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## CATASTROPHIC OXIDATION OF HIGH-TEMPERATURE ALLOYS

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### ABSTRACT

The growth of nonprotective, crust-like oxide films is encountered in high-temperature alloy systems that contain molybdenum, vanadium, or tungsten as strengthening additions. The cause of accelerated oxidation in such alloys appears to be associated with the characteristically low melting temperatures of oxides of these refractory elements. The factors that contribute to a breakdown of oxidation protection in these systems are outlined and remedial methods which may be used to avoid catastrophic oxidation are discussed. Commonly encountered service failures that have resulted from catastrophic oxidation are also described.

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# CATASTROPHIC OXIDATION OF HIGH-TEMPERATURE ALLOYS

## INTRODUCTION

The components tungsten and molybdenum are routinely utilized in commercial alloy systems that display outstanding strength properties at high temperatures. Typical of such alloys are those listed in Table 1. Although a thin, adherent oxide film is generally produced when alloys of this type are heated in oxidizing atmospheres, in some instances the rate of oxidation may become very rapid, and large growths of crust-like oxides appear. Because of the severity of this attack, the term catastrophic oxidation has been applied.

The essential difference between catastrophic oxidation and the oxidation usually encountered in conventional metals and alloys is that the corrosion product in the former does not act as a barrier to continued attack. The scale layer is either entirely unprotective, leading to a linear rate of oxidation; or it actually causes a more intense attack to occur as the scale layer thickens, which results in a continually accelerating rate of oxidation.

This report discusses the nature and causes of catastrophic oxidation, emphasizing particularly its ramifications in the use of molybdenum-containing stainless steels. The discussion is based on a review of published reports concerning this phenomenon and on an examination of failures caused by catastrophic oxidation that have occurred in experimental programs at the Oak Ridge National Laboratory (ORNL).

## NATURE OF CATASTROPHIC OXIDATION

As indicated above, the occurrence of catastrophic oxidation in high-temperature alloys has been traced to the incorporation of molybdenum and tungsten as alloying additions. Alloying additions of vanadium, though less widely encountered, can likewise impart susceptibility to this mode of oxidation. The effect of these additions seems to be that of opening agents; that is, they render the resultant oxide film more pervious. It is generally agreed that this effect stems from the characteristically low melting points of the oxides of these elements, especially when they are mixed with the

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Table 1. Commercial High-Temperature Alloys Susceptible to Catastrophic Oxidation

Alloy Designation	Nominal Composition (wt %)					
	Cr	Ni	Mo	W	Cb	Others
16-25-6	16	25	6			
Type 316 Stainless Steel	18	12	2.5			
Type 317 Stainless Steel	18	12	3.5			
19-9 DL	19	9	1.5	1.2	0.3	0.2 Ti, Bal Fe
N-155	20	20	3	2	1	Bal Fe
Refractaloy B	24	30	8			Bal Fe

oxides of certain of the other alloy constituents. It is also agreed that their destructive influence is associated with the formation of liquid or gaseous oxide compounds.

The presence of vanadium, tungsten, and molybdenum as external contaminants similarly serves to debilitate the protective qualities of oxide films. In this case, the destructive effect is the formation of a pervious complex or mixed oxide by reaction of atmospheric oxygen and contaminant with the metal surface. The other external contaminants that have been experimentally observed to induce catastrophic oxidation in otherwise passivated alloys include  $KF$ ,  $Bi_2O_3$ ,  $Na_2O$ , and  $PbO$  (ref 1).

Aside from an extremely rapid rate of reaction (whereby a 1/4-in.-thick section may be consumed in less than 10 hr), the process of catastrophic oxidation displays other unique characteristics. The area over which the crust-like growth develops tends to be localized, occurring at the point of highest temperature or at the site of external contaminants. It may slowly spread to other parts of the system, although failure usually occurs before substantial areas have been affected. Although localized, these areas of catastrophic attack advance uniformly through the metal cross section, i.e., are not intergranular in nature.

The oxide product associated with catastrophic oxidation, being quite spongy, is many times greater in volume than the volume of metal consumed. Thus, areas which have undergone this form of attack exhibit considerable swelling. When removed from the area, the oxide often displays a stratified appearance, as typified by the bottom photograph in Fig. 1. (The type 316 stainless steel specimen shown in this figure failed during service at 1400°F, catastrophic attack being initiated by the presence of Sauereisen cement.) In several cases it has also been noted that the scale formed during catastrophic oxidation tends to be especially porous at the metal-oxide interface, as shown in the upper portion of the photograph in Fig. 2. The gas-oxide interface, as shown in the lower portion of the photograph in Fig. 2, is generally smoother and almost free from porosity.

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<sup>1</sup>W. C. Leslie and M. G. Fontana, Trans. Am. Soc. Metals 41, 1213 (1949).

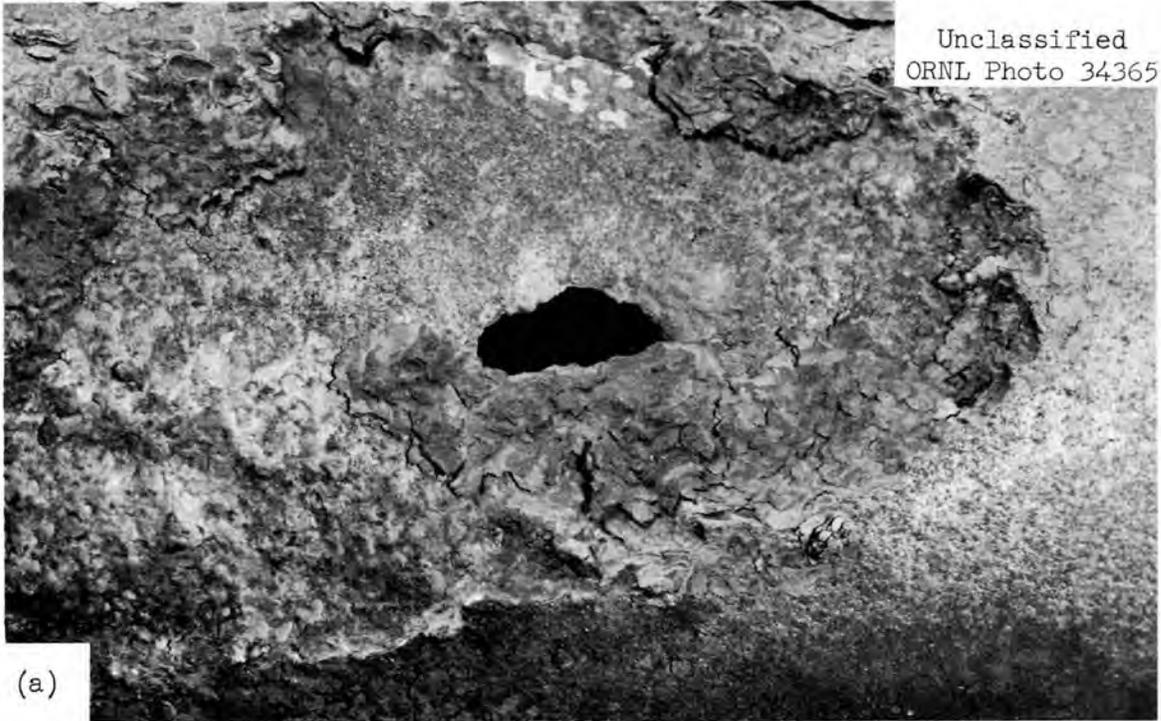


Fig. 1. Area of Catastrophic Oxidation Which Produced Failure of Type 316 Stainless Steel 2-in. Sched-40 Pipe. (a) Zone of failure after removal of oxide products. (b) Oxide Products.

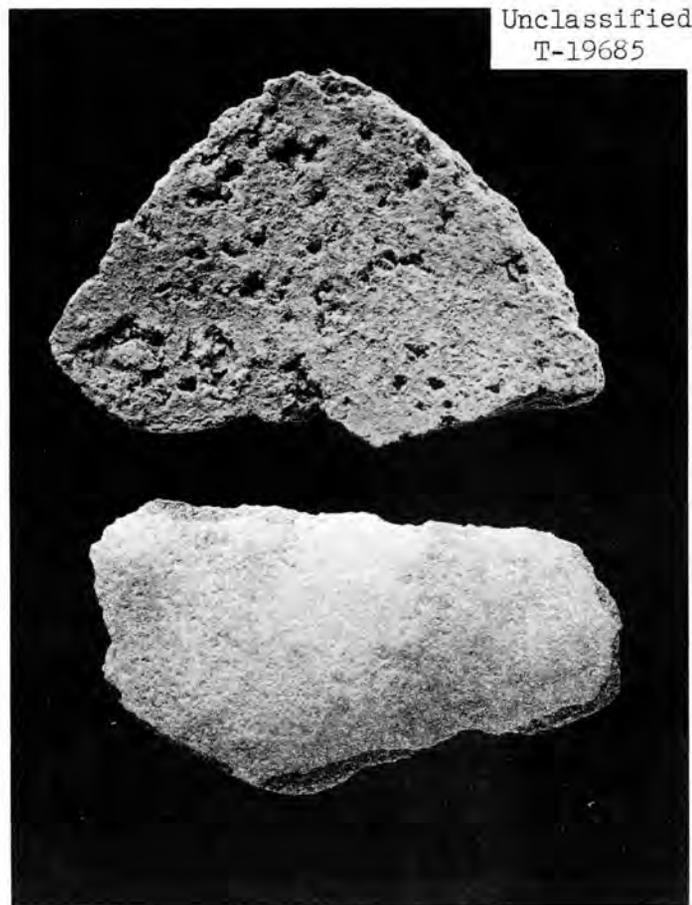


Fig. 2. Appearance of Oxide Product Produced on Type 316 Stainless Steel Specimen at 1500°F. Upper portion shows metal-oxide interface and lower portion shows gas-oxide interface. 3X.

Catastrophic oxidation, when it occurs in conjunction with iron-base alloys, generally produces a magnetic oxide, as demonstrated in Fig. 3. The contents of various metals in the oxide product usually approximate stoichiometrically the contents of the metals comprising the alloy. In the case of 18-8 stainless steels, the oxide product consists mainly of  $Fe_2O_3$  and  $Fe_3O_4$ .

## FACTORS AFFECTING CATASTROPHIC OXIDATION

### Effect of Temperature

The onset of catastrophic oxidation in alloys contaminated by or containing tungsten, molybdenum, and vanadium shows a direct correlation with the melting points of oxides formed by these elements. Table 2 compares the melting temperatures of the pure oxide of these elements and combinations thereof. Stipulating that a molten oxide must be present to induce catastrophic oxidation, it is apparent that alloys, if free from copper, should not encounter this mode of attack at temperatures below  $1200^{\circ}F$  and, if free from vanadium, should be immune below  $1300^{\circ}F$ . Experimental evidence bears out these conclusions. It has also been observed, again concurring with Table 2, that the threshold temperature for catastrophic oxidation is lowest when associated with vanadium, intermediate for molybdenum, and highest for tungsten.<sup>2</sup>

If external contaminants are absent, the lower temperature of "spongy" oxide formation for molybdenum-containing alloys in stagnant air or oxygen appears on the basis of experimental studies<sup>1,2</sup> to be between  $1400$  and  $1500^{\circ}F$ . (In one recent reference,<sup>3</sup> mention is made of the occurrence of catastrophic oxidation in a type 317 stainless steel at  $1350^{\circ}F$  during an extended exposure of 46,000 hr in air. However, no details are given as to the cleanliness of the experiment or to the reliability of temperature measurements during this period.) This temperature range corresponds closely to the melting point of  $MoO_3$ . However, a spongy oxide has formed as low as

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<sup>2</sup>A. de S. Brasunas and N. J. Grant, Iron Age 166(7), 85 (1950).

<sup>3</sup>E. A. Sticha, Proceedings of the American Power Conference 22, 288 (1960).

Unclassified  
T-19684



Fig. 3. Magnetic Attraction Displayed by Product of Catastrophic Oxidation. 2 1/4 X.

Table 2. Melting Points<sup>a</sup> of Various Oxide Compounds Containing Vanadium, Molybdenum, or Tungsten<sup>b,c,d,e</sup>

Pure Oxides	Mixed Oxides	Melting Point	
		°C	°F
WO <sub>3</sub>	(No data on mixed oxides of W were found)	1471	2683
MoO <sub>3</sub>		795	1463
	V <sub>2</sub> O <sub>5</sub> -MoO <sub>3</sub>	610-718	1130-1325
	MoO <sub>2</sub> -MoO <sub>3</sub>	778	1432
	MoO <sub>2</sub> -MoO <sub>3</sub> -Cr <sub>2</sub> O <sub>3</sub>	772	1422
	MoO <sub>2</sub> -MoO <sub>3</sub> -NiO	764	1405
	Fe <sub>2</sub> O <sub>3</sub> -MoO <sub>3</sub>	730	1346
	Fe <sub>2</sub> O <sub>3</sub> -Fe-MoO <sub>3</sub>	725	1339
	Na <sub>2</sub> O-MoO <sub>3</sub>	499	930
	Cu <sub>2</sub> O-MoO <sub>2</sub> -MoO <sub>3</sub>	470	878
V <sub>2</sub> O <sub>5</sub>		670	1240
	V <sub>2</sub> O <sub>5</sub> -Na <sub>2</sub> SO <sub>4</sub>	600-619	1110-1150

<sup>a</sup>Temperatures generally represent the lowest melting points attainable in the systems listed.

<sup>b</sup>A. de S. Brasunas and N. J. Grant, Iron Age 166(7), 85 (1950).

<sup>c</sup>G. W. Rathenau and J. L. Meijering, Metallurgia 42, 167 (1950).

<sup>d</sup>A. de S. Brasunas and N. J. Grant, Trans Am. Soc. Metals 44, 1117 (1952).

<sup>e</sup>G. M. Adamson, Jr., ORNL-1692, p 74 (1954). Classified.

1200°F on the Timken 16-25-6 alloy when in contact with V<sub>2</sub>O<sub>5</sub> (ref 1). Catastrophic failure of type 316 stainless steel in contact with Sauereisen cement also has been encountered in experiments operated by ORNL at temperatures slightly below 1400°F.

Experiments performed by Rathenau and Meijering<sup>4</sup> on 19-9 chromium-nickel steels in the presence of MoO<sub>3</sub> showed an abrupt increase in the air-oxidation rate vs temperature curves at 1420°F. This temperature corresponds closely to the MoO<sub>3</sub>-MoO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub> eutectic temperature (Table 2). Steels containing 25% Cr in the presence of MoO<sub>3</sub> exhibited a "break-away" temperature at 1450°F.

It has been noted that, during the progress of accelerated oxidation, the oxidizing specimens frequently appear to be hotter than their surrounding. Thermocouple measurements by one experimenter<sup>5</sup> showed the effect to be real and that the temperature increase corresponded to that predicted on the basis of oxidation rates and heats of formation of oxides from their elements. This effect at least partially accounts for observation that metals undergoing catastrophic oxidation may exhibit continually increasing oxidation rates as a function of time.

#### Effect of Time

In the absence of external contamination, a finite period of time is generally required to initiate the process of catastrophic attack. Temperature strongly controls the duration of this "quiescent" period. In their investigation of stainless steels, McCullough et al.<sup>6</sup> found that at 1800°F there was an abrupt increase in the oxygen pickup after an initial period ranging from 10 to 45 min. At 1700°F, the abrupt increase did not take place until after about 4 hr.

Once catastrophic attack is initiated, the rate of oxidation rapidly increases as a function of time. In certain cases, this accelerating rate

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<sup>4</sup>G. W. Rathenau and J. L. Meijering, Metallurgia 42, 167 (1950).

<sup>5</sup>A. de S. Brasunas and N. J. Grant, Trans. Am. Soc. Metals 44, 1117 (1952).

<sup>6</sup>H. M. McCullough et al., Trans. Am. Soc. Metals 43, 404 (1951).

of oxidation finally reverts to a linear rate; in other cases, particularly at relatively high temperatures, the acceleration continues until the specimen is completely consumed. In most instances, the final rate of oxidation is notably higher than the initial (zero time) rate.

When catastrophic oxidation is instigated by an external contaminant, dilution of the contaminant during oxidation depending on the initial amount and regenerative nature of the contaminant may eventually effect a slowdown of oxidation.

#### Effect of Alloy Composition

Investigations of the effect of alloy composition on susceptibility to catastrophic oxidation have been confined largely to molybdenum-containing systems. Several important effects regarding the role of alloy composition were demonstrated in experiments with iron-molybdenum and nickel-molybdenum systems performed by Brenner.<sup>7</sup> These studies, which were conducted at 1000°C (1832°F), led to the following conclusions:<sup>8</sup>

1. Binary iron-molybdenum alloys containing up to 12.5 at. % Mo showed no evidence of catastrophic oxidation on exposure to air.
2. Likewise, binary nickel-molybdenum alloys containing up to 18.7 at. % Mo effectively resisted catastrophic attack by air.
3. The addition of chromium in the range from 5 to 25 at. % to iron-molybdenum alloys imparted susceptibility to catastrophic attack.
4. Nickel additions above 10 at. % and below 30 at. % similarly produced catastrophic attack in iron-molybdenum alloys. The most severe rate of oxidation was encountered at a nickel content of 25 at. %.
5. Alloys containing more than 30 at. % Ni, whether of the type nickel-molybdenum, nickel-iron-molybdenum, or nickel-chromium-iron-molybdenum, were completely resistant to catastrophic attack by air.

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<sup>7</sup>S. S. Brenner, J. Electrochem. Soc. 102, 16(1955).

<sup>8</sup>An explanation of these findings is presented in "Correlation Between Theory and Observation," p 18 in this report.

The last conclusion bears special attention, in view of the widespread use of the alloy INOR-8 (17 wt % Mo-7 wt % Cr-5 wt % Fe-bal Ni) in reactor programs at ORNL. Oxidation studies conducted by Inouye<sup>9</sup> on this alloy composition corroborate the finding that nickel-base molybdenum systems (in the absence of external impurities) are not susceptible to catastrophic attack in air at temperatures up to 1800°F.

Oxidation studies performed on modifications of the Timken 16-25-6 alloy (16 Cr-25 Ni-6 Mo-bal Fe) similarly have shown an important effect of composition on oxidation resistance.<sup>10</sup> By successively increasing the chromium content from 16 to 20% and then to 25%, a noticeable improvement in the oxidation resistance occurred. A similar improvement was observed when the nickel content was increased from 25 to 30%. However, only in alloys containing greater than 30% Ni was catastrophic oxidation completely suppressed.<sup>11</sup>

Only limited studies have as yet been made regarding the lowest (threshold) concentration of molybdenum that will spontaneously trigger catastrophic oxidation in iron-base systems. This limit assuredly depends on the temperature at which oxidation takes place and on surface cleanliness. Concentrations as low as 2% Mo are observed consistently to produce catastrophic oxidation at 1000°C (1832°F) in alloys of the 18-8 or 16-25 type;<sup>10</sup> however, the occurrence of catastrophic oxidation with a molybdenum concentration this low is less predictable at lower temperatures and, it must be assumed, depends on external factors, such as surface contamination and whether the oxidizing atmosphere is stagnant or moving. The threshold molybdenum concentration, as might be expected, is also dependent on alloy composition. A study was reported<sup>10</sup> of the oxidation behavior of type 316 (18 Cr-12 Ni-2.5 Mo-bal Fe) stainless steel and type 310 (25 Cr-20 Ni-bal Fe) stainless steel having varying amounts of molybdenum. Type 316 stainless steel retained a protective oxide only below 1800°F, whereas type 310 stainless steel modified with 3 and 6% Mo withstood 2000°F without evidence of accelerated oxidation after a 60-hr period.

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<sup>9</sup>Personal communication from H. Inouye, Oak Ridge National Laboratory, January 31, 1961.

<sup>10</sup>A. de S. Brasunas and N. J. Grant, Iron Age 166(7), 85-90 (1950).

<sup>11</sup>A. de S. Brasunas and N. J. Grant, Trans. Am. Soc. Metals 44, 1129 (1952).

### Effect of External Contamination

The conclusions reached above regarding the dependence of catastrophic oxidation on alloy composition refer specifically to systems whose surfaces are free from external contaminants. The introduction of foreign substances of the types listed earlier<sup>12</sup> serves both to reduce the temperature at which catastrophic oxidation is initiated in the "susceptible" alloy systems listed in Table 1 and to induce accelerated oxidation in many types of alloy systems where this form of attack does not otherwise occur. Susceptibility to catastrophic oxidation in the presence of surface impurities has been encountered in both 300 and 400 series stainless steels<sup>13</sup> and in nickel-base alloys containing appreciable amounts of molybdenum.<sup>14</sup>

It is apparently immaterial in the case of most sources of contamination whether they result as a product of oxidation of an adjacent alloy, a foreign material on the metal surface, or a constituent of the ambient atmosphere. The essential condition has been shown to be its presence in the proximity of the metal surface.<sup>15</sup>

The commonplace occurrence of impurities that may cause accelerated oxidation forbids a comprehensive listing of all potentially harmful sources; however, three sources that have been particularly damaging in high-temperature applications will be noted. The first of these has been identified with certain fuel oils and fuel ashes which nominally contain an appreciable concentration of vanadium compounds. Almost all heat-resisting alloys that depend on chromium for oxidation resistance are found to undergo catastrophic destruction in the presence of vanadium pentoxide.<sup>16</sup> Risk of destruction by vanadium compounds is greatly increased if sodium sulfate also is present.<sup>17</sup>

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<sup>12</sup>"Nature of Catastrophic Oxidation," p 2 of this report.

<sup>13</sup>W. C. Leslie and M. G. Fontana, Trans. Am. Soc. Metals 41, 1213 (1949).

<sup>14</sup>A. de S. Brasunas and N. J. Grant, Trans. Am. Soc. Metals 44, 1131 (1950).

<sup>15</sup>G. M. Adamson, Jr., ORNL-1692, p 74 (1954). Classified.

<sup>16</sup>G. W. Cunningham and A. de S. Brasunas, Corrosion 12, 389t (1956).

<sup>17</sup>W. R. Foster et al., Corrosion 12, 539t (1956).

A second class of commercially derived oxidation "catalysts" has been identified with certain types of high-temperature ceramic cements. Figure 1 illustrates the extent of oxidation that was incurred by a type 316 stainless steel pipe beneath an area of Sauereisen cement (type 1) in air at 1400°F. Hastelloy B, a nickel-molybdenum alloy which ordinarily resists catastrophic attack, also has been sensitized to excessive oxidation at areas overlaid by Sauereisen cement.<sup>15</sup> Although varying compositions of air-setting high-temperature cements are available, those which have been popularly employed at ORNL consist of feldspars mixed in water glass (sodium silicate). The effect on oxidation identified with such mixtures no doubt stems from the fluxing action of sodium silicate ( $\text{Na}_2\text{O}\cdot\text{SiO}_2$ ). (Since high-temperature cements play an important role in the experimental program at ORNL, a review of commercially available compositions to weed out incompatible systems is badly needed.)

A final source of contamination deserving special attention concerns the oxidation products associated with alloys that are naturally susceptible to catastrophic oxidation ( $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{WO}_3$ ). Catastrophic oxidation, after initiating in a material such as type 316 stainless steel, has been observed to spread to an adjacent type 347 stainless steel component, not normally susceptible to this form of oxidation. If a furnace atmosphere becomes contaminated with  $\text{MoO}_3$  (e.g., owing to the presence of molybdenum windings), oxidation of alloys subsequently heat treated in the furnace is found to be greatly enhanced.<sup>4</sup> Materials whose oxidation rate has been increased by the presence of  $\text{MoO}_3$  include types 304, 309, 410, 430, and SAE 4130 steels. The oxidation of Inconel, chromium, and nickel, on the other hand, appears to be little affected by the presence of  $\text{MoO}_3$  (ref 13).

A further illustration of the deleterious effects of oxide contaminants resulting from vapor transport is provided in Table 3. Weight gain data shown in this table were recorded for 16-25-6 alloy specimens placed adjacent to (but not in contact with) 1/2-g samples of oxides which have been identified as instigators of accelerated attack. Note that oxidation rates were noticeably increased even in the case of contaminants of relatively low volatility (e.g.,  $\text{WO}_3$ ).

Table 3. Oxidation Rates of 16-25-6 Alloy in Contaminated Air\*

Contaminating Vapor	Average Rate of Weight Gain, g/in. <sup>2</sup> /day	
	1585°F	1785°F
None	0.0004	0.008
V <sub>2</sub> O <sub>5</sub>	0.850	1.66
MoO <sub>3</sub>	0.238	1.70
Bi <sub>2</sub> O <sub>3</sub>	0.792	2.14
WO <sub>3</sub>	0.835	1.84

\*A. de S. Brasunas and N. J. Grant, Trans. Am. Soc. Metals 44, 1133 (1950).

The presence of  $V_2O_5$  or  $MoO_3$  has precipitated catastrophic oxidation even in systems which contained no other measurable sources of oxygen. Contacting the Timken 16-25-6 alloy with either  $V_2O_5$  or  $MoO_3$  at  $1650^\circ F$  was observed by Leslie and Fontana<sup>13</sup> to effect the catastrophic destruction of this alloy, not only in air but in a helium atmosphere virtually free from oxygen or nitrogen.

#### Effect of Oxidizing Environment

The placement of surfaces in close contact with molybdenum-containing alloys has been shown to adversely affect the oxidation behavior of these alloys even when these surrounding surfaces do not contain pernicious contaminants. The most probable explanation of this effect is allied with the fact that catastrophic oxidation occurs with a much higher rate of incidence in stagnant than in moving atmospheres. In experiments by Leslie and Fontana,<sup>13</sup> the continuous movement of air effectively prohibited the occurrence of catastrophic oxidation in molybdenum-containing stainless steels below  $1650^\circ F$ . Brasunas<sup>14</sup> likewise observed that alloys of the 16-25-6 type at  $1800^\circ F$  were severely oxidized in a stagnant oxygen atmosphere, while specimens in a circulating atmosphere were attacked only where they rested on the specimen holder. On the other hand, vanadium-containing alloys showed no differences in oxidation behavior in a stagnant or moving atmosphere.

A secondary effect of contact surfaces on the occurrence of catastrophic oxidation could conceivably result from a decreased oxygen supply and an alteration of the chemistry of the resultant oxides. It is not possible to assess this effect on the basis of experimental evidence, since only limited data are available concerning the effect of oxygen partial pressures on catastrophic attack. (All tests to date have been carried out either in air or pure oxygen, with no notable difference in results being reported.) However, as discussed above, catastrophic oxidation can take place even in the complete absence of oxygen if  $MoO_3$  or  $V_2O_5$  is initially present. Thus, the partial pressure of oxygen should have little effect on catastrophic attack so long as sufficient oxygen is present to form  $MoO_3$ ; a reduction of oxygen below this limit should be beneficial rather than harmful.

As discussed in the next section, the oxidation of molybdenum- or vanadium-containing steels results in the formation of lower oxides of the type  $\text{MoO}_2$  or  $\text{VO}_2$  unless the oxidizing environment is able to penetrate directly to the area where these oxides are formed. Such penetration by air environments can then produce low-melting higher oxides of the type  $\text{MoO}_3$  or  $\text{V}_2\text{O}_5$ . However, at sufficiently low oxygen pressures, even direct contact with the environment should not affect the initial lower oxides.

#### MECHANISM OF CATASTROPHIC OXIDATION

##### Proposed Theories

Early theories advanced to explain the phenomenon of catastrophic oxidation centered around its occurrence in molybdenum-containing systems. In the first detailed analysis of this phenomenon, Leslie and Fontana<sup>1,3</sup> concluded that catastrophic oxidation of alloys of 16-25-6 type proceeded in the following manner:

1.  $\text{MoO}_3$ , which has a measurable vapor pressure, distills off the surface above  $1475^\circ\text{F}$  and prevents the formation of an impervious spinel layer.
2. In addition, gaseous  $\text{MoO}_3$  promotes the rapid attack of metals due to thermal dissociation above  $1500^\circ\text{F}$ , i. e.,  
$$\text{MoO}_3 \rightarrow \text{MoO}_2 + 1/2 \text{O}_2$$
3. Nascent oxygen formed by the latter reaction is exceptionally reactive and leads to rapid corrosion.

Since the passage of oxidizing gases through the scale is unimpeded, the regeneration of  $\text{MoO}_2$  to form gaseous  $\text{MoO}_3$  is unhindered, and  $\text{MoO}_3$  in effect serves as an oxidation catalyst.

This theory, however, did not take cognizance of the likelihood of oxide melting. Thus, it was supplanted by the more currently accepted theory which ascribes the porous nature of the oxide to a liquid oxide phase. In the case of alloys of the type iron-chromium-molybdenum, iron-nickel-chromium-molybdenum, and iron-nickel-molybdenum, experimental evidence suggests the following oxidation mechanism:<sup>7</sup>

1. Initial oxidation results in the formation of a thin protective film containing iron and/or chromium oxide products.
2. Enrichment of molybdenum occurs at surfaces undergoing oxidation and eventually results in the formation of  $\text{MoO}_2$  adjacent to the alloy surface.
3. If the outer oxide film cracks or becomes porous (caused, for example, by external contamination or after reaching a critical thickness),  $\text{MoO}_2$  converts to low-melting  $\text{MoO}_3$ .
4. As a result, the following reactions can occur at the metal interface
$$\text{MoO}_3 + 2\text{Fe} \rightarrow \text{Mo} + \text{Fe}_2\text{O}_3 \quad (1)$$
$$\text{MoO}_3 + 2\text{Cr} \rightarrow \text{Mo} + \text{Cr}_2\text{O}_3 \quad (2)$$
5.  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  are dissolved by  $\text{MoO}_3$ , which has been heated by released heat of formation resulting from reactions (1) and (2).
6.  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  may then be precipitated at the cooler  $\text{MoO}_3$ -bulk oxide interface.
7. This precipitation occurs away from the original crack or pore, so that the original film defect is not healed.

Modifications of the above theory can be advanced to explain how external contaminants that have a "fluxing" action similar to  $\text{MoO}_3$  are able to effect the rapid destruction of materials which derive their oxidation resistance from films of the type  $\text{Fe}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$ . The same general mechanism as that described above can also be assumed to govern the catastrophic oxidation of vanadium- and tungsten-containing alloys; in the latter systems higher oxides of the types  $\text{V}_2\text{O}_5$  and  $\text{WO}_3$  and lower oxides of the types  $\text{VO}_2$  and  $\text{WO}_2$  would replace  $\text{MoO}_3$  and  $\text{MoO}_2$ , respectively, in reactions (1) and (2) above.

#### Correlation Between Theory and Observation

The majority of the experimental observations noted in the preceding portion of this report are conveniently explained by the latter oxidation mechanism. The time threshold required to trigger catastrophic oxidation is in agreement with the postulate that the growth of a protective oxide film precedes the formation of molybdenum oxides. A time delay is also

suggested by the stipulation that a film defect must be present in order to produce  $\text{MoO}_3$ , since under ordinary conditions cracking of the film is not effected until a critical thickness has been reached.

The temperature dependence of catastrophic oxidation, as noted,<sup>18</sup> likewise strengthens the view that a liquid oxide phase acts as the instrument of destruction in the catastrophic oxidation process. That is, the incipient temperature for catastrophic oxidation in a given alloy system,<sup>18</sup> closely approximates the lowest melting temperature attainable for oxide products in that system. This correlation is not necessarily a conclusive argument in the case of molybdenum-containing stainless steels, since the vapor pressure of  $\text{MoO}_3$  is also significant at temperatures where catastrophic oxidation is observed. In this connection, however, Rathenau and Meijering<sup>4</sup> have reported a series of oxidation experiments that indirectly implicate oxide melting as the primary instrument of destruction in molybdenum-containing systems. Their investigations concerned the oxidation of copper and 8% Al bronze in the presence of  $\text{MoO}_3$  and air at 770 to 1020°F. At these temperatures both the vapor pressure of  $\text{MoO}_3$  and its dissociation tendency are quite small. Nevertheless, in the case of pure copper, accelerated oxidation was observed to begin at 990°F, which closely approximates the  $\text{MoO}_3$ - $\text{Cu}_2\text{O}$  eutectic temperature. In the case of the aluminum-bronze alloy, the temperature threshold was lowered to 880°F, very near the  $\text{MoO}_2$ - $\text{MoO}_3$ - $\text{Cu}_2\text{O}$  ternary eutectic temperature (Table 2).

The strongest support for the oxide-melting viewpoint is afforded by a consideration of the effects of alloying additions on catastrophic oxidation. The influences demonstrated by alloying additions in aiding or abating catastrophic oxidation, in terms of the above theory, should trace back to two factors. First is the effect of the addition on the propensity of cracking of the oxide film, and the second is the degree to which the addition inhibits the formation of  $\text{MoO}_3$ . Nickel additions afford an example of both effects. As noted previously,<sup>19</sup> iron-nickel-molybdenum alloys containing less than 15% Ni or greater than 35% Ni are completely resistant to catastrophic attack. Brenner<sup>7</sup> found that in alloys with less than 15% Ni,

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<sup>18</sup>"Effect of Temperature" p 7 of this report.

<sup>19</sup>"Effect of Time" p 10 of this report.

resistance was attained because the oxide film was generally not prone to cracking. At nickel concentrations above 15%, film cracking was introduced; however, with more than 30% Ni, sufficient nickel apparently was present at the alloy surface (i.e., the molybdenum concentration was sufficiently diluted) to prevent the formation of  $\text{MoO}_3$ . Brenner attributed the adverse effects of chromium additions on catastrophic oxidation in these same studies both to reaction (2) above and to an increased tendency for film cracking as chromium is added to the iron-molybdenum system.<sup>20</sup>

#### Vapor Effects

The volatility of  $\text{MoO}_3$ , if not a direct cause of accelerated oxidation, cannot be ruled out as an important variable in the oxidation process. This follows, of course, from the fact that oxidation of alloys containing or contaminated by  $\text{MoO}_3$  is more severe in a stagnant than in a moving atmosphere, whereas oxidation effects associated with  $\text{V}_2\text{O}_5$  are independent of the dynamics of the oxidizing gas. It is generally felt that circulation of the atmosphere will be important whenever it affects the concentration of the contaminating constituent at the metal-oxide interface. In the case of easily vaporized  $\text{MoO}_3$ , the concentration of  $\text{MoO}_3$  in the oxide near the metal surface (remembering the spongy nature of the oxide forming above it) most certainly is related to the concentration of  $\text{MoO}_3$  vapor surrounding the specimen. Conversely, atmospheric circulation in the case of  $\text{V}_2\text{O}_5$ , which is less volatile, could not have a noticeable effect on the amount remaining in the oxide near the metal surface.

#### DISCUSSION OF SERVICE FAILURES INVOLVING CATASTROPHIC OXIDATION

Occurrences of failures by catastrophic oxidation in experiments at ORNL have followed closely the classic patterns described previously.<sup>21, 22</sup>

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<sup>20</sup>In view of the improved oxidation resistance afforded chromium additions, the latter tendency may appear surprising. This indicates that the oxidation protection afforded by chromium additions is derived more from a reduction of vacancies in the resultant oxide film than from coherency effects.

<sup>21</sup>"Nature of Catastrophic Oxidation" p 2 of this report.

<sup>22</sup>"Factors Affecting Catastrophic Oxidation" p 7 of this report.

Accordingly, a detailed discussion of these failures will not be attempted, since it would add little to the information already presented. The following brief review of service failures, however, is presented to cite two especially troublesome problem areas.

#### High-Temperature Thermocouples

Various combinations of unlike refractory metals which afford relatively high-thermal emf's have been under evaluation as high-temperature thermocouple assemblies. While thermocouples of this type show much promise, the incorporation of tungsten or molybdenum elements necessitates special caution. This was recently illustrated in a calibration test of a tungsten-rhenium thermocouple in "pure" helium at 1800-2000°F (ref 23). The tungsten-rhenium wires were imbedded in beryllium oxide which in turn was encased in a type 304 stainless steel sheath. During tests the thermocouple was contained within a close-fitting quartz tube and was blanketed by a stagnant helium atmosphere which had been both charcoal filtered and cold trapped. Following a 675-hr exposure, the type 304 stainless steel sheath was found to have completely separated, as shown in Fig. 4. The cause of the break was traced to localized oxidation, the oxide products containing an inordinate amount of  $WO_3$ . Thus, the use of molybdenum or tungsten appears to necessitate either complete degassing of the well or a dynamic purge system. Substitution of a nickel-base alloy, such as Inconel as the sheath material, should also alleviate this problem.

#### Service Failure of Type 316 Stainless Steel

The majority of oxidation-connected failures of type 316 stainless steel components have been provoked by the presence of external contaminants, in particular, silicate cements. Failures of this type, as discussed in conjunction with Fig. 1, can erupt at temperatures as low as 1200°F. While less numerous, there have been at least three incidences of catastrophic oxidation of type 316 stainless steel at ORNL that evidence indicates as

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<sup>23</sup>GCR Quar. Prog. Rep. Sept. 30, 1960, ORNL-3015, p 154.

Unclassified  
ORNL Photo 51151



Fig. 4. Failure of Type 304 Stainless Steel Thermocouple Sheath Induced by Presence of  $WO_3$ . The thermocouple was comprised of tungsten and rhenium elements and was exposed at 1800-2000°F to cold-trapped and charcoal-filtered helium.

having been purely self-induced. These failures occurred at temperatures of 1500°F or above and in essentially stagnant atmospheres. Sections undergoing catastrophic oxidation were closely surrounded by heaters and/or insulation, and in no cases did failures extend to parts exposed to moving air. An insulated section of type 316 stainless steel pipe that failed during service at 1500°F and showed no evidence of surface contamination is pictured in Fig. 5. The pipe, used to contain 300 psi He, developed a pronounced bulge and longitudinal crack after less than 10 hr at temperature. Accelerated oxidation was found to have occurred along the failed section and to have caused a uniform reduction in the pipe cross section to the point where pronounced plastic deformation and ultimate rupture were effected by the high internal pressure. (It is encouraging that, while extremely rapid, this type of failure led to a slow rather than a catastrophic release of pressure.) These failures forewarn the user of molybdenum-containing stainless steels (types 316 and 317) against (1) the presence of surface contamination and (2) the use of these materials in stagnant atmospheres above 1500°F.

In summary, experience at ORNL has shown that the use of tungsten or molybdenum in high-temperature experiments demands that these materials be scrupulously protected from oxidation and, if possible, be isolated from materials that are susceptible to accelerated oxidation. Extreme discretion should be exercised in systems constructed of type 316 stainless steel to avoid contamination of the material by any substance capable of lowering the melting point of the normally protective oxide film. If type 316 stainless steel systems are to be operated above 1400°F, every effort should be made to prevent stagnation of the atmosphere surrounding the material or, if stagnation is unavoidable, to utilize an oxygen-free atmosphere.

#### CONCLUSIONS AND RECOMMENDATIONS

1. The growth of nonprotective, crust-like oxide films, termed catastrophic oxidation, has been identified with the incorporation of tungsten, vanadium, or molybdenum as strengthening additions in high-temperature alloy systems. A similar manifestation of catastrophic oxidation is induced if these elements are allowed to contaminate surfaces of otherwise oxidation resistant metals. Other external contaminants that debilitate oxidation resistance include KF, Bi<sub>2</sub>O<sub>3</sub>, PbO, and Na<sub>2</sub>O.

Unclassified  
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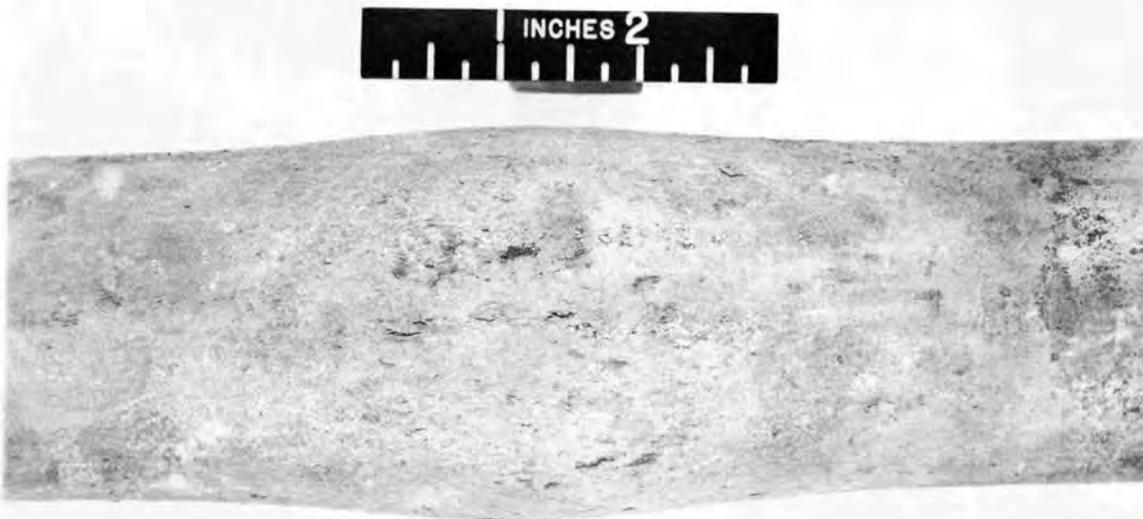


Fig. 5. Cracks and Deformation Produced in Type 316 Stainless Steel Pipe Following Loss of Metal Through Severe Oxidation. Pipe section was exposed to stagnant air above 1400°F and contained helium at 300 psi. (Oxidation products were removed to reveal cracks in pipe wall.)

2. The onset of catastrophic oxidation in alloys contaminated by or containing tungsten, molybdenum, or vanadium shows a direct correlation with the melting points of oxides formed by these elements. The threshold temperature for catastrophic oxidation is highest when instigated by tungsten, intermediate for molybdenum, and lowest for vanadium.

If external contaminants are absent, the threshold temperature for oxidation of molybdenum-containing alloys in stagnant air or oxygen is between 1400 and 1500°F.

3. Experiments have implicated oxide melting as the cause of catastrophic oxidation. It is generally accepted that oxidation of molybdenum-containing stainless steels occurs by the following mechanism:

- a. Initial oxidation of molybdenum-containing stainless steels results in the formation of a thin, protective film containing iron and/or chromium oxide products.
- b. Enrichment of molybdenum takes place at surfaces undergoing oxidation and eventually results in the formation of a pure  $\text{MoO}_2$  layer adjacent to the alloy surface.
- c. This condition is maintained unless the outer oxide film cracks or becomes porous. If, however, a film defect occurs,  $\text{MoO}_2$  is immediately converted to low-melting  $\text{MoO}_3$ , and catastrophic attack is initiated.
- d. The molten oxide layer acts as an oxygen carrier and prevents the formation of a protective film.

4. Iron-nickel-molybdenum and chromium-nickel-molybdenum alloys containing greater than 35% Ni, if free from external contaminants, are not subject to catastrophic oxidation. It is postulated that nickel, which remains at oxidized surfaces along with molybdenum, serves to restrict the molybdenum concentration and thus to prevent the formation of  $\text{MoO}_3$ .

5. The use of molybdenum-containing stainless steels (types 316 and 317) at high temperatures should be tempered by the following considerations:

- a. Above 1200°F, surfaces of these stainless steels ( and all alloys deriving oxidation resistance from iron and/or chromium oxides) should be kept scrupulously clean of external contaminants that form low-melting oxides.
- b. Above 1400°F, these materials should not be used in contact with stagnant atmospheres unless these atmospheres are virtually oxygen free.

6. High-temperature cements and insulations that are composed of sodium silicate or other low-melting oxides should be used advisedly above 1200°F. A screening program should be initiated to locate high-temperature cements compatible with alloys deriving oxidation resistance from iron and/or chromium oxides.

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