

CORROSION AND CORROSION PREVENTION IN
GAS TURBINES

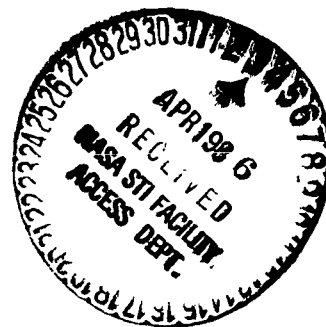
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CORROSION AND CORROSION PREVENTION IN GAS TURBINES

by

A. J. A. Mom and H. J. Kolkman

Summary

The conditions in a gas turbine that govern corrosion behavior are surveyed. /1*
Factors such as temperature, relative humidity, the presence of sulphur and nitrogen dioxide, fuel quality, etc. are discussed.

Next the different forms of corrosion in gas turbines are treated:

- electrochemical corrosion at relatively low temperature in compressors
- oxidation and hot corrosion (sulphidation) at high temperatures in turbines

There are various methods to combat these corrosion processes: washing and rinsing, the use of fuel additives, the application of corrosion-resistant materials and the application of coatings.

The background and merit of these methods are discussed.

Paper presented at the Corrosion Symposium 1982 (theme: Corrosion prevention and control in steam and electric power production), sponsored by the Netherlands Corrosion Center, held on 14 September 1982 in Arnhem.

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1. INTRODUCTION

The corrosion process in two important parts of the gas turbine (the compressor and the turbine) will be discussed. The situation in these two segments is very different. The compressor, as well as the turbine, must contend with impurities in the air entering the unit, but only the turbine comes into contact with impurities in the fuel. Because of the different temperatures involved the corrosion processes are different. Electrochemical corrosion occurs in an aqueous environment in the compressor; oxidation and sulfate corrosion in the turbine.

Still there are certain similarities in the corrosion processes in the compressor and in the turbine. In each case SO_2 and NaCl play a role. In each case as well the use of coatings is one of the possibilities used to prevent corrosion.

2. CORROSION IN COMPRESSORS

The only important corrosion process in compressors is the electrochemical corrosion in an aqueous environment. This environment arises because hygroscopic particles are drawn into the compressor and are deposited on the blades. The particles are already damp when drawn in or they become damp because of a high relative humidity (R. H.). The process is illustrated schematically in fig.1. The possible methods for the prevention of corrosion are indicated at each stage. These stages are described in the following section. 1/2

2.1 The Entry of Hygroscopic Particles

The wind in its passage over the sea carries salty droplets with it. In coastal regions these sea salt particles are drifting around and eventually lose their moisture. The most important component of sea salt is NaCl . If the relative humidity (R. H.) is greater than 78% the salt absorbs water vapor out of the air (see fig. 2). A peculiarity of NaCl is its hysteresis. As the relative humidity drops the salt loses its moisture at 35% R.H. Another component of sea salt is MgCl_2 . It begins to absorb moisture at a relative humidity of 32%.

There are also hygroscopic particles (e.g. $(\text{NH}_4)_2\text{SO}_4$) in the atmosphere in the interior of the country. Meteorologists believe that it plays an important role in cloud formation. It begins to attract moisture at an RH = 61%.

One can prevent to a certain degree the entry of hygroscopic (and erosive) particles into the compressor by the use of filters. One usually uses filters made of cloth. Inertia filters or cyclones are used on helicopters. Here use is made 1/3

of the fact that heavy particles can not readily follow any change in the direction of the air stream.

2.2 Deposition of Hygroscopic Particles on the Blades

The results of salt measurements on the 16-stage compressors used in the DC-8 aircraft^{**} are shown in fig. 3. Indeed there is evidence of the deposition of NaCl especially near the middle of the compressor. The explanation of this is as follows. The function of a compressor (the elevation of the air pressure) results in an increase in the density of salt in the air after each of its stages. The chance that a blade will strike a salt particle therefore increases at each stage. This explains the initial slope in fig. 3. The salt deposition does not only depend on the collision probability but also on its adhesion probability. If a dry salt grain strikes a blade the probability is low that it will adhere to the blade. Conversely the adhesion probability of a moist salt grain is higher. When one realizes that in the Netherlands the relative humidity is almost always greater than 30%, it follows from fig. 2, that the ingested sodium chloride particles will be damp and therefore have a large adhesion probability. The temperature as well as the pressure rises in a compressor in such a way that the salt grains become less and less moist as they progress through the compressor (see fig. 4) and they have a lower adhesion probability. The increasing collision probability together with the dropping adhesive probability result in the observed maximum deposition somewhere near the middle of the compressor.

As well, the adhesion probability for rough surfaces is greater than for smooth surfaces. In other words, a used blade which already has evidence of pitting corrosion will collect more salt than a new smooth blade. Therefore one is advised to begin with early measures against corrosion and not to wait until the corrosion is apparent. 14

Once a salt layer has been deposited it can be removed by rinsing it with water. This requires the compressor to run at a low rotation frequency. Under normal operating conditions the rinse water will evaporate in the process (see fig. 4) and the later compressor stages will not be rinsed. Also, water droplets can also cause blade erosion.

One can also add to the rinse water, liquids (e.g. BB3100, WD 40 and ARDOX 3961) which have a cleansing and water resistive action.

Interesting data can be obtained on the nature of the deposition onto the blades and on the corrosion process by analyzing the rinse water. The NLR is carrying out an investigation of the rinse water.

If the gas turbine is not used directly after the rinsing of the compressor it must still be operated at its normal frequency (and normal temperature) for a period of time in order to prevent rinse water from collecting in the compressor.

An alternative to rinsing is the addition of rice grains into the inlet air. But there is the danger that the blades will be eroded.

** More research has been done on airborne gas turbines than on industrial gas turbines. For this reason several of our examples will relate to airborne gas turbines.

2.3 The Absorption of Moisture during Salt Precipitation

Any industrial turbine in continual operation will attract moisture onto its blades because of salt precipitation. This is only possible in the first stages of a compressor (see fig. 4) and because of that this is why there is corrosion only in the first stages of the compressor.

However the salt is released during the operation of a peak-load or aircraft gas turbine. During no-load operation moisture (and its accompanying corrosion) can be deposited on the elements. Water can be present everywhere in a cooled-down compressor and then corrosion can occur anywhere in the unit. This is one of the reasons why compressors that are used intermittently show evidence of more corrosion than compressors in continual operation.

The absorption of moisture can be prevented by the use of air dryers. This is already customary [2] for the protection of steam turbines, condensers, etc. that have been removed from operation. Air driers are used on a limited scale for the protection of peak-load turbines [3,4] and jet engines. The air input and exhaust are connected in a closed loop with a drier. In this manner the compressor and the turbine can be protected. In general, this is not necessary because of the materials used in the turbine.

2.4 Acidification

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The water droplets formed on the blades absorb CO_2 and especially SO_2 and NO_2 out of the air and become acidic. In fact the water used to rinse a compressor is often acidic. This is important because many metals can dissolve in an acidic environment. Acidification in the Netherlands is especially serious -- a fact evidenced by the presence of "acid rain".

A solution to this problem can be given only if the emissions of SO_2 and NO_2 are reduced, although proposals to reduce the degree of acidity by the injection of ammonia into the inlet air have been made [4].

2.5 Corrosion

Electrochemical corrosion is schematically represented in fig.5. For every anodic reaction (in which metallic atoms give up an electron and then go into solution as a metallic ion) there must be an accompanying cathodic reaction which uses the freed electron.

The following processes are important in electrochemical corrosion:

a) Uniform Corrosion

A metal or alloy undergoes simultaneously and uniformly anodic and cathodic reactions. Here the environment is very important. The situation for a non-alloy low-carbon steel is shown in fig. 5 [5]. High relative humidity, the presence of NaCl on the steel, or the presence of SO₂ in the air each will produce only minimal corrosion. In combination, the corrosion is proportionally greater. The NLR will be carrying out research on AISI 410 (a martensitic steel with 12% Cr) which is often used in the compressors of gas turbines.

b) Galvanic Corrosion

This is the situation when two different metals (or alloys) are involved. One of them acts as an anode (and as a result becomes dissolved), the other as a cathode. Galvanic corrosion can occur in the welding between vanes and stator rings.

c) Pitting Corrosion

Anodic and cathodic reactions occur at different sites in the same metal. This type of corrosion occurs in alloys that have a passive oxide layer; for example, aluminum alloys and rust-resistant steel. The passive oxide layer provides an excellent protection against corrosion but in certain situations the layer can become weakened. At these sites pitting occurs and rapid anodic reactions and solution take place. The cathodic reaction takes place on the remaining passive surface. The weakening of the passive oxide layer can arise because of Cl⁻ions in the environment. This situation occurs when there are salty water droplets on the compressor blades. /6

The presence of this salty droplet leads to a difference in aeration. The cathodic reaction is stimulated at the edges of the droplet because of a greater oxygen supply. The anodic reaction takes place in the middle of the droplet.

Pitting is dangerous because stresses are concentrated in the vicinity of the pits. This could lead to stress fractures starting at the pit site.

A critical situation can develop especially at the foot of the blade where the stresses are the highest. The compressor can be completely destroyed if a blade should break off.

- d) Fractures occur when stress develops in a corrosive atmosphere. This phenomenon can take place in rotating compressors.

Corrosion in gas turbines can be limited by the

- 1) prevention of the formation of corrosive environments, as mentioned earlier.
- 2) use of corrosive-resistant blade materials. Titanium alloys and superalloys using nickel are excellent in the Netherlands environment (high humidity, high concentration of NaCl, SO₂ and NO₂), but they are expensive.
- 3) use of coatings on metals which are less corrosive-resistant.

2.6 Compressor Coatings

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Non-conducting high-temperature coatings no longer protect once local damage occurs in the coating and the underlying material becomes uncovered. Electrically conducting coatings, however, can protect the substrate by acting cathodically (for instance, an aluminum coating on a martensitic rust-resistant steel or a magnesium coating on a low-alloy steel). Then if a small part of the substrate does become uncovered an increasing anodic decomposition of the coating will protect the substrate.

One differentiates electrically-conducting coatings by the way in which they are applied to the substrate.

- a) spray coatings (for example, the various kinds of Sermetel, not all of which, however, are conducting). They coatings are applied using a spray gun. The thickness of the layer is not very uniform, especially on the front and back sides of the blades. An example is given in fig. 7.
- b) diffusion coatings (for example, Al2 from Turbine Support Europe - Chromalloy and HI51 from Heurchrome). Diffusion coatings have a very uniform thickness and can also be applied to cavities in the material. This type of coating is described later in the section on turbine blade coatings.
- c) galvanically applied coatings (for example, NiCd coatings [6]).
- d) electrophoretically applied coatings.

The coatings mentioned above are applied in such thin layers (12-65 μm) that the action of an existing compressor is barely affected when its blades are coated. (Sometimes the power of the compressor is improved because the blade surfaces are smoother; see fig. 7). On the other hand thin coatings are easily eroded away (see fig. 7). An inlet filter is advisable.

The application of a diffusion coating is done at high temperature. For other coatings, heat treatment after the coating is necessary; for example, in the case of spray coatings to evaporate the solvent. The heat treatment (or in the case of diffusion coatings, the brittleness of the coating as well) can detrimentally affect the fatigue resistance of the substrate. One should investigate this point further. Moreover one should compare the erosion and corrosion resistance of various coating/substrate combinations. The NLR has developed a facility (see fig. 8) in which these aspects can be simultaneously investigated in simulated conditions of actual use.

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2.7 Conclusions for Compressors

The corrosion of compressors occurs in various stages. In principle, one can prevent corrosion at each stage. But in practice one would choose one or several of the prevention measures.

3. CORROSION IN THE TURBINE SECTION

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3.1 Introduction

Electrochemical corrosion as occurring in the compressor section of a gas turbine plays almost no role in the turbine section. Materials used here have a very good resistance to that form of corrosion. One possible exception would be in the turbine rotors which are constructed out of relatively low-alloy rust-resistant steel. The corrosion process in the turbine occurs primarily during its operation. Here two types of corrosion can be differentiated.

- 1) oxidation: the point here is the fact that the speed of oxidation increases with increasing temperature.
- 2) sulphate corrosion (hot corrosion): an ever-increasing form of oxidation caused by liquid sulphates on the metal surface. In contrast to oxidation this form of corrosion occurs only in a limited range of temperatures.

3.2 Oxidation

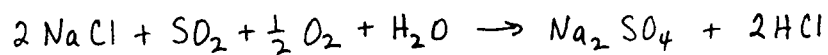
In general only superalloys are used in the turbine section. These are alloys based on Ni or Co and combine a high strength with good corrosion resistance. One usually uses Ni superalloys for rotating components because they have the higher strength (for materials used, etc., see [8]). The increased strength is achieved by the addition of Al and Ti. Cr is added for corrosion resistance. The advantage of Al, besides its effect in increasing the strength, is the improvement in

oxidation resistance. In combination Cr and Al provide a good stable, bonded and sealing oxide layer on the underlying substrate. This is shown schematically in fig. 9. The oxide layer is also suitable for the protection of the substrate from oxidation and sulphate corrosion. A layer of Al_2O_3 because of its greater stability is especially suitable for the protection against oxidation (high temperatures!). A layer of Cr_2O_3 can oxidize further (above $1100^\circ C$) to form CrO_3 and then it will evaporate. Because of this a layer of Cr_2O_3 does not offer sufficient protection. However, the Cr_2O_3 layer does provide the necessary conditions for the good sealing properties of a coating of Al_2O_3 . The presence of a thin uniform oxide layer on the surface of a component does not cause problems during operation. On the contrary, this layer protects the substrate against rapid oxidation because diffusion through the thick layer is inhibited. Any small reduction in cross-section because of the existence of the layer does not lead to unacceptable stress in the component. The situation changes when increased oxidation occurs along grain boundaries (see fig. 10). This leads to an important reduction in the cross-section of the component and to an unfavorable stress development. The fatigue resistance is unfavorably affected. An initially uniform oxide layer can be deteriorated by thermal shock (for instance, in start-stop cycles). If the oxide layer is thrown off, the substrate attempts to form a new oxide layer as quickly as possible. The substrate is somewhat deficient in Cr and Al because of the original layer, so the newly formed layer will have a somewhat more heterogeneous composition. Under variable thermal load this will lead to accelerated loosening. The oxidation will progress even more quickly. The evaporation at high temperature of the Cr_2O_3 layer, mentioned earlier, and the accompanying reduction in Cr will make the formation of a new, well-sealing layer of oxide even more difficult. In general, in spite of the processes mentioned here which could have a negative impact on the operation of a component, oxidation does not present a problem in the current generation of industrial gas turbines. The materials used have such an oxidation stability that no problems arise at the turbine inlet temperatures currently used. The situation could change if the inlet temperature is increased in an effort to achieve higher efficiency. Oxidation could also affect the expected lifetime of the component in cases where no sulphate corrosion takes place (for example, when 'clean' natural gas is used). The use of oxide coatings could increase the already long lifetime of the component (often in tens of thousands of hours).

3.3.1 Symptoms and Necessary Conditions

Sulphate corrosion is a very accelerated form of oxidation caused by liquid sulphates on the metal surface. This form of corrosion is characterized by a very rapidly developing corrosion front. (fig. 11). The upper layer consists of a porous oxide. Below there are corrosion products and even zones of uncorroded substrate. In advance of the corrosion front one often sees a zone of sulphides (usually chromium sulphides) imbedded in a somewhat chromium-deficient matrix. A necessary condition for sulphate corrosion is the presence of liquid sulphate, normally Na_2SO_4 . This has its origin in

- a) the inlet air. Na_2SO_4 occurs in sea water and is present in coastal regions.
- b) a reaction between Na and S compounds. The sulphur can originate in the fuel or be present in the inlet gas as SO_2 or SO_3 . Na is often present also in the fuel or it is drawn in with the inlet gas as NaCl. Na_2SO_4 can be formed in the following reactions:.



or



Sulphate corrosion occurs in the temperature range in which Na_2SO_4 is liquid. The lower temperature limit of this range is the melting point of Na_2SO_4 (884°C). However the melting point is reduced if other substances are dissolved in the Na_2SO_4 . The melting point of the Na_2SO_4 -NaCl eutectic is about 630°C [9]. If V_2O_5 is present the melting point is even lower. The V_2O_5 - Na_2SO_4 eutectic has a melting point of 525°C [10].

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The upper temperature limit for sulphate corrosion is the dew point of Na_2SO_4 . The dependence of the dew point on temperature, pressure in the turbine and the concentration of salt in the inlet air is illustrated in fig. 12. The reactions mentioned under b) run only to the right under normal turbine operating conditions. This means that the partial pressure of Na_2SO_4 corresponds to a specific concentration of NaCl. The horizontal axis in fig. 12 could also be expressed in terms of the partial pressure of Na_2SO_4 .

The figure shows that as the pressure increases at constant concentration of sea salt in the inlet air (vertical lines) the dew point also shifts to higher temperature. If, for efficiency reasons, higher turbine pressures are used the temperature range for sulphate corrosion is widened. One can also see that a reduction in the salt concentration in the inlet air (at constant pressure) means that the dew point falls and the upper temperature for sulphate corrosion as well. The situation is similar for Na in the fuel. The use of cleaner fuels with a lower Na content leads

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to long life expectancy (fig. 13).

The metal temperature at the first turbine stage in an industrial gas turbine lies between 700°C and 1000°C, and in some cases even higher. The pressure lies normally between 6 and 20 bar. Sulphate corrosion can probably occur even in the presence of small amounts of corrosive substances, Na and S (see fig. 12).

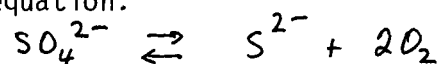
3.3.2 The Sulphate Corrosion Mechanism

The complete description of the phenomenon of sulphate corrosion has not yet been obtained in spite of extensive research (see the review articles [12,13] and also [14,15] for more details). In general it is assumed that the process goes in three stages.

- 1) the formation of a liquid sulphate layer on the surface.
- 2) an attack on and the penetration of the protective oxide layer.
- 3) a rapid or even catastrophic attack of the substrate that now comes into contact with the molten sulphate layer.

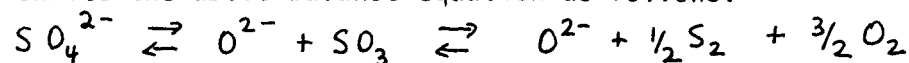
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In step (1) one assumes that a good protective oxide layer is in place (e.g. Cr_2O_3). The thermodynamic conditions in a gas turbine are such that the operation is in a gas phase. Because of the high O-activity and the low S-activity an oxide layer forms preferentially. The formation of a liquid sulphate layer occurs because of condensation of Na_2SO_4 out of the gas phase by the reactions listed in 3.3.1. The presence of a liquid sulphate layer is essential because then the relative activities of O and S can shift in favor of S. This can be seen in the following balance equation:

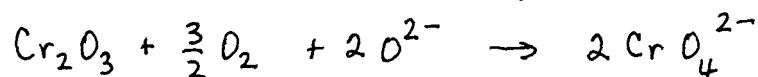


Because of oxidation a low O-activity occurs at the oxide/sulphate melt boundary. S can diffuse into the substrate through the oxide layer and form Cr-sulphates there. This, together with the previous oxidation, leads to a chromium deficiency in the matrix.

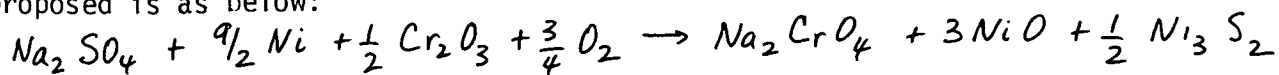
An important next step in the process is the deterioration of the oxide layer. This occurs because the activity of the oxide ion in the melt increases as the S is removed from the melt (by diffusion of S into the substrate). This is obvious if we rewrite the above balance equation as follows:



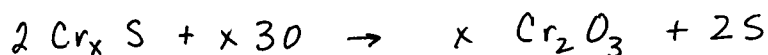
For lower S-activity the balance shifts to the right. The increase in O^{2-} -activity causes the dissolution of the oxide layer as follows:



The chromate produced here does not form a protective layer. The total reaction proposed is as below:



We see that Ni_3S_2 is formed in the substrate instead of chromium sulphides. This does not cause concern. It even occurs at a later phase when the chromium concentration in the matrix has been radically reduced by the continuing oxidation and the internal sulphidation. Because of the depletion of Cr in the matrix, NiO as well as Cr_2O_3 will be formed in an attempt to restore the original oxide layer. Because diffusion in NiO is more rapid, the oxidation will increase even further. NiO also dissolves more quickly in the presence of O^{2-} ions and this means an even more rapid oxidation process. Because of the advancing oxidation front and of the increasing inward diffusion of O, the S is forced out of the chromium sulphides in the substrate



The S released penetrates deeper into the alloy and forms Cr_xS .

In the last phase the remaining oxide layer completely deteriorates (because of the chemical reactioned above or because of thermal or mechanical load) and liquid Na_2SO_4 comes into direct contact with the metal. The formation of a protective oxide layer is no longer possible. The corrosion process continues very quickly because the reactive elements O and S can reach the metal surface almost uninhibitedly through the liquid sulphate layer because of the breakdown of the diffusion step. The corrosion front advances so quickly that uncorroded substrate remains in the corrosion products. The low-melting point eutectic Ni- Ni_3S_2 can penetrate the substrate along the grain boundaries. For completeness, we should mention that the oxides WO_3 , MoO_3 and V_2O_3 in the sulphate melt have a strong fluxing action. The solution of the protective oxide layer quickly accelerates and with it the corrosion process (see [15]).

3.4 Corrosion Prevention in the Turbine Section

3.4.1 Introduction

Corrosion in the turbine section can be prevented by:

- the use of cleaner fuels (lower S, Na and V content) and the injection of fuel additives.
- the use of materials with a high corrosion resistivity.
- the use of coatings.

3.4.2 Cleaner Fuels and the Use of Additives

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Because sulphate corrosion limits the life expectancy of industrial gas turbines one attempts to change those parameters which normally would lead to sulphate corrosion. One method is to reduce the amount of Na and S in the fuel. The corrosion can be limited to a reasonable level if the Na (and K) content is kept below 1 ppm. A reduction in the S content is also desirable but this competes with the desire to use cheaper fuels with a high S content. Sulphate corrosion can occur even at very low S content in the fuel [12]. This occurs in industrial zones and near the coast. A reduction in the V content is important because this element accelerates the corrosion process. A addition of 2 ppm to fuel with a 5 ppm Na content caused a three-fold increase in the speed of corrosion[16]. This is the reason why very low V-content fuels are chosen for marine turbines.

One could also put additives in the fuel so that the melting point of the liquid sulphate would then be increased. MgO and V would form a magnesium vanadate with a high melting point and it would not remain on the blades. This treatment must be applied if the V-content is greater than 2 ppm. Additives based on Cr (e.g. Cr_2O_3) have been tested and Na_2CrO_4 would be produced. However the use of additives can have a detrimental effect on the environment.

3.4.3 Materials with a better Corrosive Resistance

The moisture in which the sulphate corrosion occurs is strongly dependent on the substrate. Cobalt alloys in general have a much greater resistance to sulphate corrosion than nickel alloys. The reason could be that the melting point of the Co- Co_4S_3 eutectic (877°C) is higher than that for the Ni- Ni_3S_2 eutectic (645°C). The diffusion speed for S in Co is 100 times lower than in Ni. Also the oxide layer that is formed plays an important role. A Cr_2O_3 layer has a much greater resistance to sulphate corrosion than a Al_2O_3 layer [15]. A measure to this resistance to sulphate corrosion for Ni and Co alloys with varying Cr content is given in fig. 14. At higher temperatures where only oxidation plays a role, the Co alloys are much less corrosion resistant than the Ni alloys because of the deterioration of the Al. In the temperature region of sulphate corrosion a reverse effect occurs. This is caused because the Co alloys owe their corrosion resistivity primarily to the presence of a Cr_2O_3 layer. Depending on their Al or Cr content the Ni alloys will form a Cr_2O_3 layer (Ni_A) with a good sulphate corrosion resistance or an Al_2O_3 layer with a poor resistance to sulphate corrosion. A ranking of Ni alloys by their increasing sulphate corrosion resistance is given in Table 1. One sees there that the Cr

content plays an important role. A minimum of 15% is required for a reasonable /15 resistance to sulphate corrosion.

IN738 is almost exclusively used in the first stage blades of industrial gas turbines. IN939 is an important new development because it has three times the corrosive resistance of IN738 [17].

3.4.4 The Use of Coatings

A complete review of this field is given in a recent publication [18]. One can differentiate the coatings as follows:

- a) diffusion coatings
 - b) cladding or overlay coatings (metallic)
 - c) ceramic overlays
- a) The application of diffusion coatings using a 'pack cementation' process is shown schematically in fig. 15. The components are placed in a metal container in such a way that they are completely surrounded by a powder. The powder consists of an inert filling (usually Al_2O_3), a halogen salt (e.g. NH_4Cl) and the coating material (e.g. aluminum) in pure or in alloy form. The sealed container is put into an oven at the desired temperature. A halogen salt that is gaseous at high temperatures is formed and this combines with the coating element to produce a gaseous metallic halogen compound (e.g. $AlCl$). This gas diffuses through the 'pack' in the direction of the piece to be coated and decomposes on its surface. The coating (Al or Cr) now diffuses into the material. /16
- The pros and cons of diffusion coatings are listed briefly below:

<u>Pros</u>	<u>Cons</u>
relatively cheap	the part receives heat treatment
can be applied internally (in a cool channel!)	coating is brittle at low temperature
good binding to the substrate	only a small variation in composition is possible

Normally only Al is diffused. The resistance to oxidation is satisfactory but the resistance to sulphate corrosion is not. Often a two-stage process is used: the diffusion of Cr in a chromium pack followed by diffusion of Al in an aluminum pack. This could improve the resistance to sulphate corrosion.

The application of an electrolytic Pt-layer (or an other noble metal such as Pd or Rh) before the application of the Al coating improves the resistance to sulphate corrosion as well as to oxidation. The ductility of the coating, however, is reduced (fig. 16). This type of coating is especially suitable

for industrial gas turbine blades but the cost is significantly higher than for a standard Al diffusion coating.

Because of the present limitations on the composition of diffusion coatings, a project is underway to develop coatings which will have optimal protection properties. This group of coatings is called overlay coatings.

- b) There are several methods to apply overlay coatings [18]. The low pressure plasma gun is given as an example in fig. 17. An arc is created between a tungsten cathode and a water-cooled copper anode. An inert gas (usually argon) is introduced and ionized in the high temperature of the arc where it forms into a plasma. The maximum temperature in the plasma can reach 16000°C. The coating material in powder form is now introduced into the plasma beam. It melts and is sprayed onto the component at high velocity. One can introduce different powders into the plasma and as a result radical variations in the chemical composition of the coating are possible.

In this way one obtains a good oxidation resistance, good sulphidification resistance and a high ductility. These advantages are also present in other types of overlay coatings. The disadvantages are that the overlay coating can not be applied internally, that they are expensive and that shadowing (see fig. 18) can occur. Overlay coatings based on CoCrAlY seem to be the most appropriate for the present generation of industrial gas turbines. The Al serves as the agent for oxidation resistance, the Cr for sulphate corrosion resistance; Y (yttrium) is added to achieve better bonding of the oxide layer, especially when under variable thermal load. Because Al and Cr have a limited solubility in each other, Co is added as a matrix and it also serves as a good agent for sulphate corrosion resistance. /17

A typical composition is Co-21Cr-12Al-4Y, for example even though CoCrAlY coatings with a higher chromium content and a lower Al content are now receiving more attention because of their resistance to sulphate corrosion.

- c) Ceramic overlay coatings, usually based on ZrO_2 , are applied in a plasma jet. They have an excellent corrosion and oxidation resistance. A second, and in present-day practice, more important aspect is its poor heat conductivity. For this reason ceramic coatings are used as heat reflecting coatings in cooled flame tubes, for example. This limits the temperature rise of the metal. The coatings are thick and brittle and therefore are sensitive to varying thermal loads. As such, the coatings are not suitable for application to turbine blades. Currently considerable research is being carried out toward finding a ductile

ceramic coating. The expectation is that within a few years such a coating will be able to be applied to the platforms of the blades.

3.4.5 Several Examples of Corrosion Protection

An impression of how material choice can lead to improved life expectancy is given in fig. 13. Even longer life expectancy can be obtained if the blade is provided with a coating. Testing of coatings can be done in a burner rig or, in practice, by a 'rainbow test'. In this test blades with various coatings are placed in the same blade housing. All blades then will experience the same environment. After a period of time differences in deterioration of the various blades will occur. This is manifested by the appearance of different colors, and hence the name 'rainbow test'.

The results of a burner rig application are given in fig. 20. The substrate is René 80 and IN 738, the standard first stage material respectively in aircraft and marine turbines, and industrial turbines. In each case the coating was a CoCrAlY overlay which was not prepared first with a Pt layer. Such a layer does have a very positive effect on these coatings. The effect on IN 738 is especially evident.

The results of a rainbow test are given in table 2. It was carried out on a MS 8002 gas turbine in Saudi Arabia [20]. There the turbines operate under rather difficult conditions. The natural gas has a high H_2S content (sometimes as high as 12% by volume) and the inlet air contains alkali metals, chlorides and sulphates from the desert sand. The coatings in the rainbow test were: a diffusion coating of PtCrAl preceded by an electrolytic Pt application, followed by a Cr diffusion and an Al diffusion. As well, two CoCrAlY coatings, one sprayed on in a plasma, and the other plated on using an HIP (hot isostatic pressing) were also used. The last two coatings were also followed by an Al diffusion coating.

A FeCrAlY coating was also tested. All coatings protected the substrate from deterioration. The CoCrAlY overlay + Al diffusion coating and the CoCrAlY overlay coating (the plasma-sprayed coating as well as the evaporated coating) are available commercially.

3.5 Conclusions

There are two types of corrosion processes taking place in the turbine section of an industrial gas turbine (oxidation and sulphate corrosion). Sulphate corrosion especially plays an important role in the life expectancy of the equipment. This type of corrosion occurs in the presence of liquid sulphate on the metal surface

(usually Na_2SO_4). Because Na and S are present in the fuel or in the inlet air sulphate corrosion can be controlled by filtration of the inlet air or by treatment of the fuel. The latter treatment is used extensively. This is carried out by reducing the percentage of S and Na (and also V) in the fuel. But it can also be done by fuel additives which prevent the formation of liquid sulphate by shifting their melting points. Corrosion can also be prevented by the use of more corrosion-resistant materials and by the use of coatings. U 700 is replaced by IN 738 as blade material. The use of IN 939 instead of IN 738 is forecasted. Coatings are receiving ever-increasing use. An overview of the various processes for the application of coatings was given as well as the pros and cons for each type of coating. A few examples of coating use were discussed. Coatings based on Pt-Al and some CoCrAlY coatings often provide very good protection in especially corrosive atmospheres; and they are also certainly cost-effective.

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Toename corrosiebestandheid	Legering	Cr-percentage
	B 1900	8
	IN 100	10
	Nimonic 100	11
	713 C	12,5
	Udimet 700	15
	Nimonic 105	15
	IN 738	16
	Nimonic 90	20
	Udimet 500	19
a)	Waspaloy, Hastelloy I, Nimonic 80A, IN 939	19,5/22/20/22,5

TABLE 1

The Resistance of Various Ni-alloys to Sulphate Corrosion

a) (ranked by increasing resistance to corrosion)

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TABLE 2

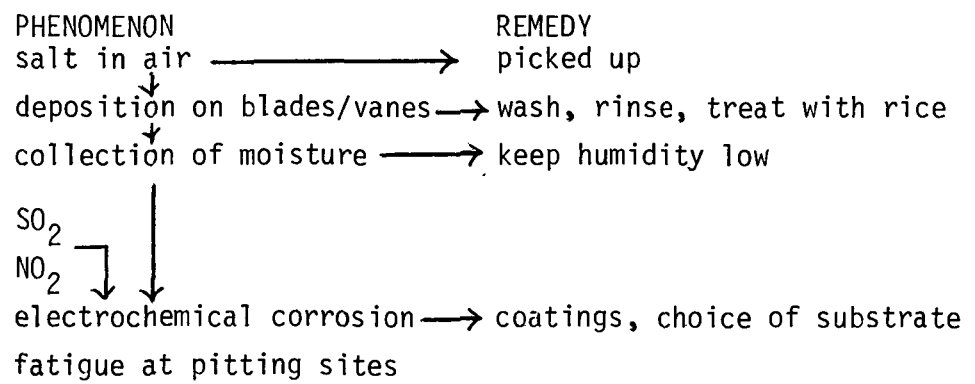
The Behavior of Various Coatings Currently in Use [20]

conditions: 26.000 hours with 502 starts
fuel: 'sour' natural gas
substrate: IN 738
turbine: MS 5002, Saudi Arabia

coating deterioration^{a)} of substrate minimum coating thickness^{b)} initial^{c)} after 26.000 hours^{d)} (μm)

COATING	AANZASTING ^{a)} BASISMETAAL	MINIMUM COATING DIKTE (μm) ^{b)}	
		initial ^{c)}	NA 26.000 UUR ^{d)}
GEEN	250 μm	-	-
PtCrAl	-	80	50
CoCrAlY (PLASMA)	-	150	25-50
CLADDING:			
CoCrAlY+Al DIFF	-	250	210
FeCrAlY	-	200-250	25-75

Fig. 1 Schematic overview of the corrosion of compressors



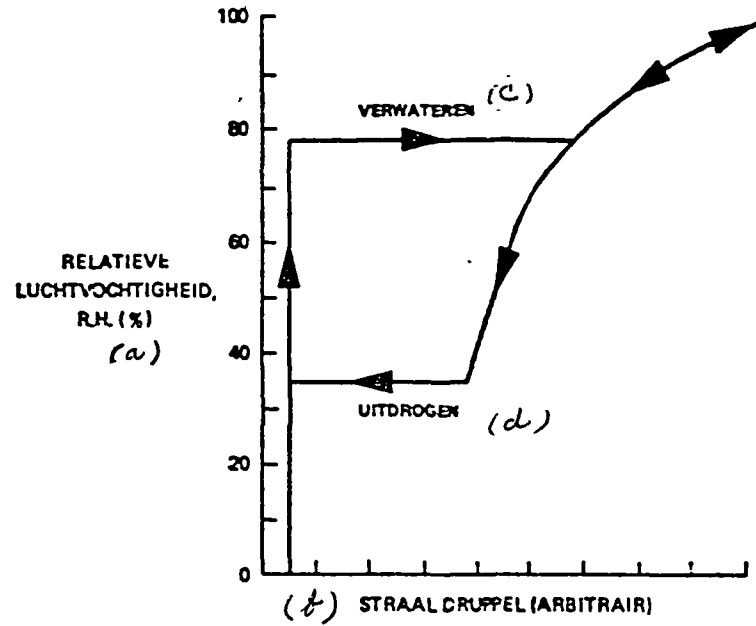


Fig. 2 Hygroscopiciteit van een NaCl deeltje

Fig. 2 Hygroscopicity of NaCl grains

- (a) relative humidity (R. H.,%)
- (b) drop radius (arb. units)
- (c) moisture absorbed
- (d) moisture released

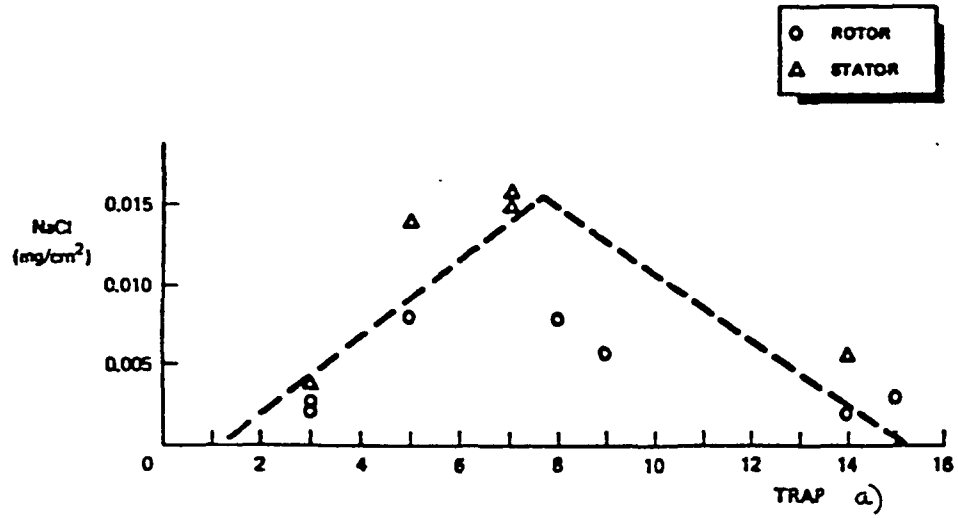


Fig. 3 Salt measurements in the compressor of a JT 4 jet engine of a DC-8 aircraft [1]

a) stage

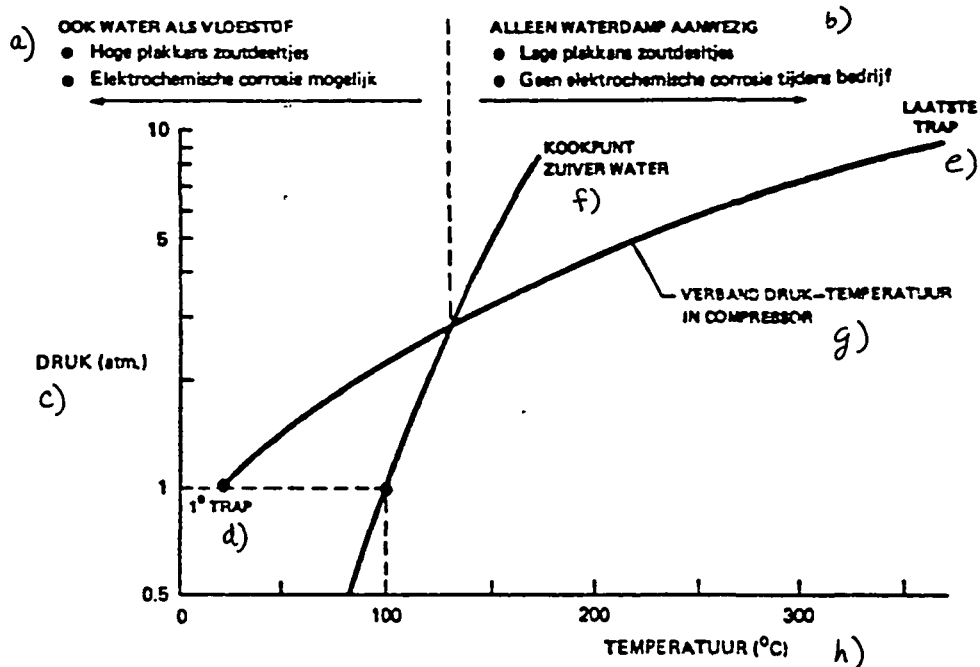


Fig. 4 Water in a compressor

At some point in the compressor the boiling point of water is exceeded. Above this point only water vapor is present. In practice this point will shift more to the right because of:

- Elevation of the boiling point because of impurities dissolved in the water
- Kinetic effects

- a) water is present in liquid form
 - high adhesion probability of salt particles
 - electrochemical corrosion is possible
- b) only water vapor is present
 - low adhesion probability of salt particles
 - no electrochemical corrosion during operation
- c) pressure (atm)
- d) 1st stage
- e) last stage
- f) boiling point of pure water
- g) pressure-temperature curve in the compressor
- h) temperature

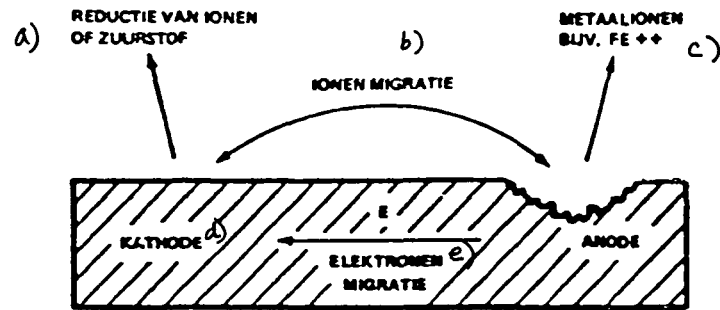


Fig. 5 Electrochemical corrosion (for clarity, the anodic and cathodic reactions are assumed to take place a large distances. This is not a necessary condition.)

- a) reduction of ions or oxygen
- b) ion migration
- c) metallic ions (e.g. Fe⁺⁺)
- d) cathode
- e) electron migration

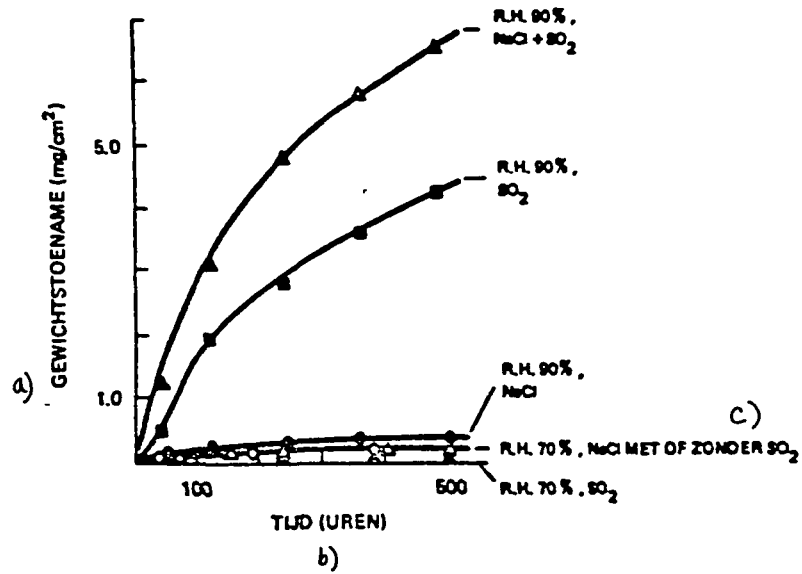


Fig. 6 Corrosion of a non-alloy low-carbon steel under various conditions:
Air humidity, 70% or 90%
SO₂ in the air, 0 or 1%
steel is not covered with moist salt [5]

- a) increase in weight
- b) time (hr)
- c) NaCl, with or without SO₂

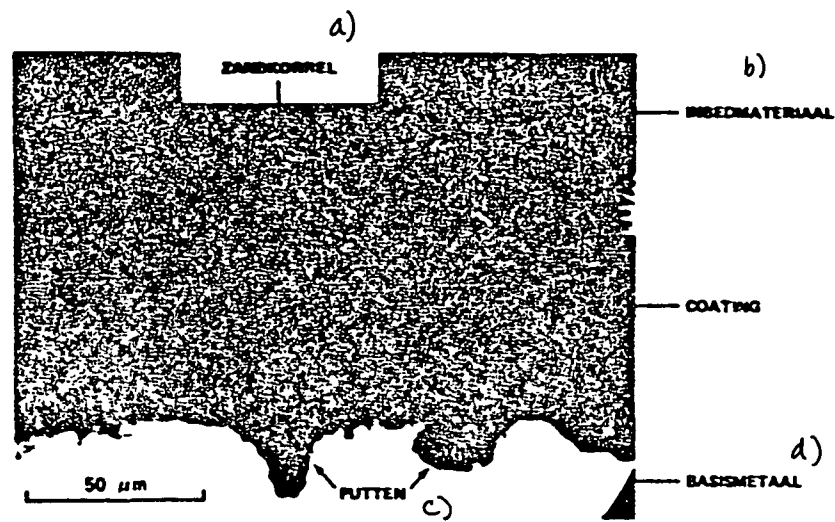
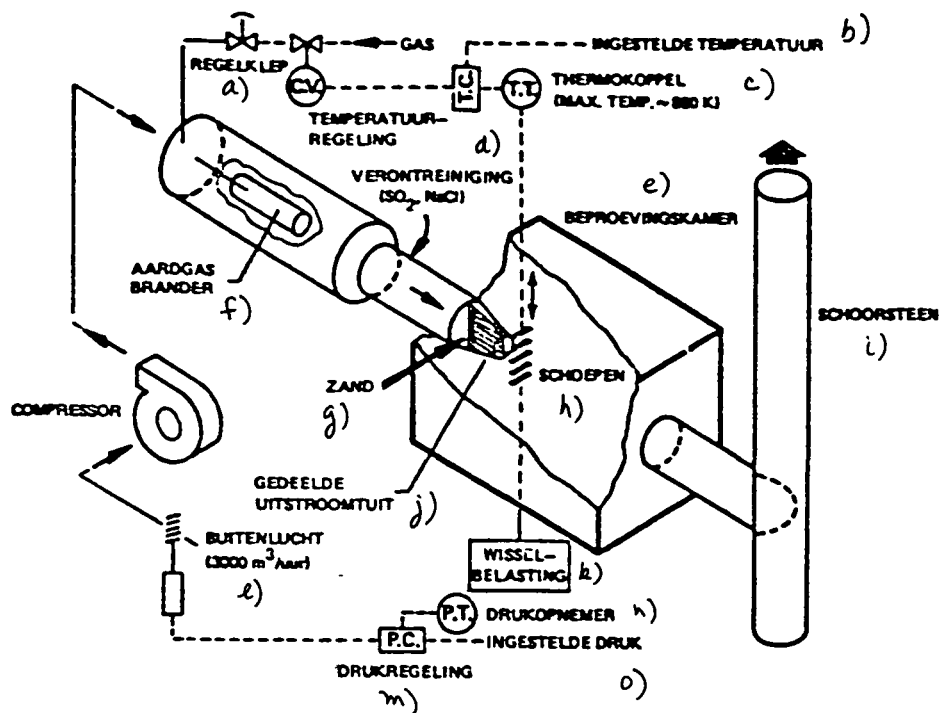


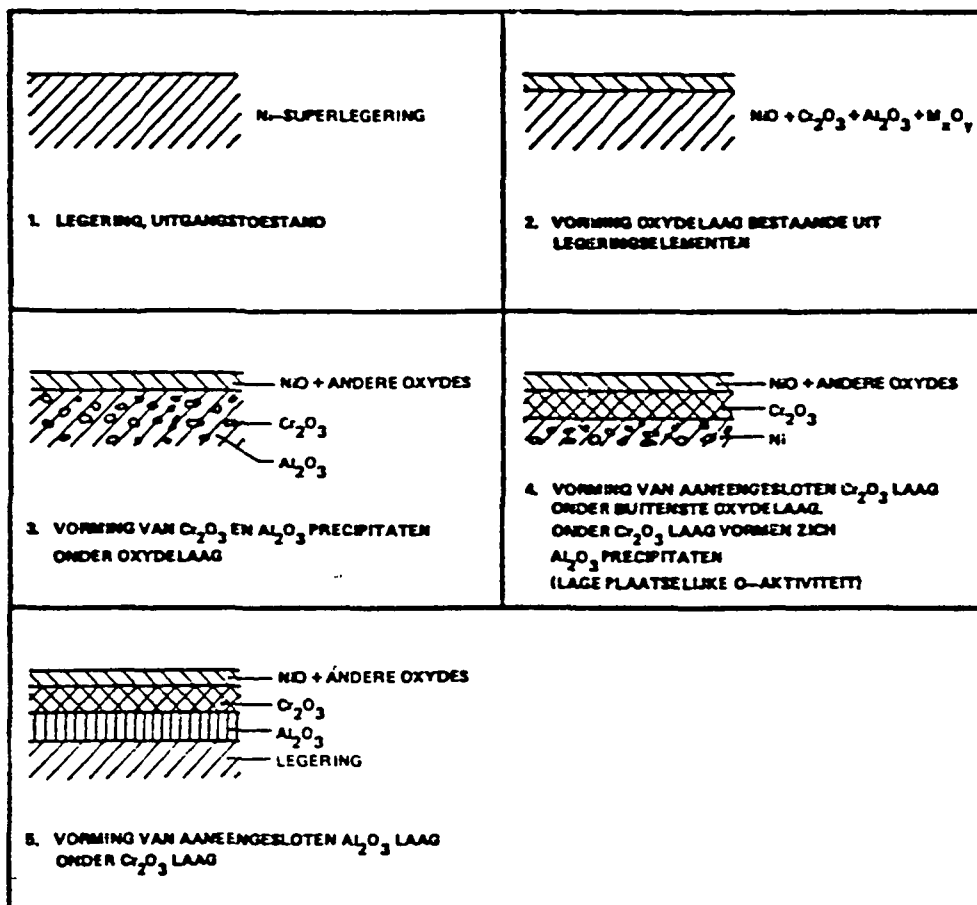
Fig. 7 Example of a spray coating. The coating matches very well the blade profile. This is obvious from the good filling of the corrosion pits that were there before the coating. The erosion by a grain of sand can be seen [7].

- a) sand grain
- b) imbedded material
- c) pits
- d) substrate



- a) regulator
- b) temperature selector
- c) thermocouple
- d) addition of pollutants
- e) testing chamber
- f) natural gas furnace
- g) sand
- h) blades
- i) chimney
- j) nozzle channels
- k) variable load
- l) outside air
3000 m³/hr
- m) pressure regulator
- n) pressure gauge
- o) pressure selector

Fig. 8 NLR test bench for compressor parts. The blade to be tested is blown with air. A natural gas furnace provides any temperature desired between 20 and 600°C. The air stream is dosed with SO₂, NaCl and sand. The blades can be fatigued during this treatment. To simulate stand-by operation the blades are periodically placed in a climate box with high relative humidity and injection of SO₂.



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Fig. 9 The formation of a protective oxide layer on a Ni-superalloy

- 1) alloy, beginning state
- 2) formation of oxide layer out of elements in the alloy
- 3) formation of Cr_2O_3 and Al_2O_3 precipitates under the oxide layer
- 4) formation of a connecting Cr_2O_3 layer under the external oxide layer. Al_2O_3 precipitates form under the Cr_2O_3 layer (low local O-activity)
- 5) formation of a connecting Al_2O_3 layer under the Cr_2O_3 layer

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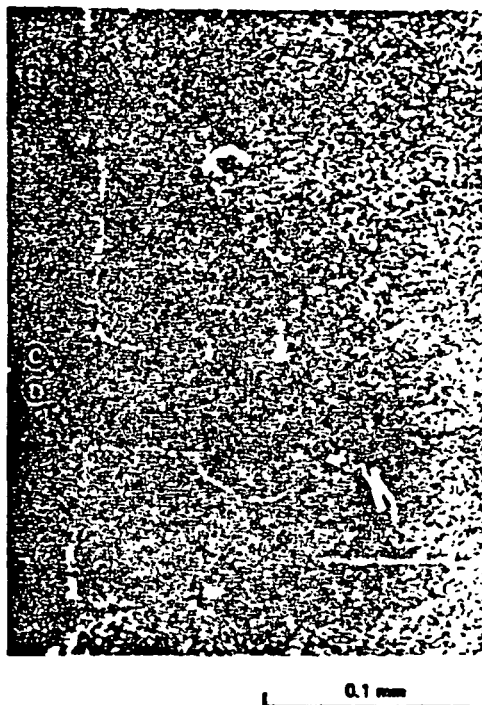
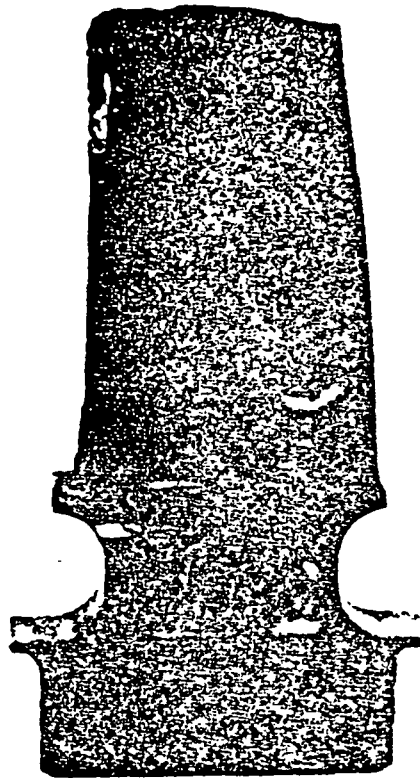


Fig. 10 The deterioration of grain boundaries of RENE 80 blade material that has been subjected to creep

According to the correlation boundaries (B and D) we can see the relatively small oxidation of the surface (C)



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Fig. 11a Deterioration by sulphate corrosion of a first stage turbine blade from an industrial gas turbine

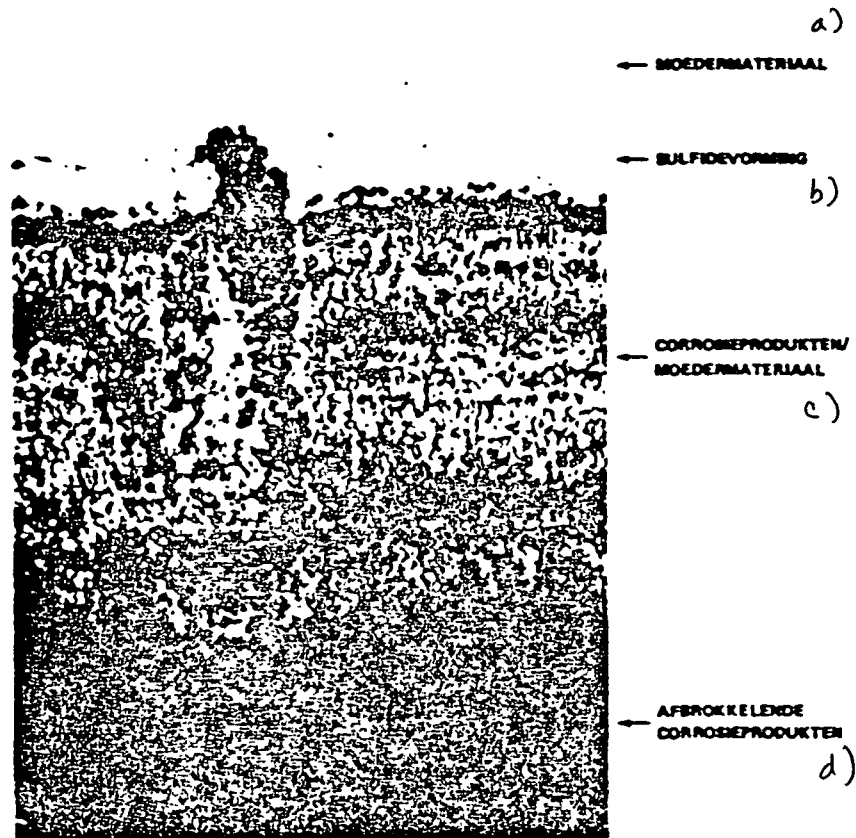
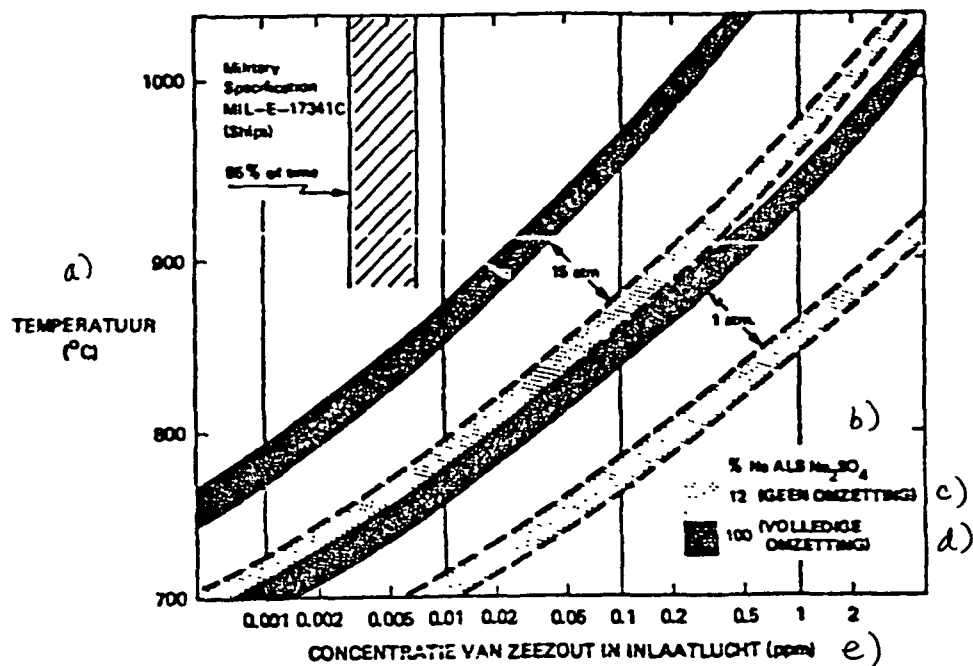


Fig. 11b Advancing corrosion front on the blade of Fig. 11a

- a) substrate
- b) sulphide formation
- c) corrosion products/substrate
- d) crumbling corrosion products



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Fig. 12 Dew point of Na_2SO_4 as a function of salt concentration and pressure [11]. N. B. Two bands are given for each pressure; for the lower band it is assumed that NaCl has not been converted to Na_2SO_4 . Normal sea salt has 12% of its Na as Na_2SO_4 . The upper band is the case for complete conversion.

- a) temperature
- b) %Na as Na_2SO_4
- c) 12% (no conversion)
- d) complete conversion
- e) concentration of sea salt in inlet air (ppm)

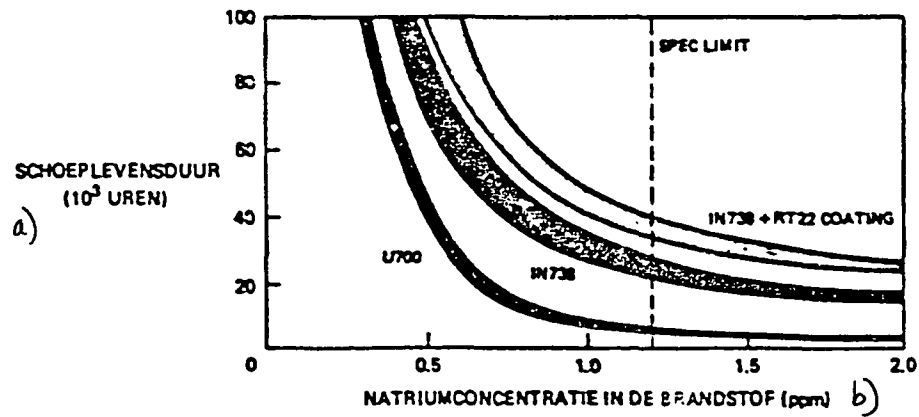


Fig. 13 Effect of Na in the fuel on the life expectancy of first stage turbine blades of a GE MS 5001N industrial gas turbine. The effect of substrate and coating choice can be seen. (RT22 coating = electrolytic Pt-layer + Al diffusion coating).

a) blade lifetime (10^3 hr)

b) sodium concentration in the fuel (ppm)

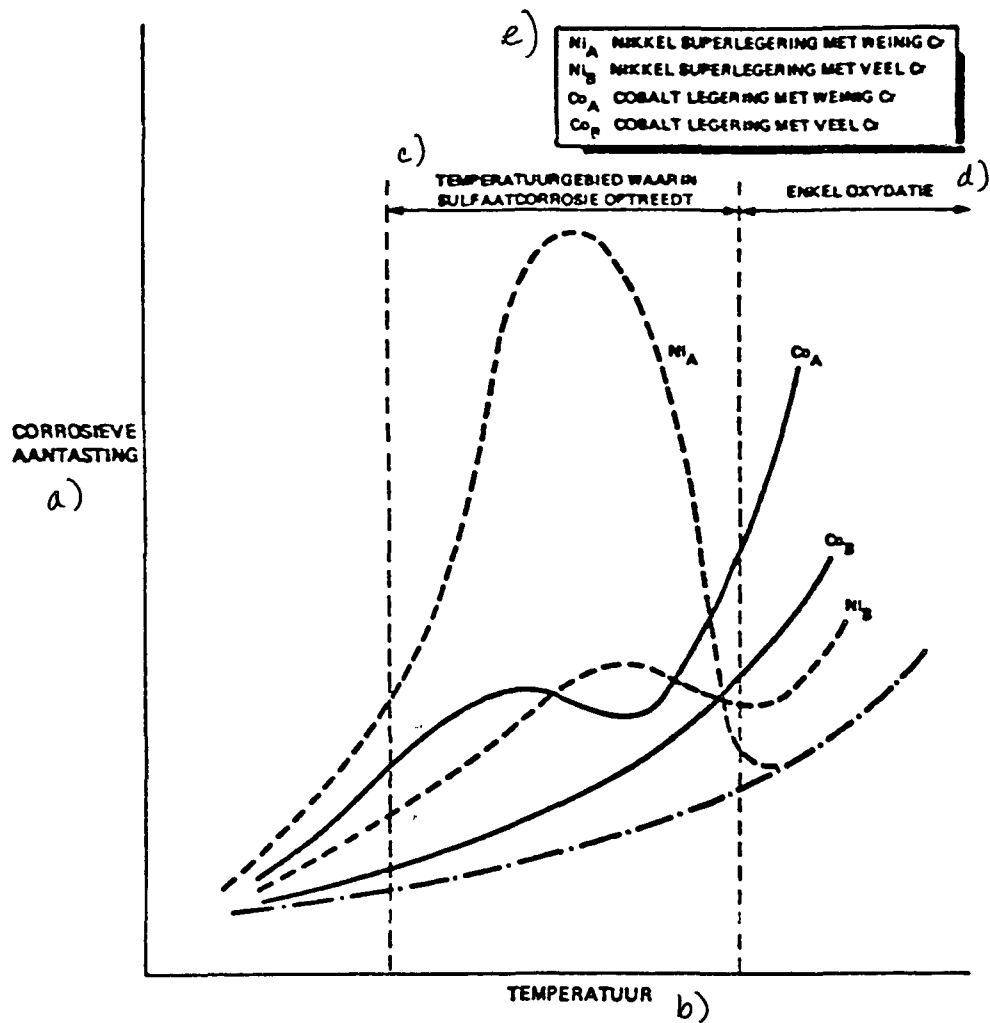


Fig. 14 Schematic representation of the relative corrosion resistance of Ni- and Co-alloys [12]

- a) deterioration by corrosion
- b) temperature
- c) temperature range where sulphate corrosion can occur
- d) oxidation only
- e) Ni_A - nickel superalloy with low Cr content
- Ni_B - nickel superalloy with high Cr content
- Co_A - cobalt alloy with low Cr content
- Co_B - cobalt alloy with high Cr content

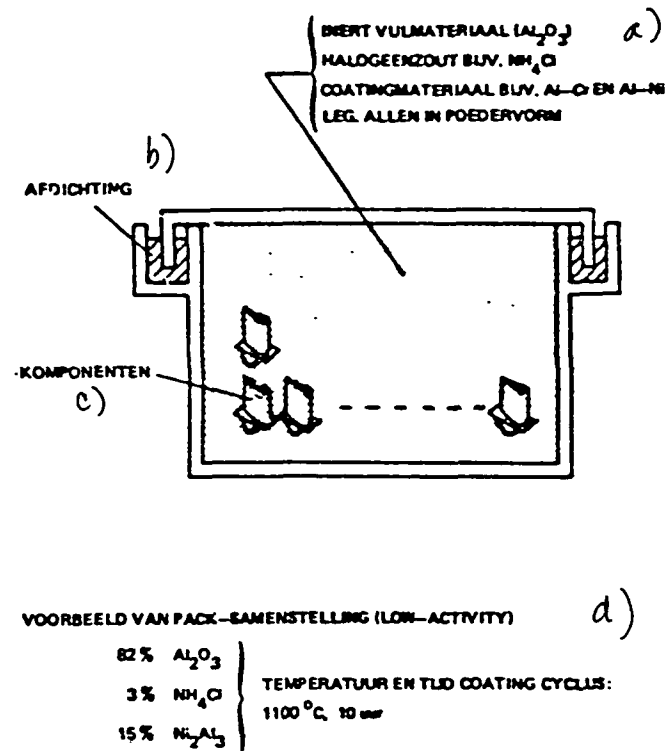
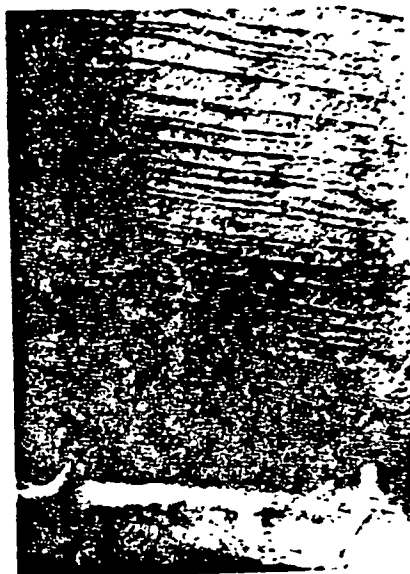


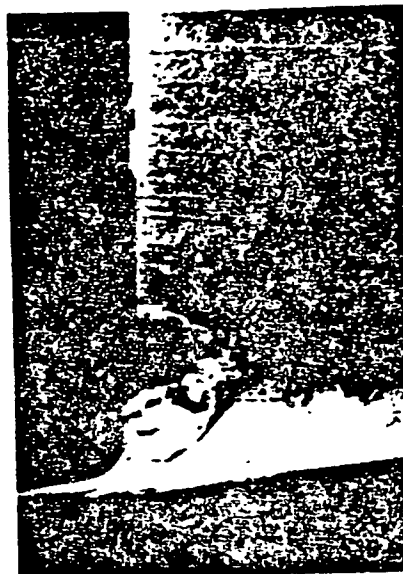
Fig. 15 Application of diffusion coatings in a Pack Cementation Process

- a) inert filling material (Al_2O_3)
 halogen salt, e.g. NH_4Cl
 coating material, e.g. $Al-Cr$ and $Al-Ni$ alloys in powder form
- b) seal
- c) components
- d) example of pack constituents (low-activity)
- | | | |
|----------------|---|---------------------|
| 82% Al_2O_3 | } | temperature: 1100°C |
| 3% NH_4Cl | | |
| 15% Ni_2Al_3 | | |
- time: 10 hr

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a)



b)

Fig. 16 Illustration of the brittleness of the 'precious' diffusion coatings (in this case Rh-electrolytic and Al-diffusion). Fig 16a shows the thermal fracture after 150 hours in the furnace installation. Fig. 16b shows the same blade after 300 hours.

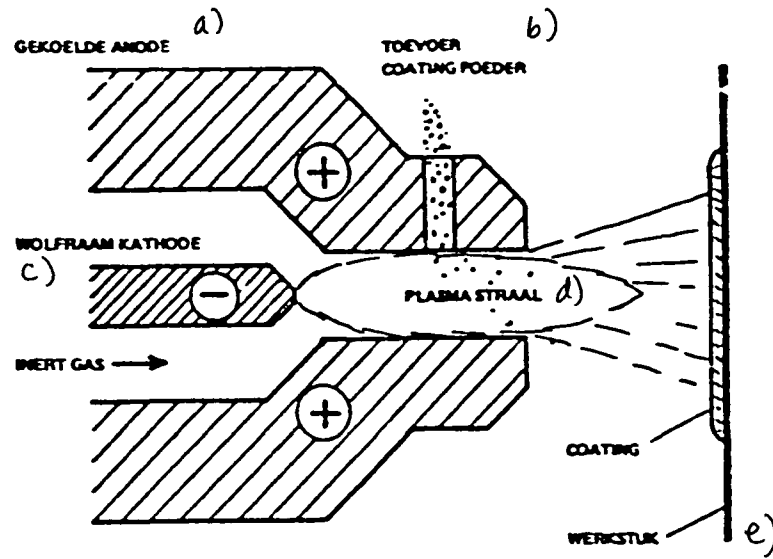


Fig. 17 The plasma jet

- a) cooled anode
- b) addition of coating powder
- c) tungsten cathode
- d) plasma beam
- e) work piece

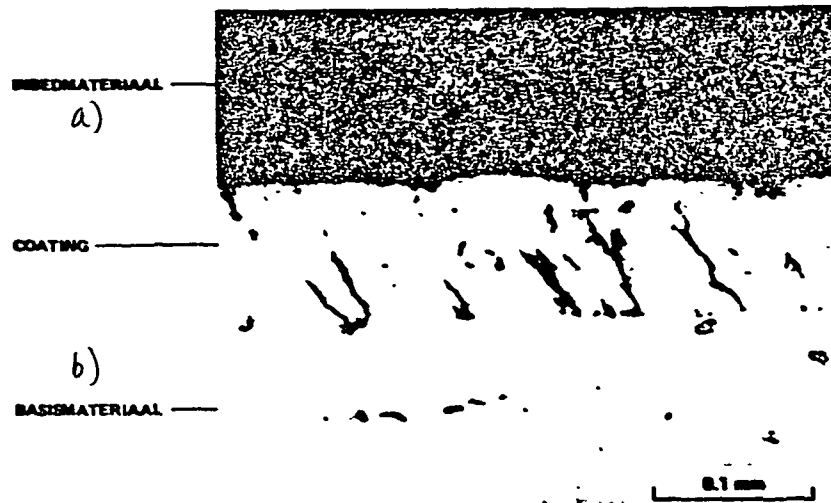


Fig. 18 Defects caused by shadowing during the application
of a NiCoCrAlY-overlay

- a) imbedded material
- b) substrate

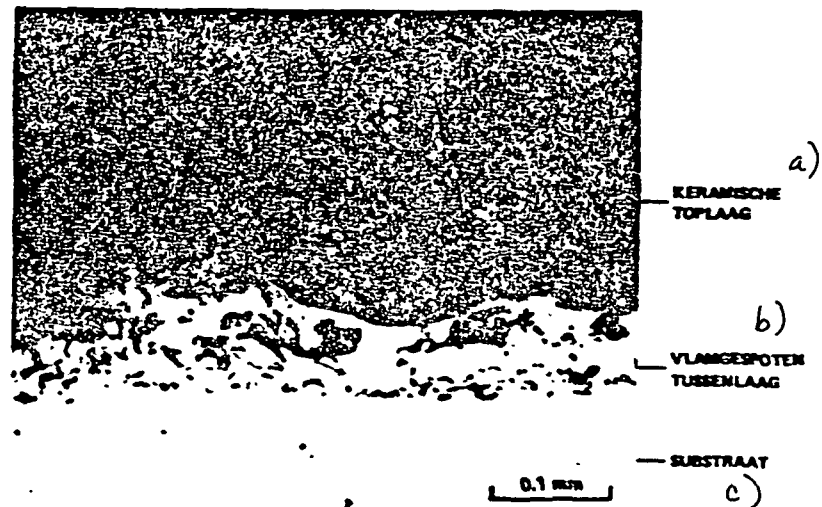


Fig. 19 Ceramic coating for use on flame pipes

- a) ceramic upper layer
- b) intermediate layer applied by a flame
- c) substrate

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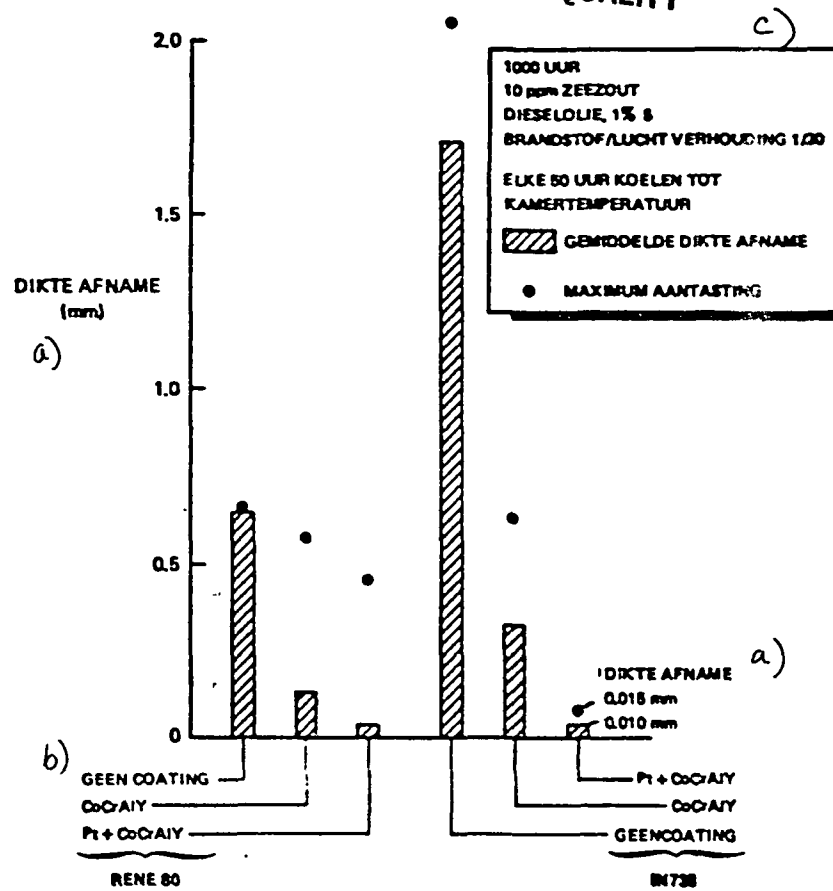
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Fig. 20 Results of the test in the furnace installation [19]

a) thickness removed

b) no coating

c) 1000 hours

10 ppm sea salt

diesel oil, 1% S

fuel/air ratio is 1/30

cooled to room temperature every 50 hours

average thickness removed



maximum deterioration