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HIGH TEMPERATURE COMPATIBILITY OF 25/20 TYPE AUSTENITIC STAINLESS STEEL WITH CARBON DIOXIDE

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ABSTRACT

The 25% Cr, 20% Ni type stainless steel has been proposed for use in the Australian High Temperature Gas Cooled Reactor in core structures, and in hot gas ducting. Thus a knowledge of the compatibility of this steel with high pressure carbon dioxide was required.

Rates and mechanisms of corrosion were investigated for machined, vapour blasted, and etched pretreated samples of this steel, exposed to carbon dioxide up to 5,000 hours in the temperature range 650 °C to 800 °C at gas pressures from 3 p.s.i.g. to 280 p.s.i.g.

Oxide film flaking was apparent at all temperatures investigated, but was only severe for pre-ground samples at 710 °C and above, and for pre-vapour blasted samples at 760 °C and above. However, severe intergranular penetration was observed in pre-etched samples on exposure to carbon dioxide at 650 °C and above.

Pressure of the gas appeared to have no systematic effect on the corrosion rate, at least in the temperature range investigated.

The maximum useful temperature for which the steel could be used would be limited by the amount of oxide flaking permissible. In reactor gas circuits where a small amount of scale flaking could be tolerated, the steel is satisfactory up to 750 °C.

CONTENTS

1. INTRODUCTION

Possible uses of 25% Cr, 20% Ni type austenitic steel in the proposed Australian High Temperature Gas Cooled Reactor (H.T.G.C.R.) are in reactor core structures and hot gas ducting. Thus a knowledge of its high temperature compatibility with high pressure carbon dioxide is required.

Previous work on the compatibility of this steel with carbon dioxide was limited and inconclusive. Bokros and Wallace (1960) found that this steel, although subjected to localised attack in the form of pitting and intergranular penetration, formed protective films at temperatures below 1500 °F (815 °C) and at 2000 p.s.i.g. pressure. In the work by General Nuclear Engineering Corporation (1960), protective films were also observed to form up to 1500 °F, 500 p.s.i.g. pressure. However, in these two investigations, exposures were limited to 2,000 hours. Billington et al. (1960) also reported the formation of protective films in the temperature range 600 °C to 750 °C up to 2,000 hours exposure, but some oxide film flaking was observed on further exposure.

This report describes a detailed study of the corrosion rates of 25% Cr, 20% Ni steel in the temperature range 650 °C to 800 °C with dry carbon dioxide ($<$ 20 p.p.m. H_2O), at pressures from 3 p.s.i.g. to 280 p.s.i.g.

2. EXPERIMENTAL METHODS

A spectrographic analysis of the steel tested in this investigation gave Cr – 25%, Ni – 20%, Si – 0.3%, Mo – 0.3%, and Cu – 0.15%, and chemical analysis gave carbon as 0.11%.

Carbon dioxide was supplied from liquid CO_2 in a six ton vessel; the main impurities were water vapour ($<$ 20 p.p.m. v/v), oxygen ($<$ 12 p.p.m. v/v), nitrogen ($<$ 50 p.p.m. v/v), sulphur dioxide ($<$ 0.3 p.p.m. v/v), oxides of nitrogen ($<$ 0.1 p.p.m. v/v), and hydrocarbons and alcohols ($<$ 1 p.p.m. v/v).

Test samples consisted of discs of approximately 17.5 mm diameter by 3 mm thick, with a 1/16 inch diameter hole for supporting prongs. Surface pretreatments investigated were:

- Machined surface:– sample turned and surface ground.
- Vapour blasted:– as machined, then subjected to a high velocity stream of 400 grade alumina in water.
- Nitric–hydrofluoric acid etched:– as machined, then etched in acid (HF : HNO_3 : H_2O is 1 : 2.5 : 4.6) at 95 °C for 30 minutes.
- Hydrochloric acid etched:– as machined, treated with 32% w/w HCl at 70 °C for 15 minutes, and then rinsed in cold 5% HNO_3 for 18 hours.
- Phosphoric acid etched:– as machined, treated with boiling 89% H_3PO_4 for 5 minutes, then rinsed in 5% HNO_3 for 18 hours.

High pressure autoclaves as described by Draycott and Smith (1960) were used for semi–static tests up to 280 p.s.i.g. pressure and 800 °C, and tube furnaces were used for runs at 3 p.s.i.g. Temperatures were held within ± 5 °C in all equipment by millivolt galvanometric controllers, and actual temperature gradients were measured on a potentiometric recorder.

Metallographic and X–ray diffraction analyses of selected samples were performed to determine type and thickness of oxide scales.

3. RESULTS

3.1 General

Examination under low magnification (X10) of exposed test samples indicated that some oxide spalling had occurred at all temperatures investigated. In the case of surface ground samples, a green oxide layer, formed initially after 100 hour exposure to carbon dioxide at temperatures of 740 °C and greater, was easily removed by brushing. However, close examination of ground samples exposed at temperatures as low as 650 °C revealed small shiny patches of metal in the oxide layer. Although the oxide films formed on pre-vapour blasted samples after 100 hour exposures were observed to be adherent, very small areas of base metal were observed in the oxide layer formed on much longer exposure (1000 hours) at 650 °C.

In the case of ground and vapour blasted samples exposed at temperatures above approximately 750 °C, the oxide layer was continuous. However lighter blue-grey patches were observed in the very dark blue grey layer, indicating that spalling could have occurred within the oxide layer.

Scale growth on surface ground samples exposed to dry carbon dioxide at 750 °C and 225 p.s.i.g., occurred mainly by increase in the number and size of multi-oxide warts. Warts were observed to grow from an average of 5 microns thick after 200 hour exposure to 10 microns thick after 1,000 hours (Figures 10, 11). However, examination of ground samples exposed at 750 °C and 280 p.s.i.g. for 4,500 hours, gave scale thicknesses of the order of 4 microns, with wart penetrations of 1 to 2 microns.

Vapour blasted samples appeared to form even oxide films of the order of 5 microns thick on exposure at 750 °C and 280 p.s.i.g. for 4,500 hours.

Little difference in oxide formation on surface ground and vapour blasted samples was observed when these were exposed for 1500 hours at 650 °C and 150 p.s.i.g., scale thicknesses being approximately 5 microns, with wart penetrations of the order of 1 micron. However, hydrofluoric - nitric acid etched specimens exposed to the same conditions were subjected to severe intergranular attack resulting in metal penetrations up to 300 microns in depth (Figure 13).

Although positive identification of scale composition was not possible because of the small quantities of oxide formed, X-ray diffraction examination did indicate that the scale formed was composed of a mixture of Fe_2O_3 and Cr_2O_3.

3.2 Sample Surface Pretreatment

Pre-etching of samples with hydrofluoric-nitric acids or hydrochloric acid increased the weight gains obtained over a given time by approximately two to eight times that of vapour blasted pretreated samples (Figure 4). As considerable scatter of the points on the weight gain-time curves was obtained, it is suggested that some flaking of the scale occurred at temperatures as low as 650 °C. However, phosphoric acid pre-etching gave weight gains of similar magnitude to those obtained with vapour blasted samples (Figure 6).

Surface effects were most marked in the comparison between surface ground and vapour blasted pre-treated samples. The chromium oxide film formed after 100 hour exposure, (spectrographic analysis gave 1% iron, 0.2% nickel, remainder chromium), flaked initially and resulted in weight losses in the case of surface ground samples exposed at temperatures of approximately 720 °C and higher (Figures 1, 2, and 3). The non-adherent green scale formed was easily removed by brushing. Further exposure of surface ground samples resulted in more stable multi-oxide scales being formed; however some scale spalling at temperatures as low as 710 °C was observed (Figure 3). Although gross spalling of oxide films produced on machined specimens did not appear below 710 °C, the point scatter on weight gain curves obtained for 650 °C suggests that simultaneous scale growth and spalling occurred (Figures 1 and 3). Oxide films produced on vapour blasted samples appeared to be protective up to 745 °C (Figure 3), but it was apparent that minor spalling of the oxide film occurred at this temperature. At 765 °C and above, severe spalling of the oxide film was observed (Figures 1, 2, and 3).

3.3 Temperature

Attempts to correlate weight gains observed at a given temperature and pressure, against time of exposure in the form:

$$(\Delta w)^n = kt ,$$

where w = weight gain, in mg/cm^2 ,

t = exposure time, in hours ,

and k, n = constants,

were not successful.

However, graphs of the rate of scale growth, $\frac{d(\Delta w)}{dt}$ (in mg/cm^2h) against time, t (hours) did indicate that little scale growth occurred on vapour blasted samples after 1000 hour exposure at temperatures up to 745 °C (Figure 8). Above this temperature negative rates of weight gain were observed (Figure 8). Results obtained for ground samples at 650 °C plotted in this way indicated the occurrence of flaking of the oxide film formed initially on exposure. (Figure 9). Thus the Arrhenius type relationship:

$$k = A\,e^{\left(-\frac{E}{RT}\right)}$$

could not be applied to the results obtained in this investigation.

Figure 7 gives weight gains obtained for vapour blasted samples at temperatures between 650 °C and 800 °C after 1,000 hour exposure to dry carbon dioxide. Weight gains observed varied from 0.1 to 0.2 mg/cm^2 at 650 °C, to approximately 0.3 mg/cm^2 at 800 °C. However no systematic temperature correlation could be obtained (Figure 7) in the case of surface ground samples, owing to the spread of weight gains observed at 750 °C and above.

3.4 Pressure

In the temperature range 650 °C to 780 °C, pressure appears to have little effect on the weight gains obtained for vapour blasted samples, at least up to 1,000 hour exposure. Values obtained for 775 °C and 3 p.s.i.g.; 760 °C and 75 p.s.i.g.; 780 °C and 150 p.s.i.g., and 765 °C and 280 p.s.i.g. were approximately 0.3 mg/cm^2 (Figure 5). However in the case of machined samples no systematic correlation of pressure could be established (Figure 6).

3.5 Summary of Results

(a) Rate of weight gain correlations and visual observations indicated that oxide film spalling occurred at temperatures of 650 °C and over. However, in the case of vapour blasted samples, significant spalling of the oxide layer only occurred at temperatures of 765 °C and greater.

(b) Metallographic examinations showed scale growth was small in ground and vapour blasted samples and occurred mainly by wart formation. This method also indicated that etched sample surfaces were subject to severe intergranular penetration on exposure to carbon dioxide at 650 °C and above.

(c) Pressure of carbon dioxide gas between 4 p.s.i.g. and 280 p.s.i.g. appeared to have no systematic effect on weight gains observed.

4. DISCUSSION

Although flaking of the chromium oxide film produced after 100 hour exposure at 720 °C or greater was observed with machined surface samples, more protective $Fe_2O_3 - Cr_2O_3$ multi-oxide films were produced on further exposure. However, some spalling of this film was apparent even at 650 °C, and became severe at temperatures of 710 °C and above.

In the case of vapour blasted samples, the oxide film formed on exposure appeared to be more adherent, at least up to 750 °C, while at 765 °C and above, severe spalling occurred.

Spalling of the oxide film in both vapour blasted and machined surface samples appeared to result from internal stresses set up between the metal and metal oxide interface. In the case of the vapour blasted samples the rough metal surface would tend to "key on" the oxide layer, at least until a smooth oxide surface was formed. Evans (1948) found that internal stresses are less with oxide films formed on finely abraded metal surfaces than on coarsely abraded surfaces, thus accounting for the greater tendency for machined surfaces to flake, compared with vapour blasted surfaces.

Differences in thermal expansion coefficients between the metal and metal oxide could also have led to oxide spalling during thermal cycles. Tylecote (1960) summarised experimentally observed mean expansion coefficients of metal oxides; Cr_2O_3 being 7.3×10^{-6} per °C and FeO being 12.2×10^{-6} per °C, both in the range 100 °C to 1000 °C. For 25% Cr, 20% Ni stainless steel, Monypenny (1951) gave a value of 17.0×10^{-6} per °C for the mean thermal expansion coefficient between 20 °C and 500 °C. Thus the ratio of the expansion coefficients for Cr_2O_3 to 25% Cr, 20% Ni will be 7.3 : 17.0. This large difference in expansion between the metal and oxide layers could explain the initial non-adherence of the Cr_2O_3 film.

Although estimation of scale thicknesses from weight gain measurements could not be accepted as being reliable, metallographic analysis indicated the order of oxide penetration. Oxide growths in the form of warts were of the order of 5 microns (0.0002 inches) after 200 hour exposure at 750 °C, increasing to 10 microns (0.0004 inches) after 1,000 hours exposure, thus indicating that scale growth was very slow.

Initial chromium carbide precipitation observed metallographically (Figure 12) in samples exposed at 750 °C for 100 hours could have resulted in the formation of the non-adherent chromium oxide film. Also, the carbide to sigma transformation noted in the metallographic results for samples exposed at 750 °C for periods greater than 100 hours could have given progressively smaller rates of intergranular attack and consequently smaller weight gain rates.

5. CONCLUSIONS

1. 25% Cr, 20% Ni stainless steel can be usefully employed up to 750 °C and 280 p.s.i.g. in reactor circuits where some oxide flaking is permissible; however in circuits where absolutely clean gas is required, the maximum temperature would be limited to 650 °C.

2. Vapour blasting of 25% Cr, 20% Ni steel surfaces before exposure to high temperatures resulted in the formation of more adherent and more uniform oxide films than those formed with machined surfaces.

3. Severe oxide film spalling occurred with pre-ground metal surfaces in exposure to carbon dioxide at 710 °C or greater, and with vapour blasted metal surfaces at 760 °C or greater.

4. Surface etching with either nitric-hydrofluoric acids or hydrochloric acid resulted in much larger weight gains than with vapour blasted surfaces, and with phosphoric acid etching little difference was observed. However, as severe intergranular penetration was observed with etched specimens, descaling of metal by this method prior to high temperature exposure must be avoided.

5. Pressure appeared to have little effect on the corrosion rate.

6. Non-adherence of oxide films produced on exposure could have resulted from any or all of the following factors:

   (a) Initial chromium carbide precipitation.

   (b) High stress concentration at metal - metal oxide interface.

   (c) Differences in thermal expansion coefficients between metal and oxide.

6. ACKNOWLEDGMENTS

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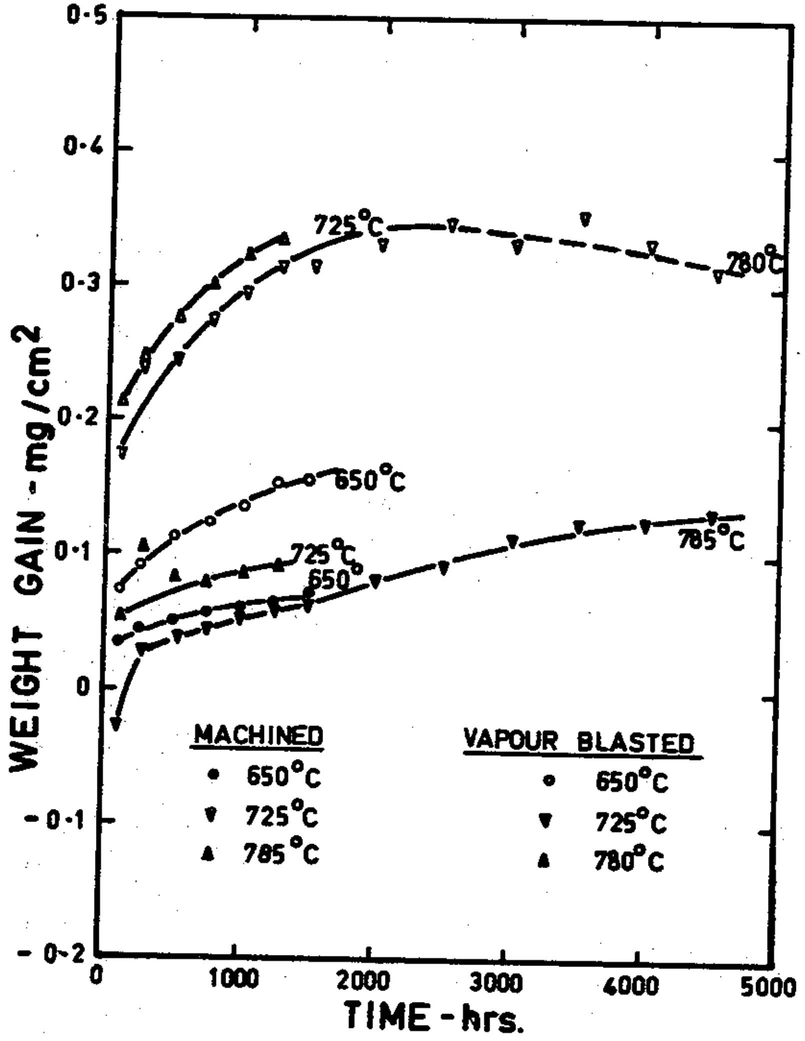


FIG.1 WEIGHT GAIN-TIME CURVES FOR 25-20 STEEL IN CO_2 AT 150 p.s.i.g.

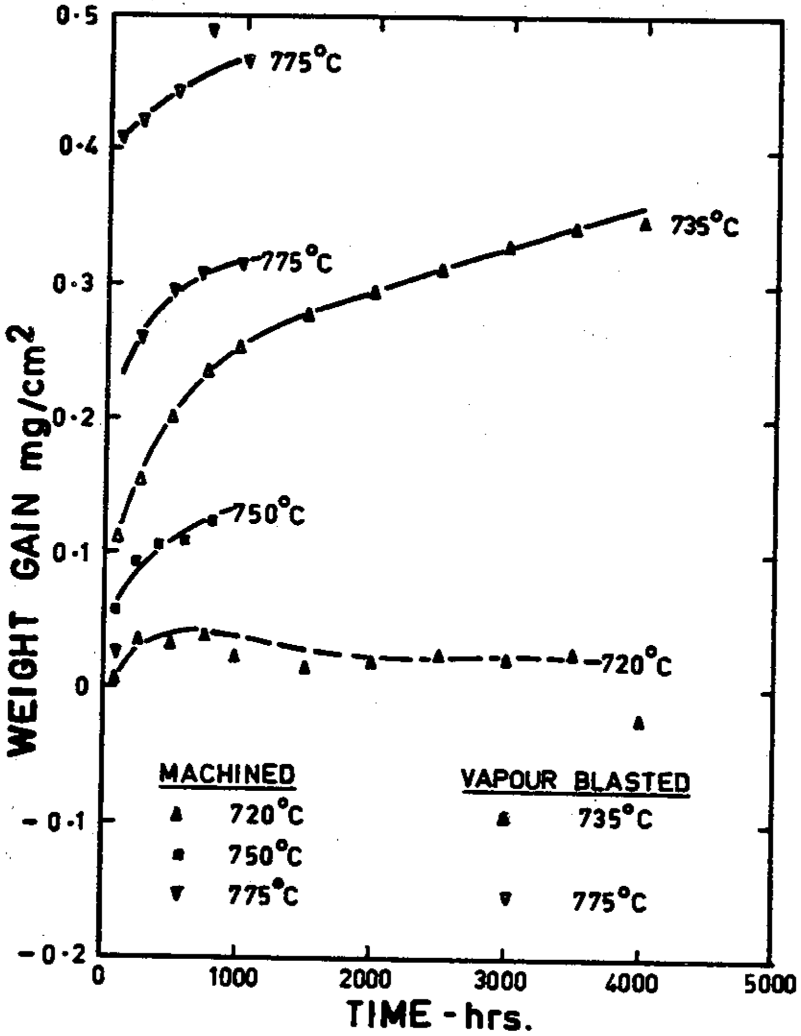


FIG. 2 WEIGHT GAIN-TIME CURVES FOR 25-20 STEEL IN CO_2 AT 225 p.s.i.g.

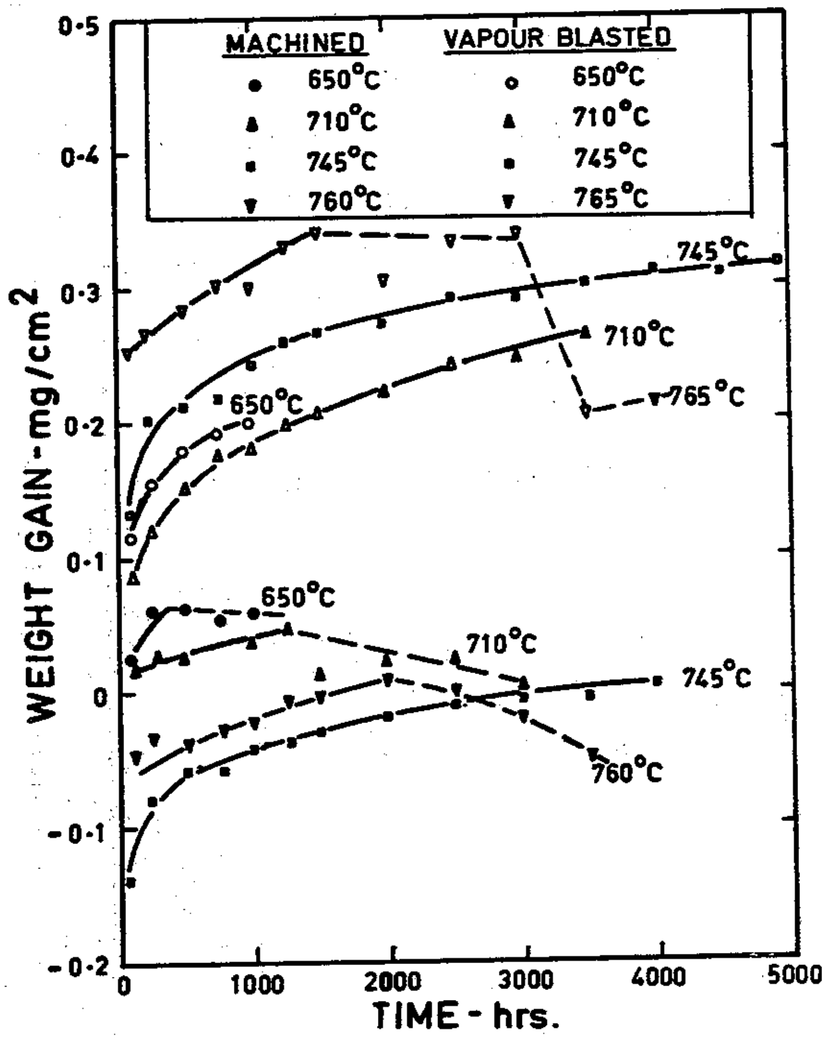


FIG 3 WEIGHT GAIN - TIME CURVES FOR 25-20 STEEL IN CO_2 AT 280 p.s.i.g.

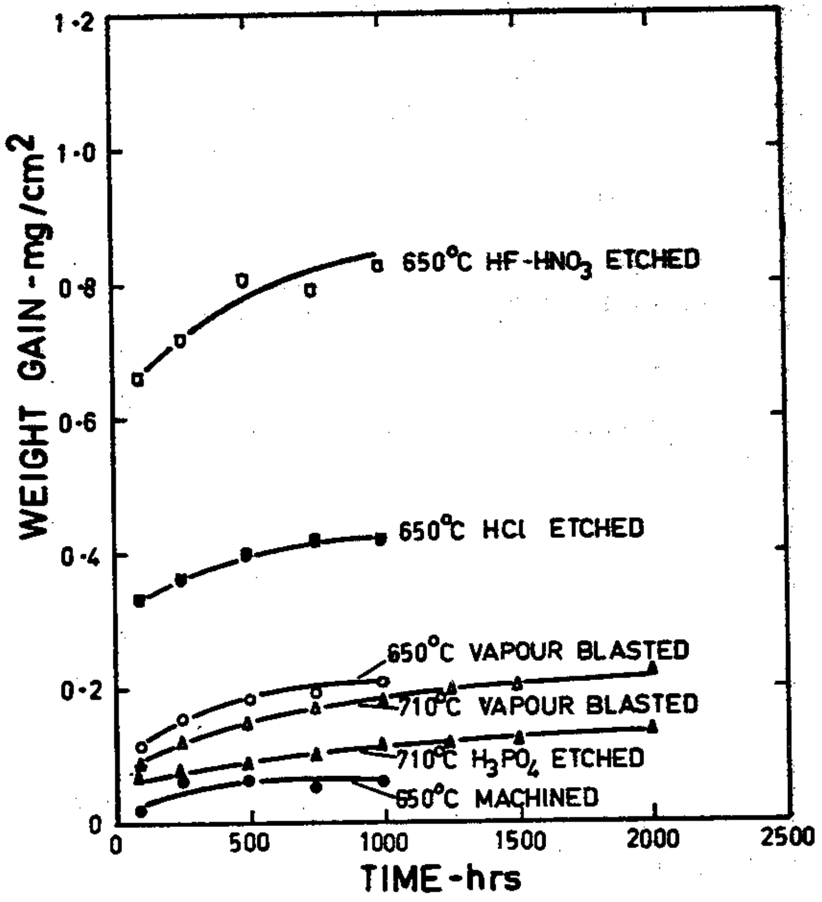


FIG 4 WEIGHT GAIN - TIME CURVES FOR 25-20 STEEL IN CO_2 AT 280p.s.i.g. (Effect of Surface Pre-treatment)

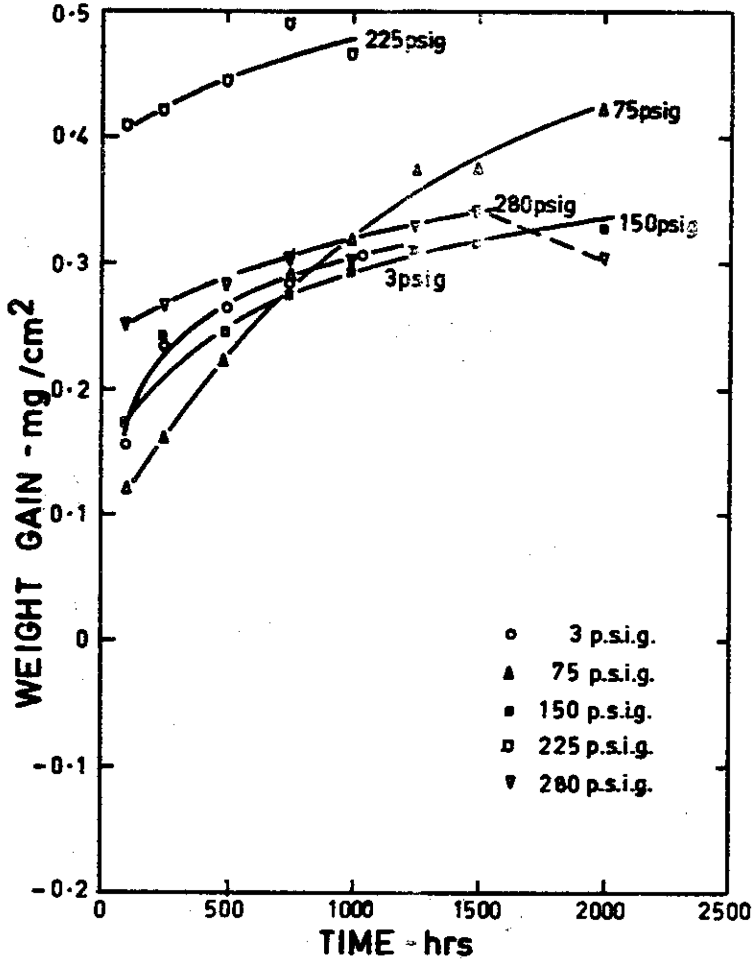


FIG 5 WEIGHT GAIN - TIME CURVES FOR VAPOUR BLASTED 25-20 STEEL IN CO_2 AT 760°C - 780°C

(Effect of Pressure)

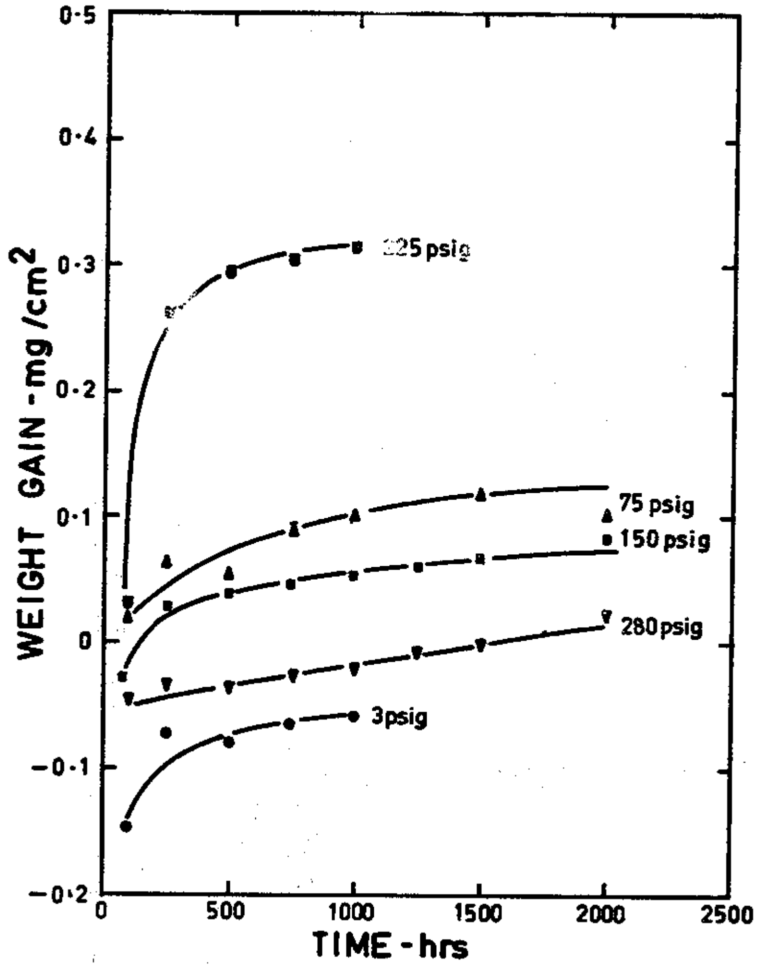


FIG 6 WEIGHT GAIN - TIME CURVES FOR MACHINED 25-20 STEEL IN CO_2 EXPOSED AT 760°C - 780°C

(Effect of Pressure)

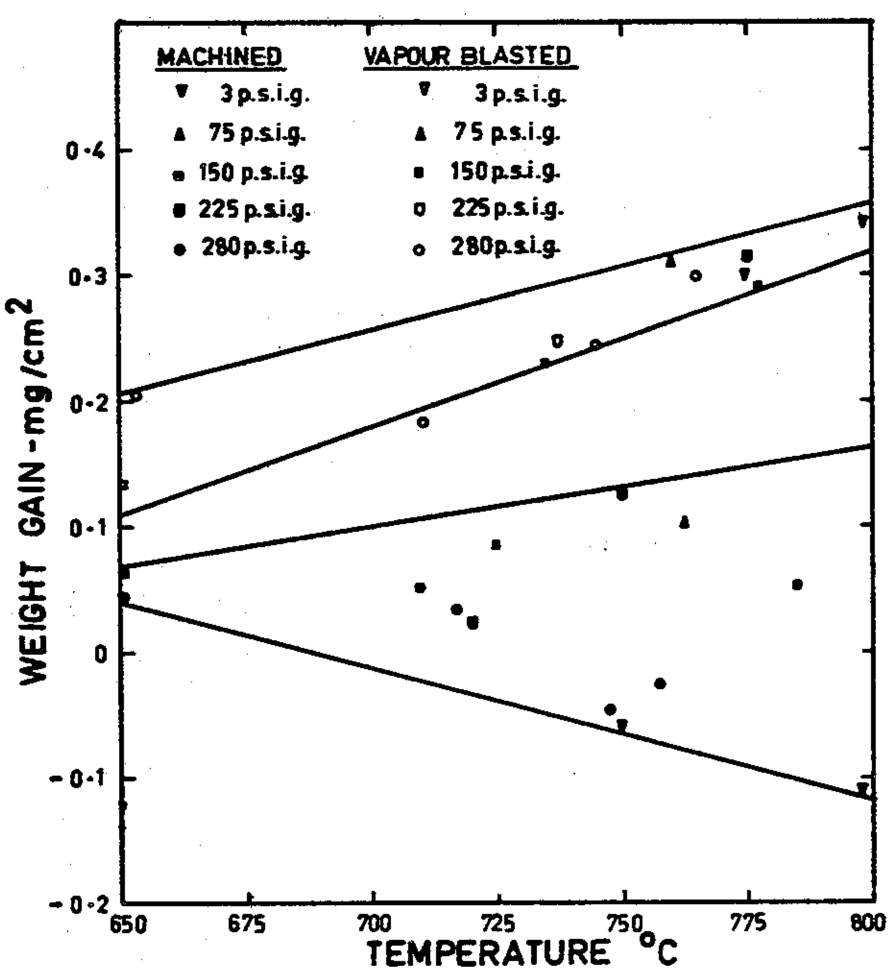


FIG 7 WEIGHT GAIN - TEMPERATURE RELATIONSHIP FOR 25-20 STEEL EXPOSED FOR 1000 HOURS IN CO_2

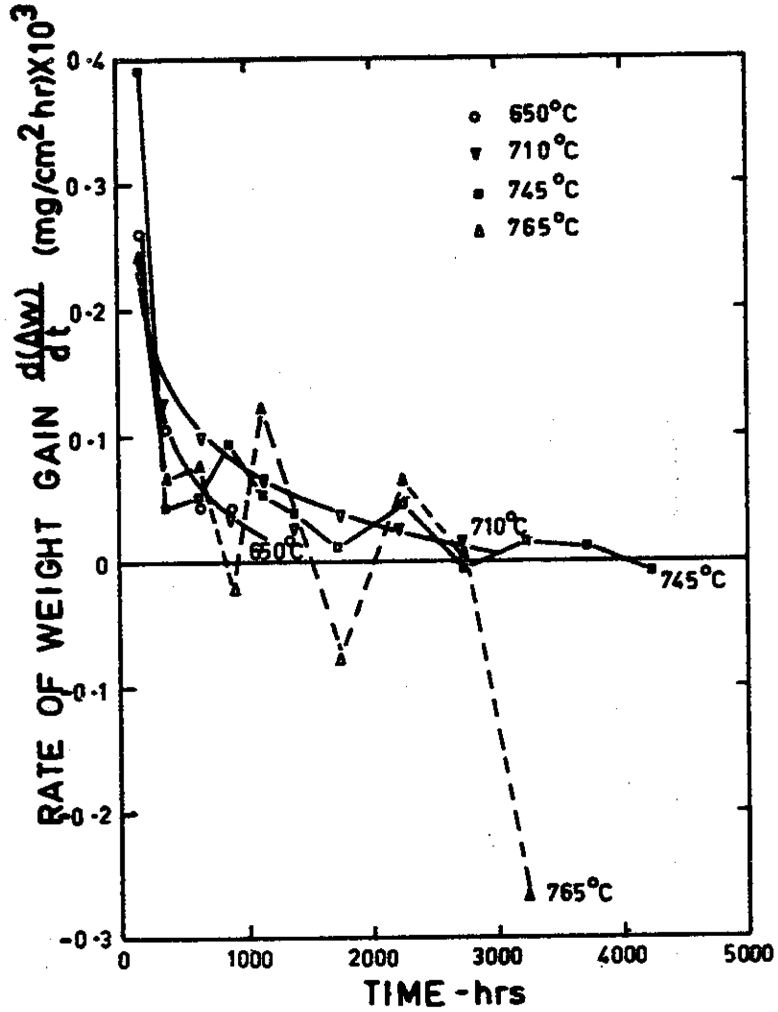


FIG 8 RATE OF WEIGHT GAIN - TIME CURVES FOR VAPOUR BLASTED 25-20 STEEL IN CO_2 AT 280 p.s.i.g.

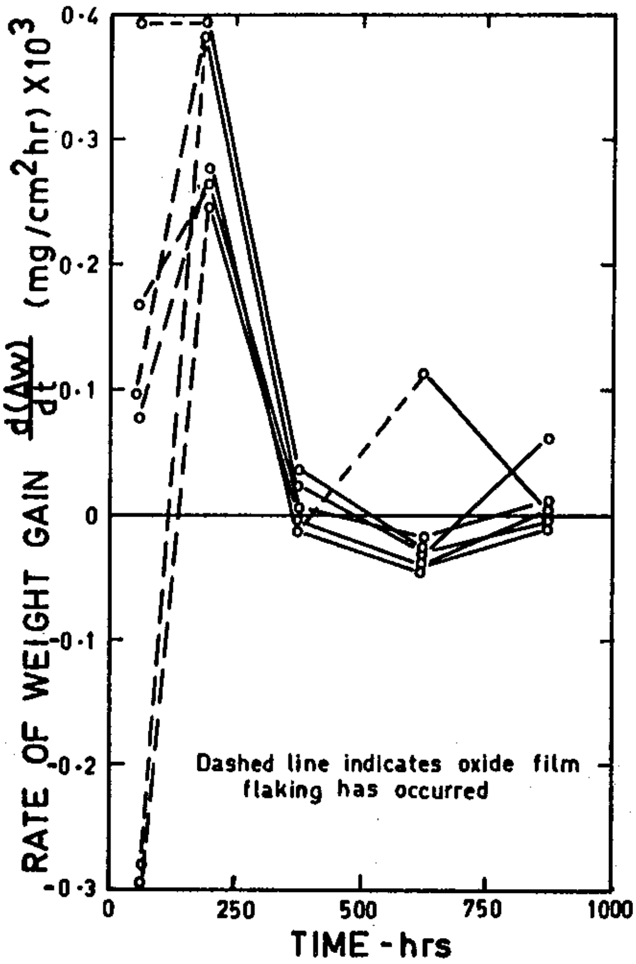
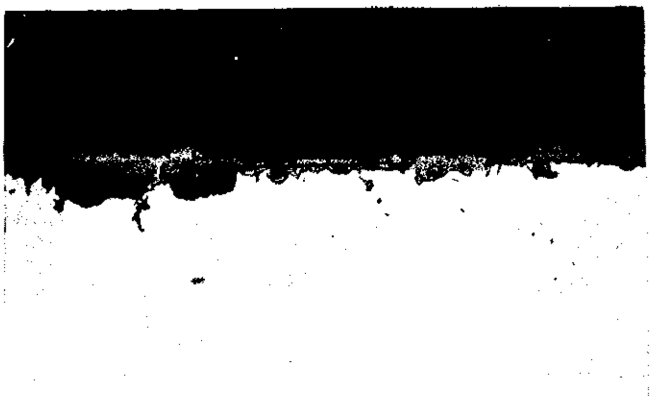


FIG 9 RATE OF WEIGHT GAIN-TIME RELATIONSHIP FOR MACHINED 25-20 STEEL IN CO_2 AT 650°C, 280 p.s.i.g.

Spec. 69 x 1000

FIGURE 10 OXIDE SCALE ON MACHINED 25/20 STEEL AFTER 200 HOUR EXPOSURE at 750°C, 225 p.s.i.g.

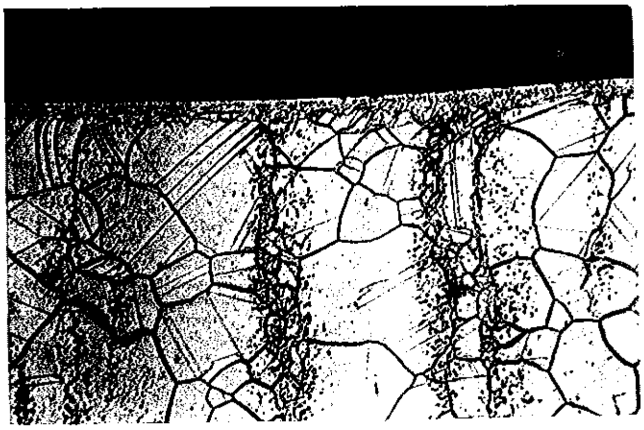
Weight gain: 0.132 mg/cm^2



Spec. 72 x 1000

FIGURE 11 OXIDE SCALE ON MACHINED 25/20 STEEL AFTER 1000 HOUR EXPOSURE AT 750°C, 225 p.s.i.g.

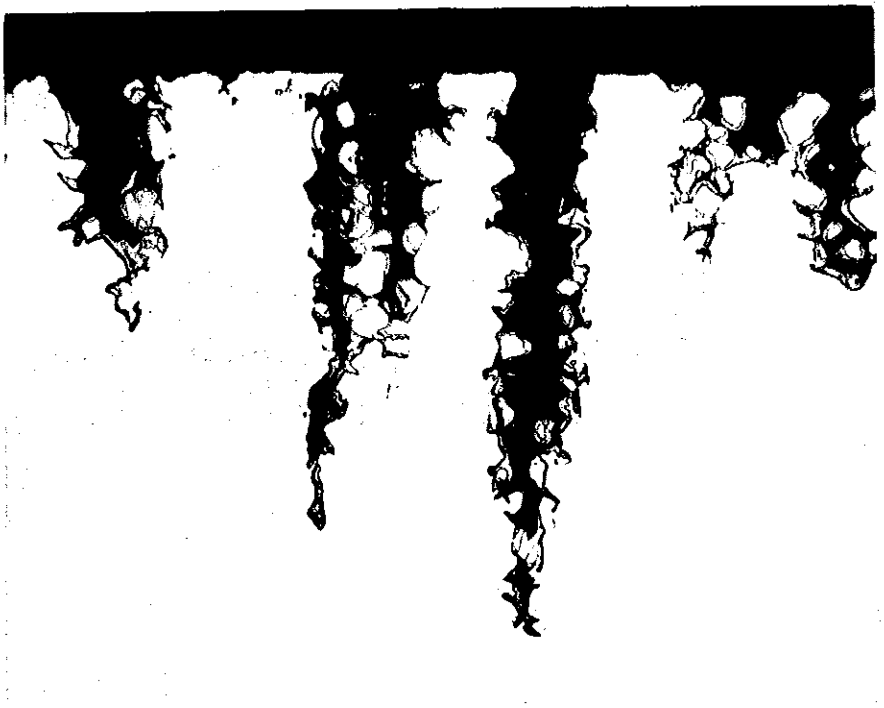
Weight gain: 0.138 mg/cm^2



Spec. 67 x 200 etched

FIGURE 12 MACHINED 25/20 STEEL AFTER 100 HOUR EXPOSURE AT 750°C, 225 p.s.i.g.

Weight gain: 0.064 mg/cm^2



Spec. 36 x 200

FIGURE 13 OXIDE SCALE ON HF–HNO_3 ETCHED 25/20 STEEL AFTER 1500 HOUR EXPOSURE AT 650°C, 150 p.s.i.g.

Weight gain: 0.886 mg/cm^2