Mechanism of the Pack Process of Chromising : Part II

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KINETICS of the pack process have been considered and it has been shown that due to chemsorption of iodine on the the iron specimens, transport step of chromium iodides is the rate determining step of the process. Relative importance of CrI_3 and its dimer Cr_2I_6 have been discussed and some methods have been suggested for the removal of the poisoning layer of iodine from the reaction zone.

KINETICS

In Part I the general mechanism of the process was described. Kinetics of the mechanism is discussed here.

The sequence of chromising may be by

1. Synthesis of chromium iodides
2. Transport of these to the specimen
3. Decomposition at or near the specimen surface to establsh dynamic equilibrium.
   The step includes :
   a) Adsorption of the gases on the surface
   b) Reactions on the surface
   c) Desorption of the products.
4. Diffusion of chromium in the iron specimen
5. Transport of the iodine liberated back to the neighbourhood of chromium source
   Steps (2) and (5) constitute the gaseous transport step.

It was stated earlier that if no other source of iron is there at the surface of the specimen, diffusion of iron through the iron-chormium alloy already formed will be the slowest rate determining step. Since iron is made available continuously by the reaction $FeI_2 + H_2 = Fe + 2HI$ very near the surface of specimens and active iron acts as the catalyst for chromium reactions. Diffusion in the solids will not control rate of chromium deposition.

Since large amount of chromium source is always present, step I is also not rate a determining step.

In a study of solid-gas reactions of different metals and alloys, Shuler and Laidler[1] report that all atoms and radicals combine on surfaces instantly even if they are poisoned, and the reactions are of first order over a wide range of temperature. Loonam[2] on a general consideration also came to the same conclusion in the iodide processes. Thus step 3 i.e. decomposition of iodides is also not the rate determining step.

Thus the transport steps are the slowest steps and the rate determining steps. Titov and Maskarov[1] confirmed this and showed that by increasing the means free path of travel of the gaseous components, the rate of chromium deposition is reduced and the exchange factor, defined by them as the quantity

$$\frac{\text{Wt. of Cr deposited}}{\text{at. wt. of Cr}} \Big/ \frac{\text{Wt. of iron loss}}{\text{at wt. of iron}}$$

changes from 27 to 0.5.

In the pack process of chromising, the transport step is not fast and the rate of chromium deposition is so slow in spite of the flow gradient between chromium source and iron surface being high can be explained thus :

For every atom of chromium deposited on the iron surface, two atoms of iodine are liberated. The iodine atoms are negatively charged and very mobile at the operating temperature. The heat liberated by this dissociation is about 90 Kcal/mole[4], the heat of formation of FeI_2, being only about 45 Kcal/mole. Thus the formation of FeI_2 will be possible but all the iodine from chromium iodide decomposition will not combine with iron to form FeI_2 since in equilibrium condition only about 0.2% FeI_2 is present in the gas phase. Thus extra iodine will remain adsorbed on the surface since heat of adsorbtion of iodine is 50 Kcal/mole. When vapour pressures of this adsorbed FeI_2 and free iodine exceed the adsorbed equilibrium value, they must evaporate out of the specimen (desorption). According to the condition of the chromising box, there is every possibility of FeI_2 thus liberated will

react with H_2 precent very near the surface with the formation of HI and Fe which drops again on the specimen surface and alloys with chromium present. Thus on the surface there will always be some iron available and surface composition will never be 100 percent chromium.

Iodine liberated by evaporation from the specimen travels to the chromium source to fulfil the pressure equibility of the chromising box. Thus the net flow of free iodine in the chromising box is upstream and opposes the flow of chromium iodide. It can be shown from geometrical consideration[5] for a cylindrical specimen, the magnitude of the poisonous effect of transport of CrI_2 increases exponentially as the specimen is approached from the chromium source. When equilibrium is attained there will be thus a layer of free iodine surrounding the specimen through which chromium iodides have to travel. Thus for the transport of chromium iodides, two things have to be considered.

1) Concentration gradient between chromium source and the specimen, and

2) Poisoning effect of the iodine layer since heat liberated and adsorbed by the various reactions practically balances each other, the temperature throughout the chromising box remains constant and thermal gradient for transport is absent. There will however, be a little pressure gradient present because of the reaction involved may cause transports of chromium iodide and iodine. Reduced pressure operation will increase chromium iodide availability and also reduce viscosity of the poisoning iodine layer and so will cause increased rate of transport.

But the main driving force of the transport in the gas phase must necessarily come from the chromium source and specimen surface. Higher this concentration difference higher will be the driving force, and hence rate of chromium availability on the specimen surface through increased transport of CrI_2.

The best possible method of removing the detrimental effects of poisoning layer will be to remove this layer from the specimen surface. The methods of breaking this layer of iodine will be by induction heating and alternate circulating of chromising gases in a special apparatus consisting of a system of three furnances and cooling device[6]. In induction heating, eddy currents break up this layer for very rapid chromium deposition on the surface[7 8 9].

Another method of improving the rate of deposition will be to create thermal gradient between the specimen and the chromium source, as is also achieved in induction heating[8]. Thermal gradient plays an important part in the rate of chromium deposition, in the German B.D.S. Process[10], French O.N.E.R.A. process[11], the Czheckoslavian process due to Povel Hibek[12]. All the three methods of improving the chromium deposition may be incorporated in the alternating circulating gas principle method[6].

Since dissociation reactions have large positive entropies the free energies of dissociation decrease rapidly with increasing temperature even though the heats of formation of iodides are moderately high. Thus for the iodides, equilibrium constant will involve $(P_I)^3$ and vapour pressure in equilibrium with the metal will be high. Thus the rate of decomposition of iodides will decrease from CrI_3 to CrI_2 and CrI. The formation of CrI as an intermediate product during dissociation of higher iodides is reported, but definitely it is very unstable otherwise chromium deposition would not have been so easily possible.

Chromium iodide is known to have a dimer Cr_2-I_4[13]. The dissociation reaction $Cr_2I_4 \rightarrow 2Cr + 4I$ will involve $(P_I)^4$ in the equilibrium constant and high rate of chromium deposition will be possible. Entropy situation is similar to iodides with the additional advantage that two atoms of chromium are deposited for every iodide molecule that decomposes. In van Arkel's process[14] of pure iodide chromium production where dissociation of chromium iodide is the only source of chromium, the rate ot chromium deposition is found to be 1.4 times than that to be expected on the basis of measurement of the vapour pressure of the iodide. The relative importance of CrI_2 and its dimer Cr_2I_4 can be as follows:

The rate of arrival of chromium per unit surface area at the iron surface will be based on the equations.

$CrI_2 = Cr + 2I$ (1) $Cr_2I_4 = 2Cr + 4I$ (2)

If d_{cr} be the rate of arrival of chromium per unit surface area, then :

$$d_{cr} = \frac{K_1 P_{crI_2}}{a_{cr}} dt + K_2 \frac{P_{cr_2 I_4}}{(a_{cr})^2} dt \quad (3)$$

where K_1 and K_2 are the rate constants of C_rI_2 and $C_{r2}I_4$ respectively.

The slopes of the time-temperature experimental data (Table I in Part-I) give us the variables K_1 and K_2. In the initial stages the slopes vary indicating that equilibrium has not yet been reached. However, in about 100 minutes, the slopes become constant and equilibrium is reached. At equilibrium, surface i. e. a_{cr} and the partial pressures of the gases are also constant and the value of a_{cr} can be taken to be unity since chromium iodides reaching surface decompose instantaneously. The relation between K_1 and K_2 can be found out from the Van Arkels process using pure chromium iodide where the rate of deposition of chromium is found to be near about 1.4 times greater than the theoretical rate. Assuming this relation is also valid for the pack process where the gas phase is much more complex, the relation approximately between K_1 and K_2 is as follows :

TABLE 2.1

Partial Pressures of CrI_2

Temp. °K	Equilibrium constant K_c for $Cr_2I_4 = 2CrI_2$	$P_{Cr\ I_4}$	Equivalent CrI_2	$PCrI_2$	Combined equivalent $PCrI_2$
1150	0.1153	0.0688	0.028	0.632	0.06
1200	0.01954	0.06557	0.036	0.036	0.072
1250	0.0597	0.0547	0.057	0.057	0.114
1300	0.126	0.0464	0.076	0.076	0.152
1350	0.2425	0.0360	0.093	0.093	0.186

$$d_{cr}/dt = 1.4\ K_1 P_{cr\ I_2}/a_{cr} \quad \text{... (4a)}$$

$$\text{or } K_1 = \frac{d_{cr}}{dt} / 1.4 \frac{P_{cr\ I_2}}{a_{cr}} \quad \text{... (4b)}$$

$$\text{also, } Cr_2I_4 = 2_{cr}\ I_2 \quad \text{... (5)}$$

Equilibrium constant, K,

$$K = (P_{cr}I_2)^2/PCr_2I_4 \quad \text{....(6)}$$

and at 1150°C. the value of the K is equal to 0.1153 and $P_{cr2}I_4$ is 0. 068 atmosphere[15].

So the equivalent partial pressure of Cr_2I_4 present in terms of CrI_2 is $(P_{cr}I_2)^2 = 0.0115 \times 0.068 = 7.82 \times 10^{-4}$ or $P_{cr}I_2 = 0.028$.

This value added to the partial pressure of CrI_2 present in the gas phase gives the combined equivalent $P_{cr}\ I_2$ which has been tabulated in Table 2.1 for different temperatures.

TABLE 2.2

Values of K_1 and K_2

Temperature °C	Temperature °K	Slope from experimental data	K_1 Cr uptake in gm per unit surface area per minute	K_2 Cr uptake in gm per unit surface area per minute
880	1153	$\left(\frac{1.528-1.225}{100}\right) \times 10^{-4}$	3.6×10^{-5}	2.87×10^{-5}
925	1198	$\left(\frac{7.44-5.3}{100}\right) \times 10^{-3}$	2.1×10^{-4}	2.11×10^{-4}
950	1253	$\frac{0.01214-01042}{100}$	1.08×10^{-4}	3.11×10^{-4}
1025	1298	$\frac{0.1446-0.01219}{100}$	1.067×10^{-4}	4.875×10^{-2}
1080	1353	$\frac{0.0170-0.01336}{100}$	1.4×10^{-4}	0.1

From the table to get approximimate combined equivalent CrI_2 pressure, partial pressure of CrI_2 is to be doubled.

Values of K_1 were obtained from the equation (4b) and substituting this value in equation (3), the values of K_2 obtained have been tabulated in table 2.2.

From Table-2.2 it is clear that higher temperature, dimer of CrI_2 becomes more important in contributing to chromium deposition eventhough its percentage decreases at higher temperature.

CONCLUSION

It has been shown that in the pack process of chromising, a mobile chemisorbed layer of dissociated iodine is formed on the specimen surface which evaporates at a rate consistant with its heat of adsorption. On the basis of analysis made, the deposition reaction of chromium should be first order with 100 percent efficiency so long as a large part of the deposition surface is free of adsorbed iodine, the rate of evaporation of iodine atoms just equalising that of deposition. With time however, the chemisorbed iodine layer covers a larger and larger fraction of the surface until ultimately it forms a complete monolayer. At this point the deposition reaction of chormium should become zero order, the deposition rate being governed solely by the rate of evaporation of iodine. As the pressure of dissociated iodine further increased, it may so happen that diffusion of chromium iodide through this stationary chemisorbed gas film may become rate controlling. Accordingly in the pack process of chromising diffusion of this metallic gaseous iodides and the reaction products through the stagnant gas film surrounding the specimen will ultimately be the slowest step.

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