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DTA STUDIES ON THE CORROSION BEHAVIOR OF TITANIUM POWDER IN NaCl AND Na_2SO_4

S. Kameswari

DEFENCE METALLURGICAL RESEARCH LABORATORY.
KANCHANBAGH, HYDERABAD - 500 258, INDIA

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The corrosion/oxidation behavior of titanium powder in air and in the presence of corrodents NaCl and Na_2SO_4 was investigated by employing the DTA technique.

The DTA results for pure and fine titanium powder in air indicate two high-temperature exotherms, one at 700° and the other at around 750°. The first exotherm is due to the formation of anatase (TiO_2) and the second to rutile (TiO_2), as evidenced by the XRD data. However, the presence of NaCl and Na_2SO_4 promote the direct oxidation of titanium to rutile, which is indicated by a large exotherm ranging between 600 and 850°. The endotherm at 690° for mixtures containing 25 to 30% NaCl to Na_2SO_4 corresponds to formation of the eutectic mixture. The DTA data clearly indicate that the presence of the corrodents not only lowers the temperature of oxidation, but also induce the catastrophic oxidation of titanium powder.

It is well-know that titanium exhibits excellent resistance to most environments, because of its strong affinity for oxygen and its tendency to form a very stable and coherent oxide film on the surface of the metal [1]. Titanium readily reacts with air/oxygen to form the stable oxide rutile (TiO_2) above 700°. During the initial stages of oxidation, the oxide layers formed on the metal surface pass through a spectrum of light interference colors depending on the thickness of the oxide film, and finally acquires a white color due to the thick oxide scale of TiO_2 [2]. The oxidation of titanium at temperatures lower than 800° leads to the formation of rutile [3], whereas at higher temperatures the scales formed involve a multilayer structure, the constituents of which are TiO_2, Ti_3O_5, etc. [4].

Titanium and its alloys are extensively employed in diverse fields, such as the aero-space, chemical and petrochemical industries, because of their excellent corrosion resistance and high strength to weight ratio. They are highly attractive materials for corrosion-resistant applications, such as off-shore drilling equipment, marine-based vessels, desalination and wast treatment plants, etc. Tough the oxidation behavior of titanium and its alloys is well documented [3, 4], very few studies have been reported on the corrosion behavior of these in the presence of corrodents such as the chlorides and sulfates of alkali metals, which are abundantly present in the marine atmospheres where many titanium-based plants and vehicles are stationed. The present work examines the corrosion behavior of titanium powder in the presence of NaCl and Na_2SO_4.

Experimental

The DTA facility employed in this investigation was assembled in the laboratory. The unit consists of a sensitive Tynseley galvanometer (England) for recording differential temperature, and a potentiometer for measuring the sample holder temperature. Platinum and platinum-10% rhodium thermocouples were used to measure temperature. The rate of heating of the sample holder was maintained throughout at 10 deg/min. A sillimanite sample holder made in the laboratory was used. Titanium powder of < -100 mesh was investigated. All the salts used were of A. R. quality, and salt mixtures were prepared by taking appropriate weights of them according to the standard equation. The characterization of oxidation products was carried out via XRD, AES and chemical analysis techniques.

Results

Oxidation of titanium powder in air

DTA of fine and coarse titanium powder was first performed in air. The DTA results recorded in air for fine and coarse titanium powder are shown in Fig. 1 (A and B). The plots in Fig. 1 indicate that the oxidation of pure titanium powder to stable titanium oxide, rutile (TiO_2), occurs above 650°. Fine titanium powder undergoes stepwise oxidation between 650° and 800° (Fig. 1A). The first exothermic peak occurs at 700° and the second at 750°. The first exothermic peak, extending between 650° and 750°, corresponds to the formation of anatase, and the second one, at 750°, to the formation of the stable rutile phase. On the other hand, coarse titanium powder oxidizes

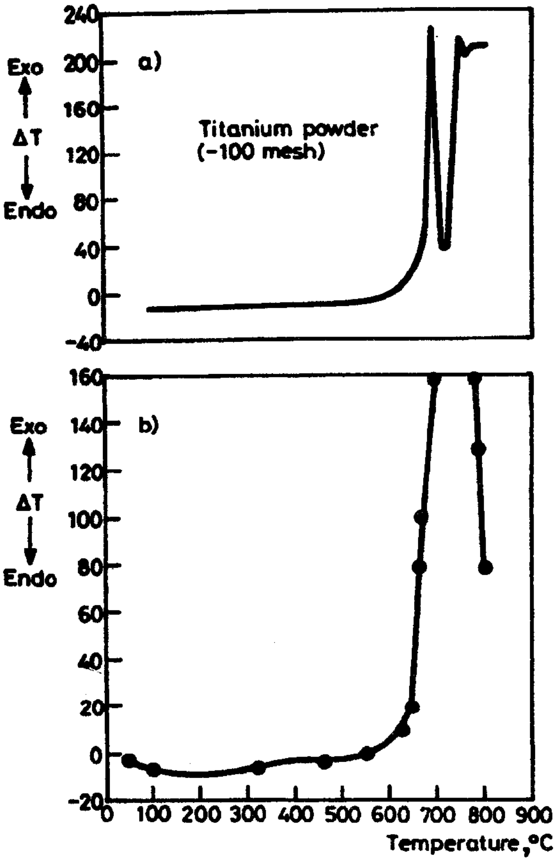

Fig. 1 DTA of fine (A) and coarse (B) titanium powders

directly to rutile in one step (Fig. 1b). The large exotherm ranging between 650° and 800° corresponds to rutile formation.

XRD analysis of samples calcined for 2 hours at 600° and at 800° shows that, though the oxidation starts at 600°, complete oxidation occurs only above 750°

Hot corrosion of titanium powder

The DTA patterns obtained for the fine titanium powder in the presence of NaCl, Na_2SO_4 and mixtures of NaCl and Na_2SO_4 in different proportions are presented in Figs 2-4. Plots 2A and 2B present the DTA patterns for titanium powder in NaCl and Na_2SO_4, respectively. The DTA plots in Fig. 2 show large exotherms ranging between 600° and 900°, with no other intermediate peaks due to the formation of a eutectic mixture (635-690°), or corrosion products such as chlorides and sulfides, or the melting of the corrodents NaCl (800°) and Na_2SO_4 (900°). Plot 2A for Ti + NaCl in Fig. 2 indicates that oxidation commences at 600° and is complete at 850°, i.e. above the m.p. of NaCl. The endotherm at 800°, due to the melting of NaCl, is masked by the highly exothermic nature of the oxidation of titanium powder. Plot 2B represents the oxidation of titanium powder in Na_2SO_4. In this case, the oxidation starts at a higher temperature, 700°, and complete oxidation takes place before the melting of Na_2SO_4. In both cases, the rate of corrosion is higher than that in air, although the effect of Na_2SO_4 is negligible at lower temperatures.

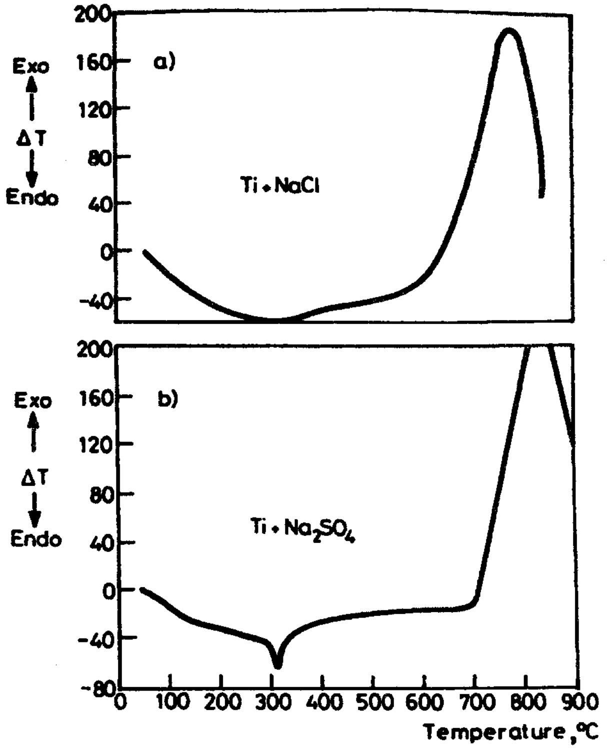

Fig. 2 DTA of titanium powders in NaCl and Na_2SO_4

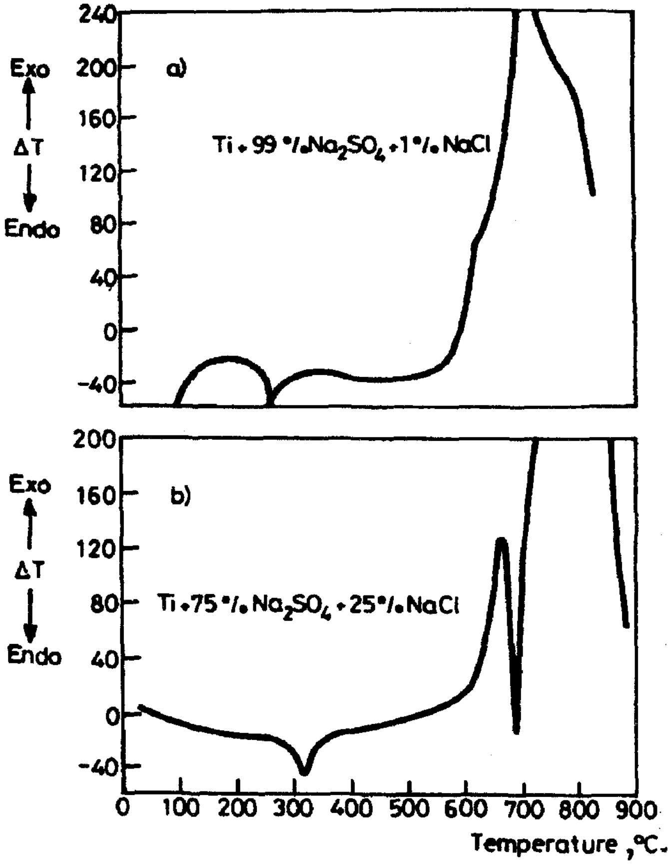

Fig. 3 DTA of titanium powder in mixtures of NaCl and Na_2SO_4

Similarly, Figs 3 and 4 represent the DTA output for the oxidation of titanium powder in the presence of corrodent mixtures. Figure 3 gives the DTA plots for titanium powder in 1% NaCl and 25% NaCl in Na_2SO_4. The DTA plot for titanium in the 1% NaCl mixture is similar to plot B in Fig. 1, which indicates the oxidation of coarse titanium powder. The endotherm due to the formation of the eutectic mixture is masked by the exothermic peak which corresponds to the oxidation of titanium powder. However, the endotherm due to eutectic formation is seen for the mixtures containing 25% NaCl (Fig. 2B) and 30% NaCl (Fig. 3A) in Na_2SO_4 at around 690°. The endotherm is prominent for these two mixtures, but is absent for the mix-

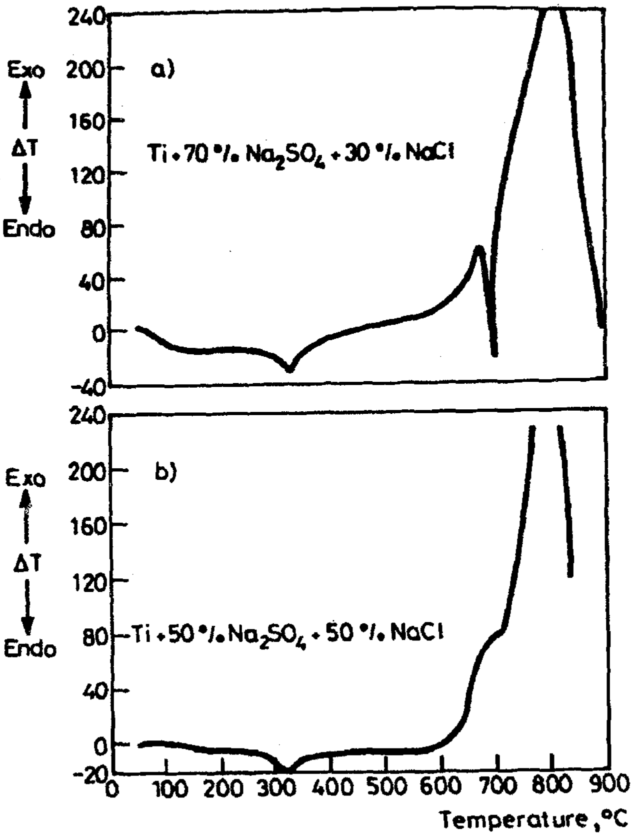

Fig. 4 DTA of titanium powder in mixtures of NaCl and Na_2SO_4

tures containing 1% NaCl and 50% NaCl. Similarly, the endotherm due to the melting of NaCl at 800° is also absent from all the plots, which clearly indicates the aggressive nature of corrosion attack on the metal powder in the presence of semi-molten (eutectic mixture) and molten corrodents (NaCl and Na_2SO_4).

Oxidation in the presence of the 50% NaCl mixture is not as severe as in the case of the other two mixtures where the eutectic formation is prominent, as shown by the sharp endotherm at 690° (Figs 2 and 3).

In order to add further to the DTA data and for a better understanding of the aggressive nature of corrosion attack by the corrodents on titanium powder, XRD patterns were taken for the three samples, i.e. pure titanium powder, Ti + NaCl, and Ti + Na_2SO_4 calcined in air at 600° for 2 hours. It can be seen from plot 2 (Fig. 5) that even at 600° most of the titanium powder is oxidized in the presence of NaCl, in contrast with the XRD patterns obtained for the mixture with Na_2SO_4 or the pure metal powder oxidized in air. The results illustrate the severe corrosion attack by NaCl on titanium powder. At higher temperatures, i.e. above 800°, all three samples gave only rutile patterns.

Discussion

Oxidation in air

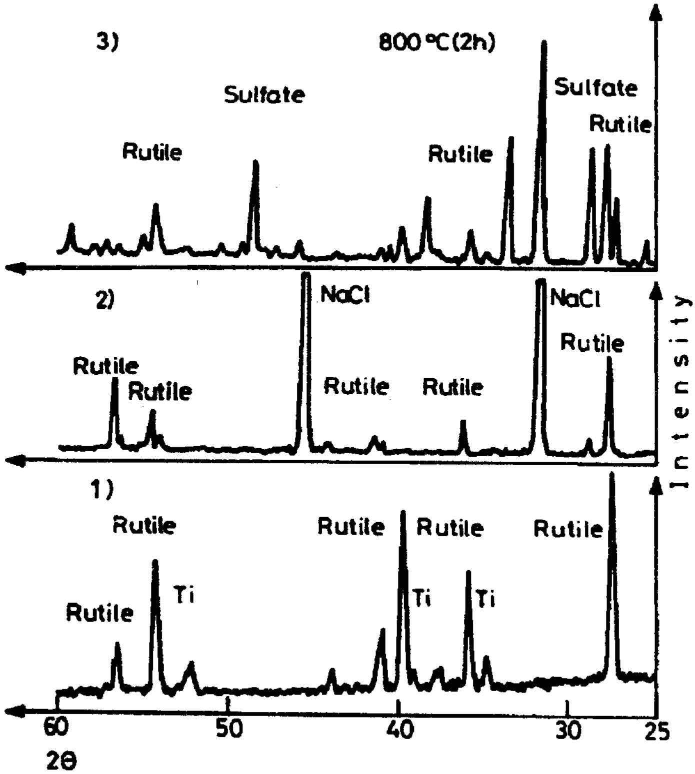

Fig. 5 XRD patterns of (1) Ti in air, (2) Ti in NaCl and (3) Ti in Na_2SO_4

The DTA results in Fig. 1 for the oxidation of fine and coarse powders differ markedly. The oxidation of fine titanium powder to rutile (Fig. 1A) occurs via anatase formation, whereas, the coarse powder proceeds directly to rutile (Fig. 1B). The two exotherms in the temperature range 600-800° are seen in Fig. 1A. The first exotherm, in the temperature range 600-700°, is ascribed to the formation of anatase, and the second one, between 710 and 750° to rutile. The DTA data also reveal that oxidation is negligible below 600°, and the formation of anatase and rutile phases occurs above 600°. Wide variations in the temperature of transformation of anatase to rutile (400-1000°) have been reported in the literature [5-7]; these variations depend mainly on the presence of impurities in the sample, the method of preparation, the time and temperature of heating, etc. According to Czanderma *et al.* [7], the anatase to rutile transition is strongly dependent on time and temperature; no appreciable conversion occurs below 610°, but above 750° the conversion proceeds very fast. Jenkins [8] showed that up to 550° oxidation is negligible; it starts at 600°, and complete oxidation to rutile occurs above 700°. Rao *et al.* [9, 10] systematically studied the transformation of pure anatase to rutile and showed that the transformations proceed according to the following scheme:

$$(620^\circ)\ \text{anatase I} \rightarrow (620\text{-}650^\circ)\ \text{anatase II} \rightarrow (650^\circ)\ \text{rutile}$$

In the case of coarse titanium powder, direct oxidation to rutile occurs in one step, (Fig. 1B). The results of Hurlen [11] and Kameswari [12] also indicated only rutile formation, and no other forms of oxides, when a thin sheet of titanium was oxidized in air. Complete oxidation of coarse powder occurs at the higher temperature of 800°, rather than at 750°, as in the case of fine titanium powder. It was observed that the powder turns deep blue on heating separately in a platinum crucible between 500 and 550°, but there was no indication of any definite oxide formation, either in the thermal curve of the sample or in the XRD pattern. However, AES analysis of the blue powder revealed a thin film oxide formation on the surface. Similar observations were reported [13] in AES analysis in the oxidation of blue chromium powder.

Hot corrosion

The addition of the corrodents NaCl and Na_2SO_4 to titanium powder enhances corrosion (Figs 2-4). It is well established [14, 15] that the presence of partially molten or completely molten salts is detrimental to the corrosion resistance of metals and alloys. The molten salts remove the protective oxide scale present on the surface of metals by fluxing and expose the fresh surface to further aggressive attack. Though titanium exhibits good resistance to air at temperatures up to 600°, the addition of even small amount of NaCl induces severe corrosion (Fig. 2). During NaCl attack, $TiCl_3$ is formed according to Eq.(1):

$$6NaCl + 2Ti + 3/2\,O_2 \rightarrow 2TiCl_3 + 3Na_2O \qquad (1)$$

The Na_2O thus formed reacts with the protective oxide scale, TiO_2, and forms sodium titanate, as shown in Eq.(2):

$$3TiO_2 + Na_2O \rightarrow Na_2Ti_3O_7 \qquad (2)$$

The presence of the reaction products Na_2O and $TiCl_3$ adds further to the aggressive environment already present, and triggers the catastrophic corrosion of pure titanium and its alloys [12], consuming the metal on long exposures. The presence of NaCl lowers the oxidation temperature from 650° to 600° (Fig. 2A), whereas the addition of pure Na_2SO_4 seems to be innocuous at lower temperature, because no corrosion products were reported to aggravate the corrosion atmosphere at this temperature (600°). The aggressive nature of NaCl attack on titanium is evident from the XRD pattern (Fig. 5) obtained for the three samples corroded in air, NaCl and Na_2SO_4. No trace of titanium is seen after NaCl corrosion at 600°. The other two patterns show that the titanium is not completely oxidized. These results support the DTA data, in that they show that the attack on titanium in the presence of NaCl is much more severe than the case of Na_2SO_4.

The addition of salt mixtures (Figs 3 and 4) to titanium powder induces severe corrosion attack as compared with the results in the presence of the pure salts, as judged from large exotherms. The endotherms at 690° (Figs 3 and 4) are due to the eutectic formation of corrosive mixtures. The large exotherms indicate the catastrophic corrosion in the presence of the mixtures, except the 50% NaCl mixture. It was shown earlier [14] that two zones of severe corrosion occur in mixtures: the first one in mixtures containing low concentrations (1-5%) of NaCl, present in the solid plus liquid state, and the other containing higher concentrations (20-30%) of NaCl, where the mixture exists in the molten state. The results are in consonanace with the earlier observations [15] and support the view that corrodents in the solid plus liquid state are detriment to the integrity of metals.

Conclusions

1. The oxidation of fine titanium powder to rutile (TiO_2) occurs via anatase formation, whereas in the case of coarse powder direct conversion to rutile occurs.
2. The presence of the pure corrodents NaCl and Na_2SO_4 promotes the direct oxidation of fine titanium powder to rutile in one step.
3. The addition of corrodent mixtures or pure corrodents lowers the temperature of oxidation of titanium powder.

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Zusammenfassung - Mittels DTA-Techniken wurde das Korrosions-/Oxydationsverhalten von Titanpulver an Luft und in Gegenwart von NaCl und Na_2SO_4 untersucht.

Die DTA-Ergebnisse für reines, feines Titanpulver zeigen bei 700° und bei etwa 750° zwei Hochtemperaturexothermen. Wie durch Röntgendiffraktionsangaben bestätigt, gehört die erste Exotherme zur Bildung von Anatas (TiO_2), die zweite zur Bildung von Rutil (TiO_2). In jedem Falle begünstigt die Gegenwart von NaCl und Na_2SO_4 die direkte Oxydation von Titanpulver zu Rutil, was durch eine breite Exotherme im Bereich von 600-850° angezeigt wird. Der Endothermen bei 690° bei Gemischen mit einem Gehalt an 25-30% NaCl oder Na_2SO_4 liegt die Bildung von eutektischen Gemischen zugrunde. Die DTA-Daten zeigen eindeutig, daß die Wirkung der korrodenten Zusätze nicht nur in einer Herabsetzung der Oxydationstemperetur, sondern auch in einem eindeutigen Vorantrieb der Oxydation besteht.