

# Plasma surface treatment of AISI 4140 steel for improved corrosion resistance

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Alloy AISI 4140 steel was plasma-nitrided in a low-pressure abnormal glow discharge in 75% N<sub>2</sub> + 25% H<sub>2</sub> atmosphere ( $P=3$  torr and  $T=540$  °C for 2 h) using a home-made laboratory reactor. The corrosion behaviour was evaluated in a chloride environment by potentiostatic and potentiodynamic polarization as a function of thermal treatment and cooling cycle. Results from potentiodynamic polarization in NaCl (3%) indicated the presence of a low anodic dissolution current of about  $1 \mu\text{A cm}^{-2}$  for ionitrided steel having layers thickness  $>5 \mu\text{m}$  as compared to  $0.1 \text{ A cm}^{-2}$  for untreated steel. In addition, the open circuit potential shifted to noble potential clearly indicating that the ionitridation process is a very efficient process for corrosion protection of AISI 4140 steel. Typical results obtained from samples oxidized during the cooling cycle showed an improvement in the corrosion resistance. The potential for pitting initiation and propagation as well as for pitting protection has been determined in a chloride environment. The use of electrochemical techniques as a control of standard parameters has been suggested.

## 1. Introduction

Plasma surface treatment has been progressing rapidly over conventional gas or salt-bath processes due to key features such as its nonpolluting, energy saving and distortion free processing. In addition, it can be automated and used on selected areas. The use of plasmas for treatment of steel surfaces has been known as early as 1940s as an important surface-hardness process on components for military use. Plasmas today are used to improve material surface properties such as hardness, strength and corrosion resistance [1–4].

Some authors have shown that the effect of nitriding on corrosion may improve or deteriorate, depending on the type of material and environment used. What is the role played on the type of material, physical and metallurgical properties of nitride layers and reactor parameters on the corrosion resistance? In this paper, we present results on the electrochemical tests performed on the nitrided and untreated AISI 4140 steel in aqueous NaCl solutions submitted to different thermal treatments. Samples oxidized in different cooling cycles have been evaluated. The potential for pitting initiation and propagation as well as pitting protection in the chloride environment was determined.

## 2. Experimental section

### 2.1. Material

The commercial AISI 4140 steel had the chemical composition as shown in Table I. The specimen as-received was divided in two lots, according to thermal treatment; the first lot was first quenched at 850 °C and tempered for 1 h at 600 °C and the second lot was annealed at 900 °C. The thermal treatment will be further referred to as Q&T for quenched and tempered and A for annealed. After thermal treatment, the material was machined to disc-shaped specimens (diameter 11 mm, thickness 5 mm) for testing. The steel samples were polished using 1  $\mu\text{m}$  alumina. After ultrasonic cleaning in petroleum ether, specimens were dried and stored under vacuum in a dessicator. Prior to the ionitriding, the samples were submitted to a supplementary cleaning in the plasma reactor using a hydrogen glow discharge at 1.6 torr and 600 V for 45 min to remove possible remaining surface impurities.

### 2.2. Chemicals

All chemicals were analytical grade reagents, and distilled water was used to prepare the solutions. Argon,

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hydrogen and nitrogen ultra pure grade, was purchased from White Martins. The samples were a commercial AISI 4140 steel; the elemental analysis is shown in Table I and agrees with the expected chemical composition for the AISI 4140 steel.

### 2.3. Plasma nitriding

The plasma nitriding unit utilized in these experiments was similar to the system described in previous studies [5]. The gas mixture was 75% N<sub>2</sub> + 25% H<sub>2</sub>. The temperature, fixed at 540 °C, was monitored using a chromel–alumel thermocouple embedded in the steel sample. All plasma nitriding experiments were performed at 3 torr, which was measured using an absolute MKS baratron gauge. The ionitriding was performed in the plasma for 120 min. Unless otherwise stated in the text, times greater than 120 min were also used. The cooling cycle procedure was performed by cooling the system in either the nitriding atmosphere or in the air atmosphere. In the former procedure, the surfaces of the samples acquired a bluish colour, probably due to the oxidation of the nitrided layer surface. Low angle X-ray spectroscopy was performed in a Philips (PW 1140) diffractometer for polycrystals, using a FeK<sub>α</sub> radiation and a manganese filter.

### 2.4. Electrochemistry

Potentiodynamic measurements were carried out in 3% NaCl solutions at 25 °C with a potential sweep rate of 0.3 mV s<sup>-1</sup>. The experiments were carried out after immersion for about 30 min when the open circuit potential became steady. In a pitting experiment, the potential scan beginning at -50 mV versus E<sub>corr</sub>, continued in the anodic direction at a threshold current which was previously set as 150 μA cm<sup>-2</sup>. When the threshold current is reached, a user-programmed potentiostat reversed the potential scanning in the

cathodic direction. All measurements were carried out with a Princeton Applied Research (PARC) Model 273A Potentionstat/Galvanostat interfaced with a DOS compatible computer through a National Instrument General Purpose Interface Board (GPIB). The commercial program, a Princeton Applied Research (PARC), Softcorr Corrosion Measurement Software Model 342 was employed for data acquisition and analyses. In a conventional electrochemical cell, a graphite rod and a home made Ag/AgCl served as the counter and reference electrode, respectively. The performance of the reference electrode was monitored by testing against a commercial Ag/AgCl electrode using a 3 1/2 digit voltmeter. The measured < 40 mV between the two reference electrodes was acceptable. To minimize the *iR* ohmic drop, a luggin capillary was employed.

## 3. Results and discussion

Since nothing is known about the thermal memory of the samples, a thermal treatment was performed. Muzart *et al.* [6] found a dependence between the microhardness and the thermal treatment. It can be advanced that, in the potentiodynamic tests, no perceptible difference between the Q&T and A lots were observed. The following discussion therefore does not emphasize the thermal treatment. By means of optical microscopy it was possible to characterize the nitride layer with respect to thickness and regularity. Fig. 1a and b show the nitride layer by means of a cut through the test samples. Nitrided samples of lots Q&T and A present a white layer (or compound layer) averaging 10 to 12 μm thickness, a little more higher than that observed for the A steels (around 9 to 10 μm). It may also be observed that the inverse in nitriding times does not alter significantly the thickness of the nitrided layer; therefore, times above 2 h became unnecessary, even when the layer maximum thickness reached around 22 μm, since the corrosion strength of the nitrided layer is determined by the layer minimum thickness. It may be observed in these figures that there are regions where the nitrided layer is thinner; there are also regions where small “isles” of non-nitrided material are present, which nearly reach the

TABLE I Elemental chemical analysis of AISI 4140 steel

Element	C	Si	Mn	Cr	Ni	Mo
Composition (%)	0.3–0.4	0.22	0.86	0.97	0.14	0.16

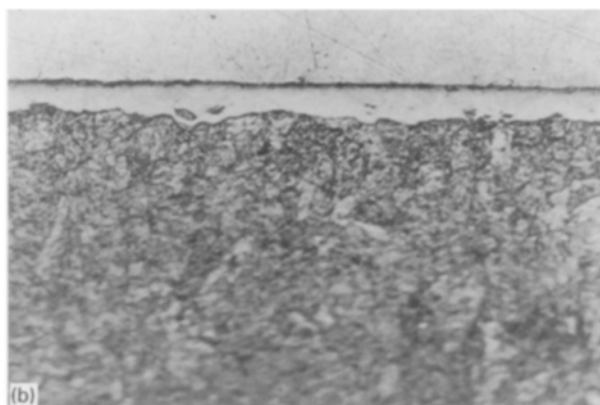
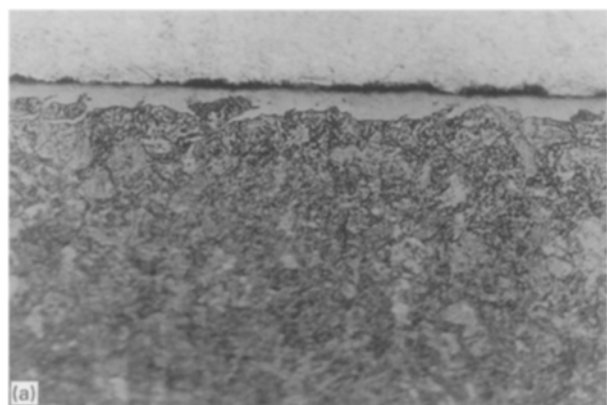
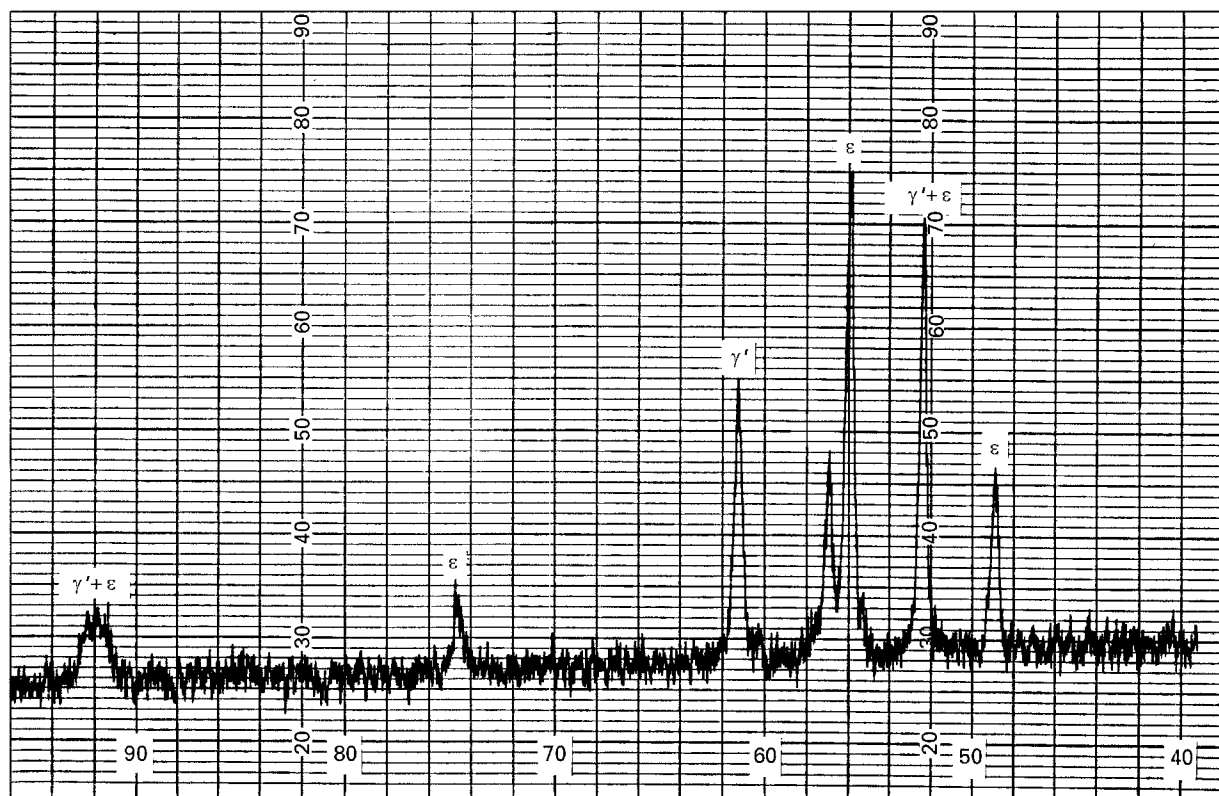


Figure 1 (a) Transversal cut in a nitrided test sample with irregular white layer. Magnification: × 500. Etchant: nital 2%. Small substrate “isles” may be observed. (b) Transversal cut through a test sample exhibiting a highly regular nitrided layer. Magnification: × 500. Etchant: nital 2%.



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Figure 2 X-ray diffractograms from a nitrided sample.

surface. These regions may represent weak points in the nitrided layer.

Fig. 2 shows an X-ray diffractogram obtained from a nitrided steel sample. The presence of the  $\gamma'$  and  $\epsilon$  phases in the nitride layer is clearly noticeable. Unfortunately, problems due to the X-ray absorption by the nitrided and oxide layers have not allowed a quantification of the  $\gamma'$ ,  $\epsilon$  and oxide phases. Thus, it was not possible to detect any relative difference between the several lots, specially for the ones exhibiting weak corrosion strength.

For lots subjected to atmospheric air cooling, the presence of oxide, probably  $\text{Fe}_3\text{O}_4$ , in the surface layer was observed. However, a definite conclusion is not possible, as only two peaks were detected, which are in accordance with the more intense peaks of these oxides. With regard to the formation of a passivating layer over the nitride layer, it was obtained through potentiostatic polarization under 380 mV versus Ag/AgCl, during three hours for subsequent evaluation. In other samples, already electrochemical tested, oxide peaks were also detected.

The  $E_{\text{corr}}$  versus time tests show a highly desirable behaviour for the nitrided steel, with a profile which is identical to one of the materials subjected to surface passivation, thus reaching a "nobler" state, as is the case of chromium, nickel and iron steel [7, 8]. The presence of the passivating layer over the nitrided steel had already been suggested by Chyou and Shih [9].

As can be seen in Fig. 3, the potentiodynamic profile represents the behaviour of a very resistant material with regard to anodic polarization, and is similar to titanium and inox steel, which generally present themselves as passivated. No transition through critical

potentials is observed, in order for passivation to occur. Curve (b) in Fig. 3 shows the potentiodynamic tests of a nitrided sample and curve (c) in Fig. 3 the white (non-nitrided) steel. A significant improvement in the corrosion strength for the nitrided steel is noticeable, when compared to the non-nitrided steel. The anodic dissolution current densities for the nitrided steel are of the order of  $10^{-6} \text{ A cm}^{-2}$ , whilst for the non-nitrided steel they are of the order of  $0.1 \text{ A cm}^{-2}$ , thus representing a difference of five orders of magnitude.

The tendency towards pit-type corrosion attacks was evaluated by the cyclic polarization technique. Fig. 4 represents the behaviour of a nitrided sample with a 12  $\mu\text{m}$  thick layer. It may be observed that  $E_{\text{pit}}$  (the pitting potential) is of the order of 580 mV versus Ag/AgCl. The hysteresis loop is relatively small and  $E_{\text{pro}}$  (the protection potential) is close to  $E_{\text{pit}}$  (500 to 560 mV). These are characteristic, associated with the high value of  $E_{\text{pit}}$ , and indicate a good material strength with respect to pitting. No differences were observed due to the employed thermal treatments.

Atmospheric sample cooling is an important alternative for it allows a more versatile use of the reactor. Samples thus cooled acquire a blue oxide surface layer. Additionally a perceptible difference between nitrided and superficially oxidized steel, with respect to normal nitrided steel, is an initial  $E_{\text{corr}}$  value already of the order of  $-130$  to  $-100$  mV versus Ag/AgCl, advancing to positive values, whilst the normal nitrided steel starts around  $-200$  to  $-170$  mV, advancing to positive values, whilst the normal nitrided steel starts around  $-140$  to  $-110$  mV versus AgCl. The most expressive results for the increase in general

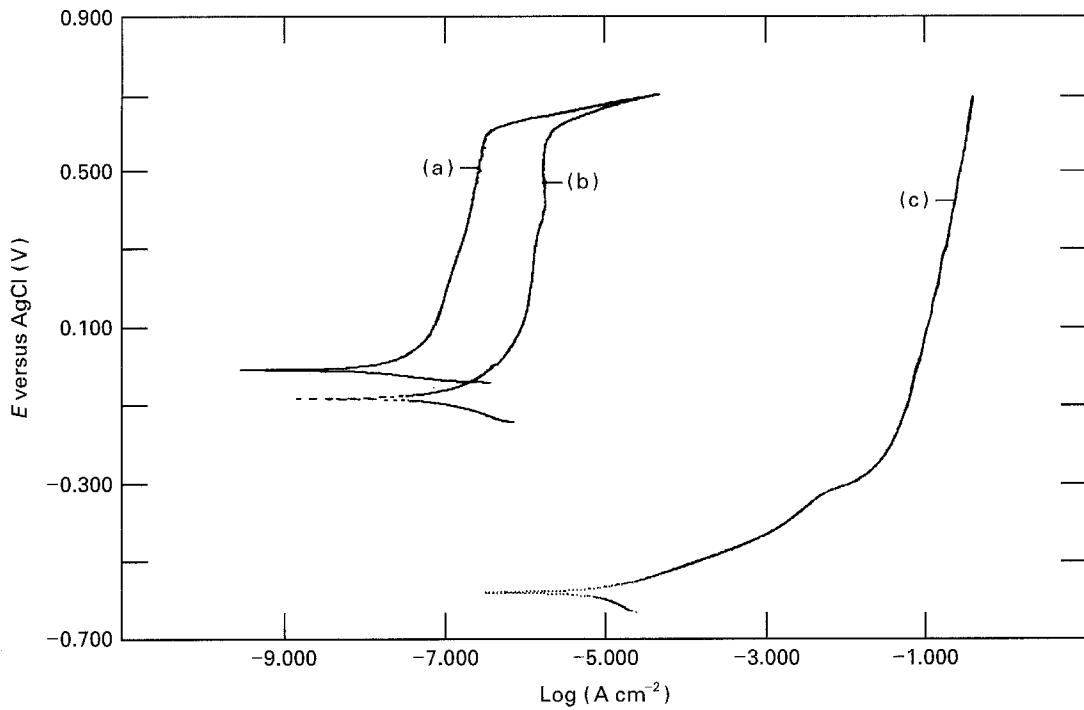


Figure 3 Potentiodynamic tests obtained in 3% NaCl from nitrided post-oxidated (a), nitrided (b) and non-nitrided (c) samples.

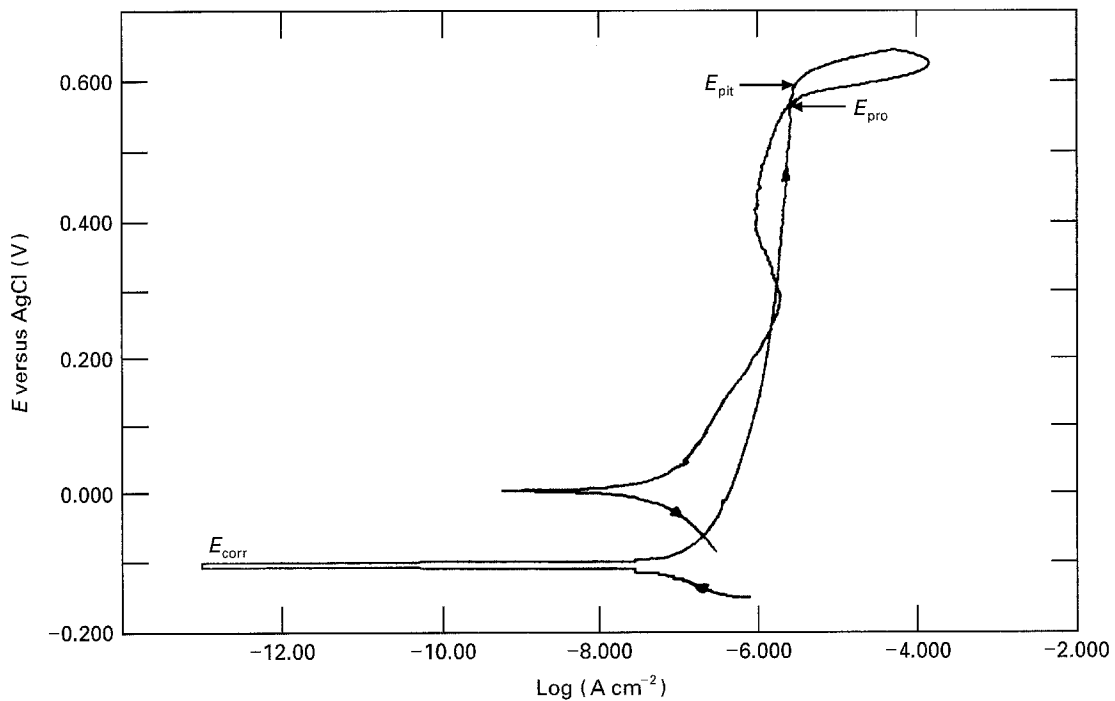


Figure 4 Cyclic polarization test obtained in 3% NaCl.

corrosion strength in nitrided-oxidized steel can be observed through potentiodynamic tests. These tests have shown that the anodic dissolution current densities have been reduced, in some cases, by one order of magnitude, reaching values between  $0.1$  to  $0.5 \mu\text{A cm}^{-2}$  as compared with those samples not submitted to the atmospheric cooling.

The behaviour of the nitrided-oxidized steel can be seen in Fig. 3 (curve (a)). The differences between the anodic dissolution current densities can be clearly seen, as well as the displacement of  $E_{\text{corr}}$  to nobler

regions. Cyclic polarization tests have shown that the oxide layer is attacked by the potentiodynamic sweep, as can be seen in Fig. 5, where a larger current density is verified in the reverse sweep than in the initial sweep. In this figure it can also be observed that the hysteresis loop closes for a  $E_{\text{pro}}$  value (approximately  $75 \text{ mV}$  versus  $\text{Ag}/\text{AgCl}$ ) which is much smaller than the values observed for normal nitrided steels, indicating a larger susceptibility to pitting attack. This behaviour may be traced to the relative fragility of the oxide layer, when subjected to the chloride ion attack [7, 8],

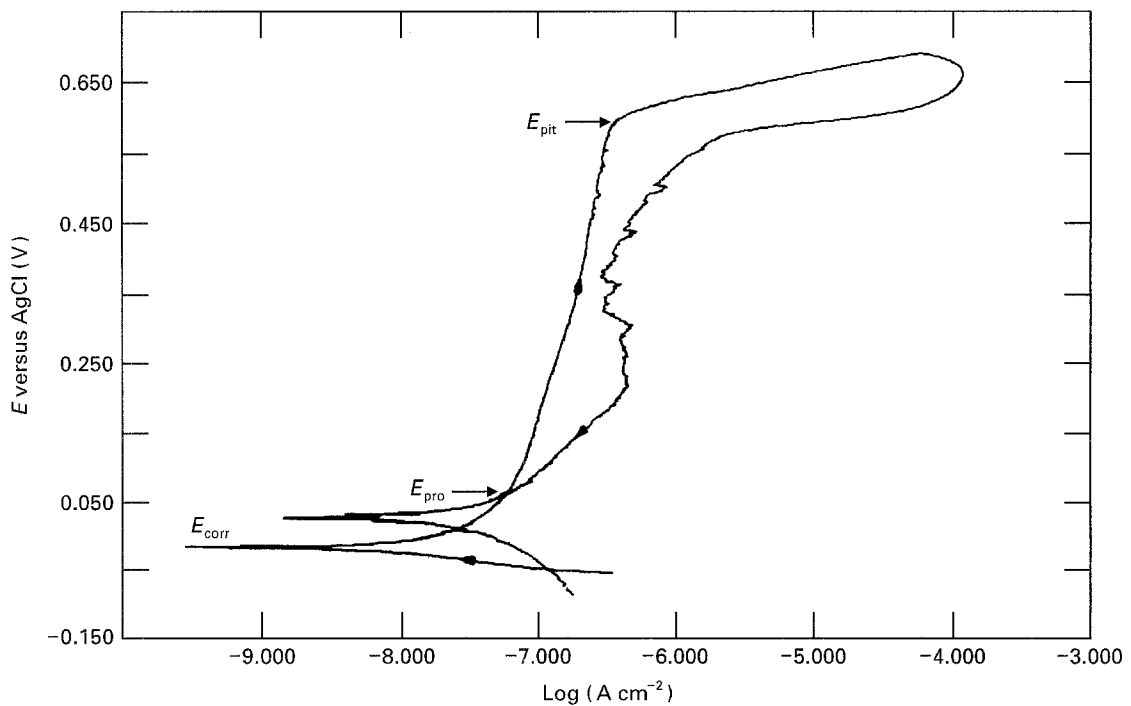


Figure 5 Cyclic polarization test obtained in 3% NaCl, with nitrated post-oxidized sample.

which may probably pierce it more easily than the nitride layer, thus initiating corrosion by potential difference between the different exposed layers.

#### 4. Conclusions

Nitrated samples have significantly lower corrosion rates in comparison with those of non-nitrated steel in 3% NaCl solution.

No observable difference between samples submitted under different thermal treatment was found.

The samples subjected to atmospheric air cooling have lower corrosion rates in comparison with those subjected to reactional atmospheric cooling.

Nitrated samples show a tendency towards pit attack in 3% NaCl solution with no observable difference due to employed thermal treatments. Samples subjected to atmospheric air cooling are more susceptible to pit attack as compared with those subjected to reactional atmospheric cooling.

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