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Metal Dusting of Stainless Steels

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Abstract : 'Metal dusting' is a catastrophic disintegration of metals (Fe, Ni, Co) occurring in carburizing atmospheres typical of reformer plants, direct reduction plants, and many chemical and petrochemical processes. In the case of stainless steels a protective chromia layer may form, but only if the chromium supply at the surface is sufficient. This is problematic at intermediate temperatures (450-700°C). Sequential exposure experiments have been done in strongly carburizing CO-H₂-H₂O mixtures at 525°C and 560°C in order to determine the influence of two factors: 1/ chromium content in the alloy and 2/ chromium diffusivity in the lattice. Seven different ferritic and austenitic steels have been tested (2.25 to 21 wt.% Cr). Diffusion to the surface was modified by two different surface preparations (600 grit or 600 grit + etching). Experimental results showed clearly the unfavorable effect of etching. These observations were interpreted by the chromium diffusion enhancement induced by the near surface deformation due to grinding. Experimental results showed also that the kinetics of 'metal dusting' were slowed down by increasing the chromium content up to the AISI 304 composition. But alloys containing more chromium experienced faster attack, and this could be related to the fact that higher Cr alloys have also a higher austenite content which is unfavorable for chromium diffusion.

Résumé : Le 'metal dusting' est une désintégration catastrophique des métaux (Fe, Ni, Co) observée dans les atmosphères carburantes de procédés chimiques et pétrochimiques. Dans le cas des aciers inoxydables, une couche protectrice d'oxyde de chrome peut se former mais seulement si l'apport de chrome à la surface est suffisant, ce qui est rendu difficile par des températures relativement basses (450-700°C). Des expositions discontinues ont été réalisées dans des atmosphères CO-H₂-H₂O (525°C et 560°C) fortement carburantes afin de déterminer l'influence de deux facteurs 1/ teneur en chrome dans l'alliage, 2/ diffusivité du chrome. Sept alliages ferritiques et austénitiques ont été testés (2,25 à 21% en masse de Cr). La diffusivité du chrome vers la surface a été modifiée par un polissage au papier abrasif grade 600 suivi ou non d'une attaque à l'acide. Les résultats expérimentaux montrent clairement l'effet défavorable de l'attaque. Ils montrent également que l'occurrence du 'metal dusting' est retardée par l'augmentation de la teneur en chrome, mais jusqu'à une valeur limite correspondant à l'alliage AISI 304. Ceci pourrait être relié au fait qu'une teneur trop élevée en chrome correspond aussi à une faible fraction volumique de ferrite, ce qui est défavorable à la diffusion.

1. INTRODUCTION :

'Metal dusting' is often referenced as a catastrophic disintegration of metals in carburizing atmospheres. This type of attack has been identified and subject to publications in the fifties [1-3]. But it was only in the seventies that Hochman [4,5] has made an attempt to understand the mechanism of 'metal dusting'. In early fundamental studies with T.E.M. observations on iron single crystals he detected the role of an intermediate carbide formation and decomposition to iron particles

and carbon. The same mechanism was assumed for nickel and cobalt but could not be observed. As a consequence of the cementite role, Hochman made the hypothesis that the beneficial role of sulfur (known empirically since the mid-fifties) was due to cementite stabilization. The last few years, facing new demands from the industry, considerable work has been done at the MPI in Düsseldorf on this subject [6-10] in order to precise the exact conditions of 'metal dusting' on several ferritic and austenitic steels with further microstructural analysis of the mechanism [11] and elucidation of the sulfur effect [12].

2. MECHANISM AND KINETICS OF METAL DUSTING :

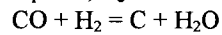
2.1. Low alloy steels :

In ferrite, and for low alloy steels, Hochman's mechanism has been confirmed and precised. It can now be detailed as follows:

step 1-oversaturation of the metal matrix with carbon. It was shown that the carbon activity in the atmosphere should be higher than the necessary carbon activity for cementite formation (a_c^*) :

$$a_c \gg a_c^* > 1 \quad (a_c = 1 \text{ for graphite})$$

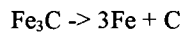
For the CO-H₂-H₂O simulation atmosphere, a_c is calculated in using the reaction of fast kinetics [13]:



step 2-precipitation of cementite at the metal surface, where the carbon concentration is highest and the nucleation is easiest. Then cementite acts as a barrier for carbon diffusion.

step 3-deposition of graphite at the cementite surface leading to an unity carbon activity, $a_c = 1$, at the surface.

step 4-at $a_c = 1 < a_c^*$, decomposition of cementite occurs according to:



step 5-the fine metal particles act as catalysts for further deposition of carbon from the atmosphere.

For low alloy steels, it was shown that the kinetics of metal loss were independent of time and environment, whereas the mass gain of the sample with its coke was increasing with the square of the time, showing the catalytic behavior for further carbon deposition of the fine metal particles found in the coke. The rate of carbon deposition furthermore is proportional to the carbon activity :

$$a_c \propto p_{\text{CO}} \cdot p_{\text{H}_2} / p_{\text{H}_2\text{O}}$$

2.2: High alloy steels :

With high alloy steels, the mechanism is not completely elucidated. It is clear that the formation of a chromia layer plays a protective role, but with all alloys studied until now the attack could not be suppressed but only delayed. One can observe chromium oxide formation followed by pitting, starting at corners and edges of the samples where a chromium depletion of the matrix is caused by selective oxidation. Another cause for chromium depletion could be the chromium carbide formation upon ingress of carbon and later on 'metal dusting' of the remaining Fe-Ni matrix. The mechanism for high alloy steels is still under study, whereas it was shown for Ni-based alloys [14] that direct precipitation and growth of graphite in and into the materials is the deteriorating process, without intermediate formation of an instable carbide.

3. PROTECTION AGAINST METAL DUSTING :

The interest of the precise description of the 'metal dusting' mechanism is to give some routes for protection. A first idea is to decrease the carbon activity (below a_c^*) of the atmosphere in contact with the steel parts experiencing temperatures between 450°C and 700°C. Second, one can think to decrease the carbon transfer and diffusion into the steel, and this could be obtained with small additions [15]. Third, the cementite could be stabilized by small additions in the atmosphere (e.g. H_2S) or through alloying in order to form mixed stable carbides. Alloying with manganese or chromium in order to stabilize the cementite was tested but without success [7]. With nickel it was shown that the solid solution decompose directly without formation of an intermediate carbide (no step 2 and 3). With manganese or chromium, 'metal dusting' occurs after a depletion of the alloying element because of selective oxidation. A last idea is obviously to form a protective surface layer which could act as barrier for carbon diffusion.

4. EXPERIMENTAL PROCEDURE :

The experimental results which are presented here concern the ability of the stainless steels to form a protective oxide scale at relatively low temperature. This ability is mainly related to the chromium contents and the chromium diffusivity in the alloy, close to the surface. For these reasons we tested seven different alloys with different chromium contents and diffusion properties. The chromium content vary between 2.25 and 20.4 wt.% (see table 1), the nickel content increasing also from 0 to 30.6 wt.%. The samples were typically 20x10x1 mm, ground to 600 grit. For each steel, two samples were prepared and only one was etched. The flowing atmosphere was strongly carburizing at 525°C or 560°C (24%CO, 73%H₂, 3%H₂O). This mixture was passed through a horizontal furnace with a silica tube. Samples were suspended on silica hooks over a silica boat. After heating the furnace in flowing argon, the sample holder was moved from the cold to the hot zone and the atmosphere switched to the CO-H₂-H₂O mixture. After each two day periods, samples were removed, weighted and cleaned. The corrosion products (coke, a dust of fine metal particles and carbon) were analyzed for iron content. The rate of metal loss was then calculated from the mass of metal found in the coke.

wt.%	Fe	Cr	Ni	Mo	Mn	Si	C	P	S	Al	V	Nb	N	Ti	Co
Alloy 800 (B163)	47.2	20.4	30.6		0.70	0.38	0.068	0.011	0.002	0.28				0.33	0.04
20Cr12Ni (AISI 309)	65	20	12		<2.0	~2	<0.20	<0.05	<0.03						
AISI 304	72.2	17.6	8.66		0.83	0.55	0.03	0.029	0.002	0.014				0.049	0.004
X12CrMo V (high)	86	11.2	0.66	0.83	0.52	0.27	0.20	0.014			0.005	0.247	0.011	0.020	0.002
X12CrMo V (low)	86.8	10.4	0.66	0.83	0.52	0.27	0.20	0.014			0.005	0.247	0.011	0.020	0.002
P91	89	8.6	0.26	0.93	0.41	0.36	0.10	0.013	0.003	0.01	0.205	0.070	0.053		
10 CrMo9 10	95.6	2.25	-	1.05	0.55	0.35	0.13	0.04	0.04						

Table 1 : Composition of the steels investigated.

5. EXPERIMENTAL RESULTS :

Figure 1 shows the rate of metal loss as a function of time, for the etched samples (solid curves, referenced as #2) and the samples which were only ground (dashed lines, #1). It can be seen that:

1- at both temperatures, a large and systematic difference is present between etched and un-etched sample for a same alloy;
 2- after a given time, the rate of metal loss seems to reach a constant value which is different at 525°C and 560°C. The constant rate of metal loss has already been observed in previous studies and fit well on an Arrhenius plot for the low alloy steels [4] with an activation energy of about 180 kJ/mol between 375 and 560°C;

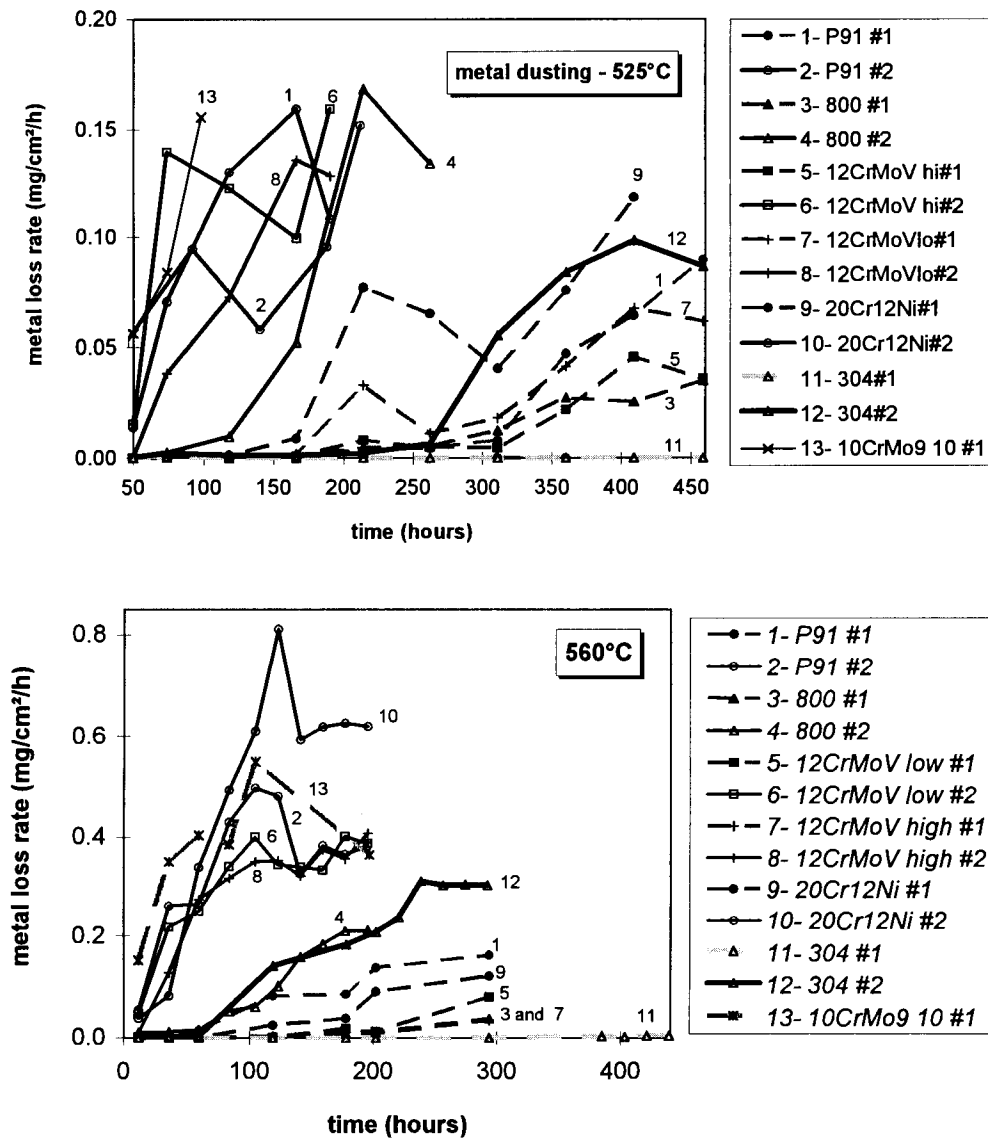
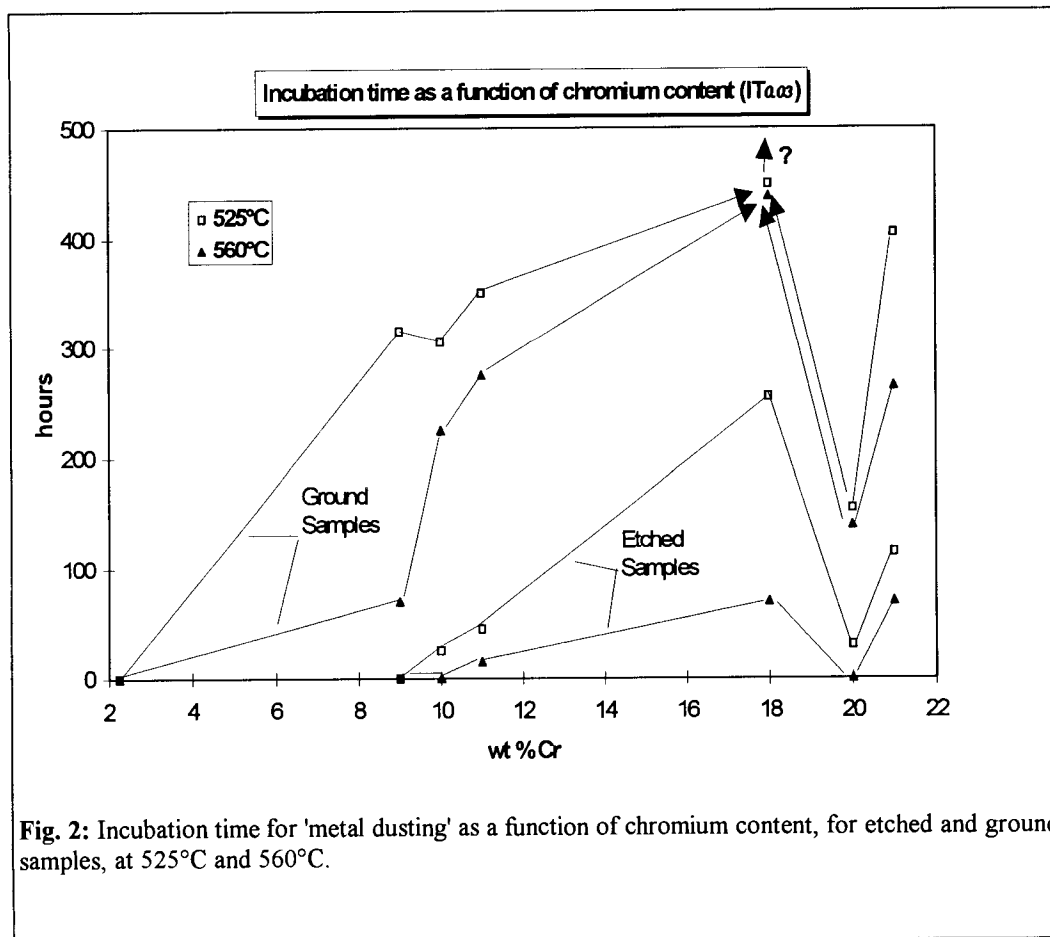


Fig 1: metal loss rate as a function of time at a)525°C and b)560°C.

3- the time needed to reach a constant rate is short for the etched low alloy steels where a general surface attack is observed already after the first exposure. This time is longer for Alloy 800 and 304.
 4-the un-etched samples which all form a visible blue oxide film (except 10CrMo9 10) experience pitting, more and more severely with time. Alloy 304 is the only one to not show pitting even after more than 400 hours, but only a very small amount of coke at the edges of the sample slowly increasing with time.

The shape of these curves offers a good opportunity to quantify the alloy resistance to 'metal dusting'. We can define an "incubation time" (IT) which is the time needed to reach a given value of the mass loss rate. For example, we present the results for a limit value of $0.03 \text{ mg/cm}^2/\text{h}$ ($IT_{0.03}$). Then, we can plot these incubation times as a function of the chromium content on Fig.2. The lower curves corresponds to the etched samples and the upper curves stands for the un-etched samples. We can see on this figure that, both at 525 and 560°C, the incubation time increases with the chromium content from 0 up to 18 wt.% (Alloy 304 shows the best performance), but then, fall down with the alloy 800 and with 20Cr12Ni which shows surprising bad resistance to 'metal dusting'. The second observation which can be done is that the two set of curves are parallel. That means that the etching decreases the incubation time of the same amount for all the considered steels (approximately 300 hours at 525°C).



6 CONCLUSION :

In this work, the beneficial effect of grinding the ferritic and austenitic steel samples was demonstrated for all compositions. This effect can certainly be related to the near surface deformation experienced by these samples which increases the chromium diffusivity and then favored the chromia scale formation. It was also shown that increasing the chromium content of the alloy was beneficial up to 18 wt%, but was not a sufficient criterion for austenitic steels. Noticeable and surprising differences between alloys 304, 800 and 20Cr12Ni were observed in term of incubation time. Placing these three austenitic alloys on a nickel equivalent-chromium equivalent Shaeffler diagram shows that 2 or 3 % of ferrite could be present in alloy 304 whereas 800 and also 20Cr12Ni should be 100% austenitic. The presence of ferrite is favorable to chromium diffusion and could explain in part the best performance of AISI 304. But this was not confirmed by x-ray diffraction, on the contrary only 20Cr12Ni showed small ferrite peaks. Metallography of this laboratory melted alloy revealed an heterogeneous microstructure with dendrites of δ -ferrite, thus the poor resistance to 'metal dusting' of this alloy can be attributed to the microstructure. Further metallography on these three austenitic alloys shows also that their grain sizes vary from 10 microns for AISI 304 to 100 microns for Alloy 800. As for the grinding which introduces surface near deformations and dislocations, a smaller grain size is favorable to chromium diffusion, then it favors the chromia scale formation. Then, the grain size could explain the superiority of Alloy 304 on Alloy 800. Current and future work include experiments at 600°C and replacement of the 20Cr12Ni alloy with a commercial alloy.

7. ACKNOWLEDGMENTS :

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