Mechanism of the Pack Process of Chromising By Thermal Diffusion Part I

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EQUILIBRIUM gas phase composition of the chromising box have been found out by considering and following gases namely, H_2, N_2, H_1 CrI_2, CrI_3, FeI_2, FeI_3, Fe_2I_4, $Fe\ I_5$, dissociated iodine at various temperatures, pressure and activity of iron specimen surfaces by computer techniques and it has been shown that out of the above gases only H_2 N_2, CrI_3 and its dimer Cr_2I_6, FeI_2, HI and dissociated iodine constitute more than 99% of the gas phase constituents and only chromium iodides iron iodide and dissociated iodine changes with variables studied. It has been shown that initially the reaction $Fe + I_2 = FeI_2$ is predominant and corrodes the specimen surface and subsequently chromium iodide reactions give the coatings. Surface diffusion of chromium plays an important role in determining the nature of this coating obtained.

THE first commercially successful Pack process of of chromising was the DAL process, reviewed by Samuel and Lockington[1]. In specially designed sealed boxes specimens were embedded in chromising compound of chromium metal and/or ferrochromium, a heat stabiliser like kaolin or alumina and a small percentage of ammonium iodide.

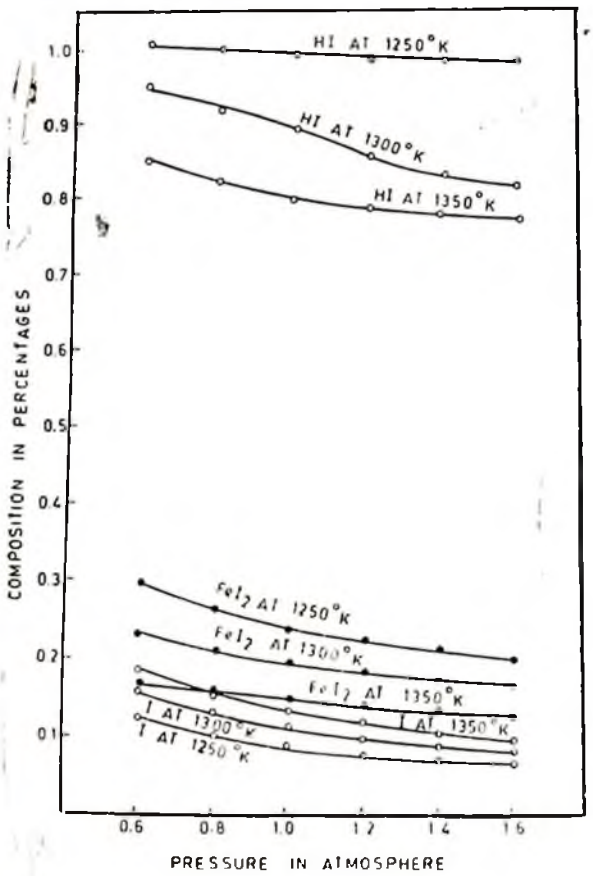


FIG. 1. VARIATION OF COMPOSITION OF HI, FeI_2 AND DISSOCIATED IODINE WITH PRESSURE AT VARIOUS TEMPERATURES.

The mechanism suggested was due to heat, solid NH_4I finally decomposes to N_2 and H_2 and HI. HI reacts with chromium to form CrI_2 which reacts with the surface of the ferrous specimen producing FeI_2 and Cr. Above the diffusion temperature, Cr diffuses into the specimen producing a true alloy coating and FeI_2 reacts with H_2 to form HI again available for further production of CrI_2. HI thus acts as a catalyst. Ammonium iodide needed is only about 3 percent of the charge. In 6 hours chromium alloy coating of 0.5 mm. at 1050°C of about 25 percent Cr is obtained. According to Hoar and Croom[2], all recations take place at the surface of the specimen as follows

1. Interchange reaction $Fe + CrI_2 = Fe\ I_2 + Cr$.
2. $Cr\ I_2 = Cr + 2I$, catalysed by the iron surface
3. $CrI_2 + H_2 = Cr + 2HI$, catalysed by the iron surface.

They showed for chromium chloride process, 50 percent of Cr uptake was the interchange reaction but in case of iodides, because of the high dissociation values of iodides, the percentage of interchange reactions will be much less and other two reactions will predominate. Manipulation of these three reactions can give us various compositions of chromium at the surface, The interchange reactions are preferred at the higher temperature and other two reactions are preferred at lower temperature. [Note – average coating means surface chromium content minus 12% Cr content (i. e. fully ferritic) divided by the coating thickness]. A new mechanism of the process has been suggested by means of experimental data and computer analysis of equilibrium conditions of the chromising box.

Experimental procedure-charge composition and operating conditions are as in Table I.

TABLE 1 : Experimental Data

Chromising composition : 80%. Alumino-thermic Cr and 20% Al_2O_3 with 3% NH_4L Chromising box was introduced in the furnace at 600°C and heated at a constant rate to the required temperature at 6.5°C/minute. Analysis of the armco iron, Si - 0.1%Mn - 1.06%C - 0 078%

Time of Treatment	Wt glain or loss Per unit surface area (original) gm/sq. cm	Wt of Cr uptake per unit surface area (original) gm/sq. cm.	Wt of iron loss per unit surface area (original) gm/sq. cm
1080°C			
0	—0.00127	0.0076	0.0088
20	—0.0006	0.0092	0.0097
50	+0.0006	0.0113	0.0106
100	+0.0030	0.0134	0.0103
200	+0.0066	0.0170	0.0103
1025°C			
0	—0.0010	0.0066	0.0076
20	—0.0006	0.0083	0.0089
50	+0.0016	0.0103	0.0087
100	+0.0040	0.0122	0.0083
200	+0 0058	0.0145	0.0088
980°C			
0	—0.0034	0.0054	0.0092
20	—0.0024	0.0071	0.0095
50	—0.0020	0.0077	0.0097
100	+0.0003	0.0104	0.0101
200	+0.0001	0.0121	0.0120
925°C			
0	—0.0038	0.0031	0 0067
20	—0.0032	0.0037	0.0070
50	—0.0025	0.0045	0.0070
100	—0.0021	0.0053	0.0068
200	—0.0018	0.0074	0.0092
880°C			
0	—0.0034	0.00013	0.0040
20	—0.0060	0.00025	0 0062
50	—0.0062	0.00086	0.0070
100	—0.0071	0.0013	0 0083
200	—0.0070	0.0015	0 0085

Computer analysis of equilibrium conditions- The following 11 gaseous constituents were considered, namely H_2, N_2, CrI, CrI_3, Cr_2I_4, FeI_2, FeI_3, HI, dissociated iodine, Fe_2I_4 and Fe_2I_6. Equations were formed according to methods suggested by Kode et al[3]. The 12 equations thus obtained consists of both linear and non-linears terms and were solved by modified Newtons method for different temperature, pressures, iodine content, and different activity of iron surface, The details of procedure for calculations can be found[4].

RESULTS AND DISCUSSION

The computer study of equilibrium gas phase composition shows that constituents, H_2, N_2, CrI_2, its dimer Cr_2I_2, HI, dissociated iodine and FeI_2 are of importance and constitute more than 99 percent of the gas phase. It was found that H_2 constitutes about 65-70 percent and N_2 about 15-17 percent under different variables studied and hence for all practical purposes can be taken to be constant. As per Fig. 1, the percentage of HI also practically

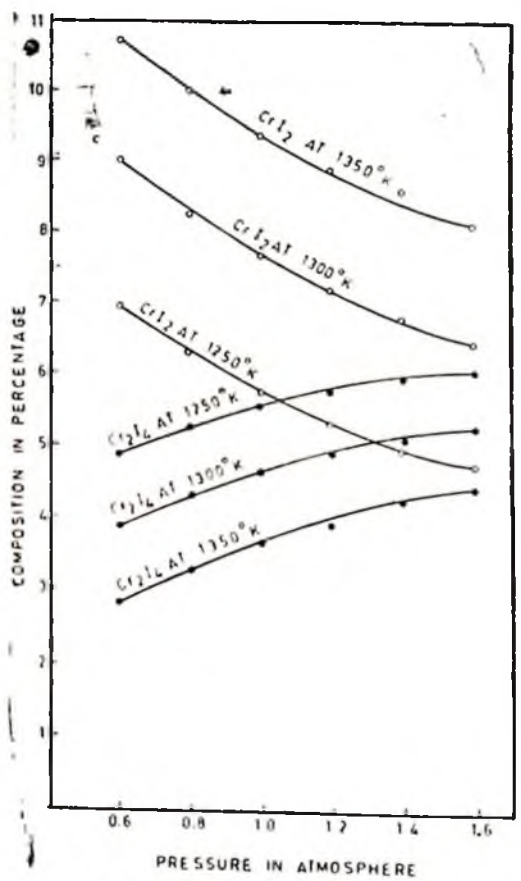


FIG. 2 .VARIATION OF COMPOSITION OF CrI_2 AND Cr_2I_4 WITH PRESSURE AT DIFFERENT TEMPERATURE (THEORETICAL)

remains constant for different variables at about 0.9 percent. Thus we find from the Figs. 1-4, that only the compositions of CrI_2, its dimer Cr_2I_4, FeI_2

and dissociated iodine change with the variables studied. Fig. 4 shows that with increasing iodine content, ratios of increase of chromium iodides (both monomer and dimer) are much more than that

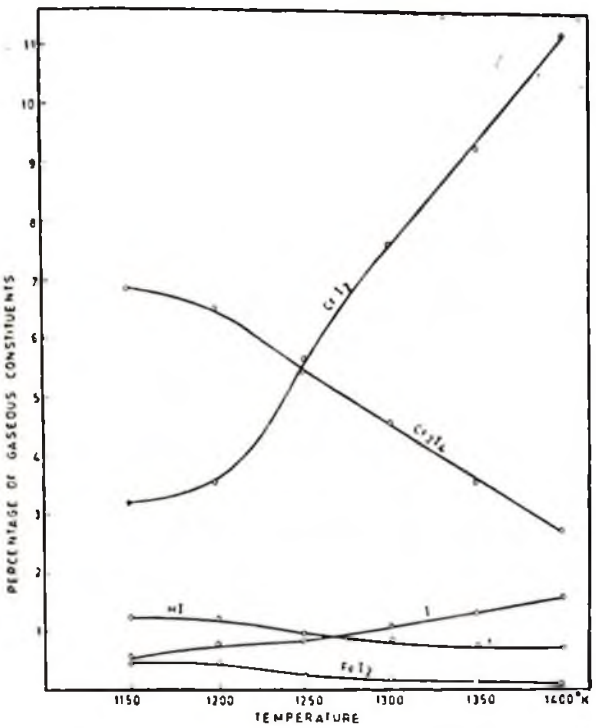


FIG.3.VARIATION OF GASEOUS COMPOSITION WITH ABSOLUTE TEMPERATURE PRESSURE 1 ATMOSPHERE ACTIVITY OF IRON 100%

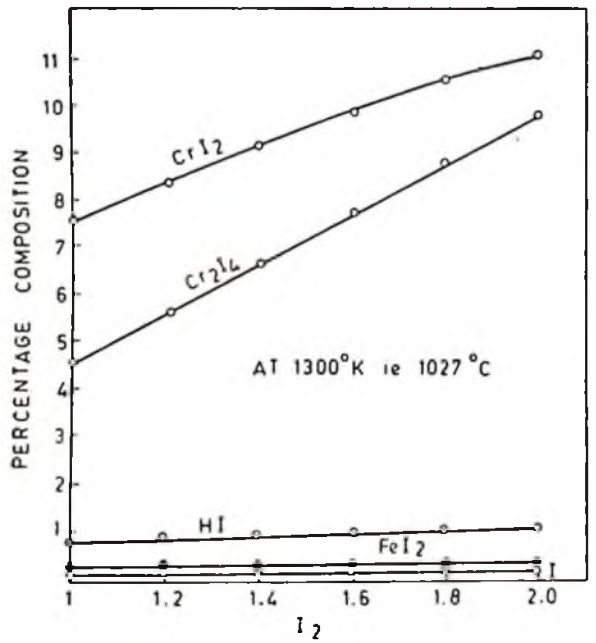


FIG.4.EFFECT OF INCREASING IODINE CONTENT ON THE EQUILIBRIUM COMPOSITION (THEORETICAL)

of FeI_2 and dissociated iodine. Thus adding extra amount of chromium in the gas phase which will in turn increase the chomium deposition rate, as in Fig. 5 and 6 wherein with an increase of NH_4I and I_2 addition, chromium uptake in the coating increased, which may be due to the lightness of N_2 and H_2 compared to HI formed from cracking of NH_4I chance of escape of these gases from the box when not yet sealed being much greater, iodine percentage thus being much greater than what has been theotically assumed.

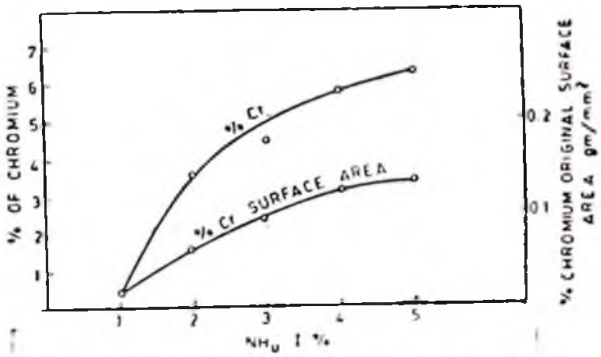


FIG.5.VARIATION OF CHROMIUM UP-TAKE PERCENTAGE WITH DIFFERENT NH_4I CONTENT AT 1020°C

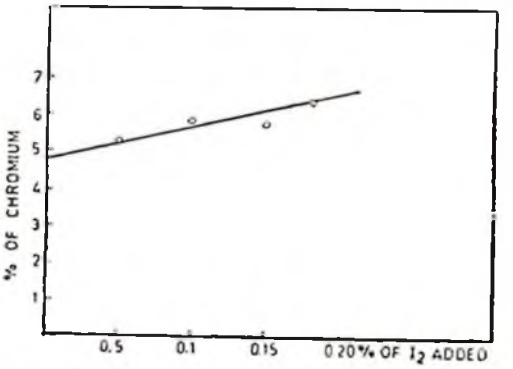


FIG 6.VARIATION OF CHROMIUM UP-TAKE PERCENTAGE WITH DIFFERENT I CONTENT (NH4I - 3%) AT 1020°C

In the DAL process solid powered glass is the sealing material which above 800°C becomes viscous seals the box, the pressure inside and outside the box being the same. But when sealing is completed iron specimens undergo α–γ phase change and thereby contract 3% by volume resulting in partial vacuum in the box which facilitates chromium deposition as is revealed from the computer analysis. But there is every likelyhood of leaks in the glass seal and oxygen from atmosphere may enter the box thereby causing point defects in the specimens. Cracks in the seals is more servere in the cooling stage and surface chromium alloys loose lustre due to this factor. These types of defects may be remedied by proper flushing of the outside of the boxes with a reducing gas or by designing better types of boxes [5,6].

When pure chromium is used instead of ferro-chromium as a chromium source, activity of iron surface plays an important role as regards FeI_2 concentration is concerned, but no other constituent in the box shows any noticeable change. Gas phase composition of FeI_2 however, changes considerably with the surface activity change of iron as in Fig. 7. From Table I it is seen that initially specimens loose weight which means that $Fe + I_2 = FeI_2$ reaction is more prominent in the early stages of thermal diffusion treatment and subsequently chromium reactions start which reduce FeI_2 reactions progressively to equilibrium value. This mechanism is confirmed by the anaiysis of iron loss unit surface area an in Table I in which it is shown that practically in all cases of treatment, iron loss remain constant.

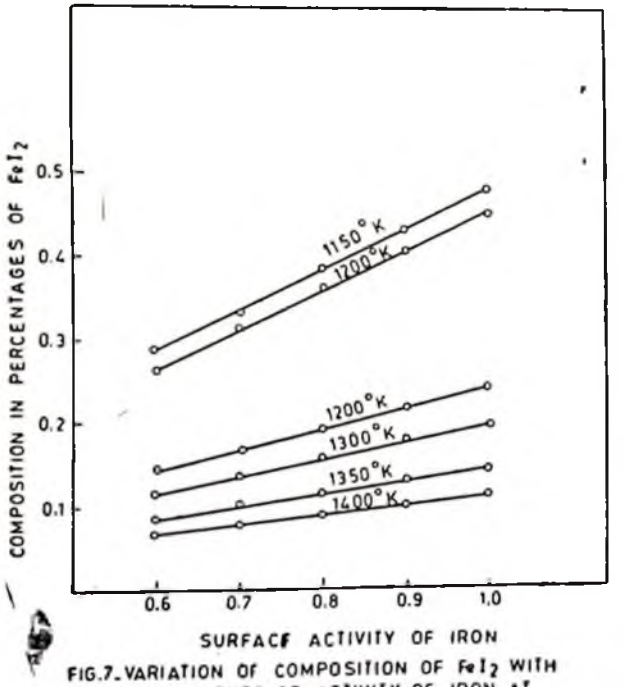


FIG.7-VARIATION OF COMPOSITION OF FeI_2 WITH VARIATION OF SURFACE ACTIVITY OF IRON AT 1 ATMOSPHERE PRESSURE (THEORETICAL)

With no iron source for the reaction $Fe + I_2 = FeI_2$, the equilibrium value of gaseous FeI_2 can only be maintained by the diffusion of iron from the interior of the specimen though the Fe-Cr alloy layer already formed and this will be the rate controlling process since all the three chromium deposition reactions depend on the availability of iron at the surface of the specimens. If however, external sources of iron be there, i.e. use of Ferro chromium as chromium source, by the reaction $FeI_2 + H_2 = Fe + 2HI$, iron may be made availeble to the specimen surface to facilitate the deposition reactions of chromium. Thus combined use of pure metalic chromium and ferro-chromium will give better deposition rate confirmed by Dubinin [7].

Surface condltions of ferrous specimens are also very important. We can assume that initially chromium deposits on some preferred sites of the iron surface and spreads along the surface by surface diffusion since the surface diffusion rate is faster than either volume or grain boundary diffusion rate. Since chromising boxes for treatment have to be introduced at about 600°C and gradually heated upto temperature of treatment nucleation of chromium will only be by two dimensional nuclei caused by surface diffusion which is the only significant mechanism initially. These two dimensional nuclei serve as the nuclei for subsequent volume diffusion of chromium into iron specimens and thus nature of iron surface which affects these two dimensional nuclei plays a significant role and structure of coating changes according to different surface treatment given[8].

CONCLUSIONS

1) Out of the 11 gas phase constituents of the chromising box at operating temperature only 5 constituents namely CrI_2, its dimer Cr_2I_4, FeI_2, HI, and dissociated iodine vary with the change in temperature, and pressure inside the box.
2) Initially the reaction $Fe + I_2 = FeI_2$ is of importance which corrodes the surfaces of ferrous specimens but subsequently with the progressive chromium deposition, this reaction looses significance.
3) Within certain limits with the increase in availability of iodine in the box chromium uptake will increase.
4) Surface diffusion of chromium plays an important role in determining the nature of the coating obtained.

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