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The Adherence of Growing Copper and Iron Oxide Scales to Quartz Glass, Corundum and Platinum

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ABSTRACT

During oxidation of metals the growing oxide or sulfide scales sometimes adhere to adjacent solid substances when mutual contact is taking place. A simple method for detection of this phenomenon has been elaborated. The adherence phenomenon was studied in the following systems: oxide scales growing on iron or copper in air at 500°C - 900°C in mutual contact with quartz glass, corundum or platinum (contact materials). From the six studied combinations of growing scale/contact material interfaces, only on the iron oxide scale/platinum interface was the adhesion effect not detected. The reaction time required to obtain adhesion dropped with increasing oxidation temperature. Subsequent decohesion was in many cases accompanied by cohesion failures either in the scale or the contact material. This is evidence that the adhesion forces on the newly developed interface are sometimes strong and can reach values of the order of cohesion forces in both substances.

INTRODUCTION

During oxidation of metals growing oxide or sulfide scales sometimes adhere to adjacent solid substances during mutual contact. For example, a growing copper oxide scale adheres to quartz glass at 1050°C /1/, and a copper sulfide scale to sodium-calcium glass at 450°C /2/. This phenomenon has not yet been thoroughly investigated. In this paper we present the results of investigations of this effect when oxide scales growing on copper and iron reach intimate contact with contact materials (CM) such as quartz glass, corundum and platinum.

METHOD OF EVALUATION OF ADHESION IN THE GROWING SCALE/CONTACT MATERIAL SYSTEM

The evaluation of adherence of the scale to the contact material surface can be carried out either during the course of the oxidation process or after stoppage and cooling of the specimen set: oxidisable metal/CM. In the first case the evaluation of adhesion presents experimental difficulties and in the second only the residual adherence is tested, but it is very easy to detect. In this work the author decided to evaluate adherence using the second system, i.e. after stopping the reaction, because these studies are only preliminary and it was necessary to ascertain the adhesion only qualitatively.

After the specimen set – oxidisable metal/CM – is taken out of the furnace, adherence discloses whether:

a. forces are needed to remove the contacting surfaces,
b. as a consequence of thermal dilatation cohesive failures are formed on the contact area scale/CM.

The geometry of the initial contact area between the oxidisable metal and the surface of CM may be:

a. two-dimensional (i.e. contact of two flat surfaces),
b. linear (i.e. knife-edge like contact), or
c. point contact.

After the oxidation process commences, the growing scale gradually covers the CM surface.

Use of an initial two-dimensional contact area is not suitable, because its oxidation conditions cannot be strictly defined. Initially, the oxidation process takes place simultaneously in the immediate vicinity of the oxidizing atmosphere and in the crevices between both surfaces (Fig. 1). In the crevice, the oxidation rate is

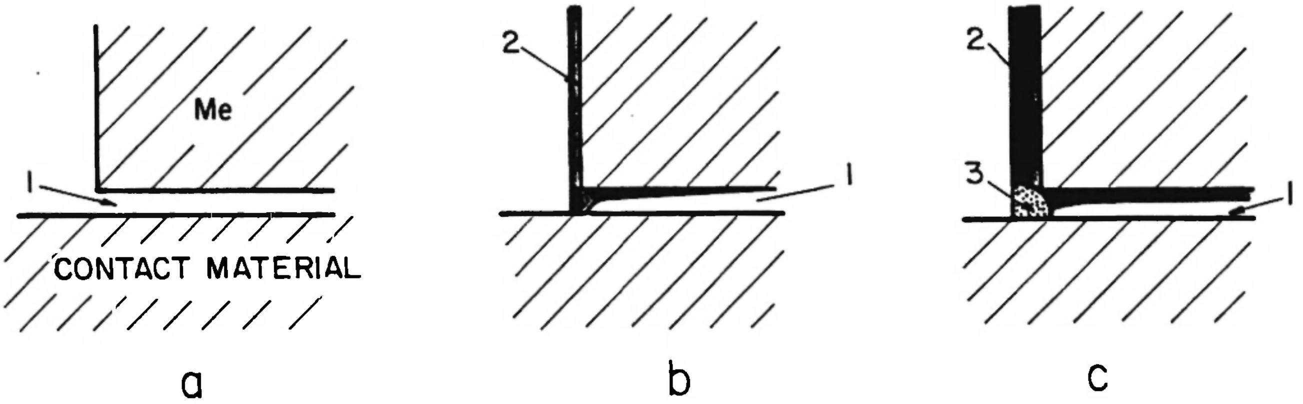

Fig. 1: Initial two-dimensional contact oxidisable metal/contact material: a. before the reaction, b. crevice is closed by the growing scale, c. partially disturbed scale, 1 – crevice, 2 – scale, 3 – disturbed region.

lower because the partial pressure of oxygen drops there. In the next stage of the reaction the oxidation product, which grows in the immediate vicinity of the oxidizing atmosphere, hinders the penetration of oxygen into the crevices, but this does not mean that the oxidation process must be completely arrested. The source of oxygen may be the process of internal dissociation of the scale, which causes its destruction /3/. In consequence, the reproducibility of contact conditions between the scale and CM are poor, as was shown during the introductory experiments.

In the case of an initial linear contact between the oxidisable metal and the CM, the oxidation process on the metal surface is not disturbed until the time at which the given part of the growing scale reaches intimate contact with the CM surface. If an "edge" from the oxidisable metal is used, the flat surface of CM gradually enters into contact with the growing scale (Fig. 2a,b). When the "edge" is from the CM, the situation is different, because during oxidation it is gradually wedged in the growing scale (Fig. 2c,d). It is not inconceivable that in this case a pure mechanical fastening of CM may occur due to the growing scale (clamping) during the oxidation process. During the cooling of the sample set the distribution of stresses in the region of contact area is also different by comparison with the first one.

The initial point contact has as many analogous properties as the linear contact, but there are essential differences, when we consider the real course of the oxidation process. When the "needle" is made from an oxidisable metal, the limited volume of metal in the region of a needle point means that after a relatively short time of oxidation it is completely consumed.

From the above considerations, it follows that the most advantageous kind of initial contact between the oxidisable metal and the CM is a knife-edge like contact, as shown in Fig. 2a,b.

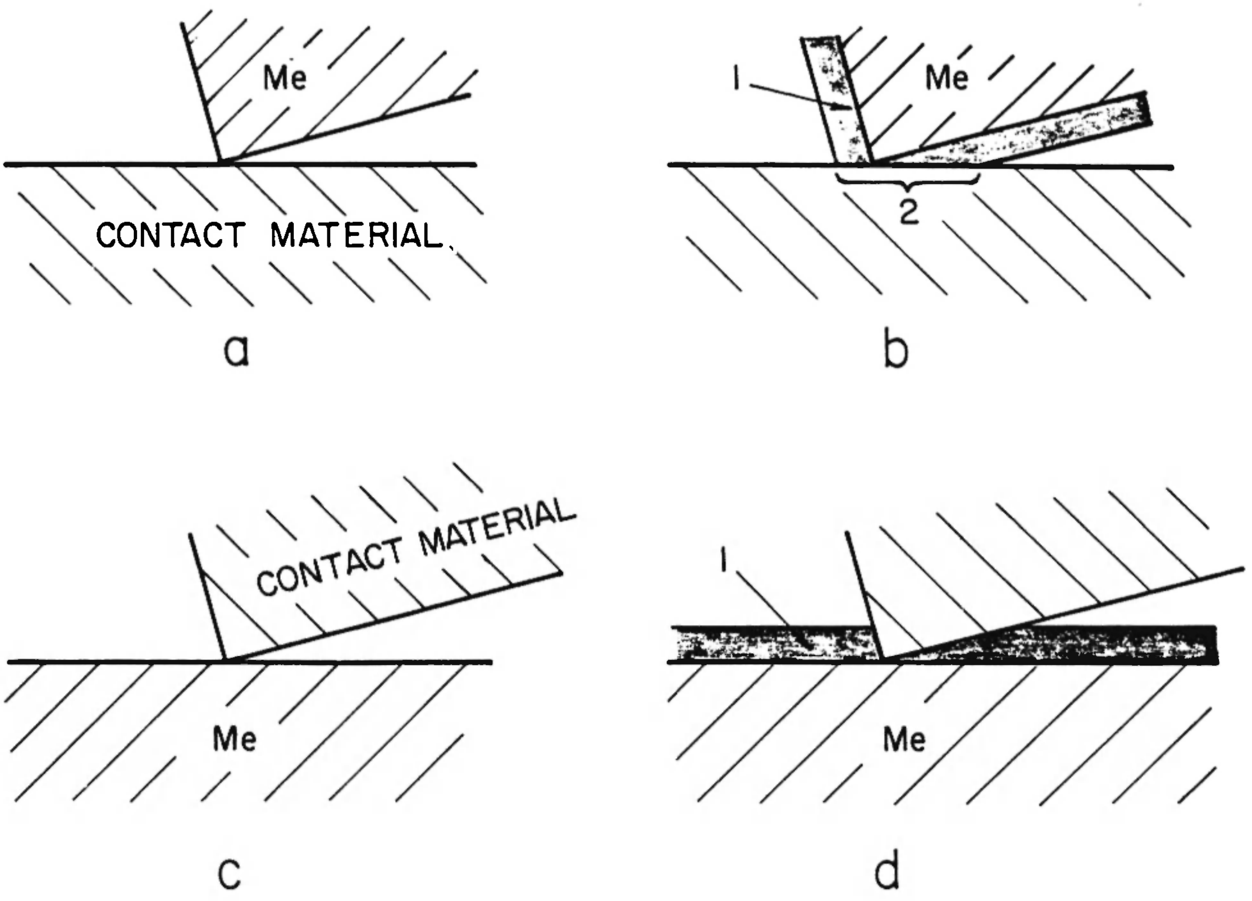

Fig. 2: Initial linear contact oxidisable metal/contact material: a, c – before reaction, b,d – scale is formed, 1 – scale, 2 – contact area interface.

EXPERIMENT AND RESULTS

Samples of oxidisable metals were prepared from ARMCO iron (99.9% Fe) and electrolytic copper (99.9% Cu) sheet. The samples were rectangular in shape (15x10x1.5 mm) and before the experiment they were first polished on grit paper to grade 800 and then degreased in ethanol and acetone. Table 1 gives specifications of the CM used. The surfaces of these were also degreased in ethanol and acetone before the experiments.

TABLE 1

Contact Materials (CM)

Material	Surface condition
Quartz glass slices for optical use	original surface from producer (Heraeus)
Corundum monocrystal split along cleavage plane	diamond polishing finished with 1 μm grains
Platinum sheet for chemical application	original surface from producer

Structure of the specimen set oxidisable metal/CM is shown in Fig. 3. The plate and prop were made from refractory ceramic whose high surface roughness preserved the shift of both samples in the specimen set during the operation of inserting and withdrawing it from the reaction chamber. Only the narrow corundum samples were mounted in assemblies with ceramic plates. The initial contact between both samples was linear. The angle between them was in the range 5°-15°.

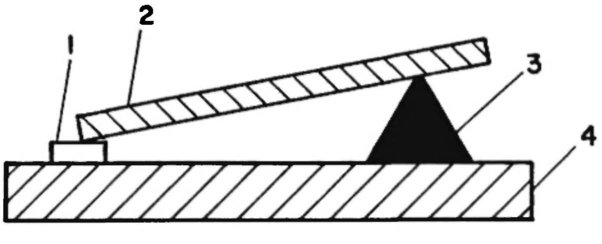

Fig. 3: Arrangement of samples in specimen set: 1 — contact material, 2 — oxidisable metal, 3 — prop, 4 — support.

The oxidation process was carried out in a chamber furnace in the temperature range 500°-900°C in air (the temperature was controlled to within an accuracy of ±5 deg). The specimen sets were removed from the furnace after three standard exposure times: 5, 10 and 24 hr. During cooling, adhesion was checked by upward movement of the oxidized metal sample, and after cooling by observation of both sides of the contact area.

Adhesion took place if the following were ascertained:

- simultaneous rising of adhering samples during upward movement,
- mechanical resistance connected with breaking of the adhesion bond (in corundum samples mounted in supports),
- adherent remainders of scale and/or CM on contact area surfaces.

Table 2 tabulates the shortest standard exposures after which the adhesion effect takes place. It can be seen that from the six combinations studied growing scale/CM interfaces only on the iron oxide scale/platinum interface was not observed. In the other cases the reaction time required to obtain adhesion decreased with increasing oxidation temperature. This did not differ significantly for the same temperatures for different kinds of contact areas.

TABLE 2

Shortest time exposures required to obtain the adhesion effect (hr)

Oxidisable metal	Contact material	500°C	600°C	700°C	800°C	900°C
Iron	quartz glass	24	24	10	5	5
	corundum*	24	24	10	5	–
	platinum	none	none	none	none	none
Copper	quartz glass	24	10	5	5	5
	corundum	24	24	5	5	–
	platinum	24	24	10	5	5

* Experiments with corundum contact were not made at 900°C.

After decohesion, adherent scale or CM< fragments were often found on the contact areas. Fig. 4 shows the microphotographs of both sides of the contact area of iron oxide scale/quartz glass formed at 500°C. From the quartz glass side losses of quartz and adherent remainders of the scale are seen, and the scale side shows adherent quartz spalls. At higher temperatures the quartz losses on the quartz glass side are reduced (Fig. 5). Fig. 6 shows the remainder of copper oxide scale on a platinum surface.

Experiments were performed in order to check the possibility of adhesive bond formation between quartz glass and scales removed from the cores. Scales formed

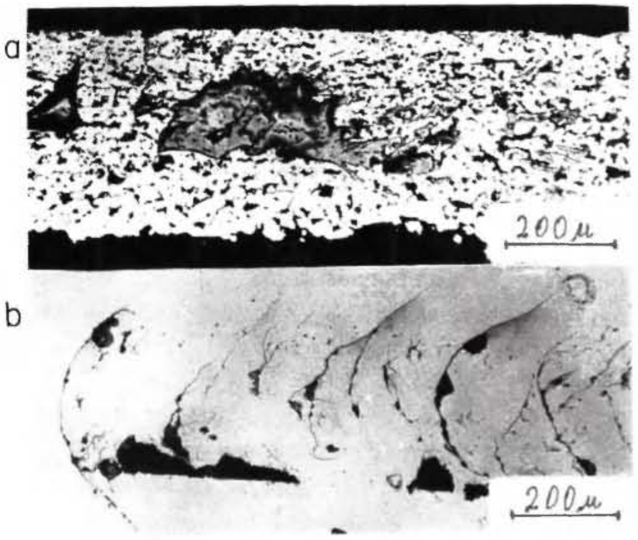

Fig. 4: Interface iron oxide scale/quartz glass (500°C, 24 h): a. scale side with quartz glass spalls, b. quartz glass side with scale remainders and quartz losses.

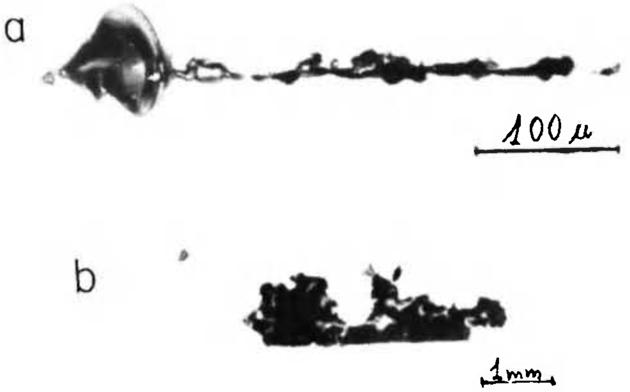

Fig. 5: Quartz glass side of iron oxide scale/quartz glass interface: a. 600°C, 24 h; b. 700°C, 10 h.

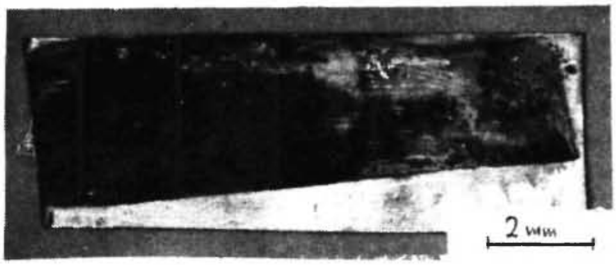

Fig. 6: Remainder of copper oxide scale on platinum (500°C, 24 h).

on iron and copper samples by heating in air at 1000°C for 20 hrs were removed from the cores and broken into pieces of –0.25 mm^2 area. The scales were placed on quartz slices and covered with similar slices. These sandwiches were held in air at 500°, 700° and 800°C respectively for 24 hrs. After heating, signs of adhesion on the contact area were not detected. In similar experiments performed with iron and copper powders, good adhesion of the oxidized metallic particles to the quartz was observed.

DISCUSSION

The results shown in Table 2 are not the true kinetic data for the formation of an adhesive bond on the interface growing scale/CM, since the evaluation of adherence took place after the reaction, and it is possible that after shorter standard exposure a rapid decohesion occurred without visible changes on the contact area. On the other hand, these results have evidently shown that the formation of an adhesion bond on the CM surfaces does occur, and that the time needed for its formation is temperature-dependent.

These results are only qualitative, but a limited estimate of strength of adhesion forces on the interface growing scale/CM is possible. When decohesion is accompanied by cohesive failures on the contact area, which are shown by material losses or adherent remainders on both surfaces (Fig. 4), there is evidence that the adhesion forces are sometimes strong and can reach values of the order of the cohesion forces in both materials. This estimate does not apply when the scale has spalled from an oxidized metal surface during cooling. In this case the scale remainder may also adhere to CM when the adhesion forces are relatively weak and do not participate in the spalling process.

Iron oxide scale had good adhesion to the iron substrate after 24 hr oxidation at 500°C. Sometimes partial spallation took place after sample cooling, but the decohesion on the interface scale/CM was always earlier. The presence of scale spalls on the quartz side of the contact area and simultaneous losses of quartz (Fig. 4) was evidence that adhesion forces were similar to cohesion force in both materials. At higher temperatures the adhesion forces on the contact area of the iron oxide scale/quartz are weaker, because the quartz loss is less (Fig. 5). On the other hand, the presence of scale spalls is no proof, since scales have a much greater tendency to spall from the surface of iron samples used at these temperatures.

At 500°C scale remains on the platinum side of copper oxide scale/platinum interface are seen (Fig. 6), but this is no indication of the magnitude of the adhesion forces, since the scale can easily be spalled from the corners of copper samples.

The lack of adhesion on the interface between scale derived from cores and quartz glass shows clearly that the adherence effect discussed here is connected with the expansion of the growing scale on the CM surface. In fact the scale pieces reacted with oxygen since they contained a preponderance of lower oxides which oxidize to higher ones under the experimental conditions given above. The primary oxide scales were formed at 1000°C in air, so that the pieces of copper oxide scale consisted only of Cu_2O /4/, while the iron oxide scale consisted of more than 95% $Fe_{1-x}O$ /5/. During heating in the temperature range 500°-800°C, oxidation of Cu_2O to CuO and $Fe_{1-x}O$ to Fe_3O_4 and Fe_2O_3 took place. The oxidation process of lower oxides is generally much slower than the oxidation of metals. Hence, the rate of contact area formation between scale pieces and CM is lower than by oxidation of metals, and no adhesive bond can form in the time available.

To continue, we would like to make a few assumptions about the probable processes which take place on growing scale/CM interfaces.

Both copper and iron-oxide scales grow by cation-transport processes, so that the scale-forming process takes place on the outer surface of the scale. The newly-produced lattice planes are not completely ordered, which can lead to the following interactions on the interface growing scale/solid substance:

1. The atom order on the CM surface enables a fitting effect to the atoms on the outer planes of growing scale, as in the effect of epitaxial growth.
2. On the incompletely ordered outer lattice planes of the growing scale, the rate of chemical reaction with CM can be higher than in conventional conditions, and thus, at relatively low temperatures, a thin intermediate compound layer can be produced.

The adhesive bond between the copper oxide scale and quartz glass may be connected with the first type of interaction because copper silicates are known to be unstable /6/. On the iron oxide scale/quartz glass interface a formation of a stable silicate such as fayalite (Fe_2SiO_4) is possible. With corundum, formation of a stable aluminium-iron spinel can occur. Aluminium-copper spinels are stable only at temperatures over 800°C /7/. The author has found no data about the formation of ternary compounds in the system Cu-Pt-O.

The chemical composition of the scale at a fixed point on the interface growing scale/CM changes during the reaction. From the moment at which the scale reaches intimate contact with CM the free supply of oxygen to it is cut, but the cation flow is not disrupted so long as the activity of oxygen there is higher than in the inner part of the scale. In consequence, the chemical composition of the scale gradually changes at this point. In copper and iron oxide scales this leads to phase transitions, because they both have more than one phase in given reaction conditions /4,5,8/. The phases with highest oxygen concentration as CuO or Fe_2O_3 are located on the edges of the contact area. In the case of copper oxide scale or iron oxide scale below 570°C, at the inner contact area Cu_2O and Fe_3O_4 respectively are located. Above this temperature in the iron oxide scale we have three phases and they are located on the contact area, as shown in Fig. 7. These considerations suggest that the chemical properties of the scale surface on the given point of contact area interface alter with duration of contact time.

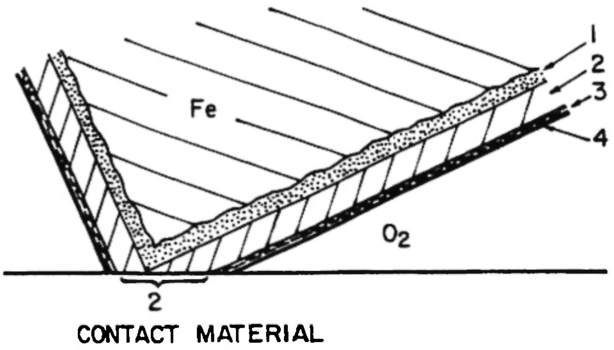

Fig. 7: Sequence of iron oxides on the contact area: 1 – $Fe_{1-x}O$ (wustit) formed in the metal consumption zone, 2 – $Fe_{1-x}O$, 3 – Fe_3O_4, 4 – Fe_2O_3.

During the exposure of the sample set (Fig. 3) in the furnace several processes can take place on the surface of CM, which are dependent on its chemical composition and the sample preparation. The surface of quartz glass and corundum are chemically stable in given experimental conditions. Because the surfaces of both materials were mechanically treated (polished) before the experiments, a recovery process is possible, which may affect surface roughness. On the other hand, on the mechanically treated surface a mechano-chemical effect can appear, leading to an increase in the rate of the chemical reaction between CM and scale. On the platinum surface the formation of a very thin PtO_2 layer takes place /9/.

The affinity of platinum to oxygen is much below that for copper and iron, and when contact between the platinum surface and growing copper or iron oxide scale was obtained, the influx of cations to this interface acted as a reducing agent. The reduction of the PtO_2 layer can change the surface roughness of platinum.

Before beginning the experiment the CM surfaces were cleaned by using the conventional degreasing technique of rinsing first in ethanol and then in acetone at room temperature. It is possible that contaminants remain on the surface which react with the scale and form a thin bonding interlayer.

When the growing scale penetrates into surface irregularities of CM, filling these spaces, the scale tongue may connect the scale to the CM, causing keying. Both the quartz glass and corundum surfaces were polished with fine grain abrasives, whereas the platinum surface was smooth-rolled (Table 1). Both surface treatments reduced the possible appearance of keying.

On the basis of the results obtained and the author's earlier observations (Table 3) we can assume that adherence of growing scale to the surface of a solid substance is a fairly common phenomenon. The mechanism of this adherence effect cannot yet be explained because there is insufficient experimental evidence to form any working hypothesis. Future research should be aimed at kinetic investigations of adhesion bond formation on the interface growing scale/CM, and evaluation of the magnitude of adhesion forces. The discussed adhesion effect must be controlled on many and various systems growing oxide or sulfide scale/CM. The surface treatment of CM must be more definite and diversified from the point of view of initial surface conditions and their influence on the adhesion effect.

TABLE 3

Systems in which the adhesion effect was observed

Growing scale	Contact material	Temperature °C
Sulfide scale on copper	KCl monocrystal	445
Sulfide scale on copper	platinum	445
Sulfide scale on silver	platinum	445
Sulfide scale on cobalt	quartz glass	700
Oxide scale on copper	silver	500
Oxide scale on iron	silver	500
Oxide scale on cobalt	quartz glass	700

CONCLUSIONS

1. A simple method for detecting the adherence effect of growing scale to solid substances was discussed.
2. Among the six combinations studied of a growing scale in contact with a solid substance (iron oxide or copper oxide scale on quartz glass, corundum or platinum) no adhesion effect was detected solely on the iron oxide scale/platinum interface.
3. The reaction time required to obtain adhesion decreased with the increase in oxidation time.

4. Adhesion forces are sometimes strong and can reach values of the order of the cohesion forces within the scale and/or within the contact material.

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