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THE BEHAVIOUR OF STEELS IN
ATMOSPHERES CONTAINING CO AND H₂
AND THE EFFECT OF PRETREATMENT
AND GASEOUS ADDITIVES

by

W. KARCHER and P. GLAUDE

1971



Joint Nuclear Research Centre
Petten Establishment - Netherlands
Reactor Materials Laboratory

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For the low alloyed steels, the effect of pretreatment with phosphoric acid, SO_2 , and silanes and the influence of the addition of CO_2 , NH_3 , N_2O , H_2O , silanes and SO_2 to the flowing gas mixture has been studied as well. The results of these experiments suggest a considerable reduction of carbon deposition both by the pretreatment and the injection technique. In both cases, the best results have been obtained with SO_2 , which suppressed carbon deposition completely even if a weighty deposit had been formed previously. Good results have been observed also with silanes and with a phosphoric acid pretreatment.

In the case of CO_2 , NH_3 , N_2O and H_2O addition relatively high concentrations are required to prevent deposition of carbon, the inhibiting effect increasing in the order CO_2 to H_2O . It is believed that the inhibition effect of phosphoric acid, silanes and SO_2 is due to the formation of a protective surface layer whereas the retarding influence of CO_2 , NH_3 , N_2O and H_2O is attributed to the competitive chemisorption of NH_3 and H_2O with CO and H_2 at the carbon deposition reaction sites.

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ABSTRACT

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For the low alloyed steels, the effect of pretreatment with phosphoric acid, SO₂ and silanes and the influence of the addition of CO₂, NH₃, N₂O, H₂O, silanes and SO₂ to the flowing gas mixture has been studied as well. The results of these experiments suggest a considerable reduction of carbon deposition both by the pretreatment and the injection technique. In both cases, the best results have been obtained with SO₂ which suppressed carbon deposition completely even if a weighty deposit had been formed previously. Good results have been observed also with silanes and with a phosphoric acid pretreatment.

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KEYWORDS

CARBON MONOXIDE
HYDROGEN
WATER
PHOSPHORIC ACID
SULFUR OXIDES
SILANES
CARBON DIOXIDE
NITROGEN OXIDES
AMMONIA
CORROSION PROTECTION
COMPATIBILITY
IMPURITIES
HEAT EXCHANGERS
STEELS
STAINLESS STEELS
NICKEL BASE ALLOY

C O N T E N T S *)

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1. INTRODUCTION	5
2. EXPERIMENTS	5
2.2 Inhibition Experiments	7
3. RESULTS	8
3.1 Long term tests	8
3.2 Inhibition Experiments	10
4. DISCUSSION	16
5. CONCLUSIONS	17

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1. INTRODUCTION

For the design of a High Temperature Gas Cooled Reactor (HTGR) the long term behaviour of structural materials under reactor conditions is an important parameter. The materials to be investigated in this direction are graphite, which is the main core component, and the steel alloys which are intended to be used in the heat exchangers. Whereas considerable work has been done about compatibility of graphite with oxidising impurities such as water vapour and carbon dioxide much less is known about the behaviour of steel alloys in presence of trace impurities in the gas phase, especially for periods of exposure comparable to the lifetime of a reactor.

Therefore, an experimental programme has been started in order to test the compatibility of various steel alloys with coolant impurities, mainly CO and H₂, for periods of exposure up to 2000 hours in the temperature range between 400 and 600°C.

Since it transpired from the results of these experiments that mild steels and alloys with a low Cr content (2.5%) invariably tend to form carbon deposits, various methods have been tested in order to decrease or prevent entirely the formation of carbon deposits on these alloys.

2. EXPERIMENTS

A survey of the steel alloys investigated is given in Table I with the manufacturers' analysis. It will be seen that A and B are mild steels, D is an 2½ % Cr alloy, E represents a ferritic and F, G and I austenitic stainless steels with increasing Ni-content, Finally, K is a Ni-based alloy. In addition, specimens of electrolytically polished pure iron have been included as a reference material as most of the experiments carried out previously at higher CO and H₂ concentrations had been done with this material.

Most of the alloys to be tested had been delivered in form of tubes with an outside diameter of 32 and an inside diameter of

TABLE I

Analysis of the Steel Alloys Employed

		C	Si	Mn	P	S	Cr	Ni	Mo	Nb	V	Fe	Cu	Ti	Al
A	DIN1.0305														
	St 35.8	0.17	0.30	≤ 0.40	max. 0.05	max. 0.05	-	-	-	-	-	Rest	-	-	-
B	DIN1.5415	0.12	0.15	0.50	max.	max.	-	-	0.25	-	-	Rest	-	-	-
	15Mo3	0.20	0.35	0.70	0.04	0.04			0.35						
D	DIN1.7380	≤	0.15	0.40	max.	max.	2.00	-	0.9	-	-	Rest	-	-	-
	10CrMo910	0.15	0.35	0.60	0.04	0.04	2.50		1.0						
E	DIN1.4922 X20CrMoV121	0.19	0.33	0.47	0.02	0.011	11.75	0.49	1.10	-	0.32	Rest	-	-	-
F	DIN1.4961 X8CrNiNb1613	0.049	0.72	1.20	0.022	0.015	16.47	13.28	0.27	0.81	-	Rest	-	-	-
G	Incoloy 800	≤ 0.1	≤ 1.0	≤ 1.5	-	max. 0.015	19-23	30-35	-	-	-	Rest	max. 0.75	0.15 -0.60	0.15 -0.6
	Incoloy 825	≤ 0.05	≤ 0.5	≤ 1.0	-	max. 0.03	19.5- 23.5	38-46	2.5- 3.5	-	-	Rest	1.5 3.0	0.6 -1.2	max. 0.2
K	Inconel 600	max. 0.15	max. 0.5	1.0	-	max. 0.015	14-16	≥ 72				6-10	max. 0.5		

22-26 mm. From these tubes 4 or 6 segments have been cut with a length of approximately 100 mm. Before the experiments rust has been removed, with the exception of the stainless steels, by treating the samples in a 10% solution of citric acid in water, which had been brought to a p_H of 7.5 - 8 with NH_3 , at $90^\circ C$ for 2-3 hours. Afterwards the specimens have been rinsed with dest. water and $CHCl_3$ and dried. 4 or 6 specimens each were then mounted on quartz hooks in 3 reaction furnaces connected in parallel for reaction temperatures of 400, 500 and $600^\circ C$ respectively.

After evacuating, filling with argon and heating the furnaces to reaction temperatures the argon gas mixture, containing 1000 vpm each of H_2 and CO , was introduced at a flow rate of 1.5 L/min. Before entering the furnaces, the mixture, which was prepared by means of flowmeters, was passed through Cu- and molecular sieve beds to remove O_2 , CO_2 and H_2O . The mixture was periodically checked by gaschromatography. Besides CO and H_2 , N_2 could be detected in trace amounts, coming from the argon carrier gas. The H_2O concentration of the purified mixture was around 10 ppm.

In the beginning, the experiment was stopped every 150-200 hours, the specimens were cooled down under argon and removed for weighing and visual examination. In the later stages, this period was extended to 200-300 hours.

2.2 Inhibition Experiments

With the inhibition experiments the CO and H_2 partial pressures have been increased from 0.1 to 1 Vol % in order to bring the time of exposure to an acceptable level.

Before each run the iron or steel samples were subjected to a reducing atmosphere overnight at $500^\circ C$ in a flow of argon containing 1% H_2 . After subsequent evacuation the sample was either pretreated with the inhibitor or directly exposed to the reaction mixture to which the inhibiting agent was added. A pretreatment step was applied

with those inhibitors showing an irreversible poisoning effect (silanes and SO_2). It consisted of an exposure of the iron or steel sample to an argon atmosphere containing less than 0.1 vol % of the inhibitor at the reaction temperature in static conditions. Otherwise, the inhibitor was added to the flow of H_2 -CO-Argon mixture; in the case of gaseous additives the inhibitor was metered into the reaction mixture by means of ball-type flowmeters. Liquid inhibitors were injected by diverting a metered fraction of the argon carrier gas through a thermostated vessel containing the liquid.

The treatment with phosphoric acid consisted of an immersion of the samples in a cold 10% solution of H_3PO_4 for 2 hours at room temperature.

The sample weight during the experiments was followed continuously by means of the recording thermobalance. The results obtained in this way have been compared to blank experiments which were run in identical conditions but in the absence of inhibiting agents.

3. RESULTS

3.1 Long term tests

The weight changes determined in this way have been plotted versus time of exposure for the various alloys investigated. The dimension selected for the weight change of the specimens, that is (mg/cm^2), is somewhat arbitrary as in some cases where carbon deposition or carbide formation did occur the attack was very much localised.

However, as the total geometric surface of the various samples was different some general term had to be introduced.

Fig.1 shows the weight changes of pure iron and the low alloyed steel specimens A, B and D in 0.1% CO and H₂ at 400° C depending on reaction time.

It can be seen that the reference material, pure iron, has the highest weight gain, due to carbon deposition which becomes noticeable after approximately 500 hours of exposure. A similar behaviour is evident for alloy B (15 Mo 3), but with a much lower rate of weight gain.

In contrast, specimens A and D exhibit an initial weight loss, due to surface oxide reduction or decarburisation, according to

$C + 2 H_2 \rightarrow CH_4$ or both, up to periods of exposure between 300 and 400 hours. After this initial period samples of type A alloy (St.35.8) do not show any further weight change whereas for type D (2 1/4 Cr alloy) a slow weight gain can be observed. This weight increase was accompanied by the appearance of a small, local carbon deposit growing from the bottom sample end where the gas mixture was entering the reaction tube, probably because the H₂/H₂O ratio was decreasing along the length of the specimen.

At reaction temperatures of 500° C, however, no further weight gain was apparent on D type samples after the initial period of a weight decrease. On the higher alloyed specimens E, F and G small weight increases could be observed which tended to fade out after an exposure of about 1000-1500 hours with the exception of the austenitic stainless steel F where an oscillation between weight loss and gain was apparent (see fig.2). For alloys K and I no appreciable weight change could be detected at 500° C.

In no case could carbon deposition be detected, therefore the small weight increase would have to be attributed to surface oxide formation which was confirmed in some instances by the observation of the characteristic blue colours.

The same was true for temperatures of 600° C, but here the formation of surface oxide films was faster and more prolonged than at 500° C, leading to considerably higher weight gains, as may be judged from fig.3. Again the austenitic stainless steels (F, G, I) behaved similarly, this time attaining a saturation stage after approximately 2000 hours.

Only the Ni-based alloy K (Inconel 600) exhibits a somewhat different behaviour. In this case the weight increases more steeply and continues even after 2000 hours leading to weight gains of more than 1 mg/cm² within the 2000 hour period.

3.2 Inhibition Experiments

The results of preliminary inhibition tests indicated a remarkable difference in the effect of silanes and SO₂ on the one hand and of H₂O, N₂O, NH₃ and CO₂ on the other hand. In the case of the silanes and SO₂ a short pretreatment is sufficient to prevent the formation of a carbon deposit for long periods of time or even indefinitely. With the other compounds, an inhibitive effect can be observed only as long as they are present in the reaction mixture in sufficiently high concentrations. In the following, the irreversible effect of silanes and SO₂ (catalyst poisoning) and the reversible effect (retardation) of H₂O, N₂O, NH₃ and CO₂ shall therefore be treated separately.

TABLE II Summary of compounds tested for carbon deposition inhibition

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Inhibitor	B.P. (°C)	Remarks
a) irreversible		
H ₃ PO ₄		
SiH(C ₂ H ₅) ₃	107	
SiCH ₃ (C ₆ H ₅) ₃	solid	
Si(C ₂ H ₅) ₂ Cl ₂	126	
Si(C ₆ H ₅) ₂ Cl ₂	302-305	
SO ₂		No carbon deposition within 300h after hour pretreatment with 0.05 Vol % SO ₂ .
b) reversible		
H ₂ O		
N ₂ O		Side reaction N ₂ O+H ₂ - H ₂ O+N ₂
NH ₃		Partial decomposition to N ₂ and H ₂
CO ₂		Side reaction CO ₂ +H ₂ = CO+H ₂ O

3.2.1 Catalyst Poisoning (Irreversible Inhibition)

In all experiments, where the steel specimens had been pickled in an aqueous solution of H_3PO_4 instead of a citric acid solution the extent of carbon deposition was always reduced (by up to 90%) as compared to the samples which had been pickled in citric acid.

Fig. 5 gives a comparison between the amount of carbon formed on an untreated iron sample and the deposition of carbon on identical iron specimens (geometric surface area 10 cm^2) which had been pretreated with less than 1 mg of various silanes for up to 16 hours. It is evident that in all cases where a silane pretreatment had been applied the formation of carbon is sharply reduced. In the case of triethylsilane, the weight gain after 120 hours exposure to 1 vol % of H_2 and CO at 500°C is less than 2 mg; whereas the untreated samples showed a weight gain of 200 mg in the same experimental conditions.

Even with the less efficient inhibitors, triphenylmethyl- and dichlorodiphenylsilane, the amount of carbon deposited is still at least one order of magnitude lower than in the uninhibited reaction. The inhibitive effect of silanes appears to be greater for silanes having high vapour pressure, low decomposition temperature, and high silicon content; e.g. the aliphatic short-chain homologs.

Comparable results were obtained without inhibition pretreatment if the inhibitor was added to the CO- H_2 reaction mixture at a concentration level CO : silane of about 10 : 1 for the first hours of the experiment. Similar inhibitive effects were found with the mild steel (St. 35.8) samples.

Addition of SO_2 to the CH-H_2 reaction mixture resulted in an immediate halting of carbon deposition. In contrast to silanes, this inhibitive influence was very effective even after a considerable carbon deposit had been formed previously. Also, a short 1 hour pretreatment with approximately 0.05 vol % of SO_2 completely prevented carbon formation in another experiment lasting 307 hours. It seems that the inhibition effect is due to a chemical reaction of SO_2 with iron since a sharp weight gain can be observed for a short period after SO_2 has been admitted. This view is supported by a visual examination of the iron samples exposed to SO_2 which shows the formation of a dark surface layer, whereas in the case of silane inhibition no superficial change was observed on the iron or steel samples after exposure. By means of an X-ray diffraction this surface layer was identified as FeS (troilite). The thickness of this layer depends largely on the concentration of the SO_2 inhibitor. With SO_2 concentrations above 0.1 vol %, the formation of several FeS layers can be observed which start to peel off after some time, whereas with lower SO_2 concentrations a very thin strongly adhering surface film of FeS is obtained.

3.2.2 Reversible Inhibition (Retardation)

It was found that H_2O , N_2O , NH_3 , and CO_2 all inhibited or retarded the deposition of carbon from the CO-H mixture, with the inhibition effect decreasing in the direction $\text{H}_2\text{O}+\text{CO}_2$. In contrast to inhibition by silanes and SO_2 , relatively high concentrations are required to suppress carbon deposition completely. In the case of CO_2 even partial pressures above those of CO and H_2 were insufficient to stop the reaction (see fig. 8).

Furthermore the effect is entirely reversible; as soon as addition of the inhibitor is discontinued the carbon deposition reaction will start up again, reaching in a short time the deposition rates of the uninhibited reaction.

This is evident from fig. 6 which presents the weight gains observed in experiments where H₂O, NH₃, and CO₂ were added to the reaction mixture intermittently. It can be seen that the discontinuance of inhibitor addition is immediately followed by a weight gain; subsequent addition of the inhibitor, with the exception of CO₂, brings carbon deposition to a halt again. Of the four compounds investigated, H₂O shows the strongest effect. As long as no carbon deposit has been formed, 0.05 vol % of H₂O in 1 vol % of CO and H₂ is sufficient to prevent deposition of carbon. After carbon formation has once begun, the H₂O partial pressure has to be raised to about 0.07 vol % in order to suppress the carbon deposition reaction. (The initial weight decrease apparent in curve I was probably due to reduction of iron oxides which were present at the start of the reaction).

The inhibitive effect of N₂O also seems to be due to the presence of H₂O, since it was observed that N₂O reacts on iron with H₂ to form H₂O and N₂. Therefore, a higher N₂O concentration (about 0.1 vol %) is needed to stop the deposition of carbon. The weak effect of CO₂, too, has very probably to be attributed to formation of H₂O according to reaction:



rather than to inhibition by CO₂ itself. This would explain why even an excess of CO₂, as long as H₂ is present, cannot stop the deposition reaction, since at 500°C equilibrium conditions of reaction III would only allow very low H₂O partial pressures. In the case of NH₃, a concentration of

about 1 vol % is necessary to suppress carbon deposition completely. After addition of NH_3 , the presence of H_2 can be detected in the off-gas line in appreciable quantities indicating partial decomposition of NH_3 into H_2 and N_2 .

Since H_2O leaking from the heat exchanger is the principal source of impurities in the coolant circuit of a HTGR, the effect of H_2O partial pressures and $\text{H}_2/\text{H}_2\text{O}$ ratios on the kinetics of carbon deposition has been studied in more detail. The effect of a variation of the H_2O concentration in 1 and 5 vol % of H_2 and CO each on the relative rate of carbon deposition (R_x/R_o ; R_o = deposition rate in the absence of H_2O) is shown in fig.7. It seems that the retarding effect of H_2O is determined by the $\text{H}_2/\text{H}_2\text{O}$ ratio and not by the absolute H_2O concentration since a plot of R_x/R_o versus $\text{H}_2/\text{H}_2\text{O}$ ratio gives almost identical curves for 1 and 5% of CO and H_2 . The retarding influence is already evident around a $\text{H}_2/\text{H}_2\text{O}$ ratio of 100. At $\text{H}_2/\text{H}_2\text{O} = 40$ the deposition rate is reduced by about 50% and the reaction stops at a $\text{H}_2/\text{H}_2\text{O}$ ratio between 15 and 20. For the same reaction conditions, thermodynamic calculations predict an equilibrium $\text{H}_2/\text{H}_2\text{O}$ ratio of 2-3 (1).

In further experiments with specimens of the 2½ Cr steel it was demonstrated that carbon deposition is prevented as long as a $\text{H}_2/\text{H}_2\text{O}$ ratio of 20 is maintained. This is true even for long periods of exposure. In this particular experiment no carbon deposit was observed on the steel sample after three months exposure at 500°C to the CO/H_2 gas mixture of 1 vol % each containing 0.05 vol % of H_2C vapour whereas in a parallel experiment where no H_2O was present a heavy carbon deposit developed during the same reaction period.

In a second experiment, where the $\text{H}_2/\text{H}_2\text{O}$ ratio had been fixed at 50, no carbon deposit was observed at 500°C after the first month of exposure (This run is still in progress).

4. DISCUSSION

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These findings would suggest that the deposition of carbon on steels can be reduced or inhibited by various methods, according to distinct mechanisms of inhibition. The most effective method seems to be the formation of a perfect surface layer which prevents contact of CO and H₂ with the steel surface proper. This mechanism is obviously followed by SO₂ and silane inhibition. With SO₂ the protective layer probably consists of FeS, in the case of silane inhibition the presence of a silicon layer with an unspecified chemical composition has been demonstrated by microprobe analysis (see fig. 9).

To afford protection over long periods of reactor operation, however, it would be necessary for this protective surface layer to stay intact in spite of changes in working temperature and chemical composition of the coolant (reducing/oxidising regime). It is felt that further experimental work in this direction and on potential side effects in corrosion behaviour (effect of SO₂ treatment on stress corrosion) would be necessary before an inhibition treatment could be confidently recommended for reactor application (2).

Since the other inhibitors like H₂O, N₂O, NH₃ and CO₂ are only effective as long as they are present in the gas mixture, a reversible inhibition mechanism is thought to be responsible in this case. The most likely cause is competitive chemisorption with the reaction partners CO and H₂ at the catalytic sites where the carbon deposition reaction proceeds.

This is in line with the observation that higher inhibitor concentrations are necessary than in the case of irreversible inhibition in order to suppress carbon deposition completely; it would at the same time explain why H_2O , which is a product of the carbon deposition reaction from CO and H_2 is the most effective of the reversible inhibitors. Finally, one would expect that with increasing deposition the inhibitive action would tend to decrease since the number of catalyst sites increases in an autocatalytic reaction such as carbon deposition. With H_2O it has indeed been observed that consecutively higher H_2O partial pressures are required to stop carbon deposition after an appreciable carbon deposit has accumulated.

5. CONCLUSIONS

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At the present state of affairs the following conclusions might be drawn from the experimental work carried out up to now:

1. Of the various heat exchanger materials which have been investigated carbon deposition occurred always in the experimental conditions which have been employed (0.1 vol % of CO and H_2 each, 400-500°C) on mild steels and steels with low Cr content (< 2.5% Cr). (This is in good agreement with earlier investigations (3, 4)).
2. Ferritic steels tended to carbide formation on grain boundaries within the first 2000 hrs of exposure which at a latter stage might lead to carbon deposition.

3. Austenitic steels and alloys with a considerable Ni content exhibited in the same experimental conditions superficial oxidation which tended to level out after approximately 2-3000h exposure. Only on alloys with very high Ni content (> 70 weight %) an appreciable weight gain due to oxidation has been observed which was still continuing after 2000h exposure. However, carbon deposits may grow on austenitic steels if they are in contact with mild or ferritic steels or if carbon deposits which developed elsewhere reach the austenitic steel surface.
4. For pickling of the heat exchanger steels a treatment with an aqueous solution of H_3PO_4 should be preferable to pickling with citric acid since the H_3PO_4 treatment seems to exert a temporary protective effect against carbon deposition. Invariably, the specimens treated with phosphoric acid exhibited a decreased deposit as compared to samples treated with citric acid which varied between a reduction of 50 to 90% in identical experimental conditions.
5. Carbon deposition can be prevented on low alloyed steels by the addition of inhibitors to the gas atmosphere. The inhibitive effect may be reversible or irreversible, depending on the inhibition mechanism.
6. Reversible inhibition is observed with H_2O and NH_3 , and less effectively with CO_2 addition. On 2½% Cr alloys a H_2/H_2O ratio of up to 50 seems tolerable in presence of equal amounts of CO and H_2 without incurring carbon deposition.

7. The most promising inhibition effects have been observed with irreversible inhibitors, such as SO₂ and silane compounds, where the inhibitive effect seems to be due to the formation of an unpermeable protective surface layer.

6. LITERATURE REFERENCES

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- (1) M.R. Everett, D.V. Kinsey and E. Römberg, Chemistry and Physics of Carbon, Vol. 3, M. Dekker New York, 1968.
- (2) W. Karcher, "A Process for the Prevention or Reduction of Carbon Deposits on Metal Surfaces in a Nuclear Reactor", Brit. Patent 1, 189, 423, April 1970.
- (3) A.B. Knutsen, J.F.G. Condé and K. Piene, Dragon Project Report 527, 1967.
- (4) W.R. Ruston, M. Warzee, J. Hennant and J. Waty, Carbon 1, 47 (1969).

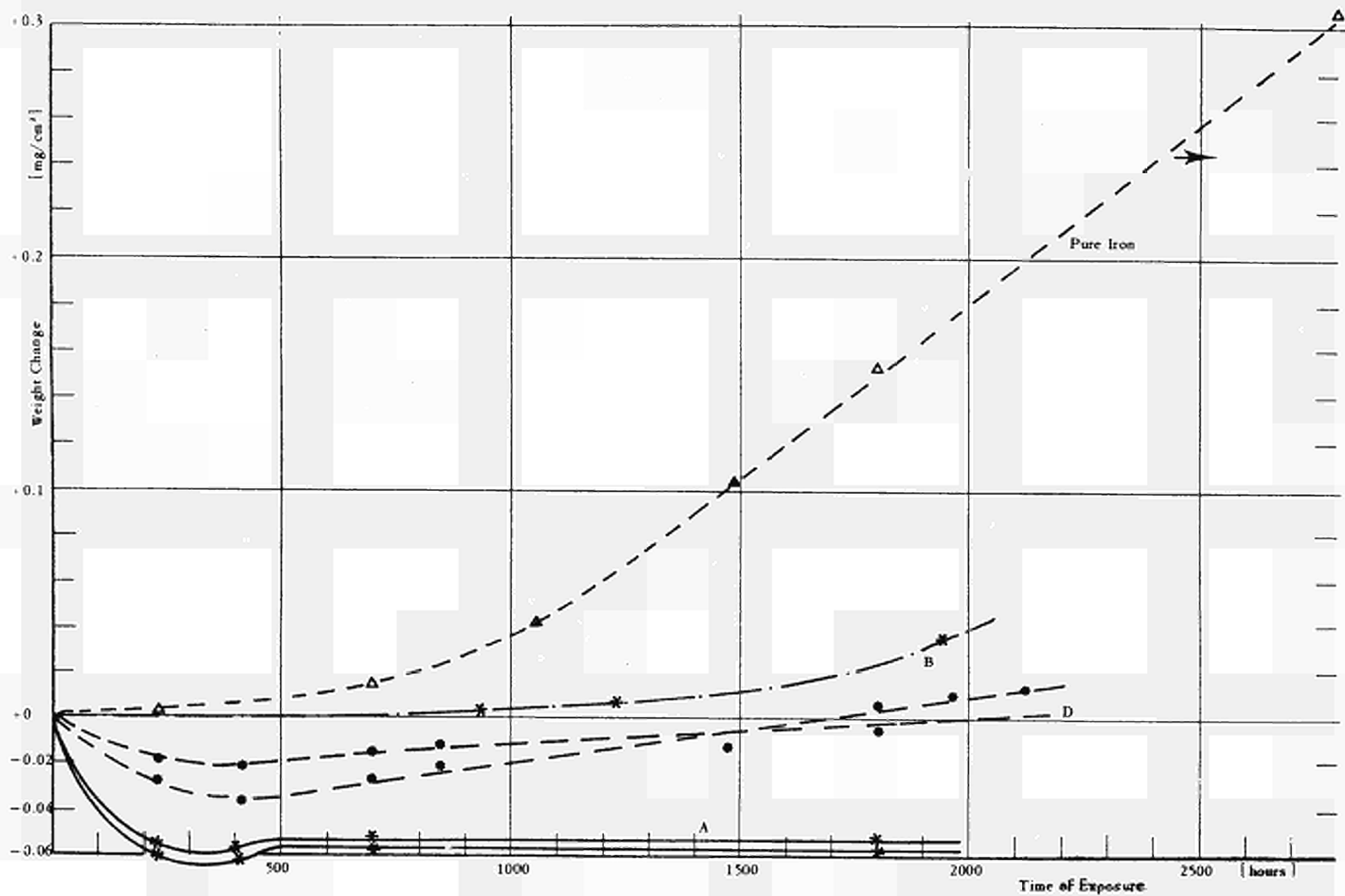


Fig. 1 Weight Change of Pure Iron, 2 1/2 Cr, 15 Mo3 and St 35.8 in 0.1% Co/H₂ at 400°C.

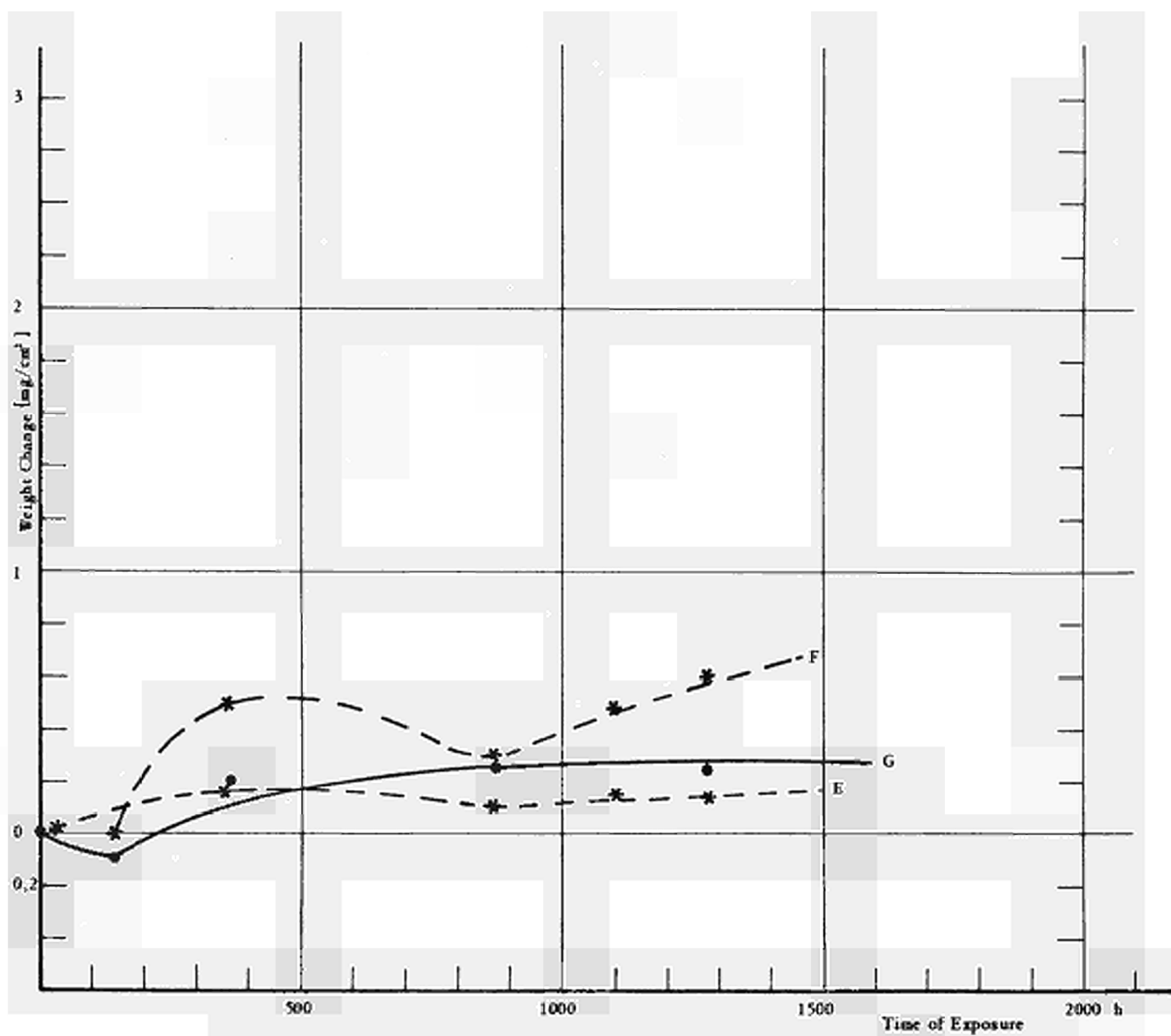


Fig. 2 Weight Change of Alloys E, F and G at 500°C.

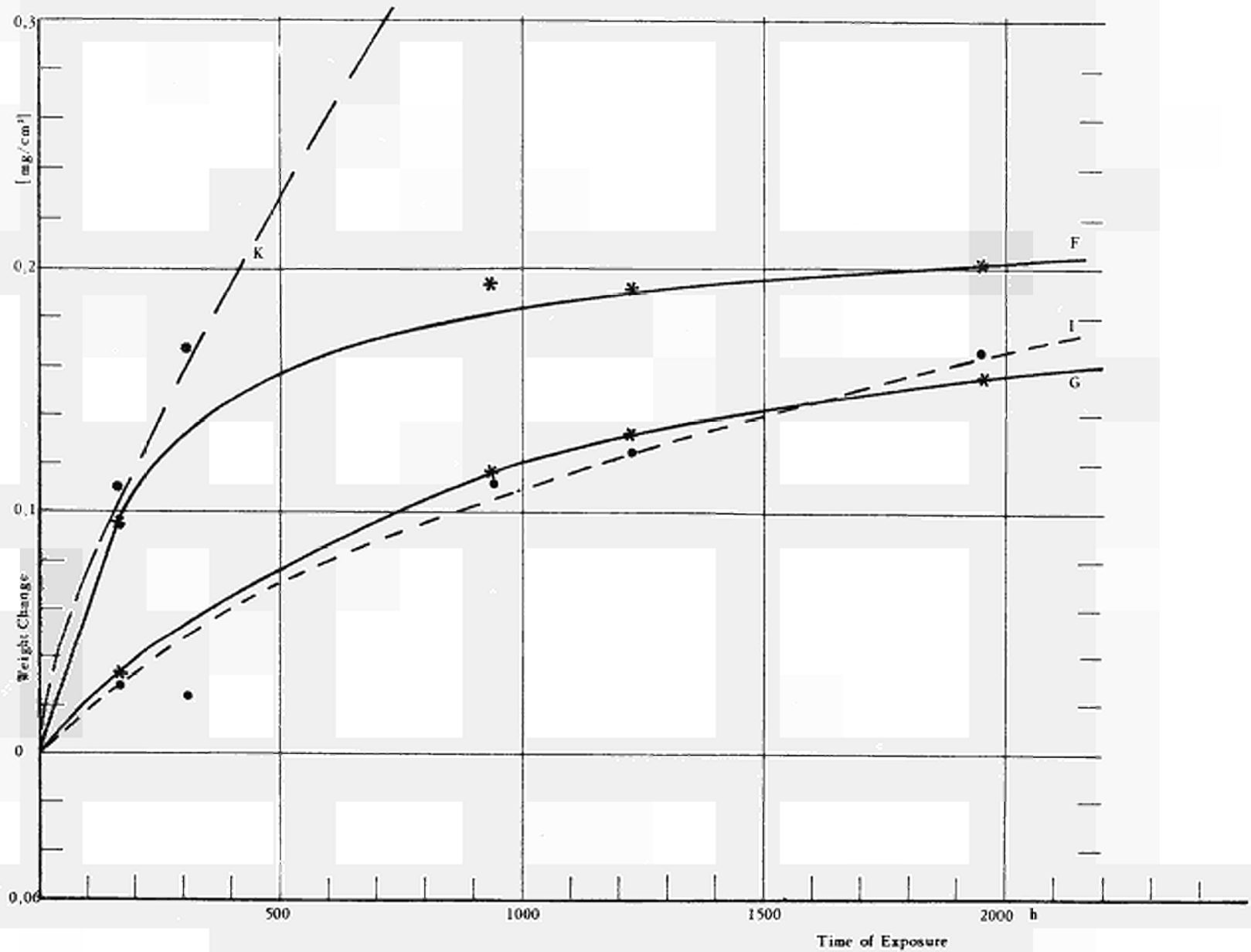


Fig. 3 Behaviour of Cr-Ni alloys in 0.1% Co/H₂ at 600°C.

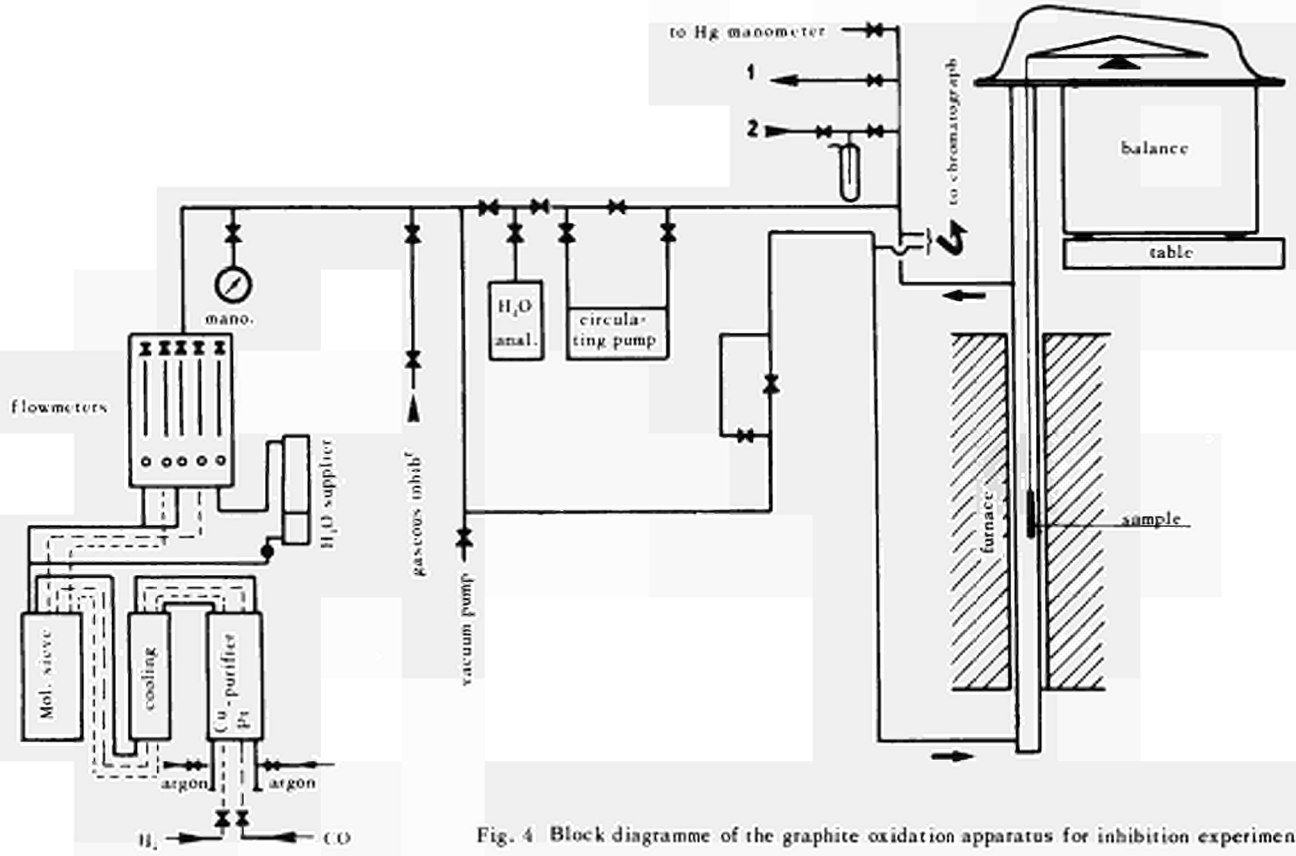


Fig. 4 Block diagramme of the graphite oxidation apparatus for inhibition experiments.

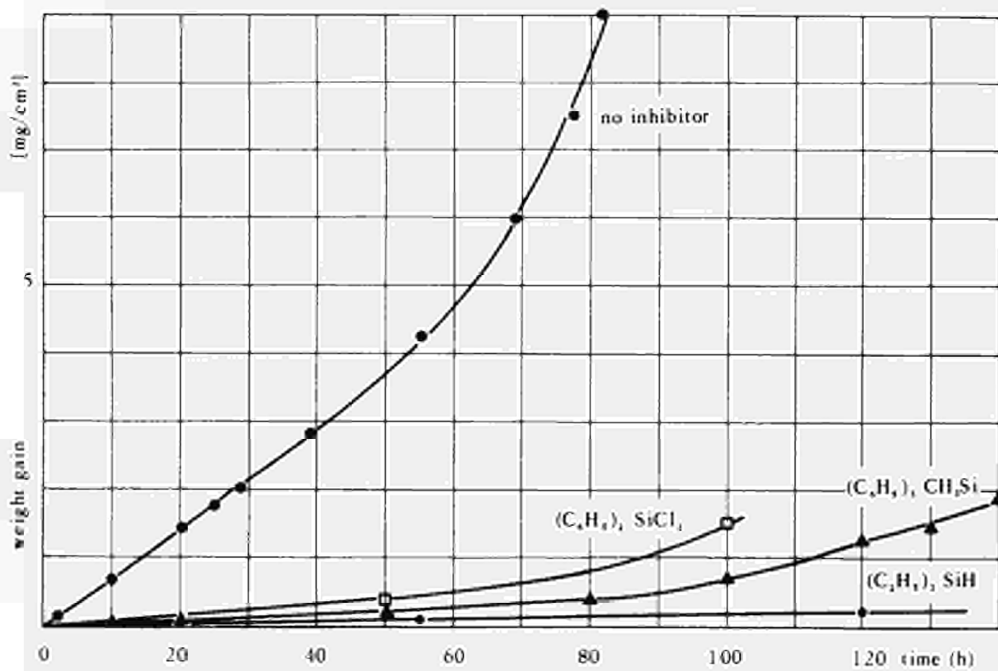


Fig. 5 Weight gain of pure iron in 1% CO and H_2 at $500^\circ C$ in presence and absence of inhibitors.

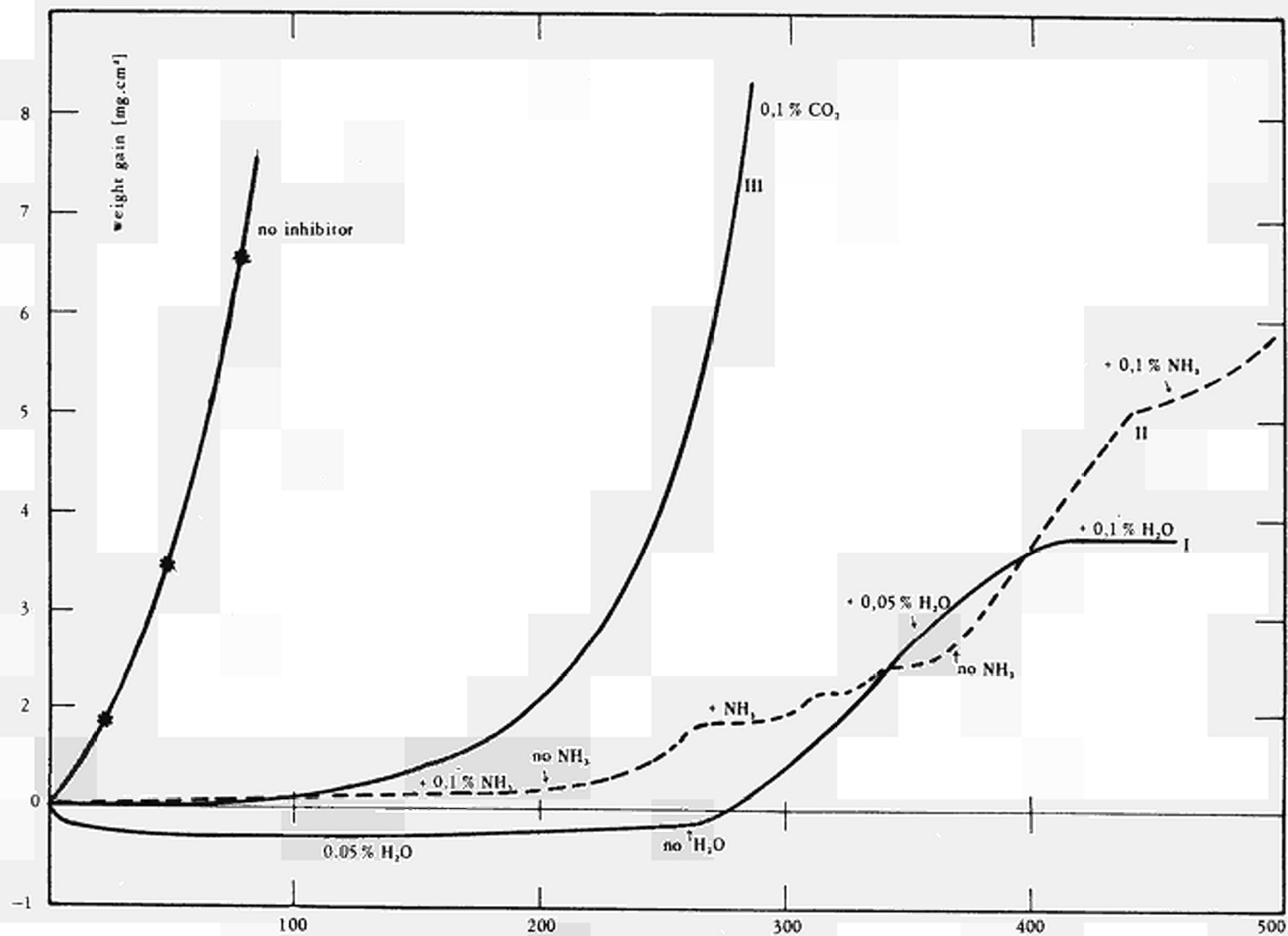


Fig. 6 Effect of CO₂, NH₃ and H₂O on carbon deposition on iron at 500°C (1 vol % of Co and H₂).

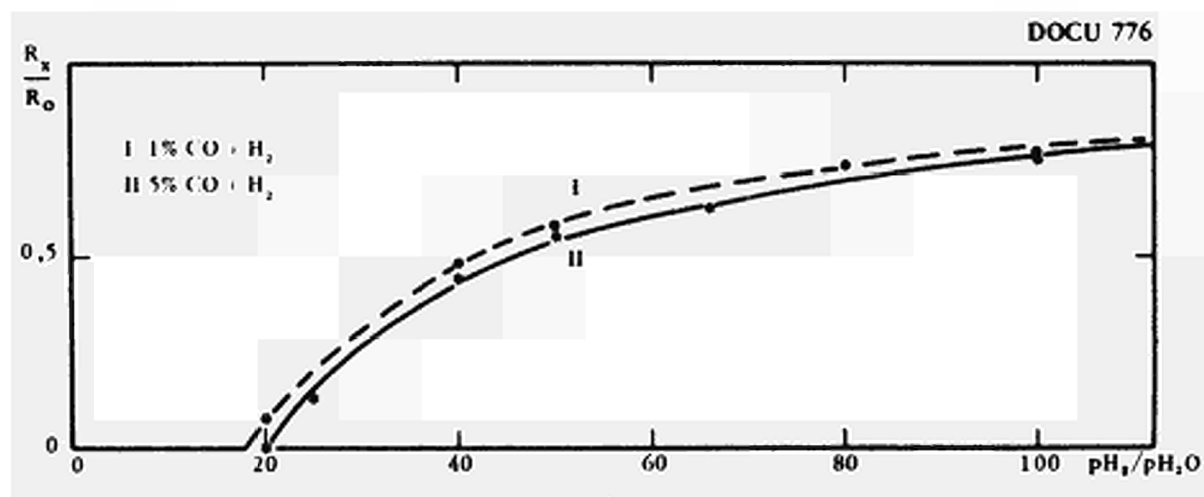
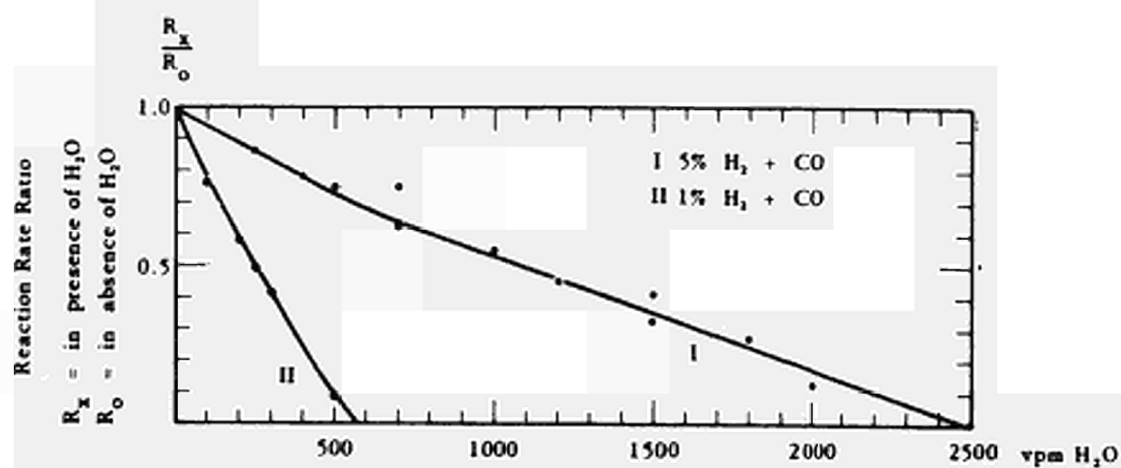


Fig. 7 H_2O retardation of carbon deposition at 550°C. on pure iron.

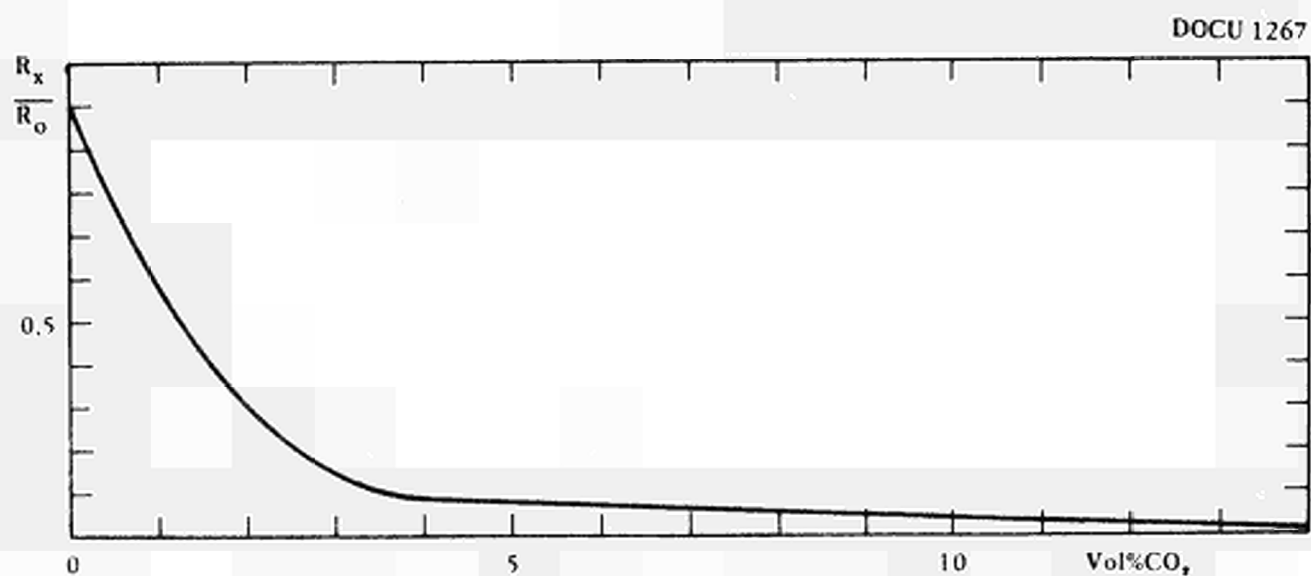


Fig. 8 Influence of CO_2 on carbon deposition (1% CO + H_2 , 500°C) on pure iron

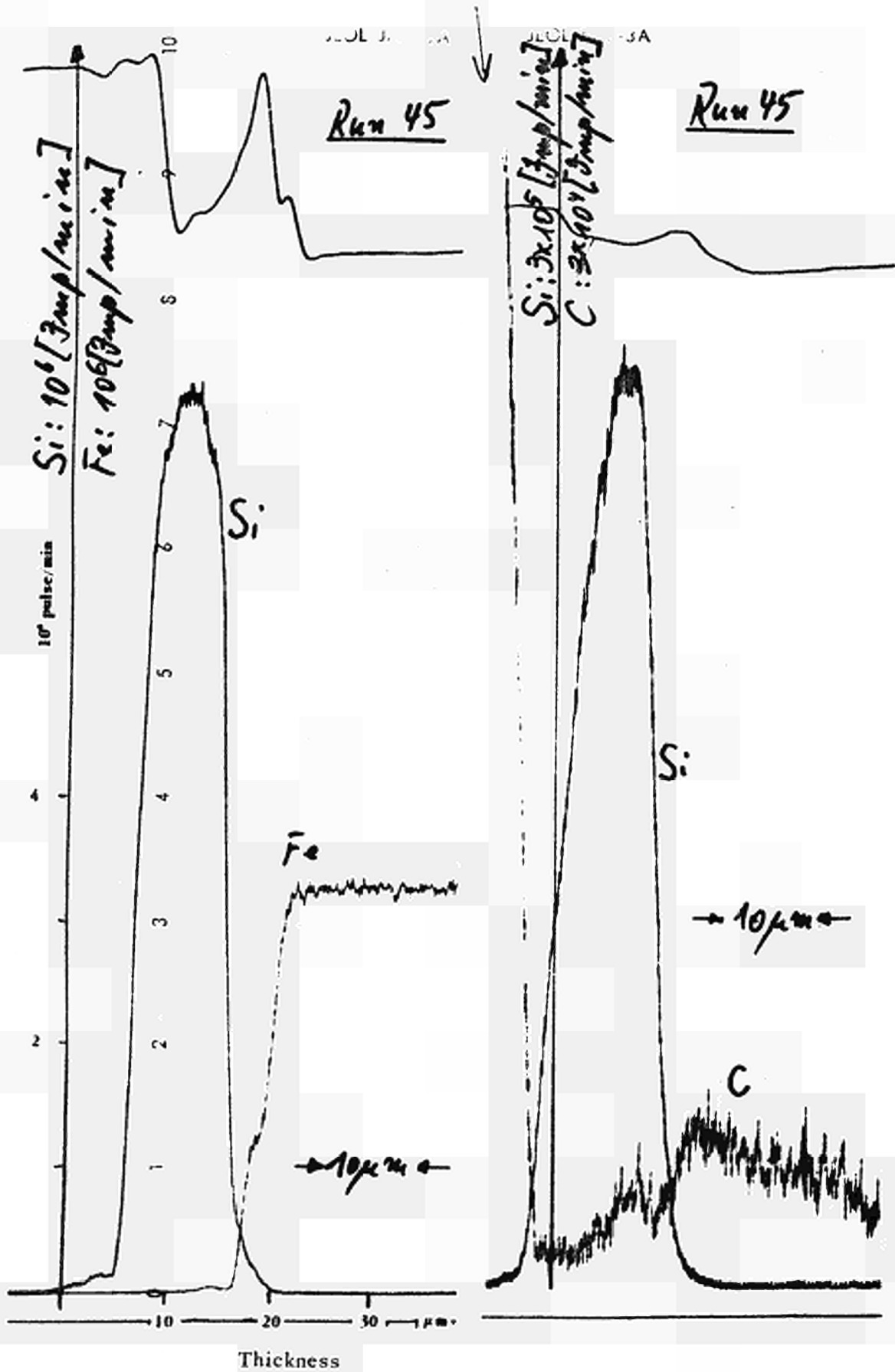


Fig. 9 Microprobe analysis of iron sample treated with silane.

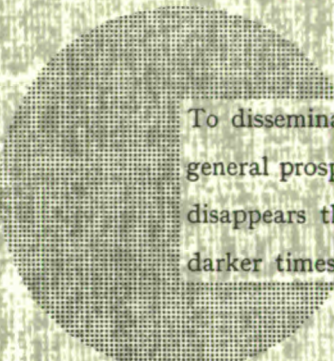
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Alfred Nobel

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