

Effects of Grain Size, Cold Working, and Surface Finish on the Metal-Dusting Resistance of Steels

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The presence of easy-diffusion paths is very important for fast formation or healing of a protective Cr-rich oxide scale for resistance of chromia-forming steels against metal dusting. Such easy-diffusion paths, grain boundaries, sub-boundaries, and dislocations are provided by a fine-grain microstructure, cold and/or surface working—polishing, grinding, machining, sand blasting. Their importance and effectiveness are demonstrated by various laboratory results and also by a failure case and their appearance is shown by TEM studies on ground steel specimens.

KEY WORDS: metal dusting; chromia-forming steels; grain size; cold rolling; near-surface deformation; easy-diffusion paths.

INTRODUCTION

Austenitic steels for components in power plants in the petrochemical, and chemical industry are generally delivered in the solution-annealed state. However, for applications at intermediate temperatures $< 700^{\circ}\text{C}$ this state is not optimal, since materials with a coarse-grain microstructure without any near-surface deformation are very susceptible to high-temperature corrosion. This was shown in earlier extended studies on the effects of cold work on the oxidation behavior and carburization resistance of Alloy 800.^{1,2} The coarse-grain material forms a thick oxide layer at 600°C of outward-growing Fe_3O_4 (and Fe_2O_3) and inward-growing layer of (Fe, Mn, Ni) chromium spinels and some Cr_2O_3 . A protective Cr-rich oxide scale was

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observed only above the grain boundaries of the alloy. This kind of oxide layer is not protective and allows considerable carbon permeation, as shown by exposures in a H_2 - H_2O - CO - CO_2 atmosphere (tagged with ^{14}C) at $700^\circ C$. The oxidation behavior and carburization resistance are greatly improved by cold working the material. The oxide thickness formed by steam oxidation at $600^\circ C$ and the carbon ingress in carburization tests significantly decrease with increasing degree of cold work.² The cold work can also be introduced by the surface finish, as well by polishing, grinding, and machining, as by sand blasting or shot-peening.³ The high-temperature corrosion of cover hoods for batch annealing, i.e., the formation of thick crusts of carbon, metallic Fe-Ni, carbides, and oxides at the inner walls due to changes in the oxidizing and reducing carburizing conditions, could be effectively suppressed by an appropriate surface finish of the material—a 20Cr-12Ni-1.9Si steel (1.4828). The positive effect of grinding (120-grit SiC) compared to pickling (in HNO_3 - H_2SO_4 , $165^\circ C$) and corroding (boiling HNO_3 - H_2SO_4 after sensitizing at $650^\circ C$ for 1 hr) has been shown for Alloy 800 in earlier studies,⁴ in carburizing-oxidizing atmospheres at $850^\circ C$. On the pickled or corroded surface the formation of significant amounts of transient Fe-oxides is favored and the scales are rather permeable to carbon. Rapid formation of Cr_2O_3 was observed on the polished surfaces, which provides a better barrier against carbon penetration than the spinels formed on the pickled or corroded specimens.

Cold deformation and surface working of the steels causes the formation of easy-diffusion paths for Cr that allow rapid formation of a dense protective oxide layer. During heating and during the first hours of operation, the dislocations introduced by surface working can serve as fast-diffusion paths, later on the grain boundaries will be important for the supply of Cr and for the formation of a protective oxide layer. In fact, a relation between mass gain after 1000 hr by steam oxidation at $600^\circ C$ versus average grain diameter of Alloy 800 was established^{1,2} clearly showing the importance of fine-grain size for application in this temperature range. For the oxidation of Ni-Cr alloys the effect of grain size on the formation of a Cr_2O_3 scale is important, even at rather high temperatures, 900 and $1100^\circ C$.⁵

It may be noted that in 1996 an ECSC project was started on the "Improvement of Stainless Steels for Application in Aggressive Environments at Intermediate Temperatures." The advantages of fine-grain materials under these conditions are demonstrated.⁶

In Japan efforts have been made to develop a fine-grain stainless steel by applying certain heat treatments, making use of the dissolution and precipitation behavior of NbC.⁷ This development led to a fine-grain TP 347 H steel (GS No 8), which proved to have improved resistance against steam oxidation and hot corrosion under alkali sulfate deposits. Moreover, further

Japanese work^{8,9} showed that the use of shot-blasting on the inner surfaces of tubing improved grain size and corrosion resistance.

A recent failure case spectacularly demonstrated the role of grain size on the resistance of austenitic steels against "metal dusting". Simultaneous research confirmed the effects of surface working on the resistance of various steels against this corrosion phenomenon.¹⁰ The failure case and these new research results will be reported here, but, first, the phenomenon of metal dusting must be reexplained.¹¹⁻²⁴

Metal dusting is a disintegration of metals to a dust of metal and graphite, mostly as an aggregate of fine particles (coke), which can also contain oxides and carbides, depending on materials and conditions. The disintegration is due to the unstable thermodynamic situation in atmospheres (syngas CO-H₂, hydrocarbons) with high-carbon activities $a_C \gg 1$, occurring in many processes. If the metal components are not protected by a dense oxide scale, carbon is transferred into the metal matrix and the subsequent oversaturation leads to disintegration—in the case of Fe-base materials, via the intermediate cementite,^{11,12,13,18} and in the case of Ni-rich materials, by direct inward growth of graphite intrusions.^{13,21,22} Basically, protection is afforded by an oxide scale, which prevents carbon ingress.^{14,21} For thermodynamic and kinetics reasons, metal dusting is mainly a problem between 400–700°C, where the formation of a protective scale on chromia-forming steels is not guaranteed, but is strongly dependent on microstructural features.

This paper presents results on the important role of cold deformation and surface working on the metal-dusting resistance of various steels, demonstrating that not only the chemical composition but also the micro-structure are important. In fact, the grain size near the surface and the availability of grain boundaries for Cr diffusion is decisive for corrosion resistance, as was demonstrated by transmission electron microscopy (TEM) studies.

FAILURE CASE STUDY

The great importance of the topic of this paper was demonstrated by a striking failure case. From a large heat exchanger in which syngas is cooled from about 575 to about 350°C, an internal gas duct was removed because of strong metal-dusting attack. The entire component was comprised of Alloy 800, with the usual coarse-grain microstructure, i.e., grain size of 200 to 300 μm (ASTM 0–1). This material was exposed to a temperature of 575°C and signs of attack were seen equally throughout—wasting from 10 mm original thickness to an average of 3 mm with local perforations. Metal-dusting attack is nearly uniform (as seen in Fig. 1a), as often

observed for Alloy 800. It must be noted that metal-dusting attack on high-Cr steels, including Alloy 800,²⁵ generally starts by pitting at defects in the scale, but for Alloy 800 this attack often spreads rapidly and uniform metal wastage occurs.

However, the most-striking observation in this failure case is that there were sections in the heat exchanger made of 18Cr–8Ni steel that were not attacked at all. These sections, eight small fastening sheets, were exposed to the same process gas and were located in places where the temperatures were in the range of 550 to 450°C. These sheets show oxidation, macroscopically indicated by interference colors. In a metallographic cross section on which an AES sputter profile was performed, a thin oxide layer was detected. Obviously these sheets were protected against metal dusting by oxide formation from the onset of operation. The reason for the different behavior is evident from the metallographic cross section (Fig. 1b), which shows a very fine-grain microstructure (average grain size 30 μm , ASTM G7), which resulted from the recrystallization of cold-rolled sheet at the operation temperature. Pieces of cold-rolled stainless steel sheet had been used. The strong deformation and many easy-diffusion paths for Cr provided better preconditions for the formation of a protective Cr-rich scale, which was effective for some years in spite of the lower Cr content of this stainless steel compared to Alloy 800.

THERMOGRAVIMETRIC STUDIES

In these studies¹⁰ the samples are hanging from the thermobalance in flowing dry hydrogen, during heating to 600°C which for reaction is switched to a mixture of 24%CO–74%H₂–2%H₂O. The mass changes observed can be due to (1) carburization, i.e., dissolution of carbon in the alloy, (2) carbon deposition, which is due mainly to metal dusting, caused by the formation of fine metal particles catalyzing the reaction $\text{CO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{C}$, and (3) oxidation of high-alloyed steels involving the formation of Cr₂O₃ and spinels. Carbon deposition (point 2) is dominant—when metal dusting starts, either locally or over wider areas, the amount of catalytically active metal particles rises linearly and the amount of carbon deposited increases quadratically with time.¹⁵ Thus, the start and extent of metal dusting can be seen clearly from the thermogravimetric curves.

Thermogravimetric studies on the effect of grain size have been conducted on a 304 stainless steel (18Cr–8Ni) and 30Cr–60Ni alloy (Alloy 690). The stainless steel was tested in the as-delivered, fine-grain state and after 1-hr annealing at 1000°C which causes an increase in the average grain size to the 30–100 μm , ASTM 3–7. The fine-grain material (ASTM 10, ca. 10 μm) was not attacked by metal dusting for 170 hr (Fig. 2a) whereas the coarse-grain

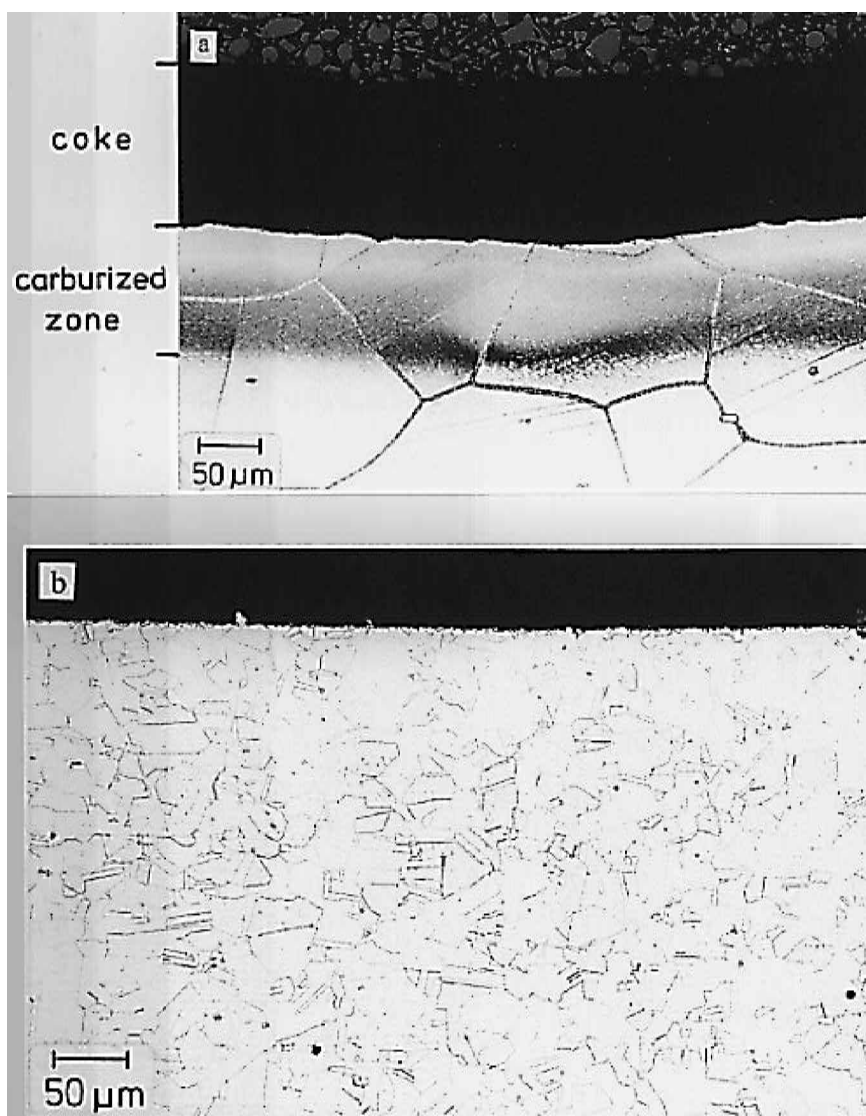


Fig. 1. Metallographic cross sections of sections of heat exchanger after several years service in syngas. (a) Coarse-grain 32Ni–20Cr steel (Alloy 800) strongly attacked by metal dusting—covered with coke and showing a carburized zone beneath (uniform metal wastage). (b) Fine-grain 18Cr–8Ni steel, not attacked under the same conditions, protected by a thin Cr-rich oxide layer.

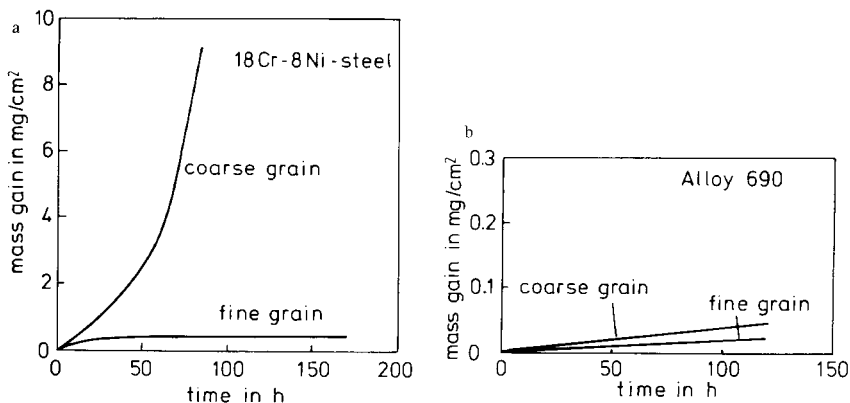


Fig. 2. Thermogravimetric studies of metal dusting in flowing $\text{CO-H}_2\text{-H}_2\text{O}$ at 600°C on materials of different grain sizes. (a) No attack on fine-grain, but strong attack on coarse-grain 18Cr-8Ni steel (304 SS). (b) No attack on either fine- or coarse-grain Ni-base alloy 690.

steel showed heavy attack by metal dusting after about 30 hr, indicating an accelerating mass gain with time.

The as-delivered, Ni-base material had a highly deformed microstructure, but after 1-hr annealing, the alloy had a globular structure with a still rather fine-grain size of 50 to 60 μm . In both states no clear metal dusting was observed after 120 hr; only a very small mass gain by oxidation, leading to a protective oxide scale (Fig. 2b), was found.

Thermogravimetric studies have also been conducted on the effect of various surface finishes on metal-dusting resistance. Three surface states were tested of the 32Ni-20Cr steel (Alloy 800) and 25Cr-20Ni steel (310 SS): (1) as-received, i.e., rolled; (2) grinding to 600 grit; and (3) electropolishing in 64% H_3PO_4 , 5% H_2SO_4 , 21% H_2O for 30 s at 10 V-4A. The tests were conducted at 600°C for 25 hr in 24% CO -74% H_2 -2% H_2O . Plots of mass gain vs. time are shown in Fig. 3. In both cases the electropolished material was attacked by metal dusting after short times and showed a large mass increase by carbon deposition. Electropolishing had removed the surface-deformation layer on these samples, this procedure causes most materials to be very susceptible to attack.¹⁴ Attack on the as-received materials was delayed by 8-10 hr, but then an accelerating mass increase clearly indicated strong metal dusting. The ground materials proved to be most resistant, especially the 25Cr-20Ni steel, which only slowly oxidized during the measurement period and was not attacked by metal dusting at all, after the experiment the sample still appeared bright metallic. In contrast, the ground sample of Alloy 800 showed some attack at the edges. This observation confirms that Alloy 800 is generally more

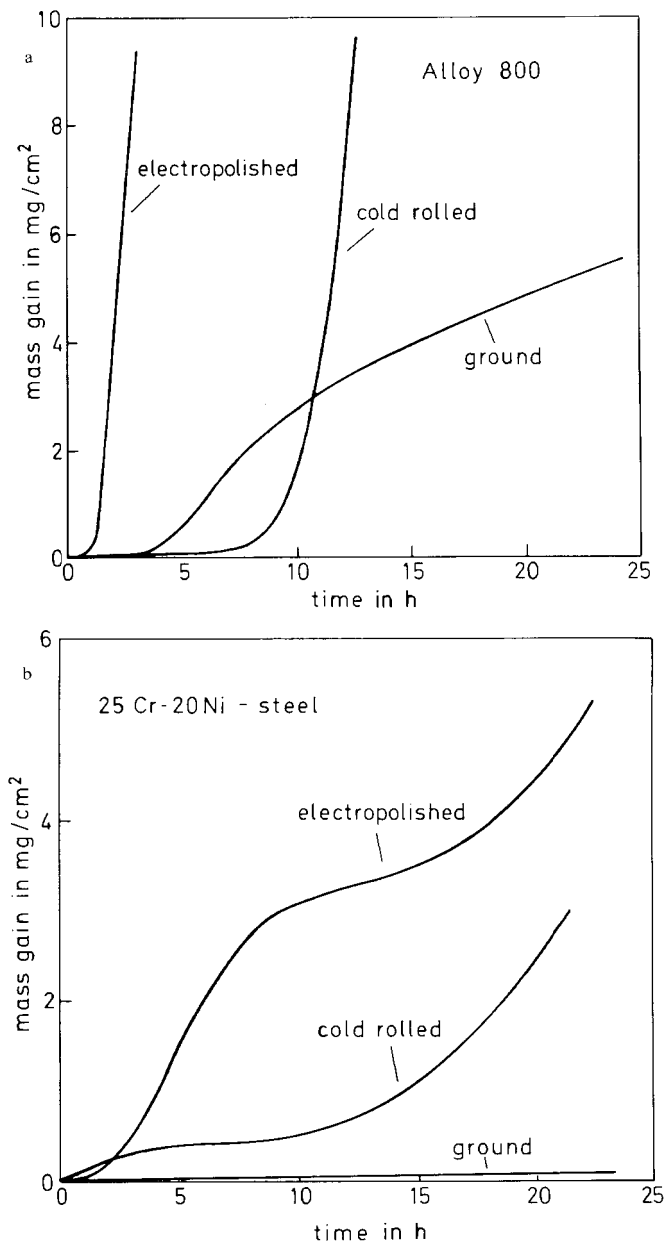


Fig. 3. Thermogravimetric studies of metal dusting in flowing $\text{CO}-\text{H}_2-\text{H}_2\text{O}$ at 600°C on materials with different surface finish: ground, as received (cold-rolled) or electropolished; attack for both the latter states, protection for the first (ground state). (a) 32Cr-20Ni steel (Alloy 800); (b) 25Cr-20Ni steel (310 SS).

Table I. Compositions (in wt.%) of the Steels Investigated in the Discontinuous Exposures

Ferritic alloys	C	Cr	Ni	Mo	V	Nb	Mn	Si	N
10CrMo 9 10	0.13	2.25		1.05			0.55	0.35	
P 91	0.10	8.6	0.26	0.93	0.205	0.07	0.41	0.36	0.053
12CrMoV lo	0.20	10.4	0.66	0.83	0.247	0.011	0.52	0.27	0.0195
12CrMoV hi	0.19	11.21	0.66	0.86	0.25		0.50	0.32	
Austenitic alloys	C	Cr	Ni	Mn	Si	Al	Ti	N	
SS 304	0.030	17.6	8.66	0.83	0.55	0.014	0.004	0.049	
Alloy 800	0.068	20.4	30.6	0.70	0.38	0.28	0.33		

susceptible to metal dusting (due to its lower Cr content) than the 25Cr–20Ni steel.

DISCONTINUOUS EXPOSURES

In these experiments 10–12 samples were exposed to the flowing CO–H₂–H₂O atmosphere, for different periods, after which the coke formed was scratched from each sample surface, collected separately, and analyzed for its iron content. From the mass of coke, iron content, sample area and time of the exposure period the rate of metal wastage was calculated (in mg/cm²h) i.e. the rate of metal transfer into the reaction product coke. Various steels (see Table I) were investigated in a ground condition and in a chemically etched surface state, i.e., with and without any surface deformation. Figure 4 shows the development of wastage rate with time, in (a) for the etched materials (and for both 10 CrMo 9 10 and P 91 in the surface-ground condition) and in (b) for the ground steels; clearly, the latter show better metal-dusting resistance. After a short time, the etched specimens approach a more or less constant wastage rate, which corresponds to general attack of the whole surface. This virtually constant rate is reached for the low-alloy 2 $\frac{1}{4}$ Cr–1 Mo steel (10 CrMo 9 10) already after the first period, since this steel cannot form a protective scale).

Metal-dusting resistance generally improves with increasing Cr content of the steels, however, in these experiments there is also clear evidence for the effect of grain size. The SS 304 is a very fine-grain material (ASTM-G9, average grain diameter 15 μ m) and behaves better than the coarse-grain Alloy 800 (ASTM-G5, average grain diameter 62 μ m), in spite of the higher Cr content of the latter (just as in the failure case described earlier). In addition, other influences become evident. For example, there are higher Cr diffusion rates in ferritic as compared with austenitic steels—this improves the resistance of 12 CrMoV hi steel. Obviously, the Cr content of this steel

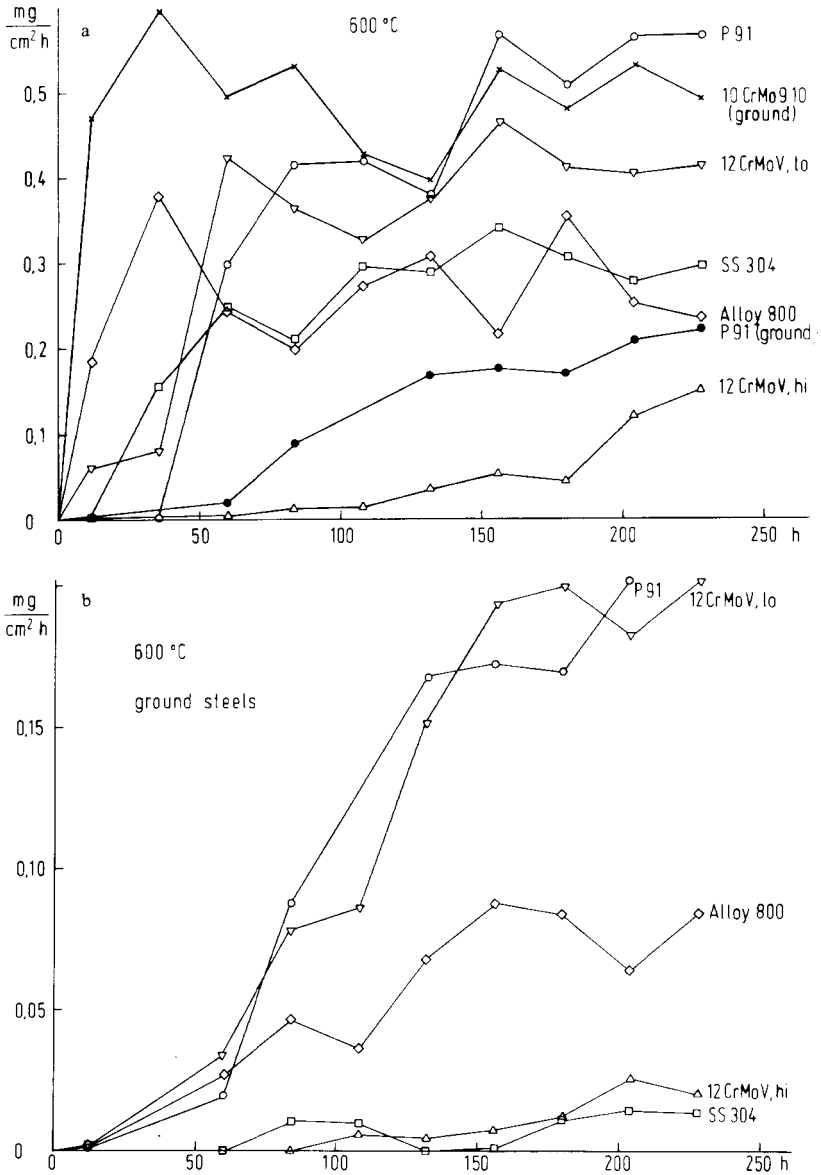


Fig. 4. Metal-wastage rates of different steels determined by discontinuous exposures in flowing CO-H₂-H₂O at 600°C. Increase of wastage rate due to the spreading of attack over the surface (a) for etched steels (and ground 2¹/₄Cr-1Mo steel and ground P 91) and (b) for ground steels. Note much slower increase for the latter.

Table II. Average Grain Size in the Bulk and at the Surface of Three Steels After Grinding (600 #) and Short Heating (1 hr) to 600°C^a

Steel	Bulk	Surface
9Cr-1Mo (P 91)	1	0.17
12Cr-Mo-V	0.54	0.2
18Cr-8Ni (SS 304)	> 10	0.1

^aUnits in μm .

(> 11% Cr) is sufficient to form a protective Cr-rich layer at 600°C, in contrast to the ferritic steels with lower Cr contents (P 91, 12 CrMoV lo, and 10 CrMo 9 10), which attain a constant maximum wastage rate after a short time.

TRANSMISSION ELECTRON MICROSCOPY STUDIES

The surface state after grinding and chemically etching was investigated by TEM to confirm the reasons for its strong influence on metal dusting. Investigations were conducted on P91, 12 CrMoV, and SS 304, which were either etched or ground using the usual procedures. To simulate the thermal treatment of samples before exposure to metal dusting, all specimens were inserted into the reaction chamber and heated as usual under flowing dry H₂ to the reaction temperature of 600°C and then held for 1 hr. Instead of changing to the reaction gas mixture, the samples were quenched in inert gas (Ar).

The TEM study showed no difference between the surface and bulk microstructure for the etched specimens (as expected). In contrast, there was a clear difference for the ground specimens—the grain size near the surface was much smaller than in the bulk (see Table II and Fig. 5) and also the dislocation density appeared to be higher at the surface. Quantitative data on dislocation densities, however, could not be obtained. However, it is quite evident that there are more grain boundaries and dislocations in the ground specimens acting as easy-diffusion paths for Cr. When the specimen is exposed to the oxidizing and carburizing atmosphere, this leads to rapid formation of a protective scale on the ground specimens. One may argue that the presence of dislocations and grain boundaries may also accelerate inward carbon diffusion. However, in the temperature range of 600°C, bulk diffusion of carbon in metals is normally very rapid. The evidence proves that rapid formation of a Cr-rich scale can avoid oversaturation with carbon and suppresses the onset of metal dusting.

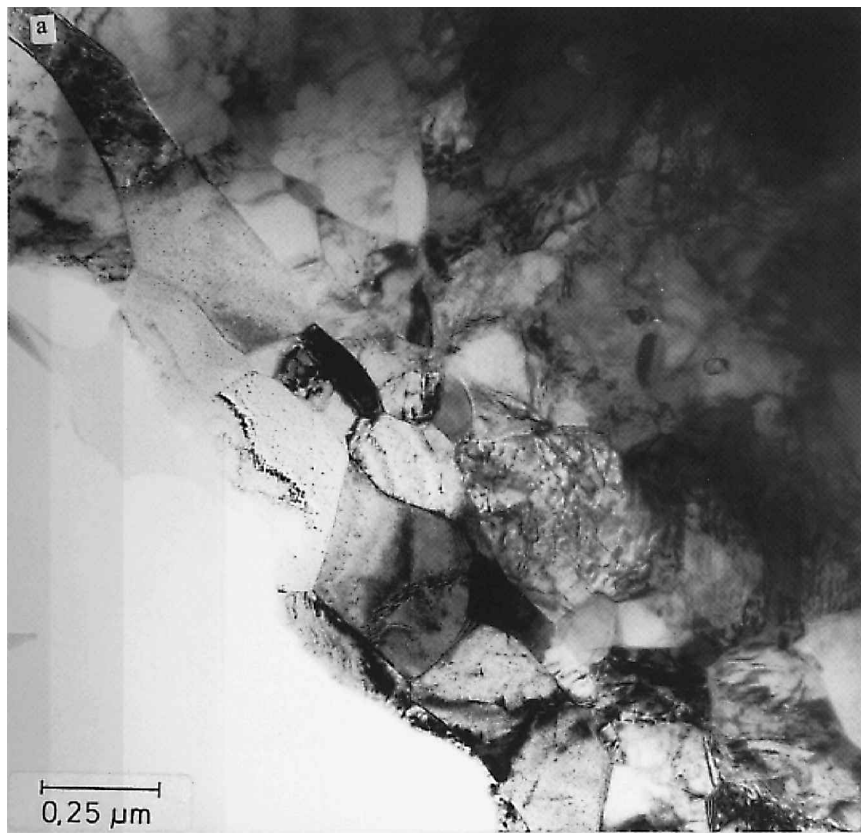


Fig. 5. Transmission electron micrographs of the surface zone of two steels—extremely fine-grain microstructure after grinding and short heating (in H_2) to $600^\circ C$. (a) 9Cr-1Mo steel (P 91); (b) 18Cr-8Ni steel (304 SS).

DISCUSSION

For ferritic and austenitic high-alloyed steels used in the temperature range $500\text{--}1000^\circ C$, the formation of a dense, well-adherent, slow-growing Cr_2O_3 layer provides optimum protection against oxidation, carburization, and sulfidation by gas atmospheres and against attack by corrosive deposits or slags. It is most advantageous if such a layer is formed in the very first operation run of a plant or even better if it is generated by a controlled preoxidation. This preoxidation must be conducted at a low P_{O_2} , e.g., in a wet $N_2\text{--}H_2$ atmosphere so that no Fe or Ni oxides are formed which would be reduced later in the process gas. Steels covered by a dense Cr_2O_3 layer are very resistant against sulfur- or carbon-bearing atmospheres, since C

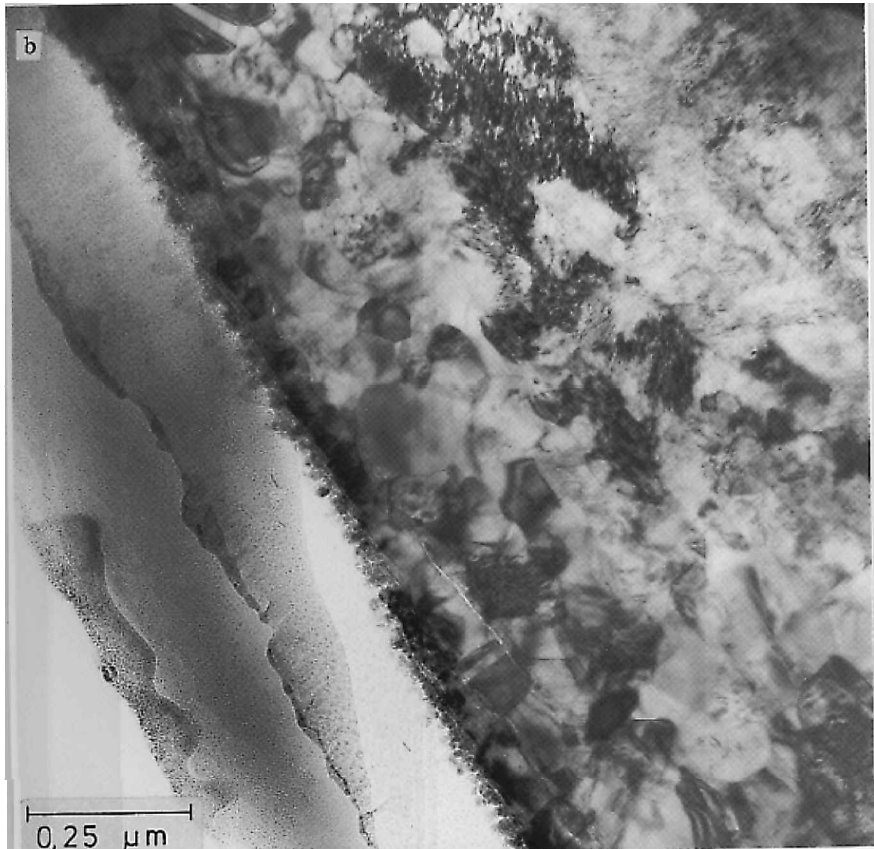


Fig. 5. Continued.

and S penetration through a perfect layer is virtually impossible.^{26,27} However, if the layer does not grow rapidly enough, there will be considerable absorption of C or S into the alloy, which can negatively affect the oxide formation.

Under metal-dusting conditions, i.e., at a high carbon activity in the atmosphere, there will be competition between carbon absorption and formation of an oxide layer. Under unfavorable conditions, i.e., rapid carbon transfer will lead to fast increase of C concentration in the alloy and the Cr is tied up in carbide precipitates—no Cr_2O_3 formation is possible. Outward diffusion of Cr must be enhanced, especially at relatively low temperatures, ($< 600^\circ\text{C}$), so that Cr “wins the race” and Cr_2O_3 can be formed.

In contrast to a coarse-grain steel, a fine-grain steel is capable of rapidly supplying chromium to the surface.²⁸ A network of regions at the intersections of grain boundaries is supplied directly with chromium, and, once at the surface, short lateral-diffusion distances on the fine-grain steel allow a rapid supply of chromium to the entire surface. On a coarse-grain steel, chromium-rich oxide grows only as ridges on the grain boundaries. Depending on oxygen pressure, on large-grain alloys either no oxide is formed for long time on a wide area of the grains or, for higher P_{O_2} , iron-rich oxides are formed that are less protective.

For steels subjected to a surface finish which introduces near-surface deformation, such as grinding, polishing, machining, sand blasting, and shot-peening, another additional transport mechanism becomes effective. Below 700°C , diffusion through dislocation pipes contributes to the transport of chromium to the surface.^{29,30} Dislocation diffusivity is dominant at short times and leads to an apparent enhancement of the bulk diffusion. For the period decisive for the formation of the oxide at temperatures $< 700^{\circ}\text{C}$, dislocation diffusion plays an important role. For longer periods, grain-boundary and bulk diffusion prevail²⁹ and the dislocations may disappear by recovery and recrystallization. However, it is clear from its effect that near-surface deformation, in fact, enhances chromium diffusion to the surface and facilitates the formation of a protective Cr-rich oxide scale. Thus, any surface finish introducing near-surface deformation can be recommended in the case of high-temperature corrosion problems. This has been helpful in several cases.^{3,23}

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