PRJ, Vol. 2 (January 1990); P. 57–62, 8 FIGS, 3 TABLES.

Short Note

HIGH TEMPERATURE CORROSION OF 316 AUSTENITIC STAINLESS STEEL IN H_2S/CO_2 CONTAINING ENVIRONMENT

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التآكل الحراري للفولاذ الأستينيتي 316 في وسط حاوي لغاز يد٢ كب وك١

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لوحظ أن أطباق الفولاذ الأستينيتي من نوع 316 ، والتي تستعمل في مصنع الإستقطاف بحقل جالو النفطي ، ذات مقاومة ضعيفة للتآكل ، وذلك عند تعرضها لغازات هيدروكربونية تحتوي على كميات ضئيلة من غازي يد٢ كب وك١ في درجات حرارة تتراوح ما بين 400 – 600 درجة مئوية .

وخصصت هذه الدراسة لفهم عملية التآكل باستعمال نسب مختلفة من يد٢ كب وك١ لتعطي وسطا من الأكسدة والكبرته في درجات حرارة تتغير من 450 إلى 600 درجة مئوية .

تمت دراسة الرقائق القشرية الناتجة عن عمليات التآكل باستخدام الفحص المجهري والأشعة السينية ، ووجد أن معدل التآكل كان أكثر فعالية في الوسط المكبرت .

INTRODUCTION

The increasing demand of alloys for use at high temperatures in sulphur bearing atmosphere has stimulated a number of investigations [1–4] on sulphidisation of metallic materials by sulphur vapours or H_2-H_2S gas mixture.

Low sulphur vapour pressures, 10^{-4}–10^{-10} atmospheres are generally encountered in actual practice such as in the petroleum industry and thermal power plants. Process gas streams generated by many petrochemical and gasification processes contain sulphur as H_2S. The sulphidisation behaviour of a variety of commercial alloys ranging from stainless steel to nickel-and cobalt-base alloys has been reported recently in a reducing sulphidising environment, mostly at temperatures exceeding 700°C [5]. Sulphidising behaviour at temperatures, less than 600°C, has not received much attention. In some petrochemical processes temperature encountered are in lower regions. The present paper reports preliminary results of a long term research on sulphidisating behaviour of 316 austenitic stainless steel in the temperature range, 450–600°C in a wide range of gas mixtures. Study being reported here was carried out in the H_2S-CO_2-N_2 gas mixture.

EXPERIMENTAL PROCEDURE

Standard AISI 316 austenitic stainless steel was used and its chemical composition is given in Table 1, specimens of the size 8 × 5 × 1 mm were cut from the sheet. They were polished on different grades of emery paper finishing with 600 grit paper, washed with water, rinsed with alcohol and weighed. Sulphidisation was performed in a gas mixture consisting of H_2S, CO_2 and N_2 at 450°, 500° and 600°C up to a period of three hours.

Fig. 1 shows a schematic diagram of the experimental set-up for carrying out sulphidisation. Flow rate of each gas was measured by capillary flowmeters. N_2, H_2S and CO_2 gases at predetermined flow rates were mixed in a gas mixer of 60 cm length and 1.2 cm diameter having four perforated glass discs fused at

Table 1. Chemical composition of 316 Austenitic Stainless Steel
(Wt %)

C	Cr	Ni	Mn	Si	P	S	Mo
0.08	16	10	2.0	1.0	0.045	0.04	2.5

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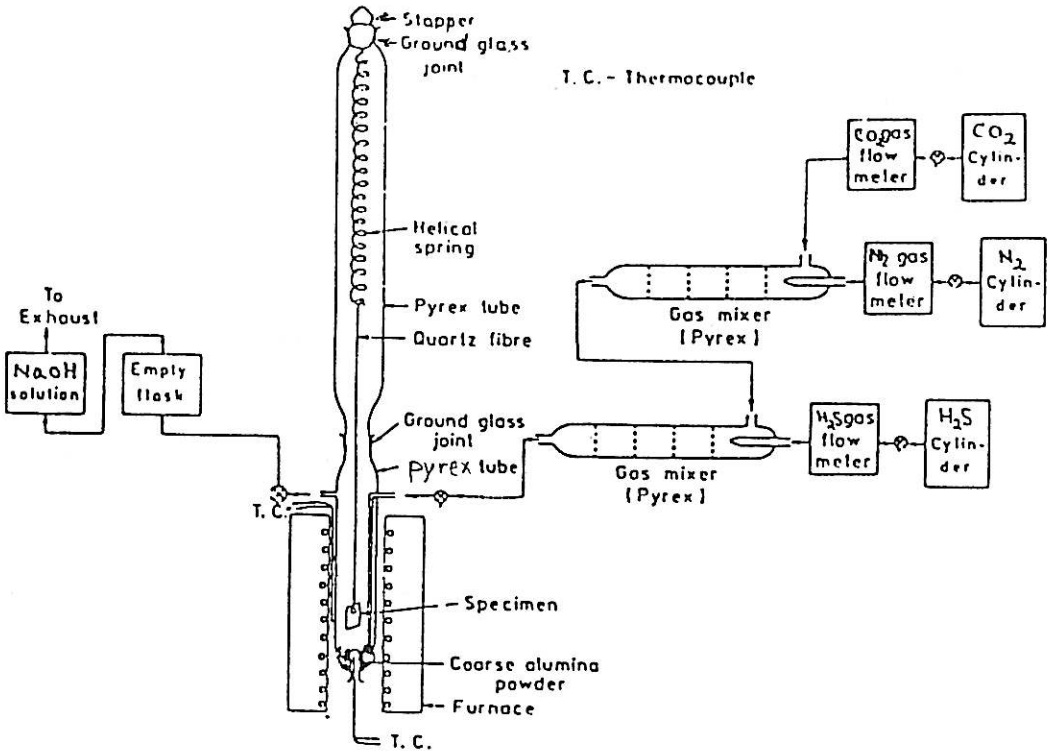

FIG. 1. Schematic diagram of experimental set-up for sulphidisation in H_2S-CO_2-N_2 environment.

equidistance. The gas mixture was introduced into pyrex glass reaction tube. The thermogravimetric set-up consisted of a borosilicate glass helical spring of sensitivity 100 μ gm. The specimen was attached with a glass fibre to the spring. Weight gain data was recorded by measuring extension of the spring with a cathetometer.

The gas mixture was first passed through the reaction tube for 30 minutes at room temperature and then, tubular furnace heated to desired temperature was raised to surround the reaction tube. After completion of the experiment, the furnace was lowered and specimen was cooled in the gas stream.

The sulphidisation samples were analysed by x-ray diffractometry and conventional metallography. Cuk_α radiation with Ni filter and a scanning speed of 2°/min. was used.

RESULTS

Kinetics of Sulphidisation

Effect of temperature on suphidisation of 316 stainless steel in higher H_2S concentration gas mixture, 30% H_2S, 30% CO_2 and 40% N_2 by volume is shown in Fig. 2. Weight gain versus time plot gave a straight line relationship revealing that sulphidisation follows the parabolic rate law. Table 2 gives parabolic rate constant as a function of temperature. Parabolic rate constant was found to depend on temperature. It increased from 0.83×10^{-9} at 450°C to 4.07×10^{-9} gm cm^{-4} s^{-1} at 600°C.

Based on this data, activation energy using Arhenius plot shown in Fig. 3 was determined to be 54 KJ/mole. KJ/mole.

In order to examine the role of CO_2 in sulphidisation of 316 stainless steel, a run was made in the gas mixture, 30% H_2S and 70% N_2 free from CO_2 at 600°C. Results are plotted in Fig. 4 which shows that presence of CO_2 decreases sulphidisation rate. Parabolic rate constant was found to be 8.61×10^{-9} gm^2 cm^{-4} s^{-1} without CO_2 compared with 4.07×10^{-9} gm cm^{-4} s^{-1} in the presence of CO_2 in the gas mixture. A test was also run at 600°C in the gas mixture, 30% CO_2 and 70% N_2 free from H_2S. Weight gain was too small and was within the sensitivity of helical spring balance.

Table 2. Parabolic rate constants of 316 Austenitic Stainless Steel in 30% H_2S, 30% CO_2 40% N_2 at different temps

Temperature (C°)	Kp (gm^2 cm^{-4} sec^{-1})
600	4.07×10^{-9}
500	2.12×10^{-9}
450	0.83×10^{-9}

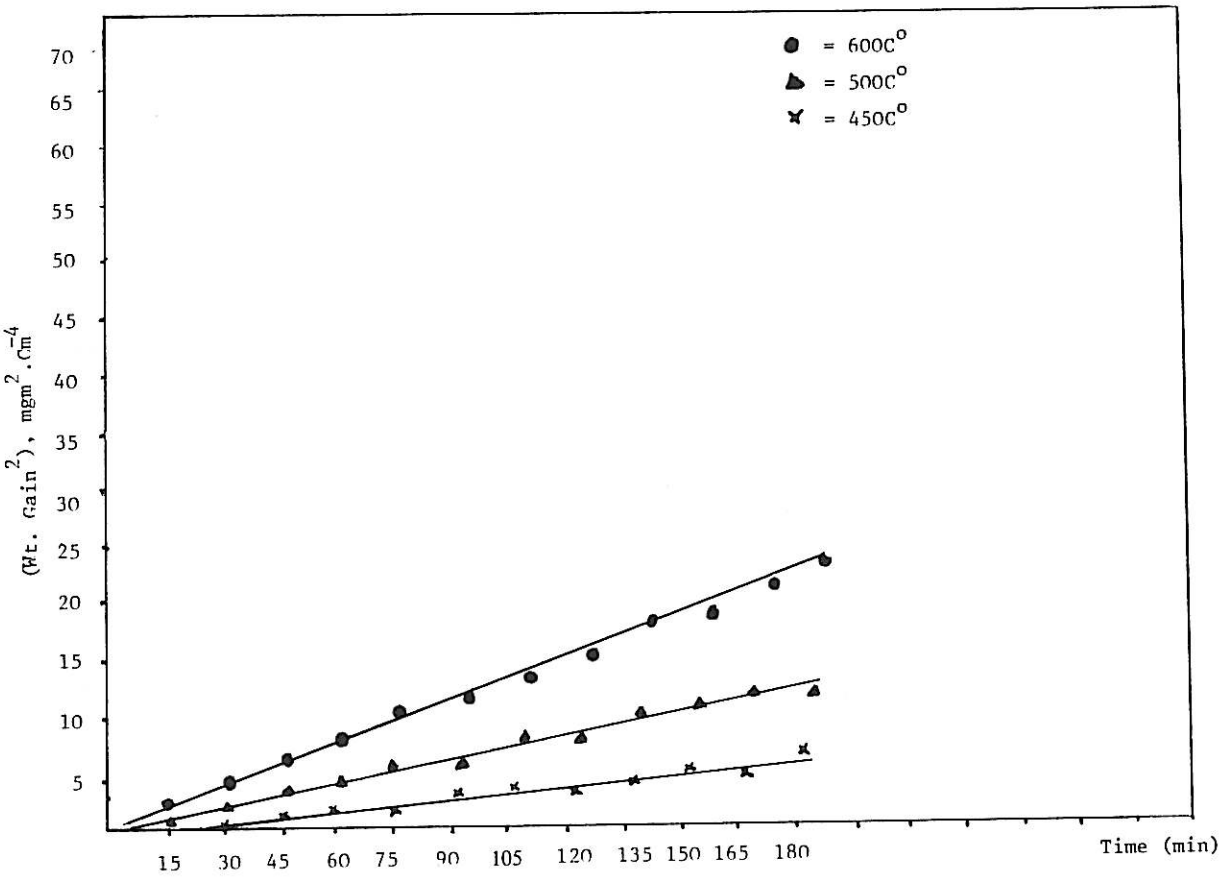

FIG. 2. Effect of temperature on sulphidisation of 316 Stainless Steel in 30%, H-30% CO_2-40% N_2.

Table 3. Parabolic rate constants at different H_2S gas composition and 600°C

Composition %	($gm^2\ cm^{-4}\ sec^{-1}$)
30	4.07×10^{-9}
10	3.15×10^{-9}
5	2.69×10^{-9}

Since H_2S concentration in the gas mixture investigated was rather too high, the effect of lower concentrations of H_2S, 5% and 10% respectively on sulphidisation at 600°C was studied. Results are plotted in Fig. 5 showing parabolic rate law at lower concentrations of H_2S. Reducing H_2S concentrations from 30% to 5% decrease parabolic rate constant from 4.07×10^{-9} to 2.69×10^{-9} gm $cm^{-4}\ s^{-1}$ (Table 3).

Scale Morphology-Fig. 6 shows macroscopic appearance of sulphidised sample. The scale formed was highly fragile particularly at 500° and 600°C as in Figs. 6b and 6c. It came off easily from the specimen surface. Visual observations revealed that the outermost scale was bright grey in colour and scale layer underneath outer layer was black in colour. Fig. 7 shows outer scale having poor adherence and inner

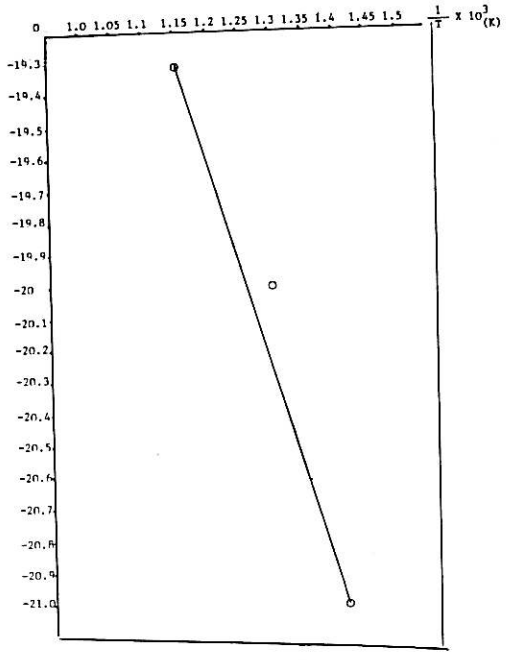

FIG. 3. Temperature dependence of the sulphidisation rate of 316 Stainless Steel in 30% H_2S-30% CO_2-40%, N_2 in the Arrhenies plot.

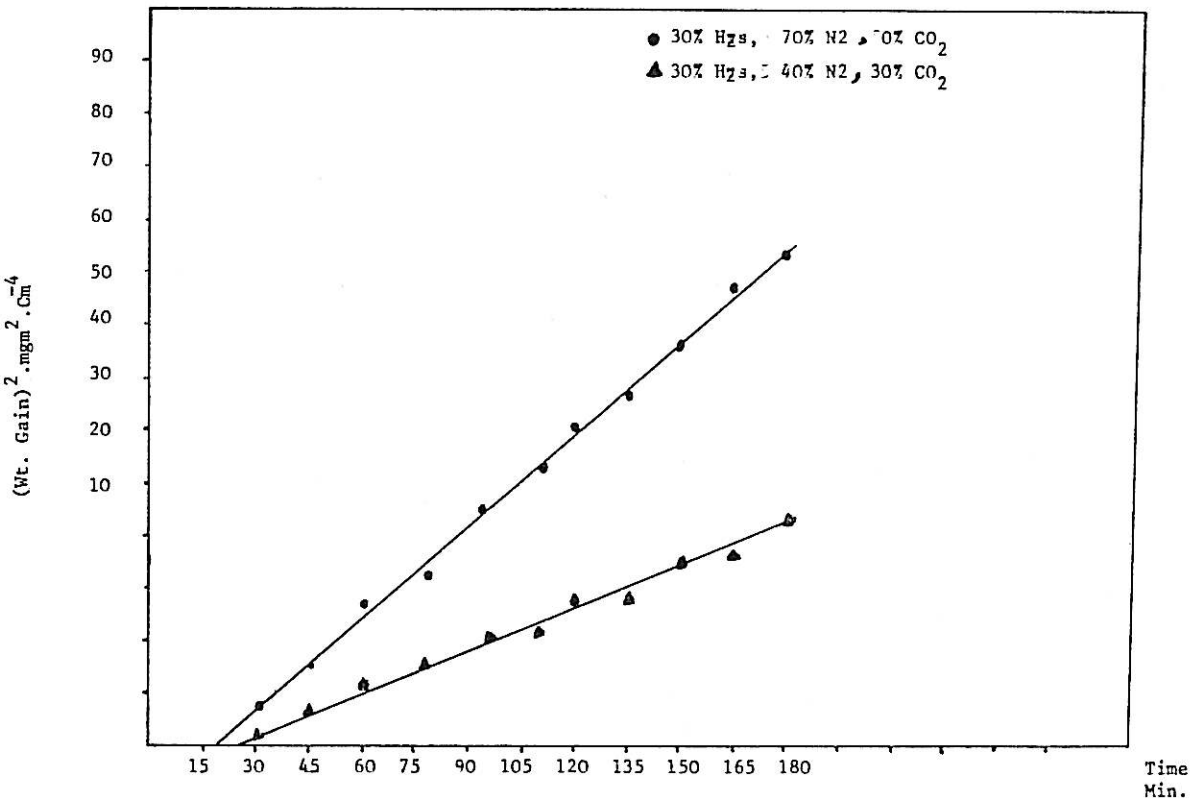

FIG. 4. Effect of CO_2 on sulphidisation of 316 Stainless Steel.

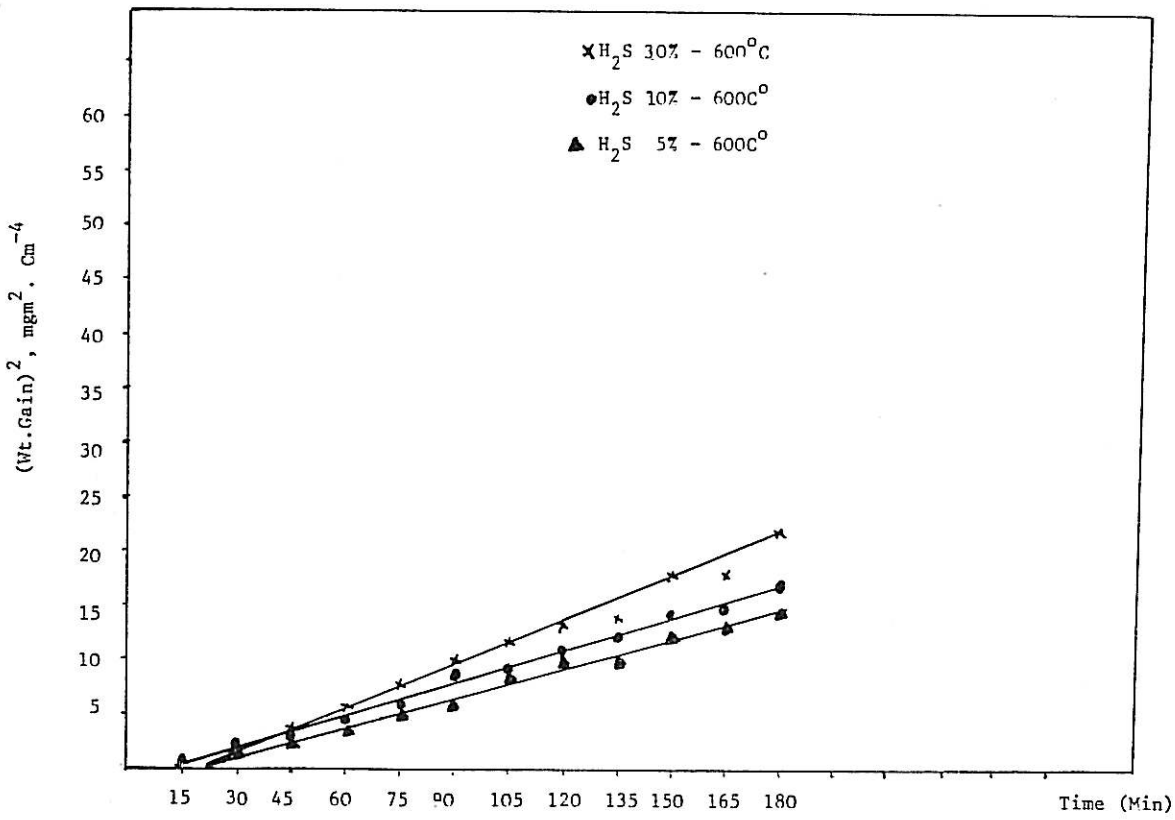

FIG. 5. Effect of H_2S concentration in the gas mixture, H_2S-CO_2-N_2 on sulphidisation of 316 Stainless Steel at 600°C.

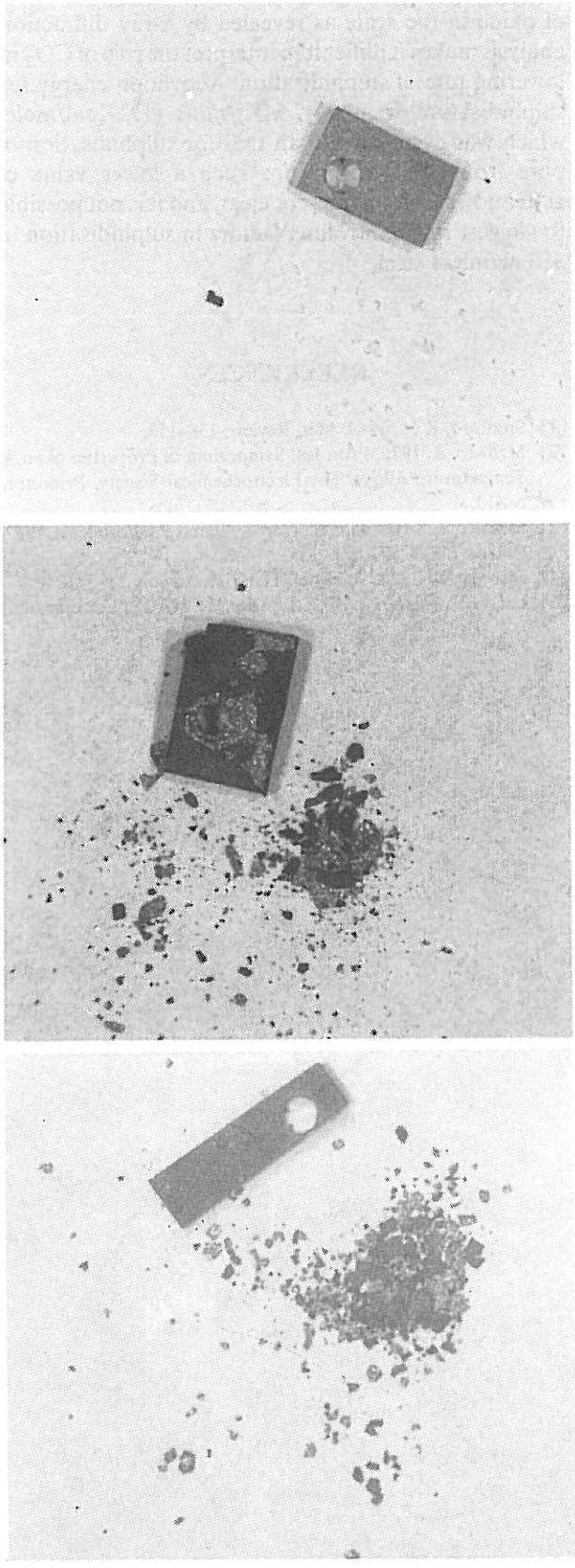

FIG. 6. Macroscopic appearance of scale formed on specimens sulphidised in 30% H_2S-30% CO_2-40% N_2 (a) 450C (b) 500°C (c) 600°C.

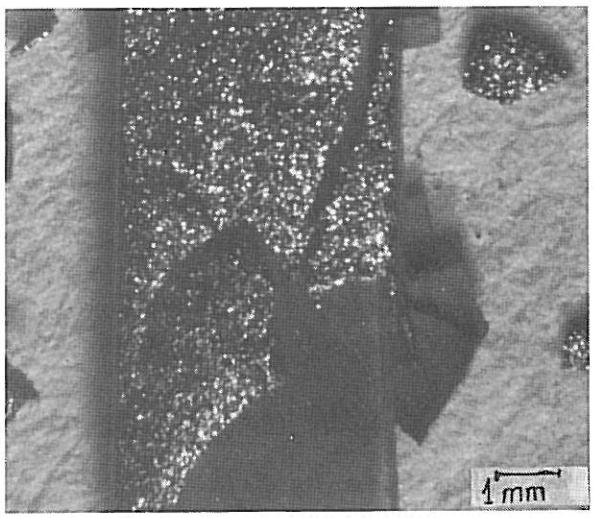

FIG. 7. Outer and inner scale formed on specimen sulphidised at 600°C in 30%, H_2S-30% CO_2-40% N_2.

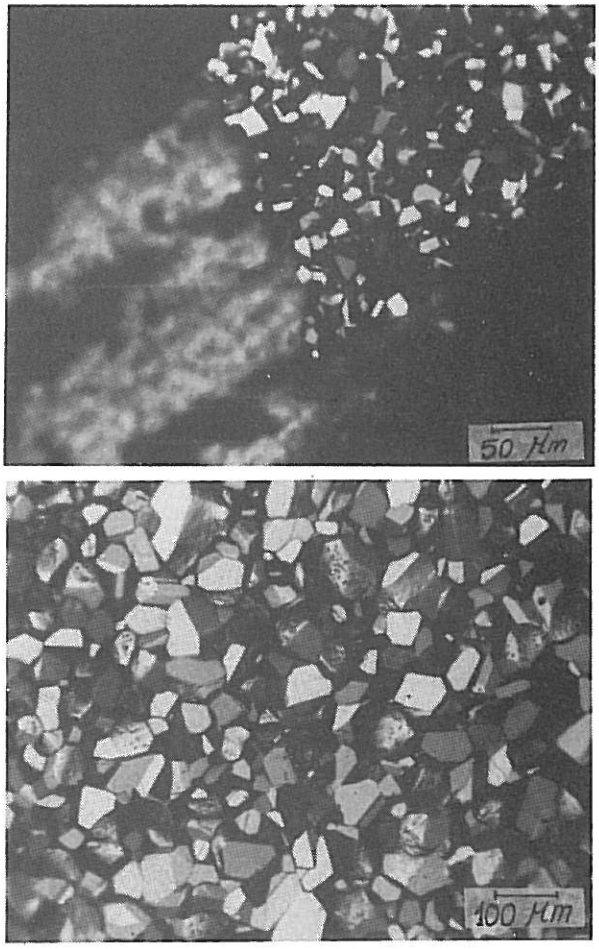

FIG. 8. (a) and (b) Microstructure of outer scale showing polyhedral crystals formed on specimen sulphidised at 500°C in 30% H_2S-30% CO_2-40% N_2.

scale, relatively smooth. Higher magnification revealed outer scale structure consisting of polyhedral crystals as seen in Figs 8a and 8b.

X-ray Diffraction Analysis: This was carried out on specimens sulphidised at 500°C for three hours in the gas mixture consisting of 30% H_2S, 30% CO_2 and 40% N_2. Spalled material consisted of $Fe_{1-x}S$ and Cr_2S_3. Scale scratched from the specimen surface was identified to have presence of $Fe_{1-x}S$, $FeCr_2S_4$ and FeS. Black scale still remaining on specimen surface showed some results as the scale scratched from the specimen surface.

CONCLUDING DISCUSSION

Results reveal that 316 stainless steel has poor resistance to sulphidisation even at lower temperatures, 450–600°C. Sulphide scale formed is highly fragile and outer scale comes off easily. Duplex sulphide scale is formed, outer scale consisting of FeS and Cr_2S_3, while inner has presence of FeS, $FeCr_2S_4$ and FeS. Absence of oxide in the scale as revealed by x-ray diffraction analysis makes it difficult to interpret the role of CO_2 in lowering rate of sulphidisation. Activation energy for sulphidisation was only 54Kj/mole (13 Kcal/mole) which was even lower than that for sulphidisation of pure iron [4]. Reasons for such a lower value of activation are not at present clear, and it is not possible to suggest rate controlling factors in sulphidisation of 316 stainless steel.

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