

THE APPLICATION OF DTA TO HOT CORROSION STUDIES OF CHROMIUM AND NICKEL POWDERS AND NIMONIC 80A*

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DTA has been successfully employed to study the hot corrosion behaviour of chromium and nickel powders and Nimonic 80A alloy samples in the presence of corrodants such as NaCl and Na₂SO₄.

The DTA data indicate a large high-temperature exotherm due to oxidation in air; the onset of oxidation occurs at much lower temperatures when additional oxidants are added. The results also show that NaCl attacks chromium much more aggressively than does either Na₂SO₄ or the salt mixture. The reverse has been observed for nickel, i.e. enhanced corrosion in the presence of Na₂SO₄ and the mixtures. Both Cr and Ni are oxidized to their respective oxides, via chloride formation in the presence of NaCl, and via sulphide formation in the presence of Na₂SO₄. Sodium chromate formation was confirmed with chromium in addition to the above compounds in the presence of sodium salts.

On the other hand, the DTA results on Nimonic 80A alloy samples indicate that the corrosion attack is negligible as long as the salt is in the solid form, but once the salt is molten it triggers catastrophic corrosion. The mechanism of hot corrosion is discussed.

Investigations on the oxidation/hot corrosion behaviour of chromium, nickel and nimonic alloy 80A are of great interest because of their use in gas turbine components. The presence of chromium in Nimonic alloys offers resistance to high-temperature corrosion, particularly in sulphur-bearing atmospheres [1]. Though turbine atmospheres contain several other impurities, hot corrosion in gas turbines has been attributed mainly to the presence of condensed deposits of sodium sulphate and chloride [2, 3]. It is generally accepted that impurities present in molten form flux with the protective oxide scale formed on the surface of the turbine components and thus expose the bare alloy surface for further oxidation [4, 5]. Though several investigations have been made employing various techniques, the literature is meagre on application of the DTA technique for hot corrosion studies.

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The present DTA investigation focuses on the oxidation behaviour of chromium, nickel and Nimonic alloy 80A. The hot corrosion studies in the presence of NaCl and Na₂SO₄ were undertaken with a view to assessing the aggressive nature of the attack by these salts on turbine hardware.

Experimental

The DTA unit employed in this investigation was assembled in the laboratory. The unit consists mainly of a sensitive Tynseley galvanometer (England) for recording the differential temperature, and a potentiometer for measuring the sample holder temperature. Platinum and platinum versus 10% rhodium thermocouples were employed to measure temperature. The rate of heating of the sample holder was maintained throughout at 10 deg/min., and the cooling rate was not programmed. Al₂O₃ was used as the reference material. Two types of sample holders were employed in this investigation. For powdered samples a sillimanite block made in the laboratory was used, and for the Nimonic alloy studies a nimonic alloy block itself was used as sample. All the salts employed were of A.R. grade and the salt mixtures were prepared by taking the weights according to the standard equation. Metal powders used were of - 100 mesh in size. The methods used for characterization were XRD, AES and chemical analysis.

Results and discussion

1. Hot corrosion of chromium powder

Prior to the hot corrosion tests on the samples, the DTA data on fine and coarse chromium powder were obtained in air in order to understand the oxidation behaviour. The results on the oxidation of chromium powder in air are presented in Fig. 1. Curves 1 and 2 in Fig. 1 illustrate oxidation behaviour of fine electrolytic chromium powder and imported coarse chromium powder, respectively.

Fine chromium powder undergoes stepwise oxidation, as shown by the three exotherms in curve 1. During the initial stages of oxidation, as indicated by the low-temperature exotherm at 290°, only the surface oxidation of chromium powder takes place; the powder acquires a navy-blue tinge at about 470° and then turns bluish-green at 600°. The second exotherm, at 600°, is ascribed to the formation of α -Cr₂O₃. The third exotherm, ranging between 700 and 800°, corresponds to the complete oxidation of chromium to the green, stable β -Cr₂O₃. The formation of a thin film of oxide on chromium powder particles during the early stages of

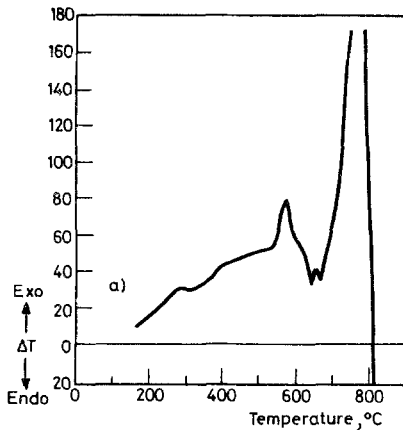


Fig. 1a DTA curve of fine chromium powder

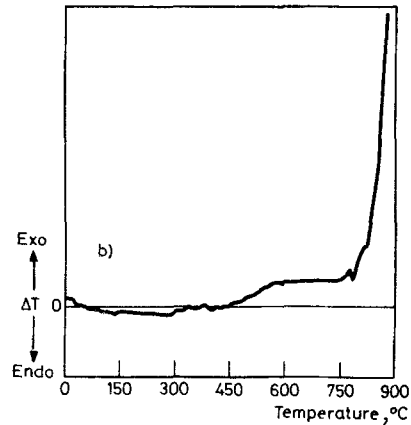


Fig. 1b DTA curve of coarse chromium powder

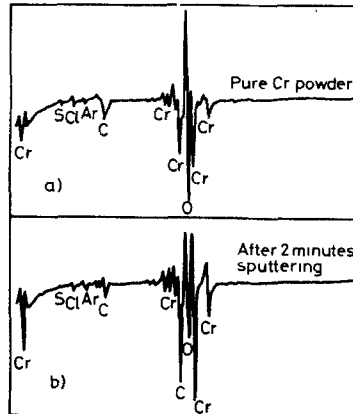


Fig. 2 Auger electron spectra of chromium powder

oxidation has been confirmed both by AES and by XRD. XRD analysis of the powder heated at 470° and 500° for 2-hr intervals in platinum crucibles indicated only the chromium pattern and no oxide of chromium was found; this observation was confirmed by AES analysis (Figs 2 and 4). On the other hand, the XRD pattern obtained for the sample heated for 2-hr at 800° revealed only Cr_2O_3 .

In order to examine the extent of surface oxidation, as indicated by the first two exothermic peaks in the DTA pattern of the fine powder, the AES spectra of pure chromium powder and of the powder heated to 470° for 4-hr were taken (Figs 2–4). The extent of surface oxidation which occurs even at room temperature on storing is shown in Fig. 2. Figure 2B present the spectrum for the same powder after 2 min of ion etching (equivalent to the removal of surface layers, i.e. 60 Å of Ta_2O_5). The peak height ratio for O/Cr is 0.64 for the etched powder. Similarly, Figs 3A and 3B

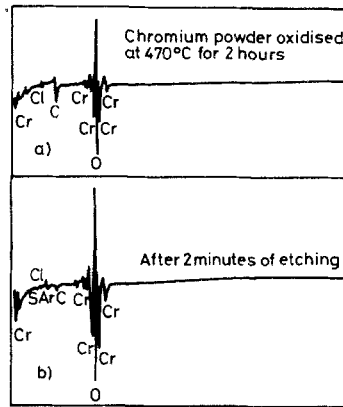


Fig. 3 AES of chromium powder

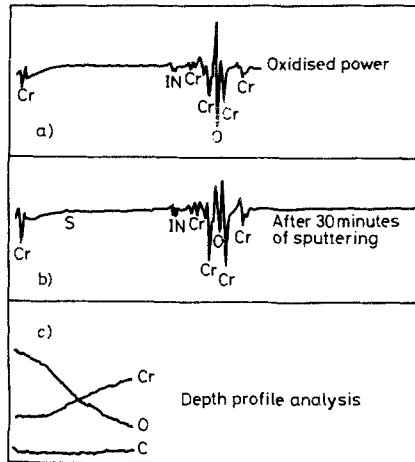


Fig. 4 AES of Cr powder oxidized at 475° for 2 hours

present AES spectra for the chromium powder oxidized at 470° for 4 hr and for the same powder ion etched for 2 min, respectively. The peak height ratio for the etched powder in this case is 2.57. However, 20 min of ion etching was necessary for removal of most of the surface oxide layers, as is seen from the depth profile analysis (Fig. 4). These results clearly indicate that the oxidation is restricted to the surface and does not extend to the bulk at low temperatures.

It is clear from the exothermic trend of curve a, Fig. 1 that the oxidation of fine chromium powder, sample 1 commences at a much lower temperature (300°) and continues in steps until the powder is completely oxidized to green chromic oxide at about 800°. On the other hand, no stepwise oxidation has been observed for the

coarse imported chromium powder, sample 2. Oxidation commences in this case at a much higher temperature, 825° rather than at 700° observed in the case of fine chromium powder. It is well known that the oxidation of chromium powder in air depends on the mode of preparation and on the particle size [6]. The DTA data clearly indicate the difference in the thermal behaviour of the fine and the coarse powders, during oxidation of chromium to green chromic oxide. According to Wohler [7], when heated in air chromium becomes yellow at first, then blue and finally acquires a crust of green chromic oxide. Our experimental observations show that grey chromium powder turns navy-blue at around 475° in air, then light-green at 600° and finally yields dark-green chromic oxide at 800° .

The influence of NaCl, Na_2SO_4 and a mixture containing 1% NaCl in Na_2SO_4 on the oxidation behaviour of chromium powder is illustrated in Fig. 5. Enhanced oxidation of chromium powder occurs in the presence of these corrodants, and the attack seems to be the highest in the case of contamination with pure NaCl. Curve a in Fig. 5 indicates the aggressive nature of the attack in the presence of NaCl. The

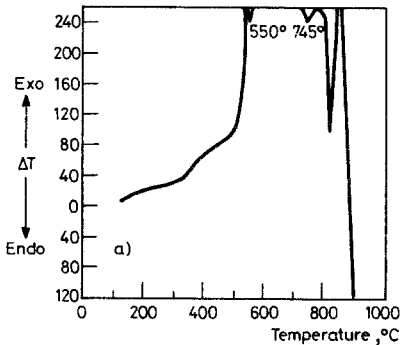


Fig. 5a DTA curve of Cr + NaCl

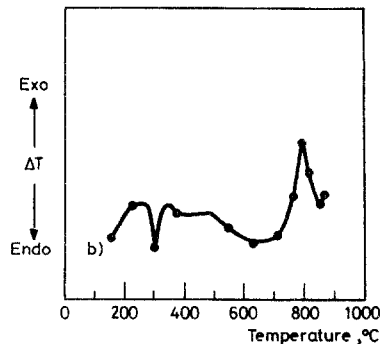


Fig. 5b DTA curve of Cr + Na_2SO_4

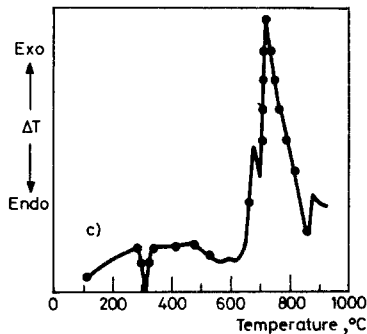
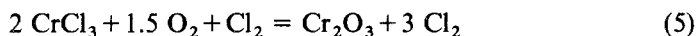
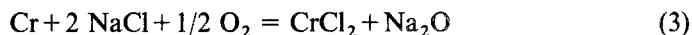
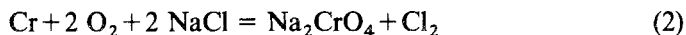


Fig. 5c DTA curve of Cr + 1% NaCl mixture

oxidation of chromium commences at around 300°, and a large exotherm at about 550° shows the catastrophic nature of the oxidation. A comparison of the curves in Fig. 1 and Fig. 5 shows that the oxidation of pure chromium is negligible at 550° in air, whereas the presence of NaCl favours the catastrophic oxidation of chromium to Cr₂O₃ at that temperature.

There is a small reversible endotherm at 550°, which may be due to the combined effect of the formation of a low-melting volatile chloride and the allotropic transformation of α -Cr₂O₃ to β -Cr₂O₃. Blanc [8] found that the allotropic transformation of α -Cr₂O₃ to β -Cr₂O₃ occurs at around 550°. The other large endotherm, at 800°, represents the molten phase of NaCl. The formation of Na₂CrO₄, depicted by an endotherm at 750°, was confirmed by heating chromium powder with NaCl and Na₂SO₄ separately for 2 hr at different temperatures in platinum crucibles and analysing the end-products by both XRD and chemical analysis. This observation was also confirmed from the reversible exotherm (recorded during cooling of the sample to 420°), which is attributed to the polymorphic phase transition of Na₂CrO₄. These results prove that the oxidation of chromium powder to Cr₂O₃ occurs below the m.p. of NaCl. The oxidation of chromium powder in the presence of NaCl can be represented in the following sequence:



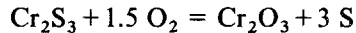
No difference in the oxidation behaviour of fine and coarse chromium powders in the presence of NaCl was observed in this case.

The reaction products, Na₂CrO₄, CrCl₃ and Cl₂, are all highly oxidizing agents, which can trigger catastrophic corrosion. It has been shown by Wohler [7] that chromium burns in liberated chlorine and forms CrCl₃ at around 600°, and is also subject to rapid oxidation in contact with air, to form Cr₂O₃. The DTA output for CrCl₃ in the laboratory showed a large exotherm at 670°, due to oxidation to Cr₂O₃ [9].

Cr-Na₂SO₄

Curve b in Fig. 6 is the DTA plot for the oxidation of chromium in the presence of Na₂SO₄. The DTA output for chromium powder shows a large endotherm between 500° and 750°. This may be due to the formation of chromium sulphides and

sodium chromate. The exotherm at 780° may be ascribed to the oxidation of both chromium sulphides and chromium in the presence of additional oxidizing agents such as Na₂CrO₄ and oxides of sulfur. Chromium reacts with Na₂SO₄ to form sulphides and oxides and these sulphides are often formed at the grain boundaries [10]. It has been shown that preferential chromium sulphide oxidation is the key process to the drastic attack characteristic of hot corrosion [10]. Chromium sulphides are oxidized directly to Cr₂O₃:



Curve c in Fig. 5 presents results on the influence of 1% NaCl in Na₂SO₄ on the oxidation behaviour of chromium. A small endothermic dip at 630° and another one at about 690° are seen. The former corresponds to the eutectic formation of the salt mixture, and the latter to the conversion of α-Cr₂O₃ to β-Cr₂O₃. The large exotherm reveals the oxidation of chromium to Cr₂O₃ below the m.p. of the mixture.

From the results obtained, it can be seen that the aggressive nature of the attack by the three corrodants studied follows the sequence NaCl > 1% NaCl mixture > Na₂SO₄. Experimental investigations carried out on the hot corrosion behaviour of Nimonic alloys using crucible tests [11] confirm that NaCl not only attacks chromium, but also lowers the oxidation temperature considerably. The DTA results have shown that the presence of the corrodants studied lowers oxidation.

2. Hot corrosion of nickel powder

The oxidation behaviour of nickel powder is illustrated in Fig. 6, curve 1. Nickel is oxidized to nickel oxide at a temperature of 900° in air. It undergoes a magnetic phase transition at around 350°, indicated by a small endothermic dip at the Curie temperature, with a large exotherm due to the oxidation of nickel powder to NiO at about 900°. The final oxidation product identified is NiO. Nickel loses its oxidation resistance above 900°, due to non-protective NiO formation.

Ni + NaCl

Figure 6 also presents the DTA results for the oxidation of nickel in the presence of NaCl, Na₂SO₄ and 1% NaCl in Na₂SO₄. DTA curve b exhibits an initial exothermic trend, and then three distinct endothermic peaks before the nickel is oxidized to NiO above the m.p. of NaCl at 800°. Three endotherms, at 610°, 680° and 780°, may correspond to NiCl₂ formation, melting and decomposition, respectively. Yet another endotherm at 800° indicates the molten NaCl phase. The high-temperature exotherm which appears immediately after the endotherm at 800° is due to the oxidation of nickel powder in the presence of molten NaCl.

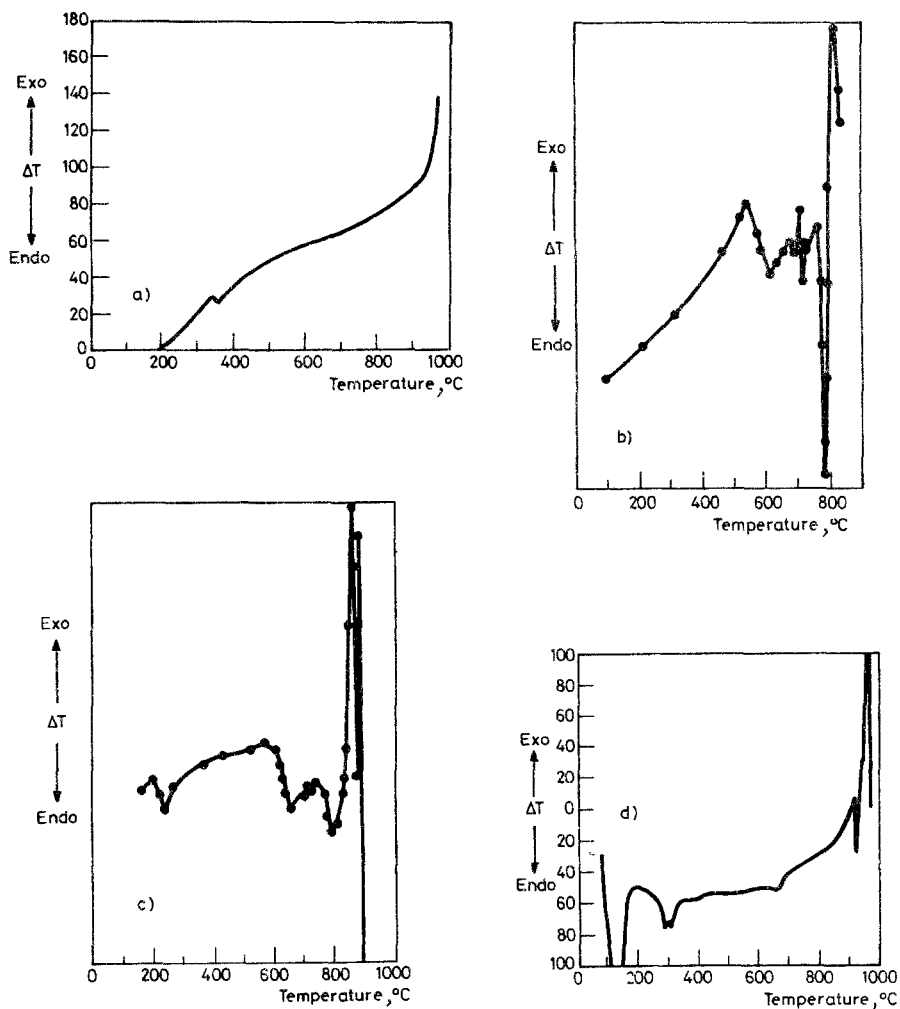
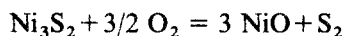
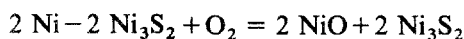


Fig. 6.

$Ni + Na_2SO_4$

The DTA pattern for the oxidation of nickel in the presence of Na_2SO_4 is exhibited in curve c, Fig. 6. After an initial endotherm at 250° , the curve takes an upward trend up to 600° , due to the slow oxidation of nickel powder. The reversible endotherm at 640° corresponds to the eutectic formation of $Ni-Ni_3S_2$. The second endotherm, at 790° , is ascribed to the presence of Ni -liquid = liquid phase [12]. This is followed by an exotherm due to the oxidation of nickel to NiO . The presence of molten sulphide accelerates the oxidation of nickel at the lower temperature of

850° instead of at above 900° as in air. The end-product of the reaction at 900° contains only nickel oxide and no sulphides. These results suggest that, though initially oxides and sulphides form simultaneously, the final oxidation product is NiO. According to Goebel and Pettit [13], the Na₂SO₄-accelerated oxidation of nickel is caused by the reaction between NiO and Na₂O rather than by the oxidation of nickel sulphide. Our DTA results suggest that the enhanced oxidation of nickel proceeds via sulphide formation. Though both sulphidation and oxidation occur at first, the accelerated oxidation of sulphides of nickel takes place in the presence of the liquid sulphide phase at higher temperatures. Enhanced oxidation occurs according to the following reaction:



Ni + (1% NaCl + 99% Na₂SO₄) mixture

The oxidation of nickel in the presence of a mixture containing 1% NaCl in Na₂SO₄ is illustrated in Fig. 6. DTA curve d shows an endotherm at 640° and another one at 900°. The first endotherm is due to the eutectic formation of Ni-Ni₃S₂, and the other one to the molten state of the salt mixture. The exotherm above 900° shows the oxidation of nickel.

The DTA data on the oxidation of nickel in the presence of the three corrodants studied clearly show that molten salts are detrimental to nickel. Though both chlorides and sulphides of nickel are formed below the molten state of the corrodants, the final oxidation product formed is always pure nickel oxide. The results in Fig. 6 illustrate that the presence of molten corrodant promotes the enhanced oxidation of nickel.

Hot corrosion of Nimonic 80A

Figure 7 presents DTA data on Nimonic 80A in the presence of NaCl, Na₂SO₄ and a mixture containing 1% NaCl in Na₂SO₄. Curve 1 in Fig. 7 exhibits a sharp endotherm at 800°, due to the melting of NaCl, followed by a large exotherm ranging between 810° and 970°. The large exotherm corresponds to the enhanced oxidation of the alloy specimen in the presence of molten NaCl. It can be seen from Fig. 7, curve a, that there is no change in the DTA pattern up to 800°, except for an upward trend from the base line, but once the salt is molten an abrupt change in the DTA pattern takes place. The large exotherm which appears immediately after the endotherm at 800° clearly indicates the aggressive nature of the attack on the sample in the presence of molten salt.

In a similar way, the presence of Na₂SO₄ (curve b, Fig. 7) causes an exotherm

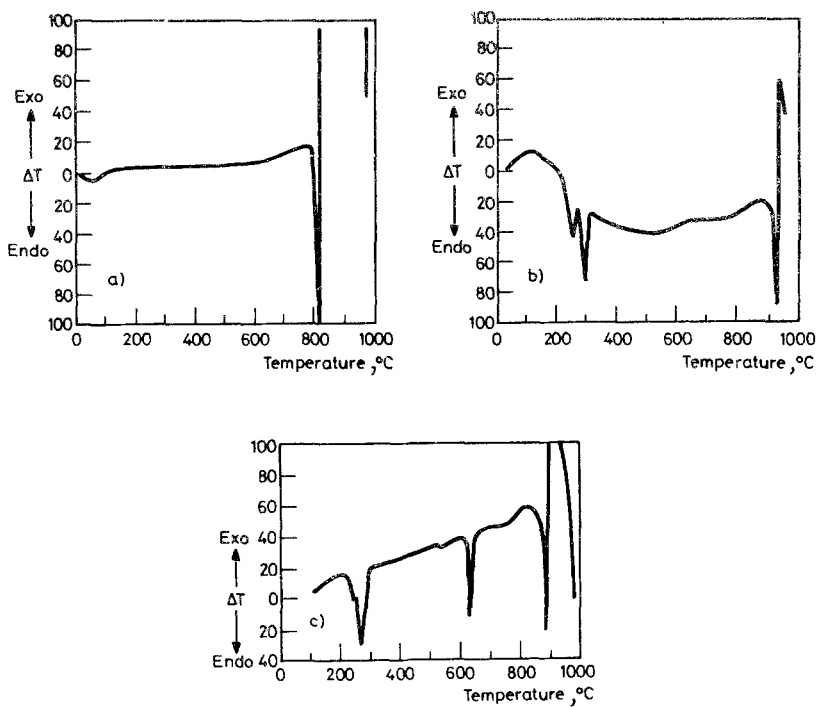


Fig. 7.

after the salt is molten at 900° , this relating to the oxidation of the sample. The curve also shows an endothermic trend between 500° and 760° . This is probably due to the formation of small amounts of sulphides. The formation of nickel and chromium sulphides in the temperature region 500 – 760° in the presence of Na_2SO_4 is well documented in the literature [14, 15].

The oxidation in the presence of the 1% NaCl in Na_2SO_4 mixture is shown in curve c, Fig. 7. The endotherm at 636° is ascribed to the eutectic formation and that at 900° to the melting of Na_2SO_4 . The results indicate that NaCl is certainly more aggressive than Na_2SO_4 . The addition of even small amounts of NaCl to Na_2SO_4 enhances the corrosion considerably. Both Simons et al. [16] and Goebel and Pettit [13] have shown that pure Na_2SO_4 is innocuous, but the addition of small amount of NaCl aggravates corrosion. The large exotherm obtained in the presence of NaCl not only indicates the catastrophic nature of the attack, but also shows that it is more aggressive than the other two corrodants studied.

Conclusions

- (1) The presence of molten salts is detrimental to all of the metals studied.
- (2) Products of oxidation are voluminous because of hot corrosion attack.
- (3) Material degradation occurs due to the preferential removal of alloying elements during corrosion.
- (4) Na_2SO_4 is innocuous in comparison to NaCl .
- (5) Addition of NaCl to Na_2SO_4 yields a more harmful corrodant than pure Na_2SO_4 .

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Zusammenfassung — Die DTA-Methode wurde mit Erfolg zur Untersuchung des heißen Korrosionsverhaltens von Chrom- und Nickelpulvern und Proben der Nimonic 80A-Legierung in Anwesenheit von Korrosionsmitteln wie NaCl und Na_2SO_4 angewandt. Die DTA-Kurven weisen einen breiten exothermen Hochtemperaturpeak auf, der der Oxydation in Luft zugeschrieben wird. Die Oxydation setzt bei viel tieferen Temperaturen ein, wenn zusätzliche Oxydationsmittel zugegeben werden. NaCl greift Chrom stärker an als Na_2SO_4 oder Gemische der Salze. Das Gegenteil wurde für Nickel festgestellt, d. h. verstärkte Korrosion bei Anwesenheit von Na_2SO_4 und Gemischen der Salze. In Anwesenheit von NaCl werden Cr und Ni zu den entsprechenden Oxiden über die Chloride oxydiert, in

Gegenwart von Na_2SO_4 dagegen über die Bildung von Sulfiden. DTA-Untersuchungen der Nimonic 80A-Legierungsproben zeigen andererseits, daß eine vernachlässigbar geringe Korrosion erfolgt, solange das Salz in fester Form vorliegt, in geschmolzenem Zustand löst es jedoch eine katastrophale Korrosion aus. Der Mechanismus der heißen Korrosion wird diskutiert.

Резюме — ДТА метод был использован для изучения высокотемпературной коррозии порошкообразных хрома и никеля, а также образцов сплава Нимоник 80А в присутствии хлорида и сульфата натрия, как корродирующих веществ. Данные ДТА показали наличие высокотемпературной экзотермы, обусловленной окислением в атмосфере воздуха, причем в случае наличия окислителей начало окисления происходит при более низких температурах. Результаты также показали, что хлорид натрия значительно интенсивнее корродирует хром, чем сульфат натрия или же смесь хлорида и сульфата натрия. Противоположное явление наблюдалось для никеля, который более интенсивно подвергался коррозии в присутствии сульфата натрия или же смеси его с хлоридом натрия. Как никель, так и хром окисляются до соответствующих окислов через промежуточную стадию образования хлоридов в присутствии хлористого натрия и с образованием сульфидов в присутствии сульфата натрия. Кроме того для хрома, в присутствии натриевых солей, было подтверждено образование хромата натрия. ДТА исследования образцов сплава Нимоник 80А показали, что соли в твердом состоянии вызывали незначительную коррозию, тогда как в расплавленном состоянии — очень сильную коррозию. Обсужден механизм высокотемпературной коррозии.