is an increase in minimum creep rate and drastic reduction of rupture life with corrosive coating. The plots of secondary creep rate vs stress, and rupture life vs secondary creep rate on log-log scales exhibit straight line relationships. XRD analysis of the corroded surface reveals the formation of simple and complex oxides such as NiO, Cr_2O_3, etc. The hot corrosion reactions indicate that hot corrosion occurs by salt fluxing actions where as the presence of chloride ions modifies and causes cracking of the protective oxide layers and also leads to the formation of volatile compounds resulting numerous pits. Hot corrosion causes severe materials degradation due to oxidation, sulphidation and chlorination reactions occurring simultaneously.

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