

PROBLEMS IN USING METALLIC MATERIALS
AT ELEVATED TEMPERATURESA. M. Hall
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Factors Involved in Elevated-Temperature Service

The characteristics of the applications in which metals and alloys are used at high temperatures can be catalogue in various ways. They can be delineated by the temperature range involved, by the nature of the environment in which the material is to function, by the kind of function involved, by the presence or absence of thermal gradients, and by the magnitudes and types of applied stress involved. Of course, all of these factors, as well as others, must be considered in defining the conditions of a given elevated-temperature service.

In designing a component for use at elevated temperatures, and in selecting the material and the method of manufacture, it is general practice to place early emphasis on the kinds and magnitudes of the applied stresses. The materials engineer has reacted to this situation by developing considerable quantities of data on high-temperature tensile strength, and on creep and rupture properties. In fact, much more is known about these kinds of mechanical properties than about such other important considerations as high-temperature corrosion resistance, damping capacity, or thermal fatigue resistance. The simpler mechanical properties are easier to measure and the numbers obtained are more easily understood and used. Therefore, it is reasonably appropriate to use applied stress as the first criterion to catalogue the high-temperature applications, and to introduce other operative factors in some kind of cohesive order, though not necessarily in the order of their importance. The latter varies with the application.

Applied Stresses

In the category of applied stresses are those intentionally imposed upon the component. They are the stresses the component is expected to support as a direct consequence of the function for which it was designed.

Static Loading. There are a number of cases in which the applied load on the component is essentially constant in sign and magnitude. In some cases, the load is actually no more than the component's own weight. An example is the cover of a bell-type annealing furnace. In other cases, the component is a structural member expected to sustain loads additional to its own weight. Such a component is illustrated by the work-supporting fixtures used in molten-salt-bath heat-treating equipment.

Dynamic Loading. A frequent case of dynamic loading in elevated temperature service is rotational. The discs and blades of turbosuperchargers, turbojet engines, and centrifugal pumps are common examples. Reciprocating motion is illustrated by the action of the pistons in an internal combustion engine.

Combinations. There is a considerable variety of cases where the loading situation is complex and often difficult to analyze. The loading on the hearth of a roller-type continuous annealing furnace is a complex case where a series of rotating members supports, in essence, a sustained load. Another type of situation is illustrated by the grate bars in a coal-fired boiler furnace. The bulk of the time these members are expected to

support a more or less static load of burning coal, but periodically they must rotate or reciprocate to discharge ash and clinker.

Unintended and Environmental Stresses

Components operating at elevated temperatures are frequently required to sustain stresses which are not directly associated with their function, though they may be inherent in the application or in the behavior of the material. They are not wanted because they often are critically important to the performance of the component. They are therefore unintended, but have to be put up with because of their association with the service conditions or the material.

Vibration. Cyclic stresses of various frequencies from moderate to high, which may be termed vibrational, are often encountered in high-temperature applications. Because it is impossible to make exactly balanced components and perfect bearings, vibration is inevitable in rotating parts. Vibration during rotation, of course, extends to housings and other more or less rigidly attached components.

Vibration is often encountered in otherwise statically loaded structures. The steam line from the superheater to the turbine in a central power station is in a state of continuous vibration because of the pulsations in the pressure of the steam it is delivering. An autoclave may vibrate because the system contains reciprocating pumps.

Thermal Stresses. A whole host of unintended, environmentally controlled states of stress replete with many consequences may stem from the thermal factors in the high-temperature application. With rare exceptions, the thermally induced stresses discussed here arise from the existence of thermal gradients and the characteristic of metallic materials to expand on heating and contract on cooling. On heating, surfaces and thin components get hot faster than interiors and thick sections. In consequence, they expand more rapidly and, in doing so, place the cooler regions in a state of tension. The latter areas, in turn, react on the hotter parts to put them in compression. When the structure obtains the operating temperature, thermal gradients and hence thermal stresses tend to disappear. Surfaces and thin sections cool faster, contract more rapidly and place the hotter regions in compression. By reaction, tension builds up in the cooler areas. If the hotter regions upset (deform plastically) because the compressive stress exceeds the yield strength, then on further cooling, the surface may go into tension. This is the type of cycle undergone by the trays and fixtures used to support loads of steel parts in a carburizing furnace. If the work is to be slow cooled after carburizing, the thermal cycle is relatively mild; if the work is quenched from the carburizing temperature, the thermal cycle is quite severe.

A more rapid thermal cycle, but usually quite mild in terms of the magnitudes of the stresses induced, is that experienced by the muffle in a "casually" controlled heat treating furnace where the temperature is continually fluctuating.

The start-up of high-temperature equipment frequently involves drastic temperature changes. Such changes are commonly called "thermal shock". Thermal shock and the high degree of thermal stress which it induces often occur in starting up such equipment as stationary gas turbines. The combustion chambers, ducts, turbine rotor, blades and guide vanes may go from room temperature to operating temperature in a matter of seconds. The cooling phase of the cycle is usually relatively mild.

A slightly different situation, arising from the same basic causes, prevails in cases where, even when the structure has attained operating temperature, some parts of it remain colder than others. If the cold parts are held quite rigidly, they may force the hot components to buckle or upset. Then, during a subsequent cooling period, these hot components may experience unusually severe tensile stresses as they attempt to contract in the face of the restraint imposed by the cold components. Chemical processing equipment involving reactions occurring at different temperatures in the same system must be so designed as to guard against the consequences of this type of situation.

Transformation Stresses. The materials of construction may provide another source of uninvited stress. For example, if the thermal cycle imposed on a hardenable steel causes it to soften or harden, it will undergo corresponding changes in specific volume. The hardening reaction in steel, that is, the transformation of the austenite phase to martensite, involves a substantial increase in specific volume. Tempering and annealing tend to induce a decrease in specific volume.

Many of the high-strength, high-temperature alloys such as the so-called superalloys are strengthened by the precipitation of a second phase from the matrix. Such alloys are normally precipitation hardened before service, but the precipitation process may continue during service. If so, a small degree of contraction usually occurs.

If the components undergoing these changes in specific volume are restrained, then stresses will build up in them. Likewise, if thermal gradients prevail while these changes are occurring so that different parts of the same component undergo the changes at different times or to different degrees, stresses also will develop.

Corrosion

Stress as a factor in high-temperature applications has been briefly treated, first in terms of applied stress and second in terms of unintended stress. Another general factor which must always be considered is chemical in nature. This is the matter of the chemical activity of the environment, that is, its corrosiveness. Considerable data are available on the reaction between metallic materials and various environments at elevated temperatures. Nonetheless, the information frequently is inadequate and difficult to apply to complex practical situations.

General Corrosion. More or less uniform wastage or loss in thickness by corrosive action is what is meant by general corrosion. In many applications, this factor is readily measured and anticipated. An example is the slow reduction in the wall thickness of the steel tubes in a high-pressure water-tube boiler by oxidation. The conversion of the metal to oxide usually follows the parabolic rate law. While in some environments the major reaction is oxidation, in other media other reactions such as carburization, nitriding, sulfidation or hydrogenation may be dominant. Sometimes the environment has a surprising influence on mechanical properties. For example, some alloys when statically loaded in tension have greater creep resistance in an oxidizing medium than in one that is inert.

Stress Corrosion. It is not uncommon, in the presence of surface tensile stresses, for a progressive localized corrosion attack to occur in a component. The other factors which must cooperate to develop this situation are the chemical nature of the medium, the temperature, and the character of the resistance put up by the material toward the environment. In essence, the localized attack produces a notch which acts as a stress raiser; this, in turn, augments the prevailing tensile stress to open the notch into a

crack; the fresh metal exposed is ripe for further corrosive attack which deepens the crack and raises the stress; again, the crack deepens under the stress and the process goes forward whipsawed between the corrosive attack and the tensile stress.

Plain carbon steel scales quite readily in air at 1000 F, the attack being classified as general corrosion. However, when the temperature is raised to perhaps 1300-1400 F the advancing corrosive front tends to prefer grain boundaries. Thus, an element of localization enters the picture and, if surface tensile stress is present, the circumstances for stress corrosion exist.

Corrosion Fatigue. If the situation is essentially as described in the preceding paragraphs but the stress is cyclic, as in vibration, the phenomenon is known as corrosion fatigue.

DISCUSSION OF FAILURES

The factors in high-temperature service have been catalogued in terms of those giving rise to stress and those introducing corrosion. The material of construction has not been considered beyond thermal expansion and contraction characteristics and phase changes inducing stress. Some additional comments on materials are given later.

Much is known about the design of structures for elevated-temperature applications as well as about the behavior of metallic materials at high temperatures. As mentioned earlier, a considerable body of information on high-temperature tensile strength, creep and rupture properties exists. In addition, there are data on oxidation and other high-temperature chemical reactions, some information on high-temperature fatigue, and less data on other factors.

Enough information and experience have been accumulated so that, in the majority of cases, structures can be designed and appropriate materials selected and fabricated with reasonable assurance of acceptable performance. Sometimes, however, failures occur. The question is why. It would seem that there are two basic reasons. One is ignorance and the other is the deliberate decision that the component has failed.

The latter circumstance is not easily defined, but it frequently hinges on what becomes regarded as the limit of acceptable performance in a particular application. As an example, after being in service the normally expected number of months a high-temperature retort is taken out of service. It has not actually failed, but has become increasingly distorted from the repeated heating and cooling cycles and, in consequence, has become increasingly difficult to charge and empty. Or, during several thousand hours of high-temperature service, the microstructure near a weld in a steam line has changed causing a localized reduction in strength. Though it did not actually fail, the joint is replaced because the decision was made that it had become a safety hazard. Again, during a periodic shut-down, sections of a few of the superheater tubes in a high-pressure boiler are replaced. Though no failures had occurred in reality, the tube walls had wasted from oxidation to the point where doubt existed that they would last till the next shutdown without perforation. They were replaced because the operating personnel wished to avoid the nuisance attendant to a leak.

In sum, there are various reasons for deliberately declaring that a failure has occurred. The reasons relate to such matters as economics, safety, and operating convenience.

Ignorance is the biggest factor in unexpected failures. This factor may assume a number of forms. Commonly, it is revealed as a lack of important information on the service conditions or the properties of the material of construction. It also shows in the form of mistakes in design, of lack of awareness or appreciation of the quality of material required, of lack of understanding of the care required in the manufacture of the component, and of lack of appreciation of the consequences of misusing equipment.

The relationship between ignorance and the incidence of failure may be emphasized by considering the proposition negatively. For example, where a high degree of knowledge about an application prevails and is intelligently used, the incidence of failure is extremely low. Likewise, where much is known about a particular factor in the application and the behavior of the candidate materials of construction with respect to that factor, failures due to that factor are rare.

An example of the former situation is the aircraft turbojet engine. When first brought into production and use, failures of many sorts were quite common. Ignorance of the factors involved was reflected in the establishment of the practice of completely overhauling and reblading an engine every 100 hours. To-day the state of knowledge of this application has advanced to the point where performance reliability is high, failures are few, and the spacing between complete overhauls has extended beyond 500 hours for engines in commercial use.

The latter situation can be illustrated this way. In general, between the use of design safety factors well established by experience and the capability to calculate applied stresses reasonably well, the situation imposed on a structure by intentional loads can be accounted for. Otherwise, they would fail from rupture or excessive creep. On the other hand, much is known about the creep and rupture properties of many candidate constructional materials. Considering the capabilities of the designer and the knowledge of the materials engineer with respect to applied loads and the corresponding response of materials, it is not surprising that few failures occur from the action of applied stress. Simple rupture and creep failures are extremely uncommon.

The same situation prevails with respect to general corrosion by oxidation. Enough is known about general uniform wastage of many materials by oxidation that the influence of this factor usually can be anticipated and taken into proper account. Failures due to this factor are rare, unless the temperature was higher than anticipated or an unexpected change occurred in the environment.

Ignorance in the form of a lack of information on an important factor in the service conditions can be illustrated by the experience of a public utility. Some years ago the company had a mercury boiler installed and it was designed to be fired with Bunker-C oil. After some months of operation, it was noted that the furnace tubes were wasting in a peculiar nonuniform manner and at an alarming rate. The tubes looked as if they had been gouged or eaten by worms, and some perforations occurred. It had been expected that the tubes would oxidize uniformly and slowly in a reasonably predictable manner that would insure satisfactory service for some 20 years. Instead, the normally protective oxide coating on the tubes had been fluxed by products of the combustion of the oil to form a low melting slag which periodically sloughed off exposing fresh metal for further attack. The general condition is shown in figure 1. Research revealed that the unknown factor which had produced the unexpected failures was the presence of vanadium in the oil. This metal forms a series of oxides which are capable of combining with other oxides, such as the scale on steel, to produce slage of low melting point. Some of the

complexes so formed melt at temperatures below the temperature at the outside surface of the furnace tubes. Being viscous, they sloughed off.

A common mode of failure in the blades of a gas turbine is fatigue. This type of failure occurs stepwise, that is, a little at a time. A fatigue failure is recognizable because its stop-and-go characteristic is recorded on the fracture surface in the form of rings or annular markings which tend to spread from the point of initiation. See figure 2. When the fatigue crack has progressed to the point where the stress on the remaining metal exceeds the fracture strength, rapid failure like that in a standard tension test occurs. Fatigue failures usually reflect incomplete knowledge of the vibrational factor in the application as well as incomplete information on the fatigue resistance of the material. Occasionally, the cause can be attributed to defective material or defects introduced during manufacture.

While considerable information is available on uniform oxidation, much remains to be learned about localized high-temperature corrosion especially when a suitable state of stress exists. For example, Inconel has a well-earned reputation for oxidation resistance and, on that basis, tubing of this alloy was used in an aircraft cabin heater. It was not appreciated that the alloy might behave differently when the factor of vibration was introduced. The result was a corrosion-fatigue failure, as shown in figure 3. The combination of the oxidizing environment and the vibrational stresses caused cracks to develop along the grain boundaries of the metal.

Sometimes ignorance of the degree of stability of the material of construction, as a function of time at elevated temperatures, can lead to unexpected failures. The precipitation of carbides (figures 4 and 5), or the gradual formation of the sigma phase (figure 6), in certain stainless steels can convert what started out as a ductile alloy into a brittle material. Because the design concept was based on ductility and toughness in the material, the structure eventually failed. It had been considered that little attention need be paid to the presence of designed-in notches or adventitious stress raisers. Had it been known that the alloy would become brittle and notch sensitive, a different material might have been selected, the design might have been changed, and the quality control standards used in manufacture might have been raised.

The history of steam piping affords a classical example of a failure due to the unexpected influence of long times at elevated temperatures on the microstructure of steel. Until 1945, it was not thoroughly appreciated that the normally observed microstructure of plain and low-alloy steels, that is, a mixture of ferrite and pearlite, is actually metastable, even through thermodynamic calculations had shown that such is the case. Then, a steam line leading from one of the boilers at the Springdale Station of the West Penn Power Company came apart near a welded joint. The fact that the boiler was going off the line averted what would otherwise have been a catastrophe. During the years, the microstructure of the steel changed from ferrite and pearlite to the stable state of ferrite and graphite. The latter had concentrated along the low-temperature edge of the weld-heat-affected zone to the point that a narrow section of the pipe had become converted essentially to graphite. Examples of graphitization are shown in figures 7, 8 and 9. Through research it was established that the addition of a small amount of chromium to the steel would stabilize the ferrite-plus-pearlite structure.

Failures sometimes reveal misconceptions and oversights relating to design. The fatigue failure of a disk in a stationary gas turbine illustrates a design oversight. As shown in figure 10, the crack initiated at the corner of the bottom serration of one of the fir trees into which the blades were locked. Considering the high operating stresses and

the fact that the blades were force fit into place, the corners of the serrations were too sharp. They acted as stress raisers, providing stress concentration factors too large to be tolerated. If these corners had been rounded, the stress concentration factor would have been considerably reduced and failure would probably have been avoided.

An example of a design misconception is illustrated by the failure of a bell-type retort made of AISI 304 stainless steel. The mechanism of failure can be described as low-cycle corrosion fatigue. The corrosive medium was air at 1400 F, while the fatigue factor arose from cyclic stressing during operation. The resulting destruction of the metal is illustrated in figure 11. The stress condition was aggravated by the existence of a thermal gradient through the wall of the retort. An attempt was made to eliminate failures by increasing the wall thickness of the retort, on the theory that the unit stresses involved would decrease correspondingly. What happened, of course, was that the thermal gradient was increased, thereby increasing the contribution made by thermal stresses. The inherent misconception regarding the factors controlling thermal stress led to an increase in the frequency of failures. The problem ultimately was eliminated by selecting a stronger stainless steel and drastically reducing the wall thickness of the retort.

This case illustrates a common fallacy which results from superficial thinking or incomplete knowledge. "If the structure breaks, beef it up where it broke." Using such a main-strength-and-awkwardness approach to a problem often is the worst possible course of action.

Experience teaches the quality required in a material for a given application. The quality factor often may be operative in early failures encountered in a markedly new type of application, but disappears as experience is gained. However, the quality factor may be responsible for failures in well-known applications when defective material has escaped through the inspection process or when an important feature of quality is difficult to define and inspect for. Of course, quality requirements vary with the application. What is acceptable in one case may be intolerable in another. Carburizing trays need be little more than so much air surrounded by a skin of metal. On the other hand, a high-pressure retort must be made of completely sound, clean, homogeneous metal.

Another area of ignorance relates to the manufacture of components. Sometimes a step in the manufacturing process will cause damage that leads to failure in service. The component may be improperly forged, annealed, stress relieved, or welded. Disasterous notches may be put in the metal by grinding, machining, rough handling, or stamping of identification marks. In the case of some investment-cast Stellite 31 super-charger rotors, it was observed that some operated satisfactorily but others cracked in the hub section. Investigation revealed that the rotors which failed were always those that had been severely ground. Further, the grinding was a high-speed operation which caused considerable local heating of the metal with attendant heat checking, the cracks following along the eutectic carbides in the material. See figure 12. When the rotors were subsequently "run-in" or put in service, these cracks acted as highly effective stress raisers, as shown in figure 13. Several ways to solve the problem were open; namely, hot grind, machine instead of grinding, use a belt grinder instead of a high-speed wheel, redesign the casting to reduce the amount of stock needing removal.

Finally, it is not uncommon to observe failures resulting from misuse of equipment. A particular structure may be designed to operate at a certain maximum temperature, but after a while this limitation is ignored. The N-155 guide vanes of a stationary gas turbine buckled, cracked, and scaled badly after a moderate length of time in service.

This situation was not surprising when account was taken of the fact that the turbine had been operated 350 F above the design temperature. Of course, it took some technical detective work to demonstrate that such misuse had actually occurred. Figures 14 and 15 show the types of damage done.

There are many forms of misuse and abuse. Overloading a structure mechanically is not unknown. Switching from the high-grade fuel for which the equipment was designed to a low-grade substitute is occasionally indulged in with disastrous corrosion problems ensuing.

It may seem to be implied in all the foregoing discussion of failures that it is usual to find a single cause and a fairly direct relationship between the cause and the failure. Such a situation is unusual. Normally, a combination of causative factors exists and it is difficult to decide their relative importance, or a primary cause is identified along with a number of important contributory factors. Over-speeding may have been associated with the fatigue failure. Sulfidation may have accompanied the attack by oxygen.

COMMENTS ON MATERIALS

A number of factors relating to the metallic materials selected for high-temperature applications have already been touched on. In selecting a constructional material, it goes without saying that the choice should be based on a maximum of information about the intended application. So far as the material is concerned, it is often not enough to consider only its properties; rather, it is frequently advisable also to consider how best to make the desired component from the material. And, of course, the importance of determining the required level of quality and the establishment of suitable quality control procedures are far more appreciated today than ever before.

It is evident that much more needs to be learned about high-temperature fatigue resistance, corrosion-fatigue resistance and stress corrosion as it occurs at elevated temperatures. The combined factors of corrosion and stress are prominent in a large number of high-temperature failures.

It is not wise to assume that because a material has good general oxidation resistance, it will resist attack when surface tensile stresses are present. Often, such a material is quite susceptible. This is especially true if, during service, microstructural changes occur which make certain features of the structure more susceptible than others to attack. Depending on the environment and the temperature, this may occur when inter-granular carbide precipitation takes place in a stainless steel; the grain boundary region becomes more susceptible to oxidation. In some cases, then, it may be wise to resort to the stabilized grades of stainless steel.

It should be noted also that the type of chemical reaction between a metal and its environment may change with temperature and the concentration of the reactants. For example, Rene' 41 usually forms a tight oxide coating on exposure at temperatures up to 1850 F in oxidizing atmospheres. However, above this temperature it is susceptible to inter-granular oxidation, which tends to impair its usefulness at such temperatures when in the form of thin sections.

In applications involving fatigue it is advisable to consider the damping capacity of the material whenever possible. Those with high damping capacities alleviate the fatigue

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problem. The 400 series stainless steels and the cobalt-base alloys have good reputations in this respect.

In the realm of producibility, a casting is sometimes preferable to a wrought product from the standpoint of cost and freedom from anisotropy. However, depending on the design of the component, a sounder product may be made from one alloy than from another. In such a case, the method of manufacture becomes critically important in selecting the material. And, of course, it often occurs that a design which is satisfactory for a wrought product is unsuitable for a casting. The design should be changed in deference to the requirements of casting when a switch is made from a wrought to a cast product.

In both wrought and cast components it is important to pay close attention to welding when the process of welding is required. Proper techniques and compatible filler metal are mandatory. What happens to the weld-heat-affected zone is sometimes just as important in high-temperature service as in room-temperature corrosive environments. In some stainless steels, detrimental carbide precipitation or sigma formation may occur in this zone.

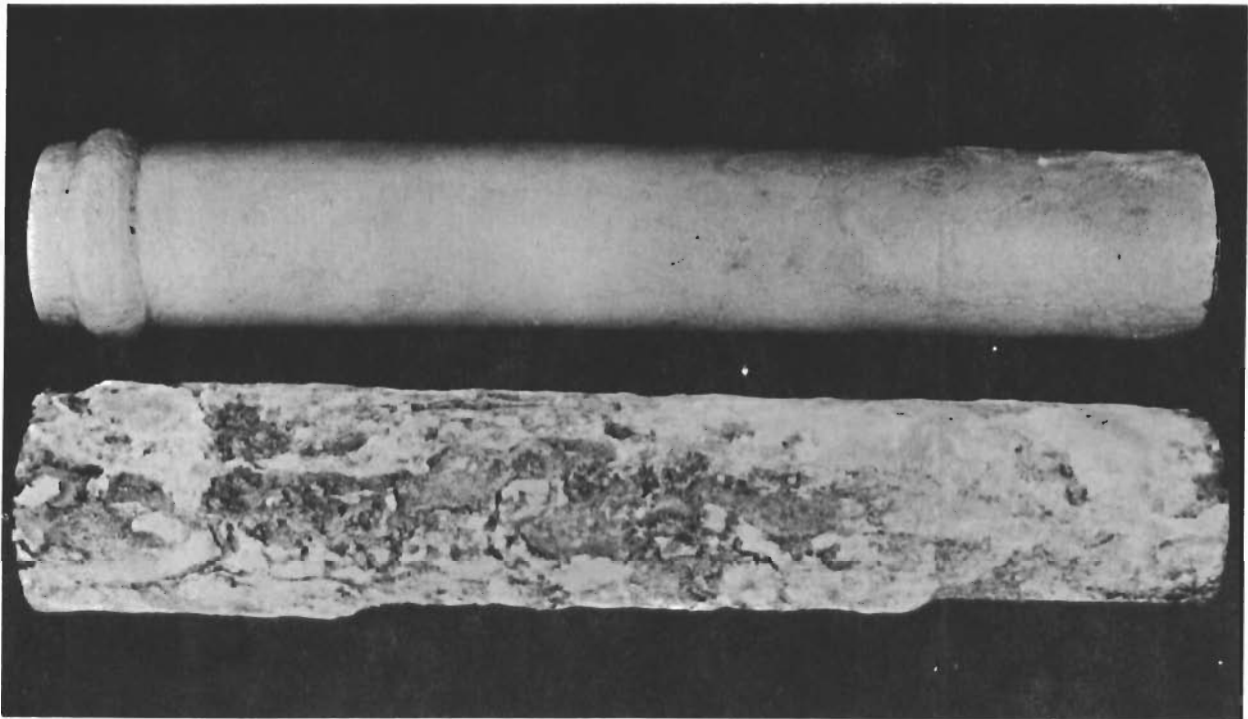


Figure 1. Furnace Tubes from Mercury Boiler. Top Tube is Coated with High-Vanadium, High-Sulfur Slag. Bottom Tube, Containing Weld, was Grit Blasted; it Shows Evidence of Mild Attack

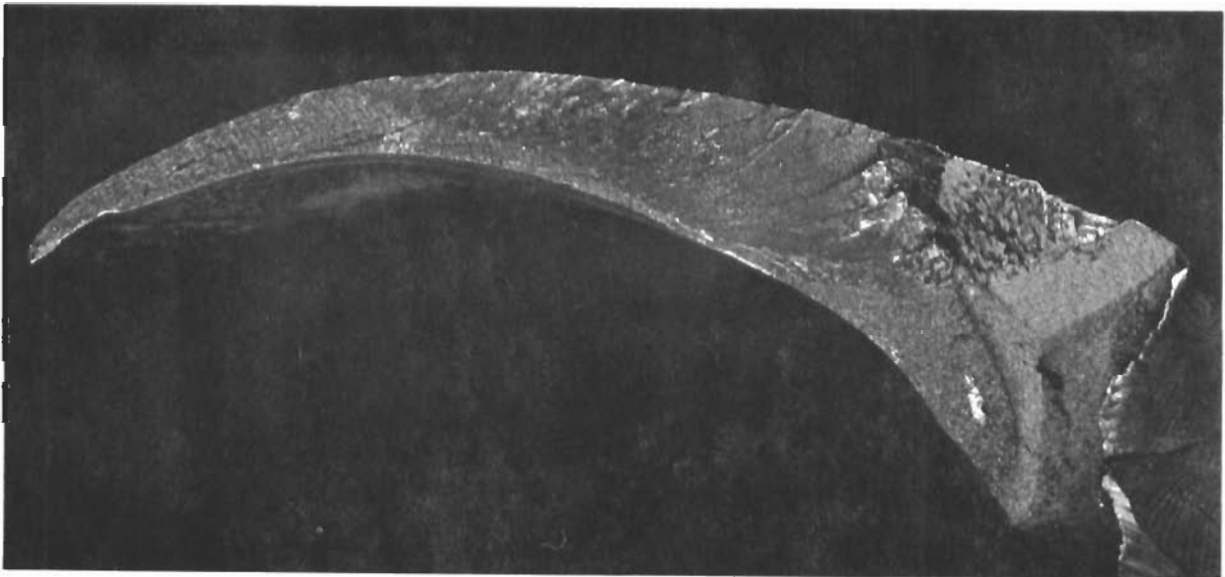


Figure 2. Fatigue Failure in Blade of Stationary Gas Turbine. Failure Started on Convex Side Near Tip.

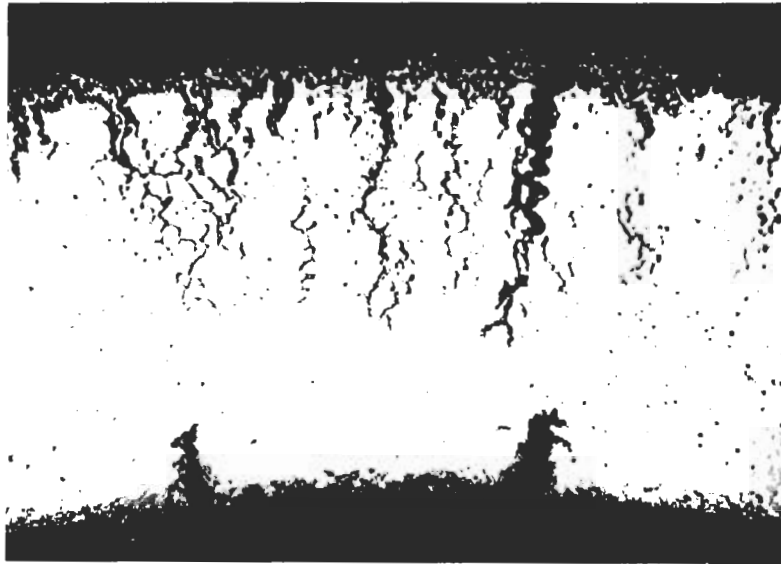


Figure 3. Oxidation-Fatigue Cracks Penetrating the Wall of an Inconel Tube, Oxide is Visible in Some of the Cracks.



Figure 4. A 20 Cr-9 Ni Alloy as Cast. Eutectic Carbides, Some Intergranular Carbides and Occasional Islands of Delta Ferrite are Present

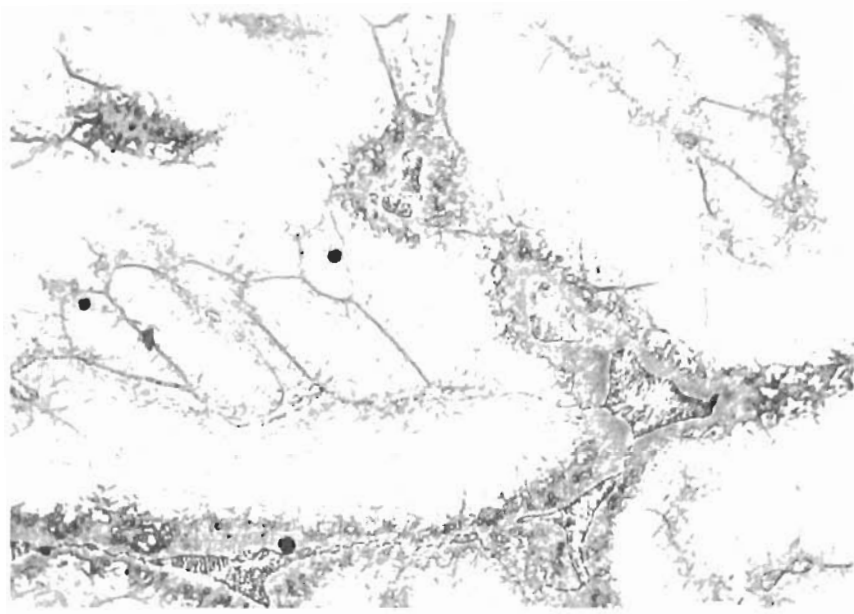


Figure 5. Same Material as in Figure 4 After Prolonged Heating at 1400 F. Heavy Carbide Precipitation has Occurred

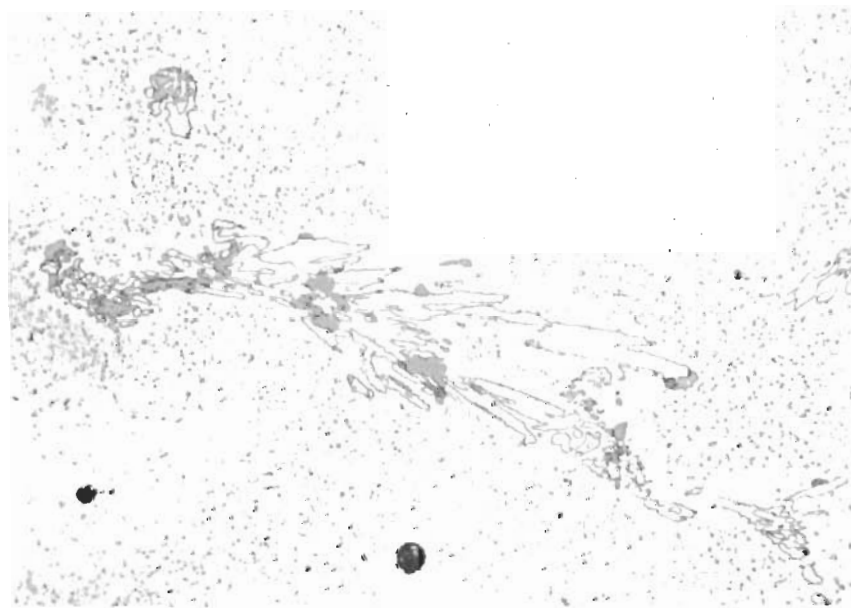


Figure 6. A Cast Fe-Cr-Ni Alloy After Long-Time Service at Elevated Temperature. Sigma Phase (Light Gray) has Formed

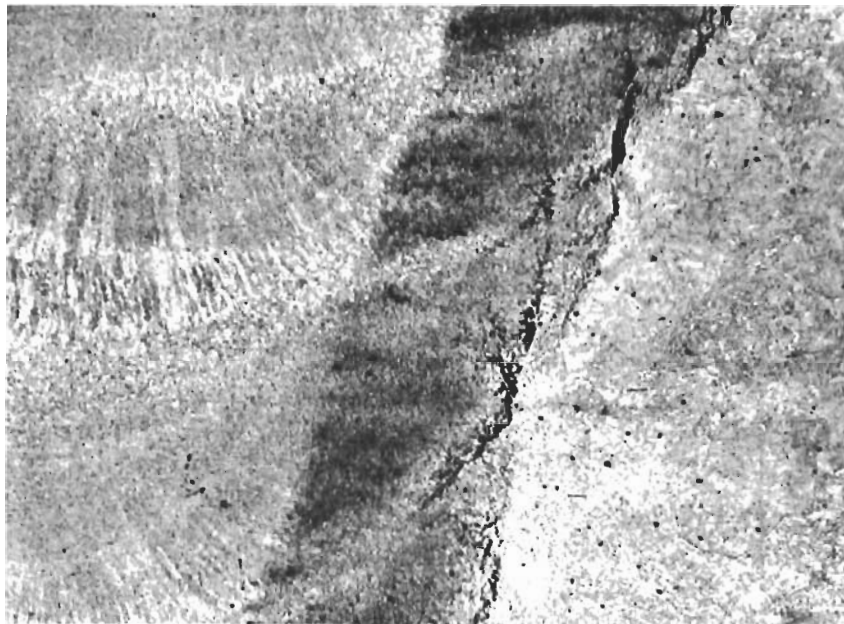


Figure 7. Portion of Welded Joint in Steam Pipe. Weld is at Left; Parent Metal at Right. Graphite has Formed at Low-Temperature Edge of Weld-Heat-Affected Zone



Figure 8. An Example of Moderate Graphitization at the Low-Temperature Edge of a Weld-Heat-Affected Zone

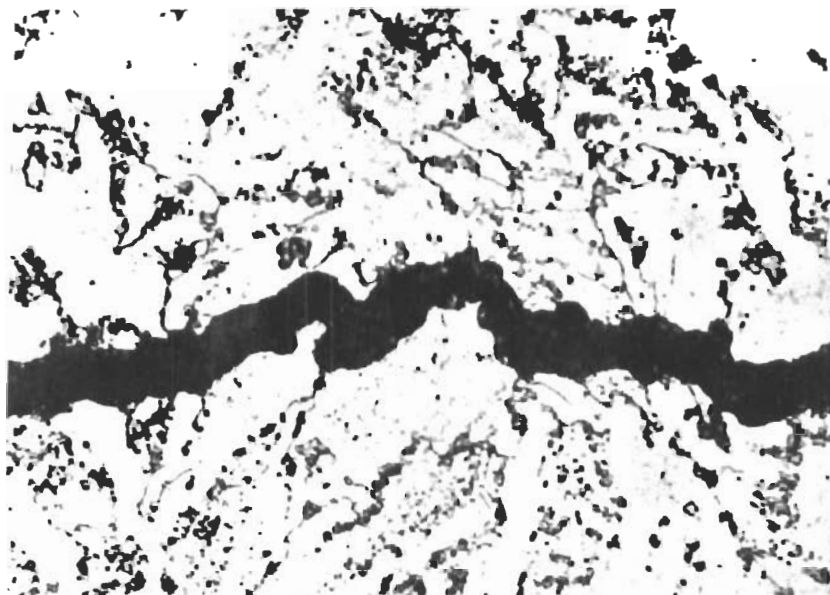


Figure 9. Extremely Severe Graphitization

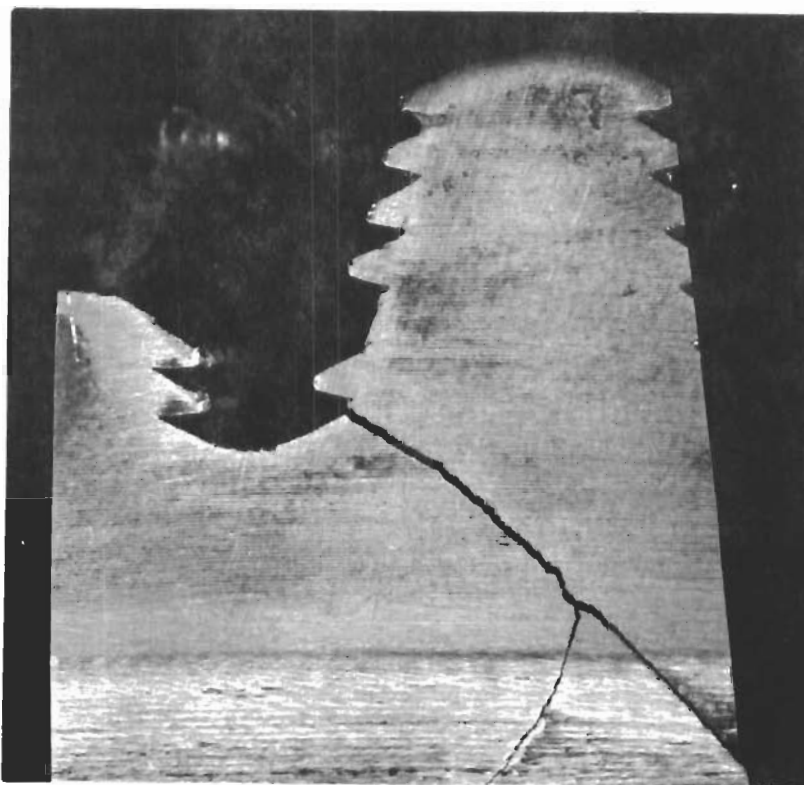


Figure 10. Section from the Disk of a Stationary Gas Turbine. The Crack Started at the Corner of the Bottom Serration of a Fir Tree

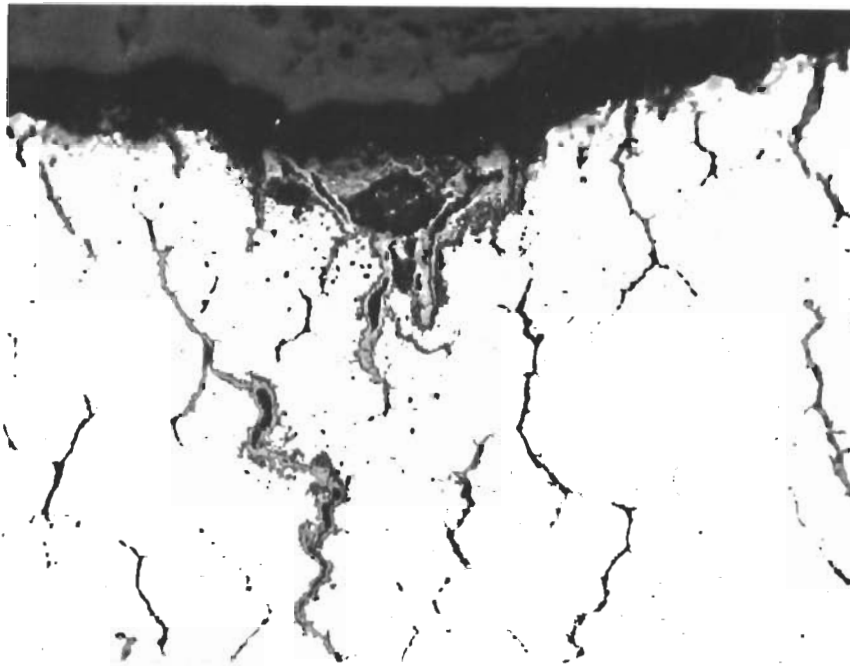


Figure 11. Low-Cycle Oxidation Fatigue in a Stainless Steel Retort. Oxide is Evident in the Cracks

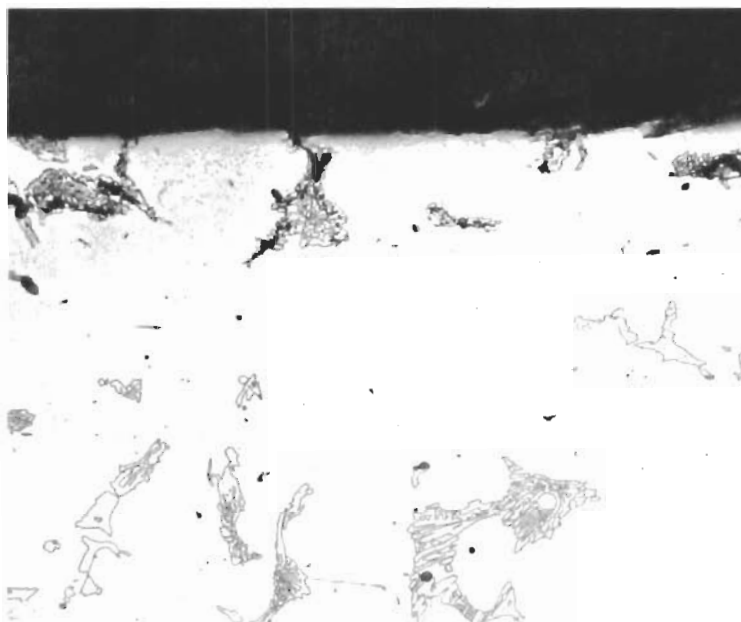


Figure 12. Grinding Cracks in an Investment Cast Stellite 31 Supercharger Rotor

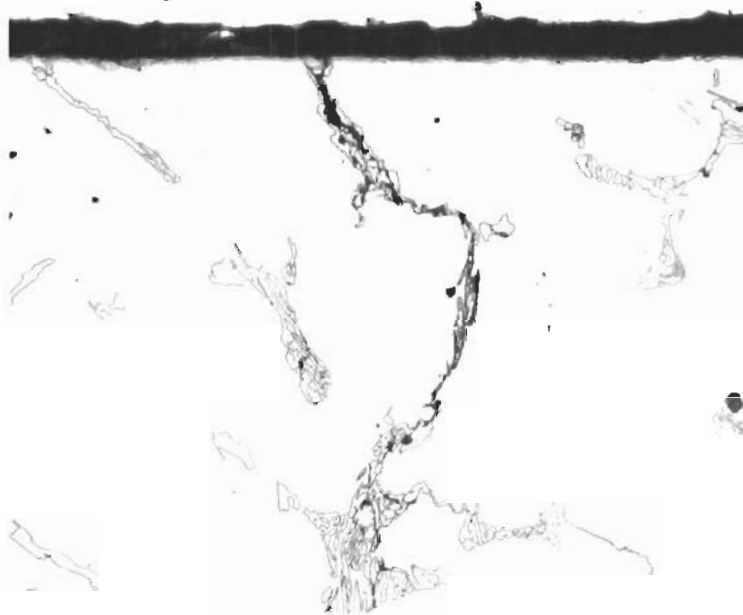


Figure 13. Supercharger Rotor After Run-In. Compare with Figure 12 to Note How the Original Grinding Cracks Extended

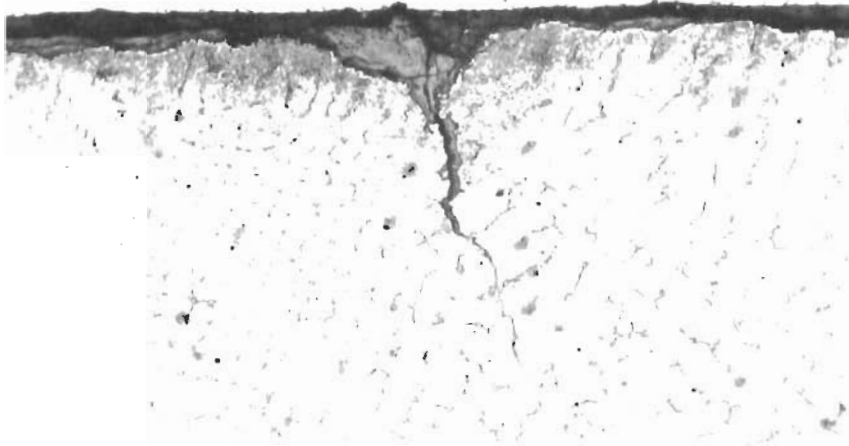


Figure 14. Severe Localized Oxidation in an Overheated N-155 Nozzle Guide Vane

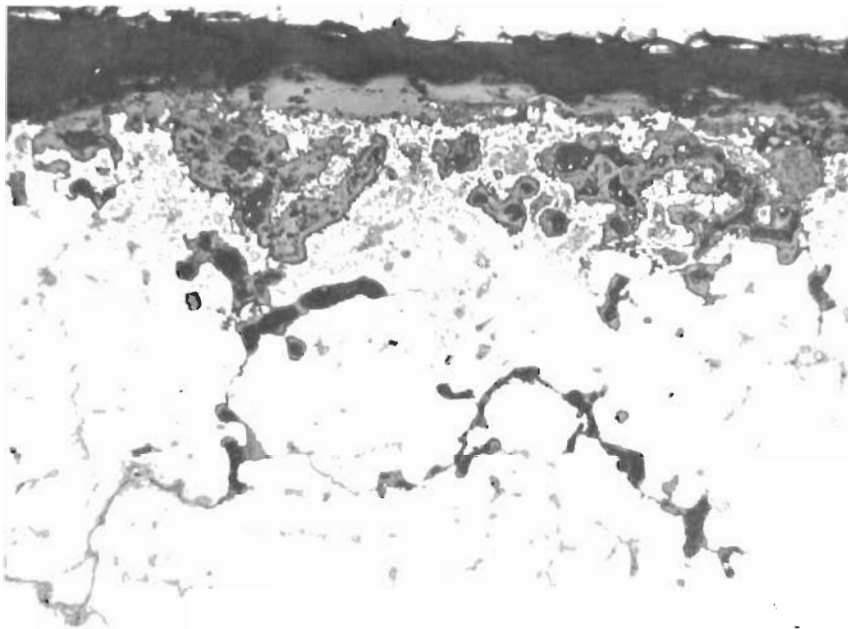


Figure 15. Severe Corrosive Attack on an Overheated N-155 Nozzle Guide Vane