Deposition and Study of Niobium Coating on Iron and Copper Substrates from Reduction of NbCl_5 by Hydrogen or Vapors of Zinc

S. Audisio, H. Hamed and D. Hertz*

INSA Lyon, Laboratoire de Physicochimie Industrielle, 69621 Villeurbanne cedex, France

** FRAGEMA, 10 rue Juliette Récamier, 69006 Lyon, France*

Abstract: The chemical vapor deposition technique is used to form niobium deposits on Armco iron or copper substrate. A thermodynamic study confirms the possibility of reducing pentachloride of niobium (NbCl_5) by hydrogen (at a temperature superior to 750°C) or by vapor of zinc (at approximately 500°C). The influence of the substrates on the reaction is shown. The kinetics of the deposit is studied.

The resulting coatings are very adherent. A folding (superior to 90°C) does not cause any cracking. Microhardness tests, X-ray diffraction, Glow discharge analysis, SIMS, ..., as well as observations by light or scanning microscopy have made it possible to characterize the formed layers (their nature, composition, thickness, continuity and porosity). The coatings obtained by hydrogenous reduction are thick (deposition rate: $22\mu\text{m/hr}$ on copper, $50\mu\text{m/hr}$ on iron). They are constituted of pure niobium, with only a few traces of copper or iron. This technique requires a high temperature treatment (950°C). The reduction treatment by vapor of zinc, made on copper substrate, leads to a deposition rate which does not exceed $5\mu\text{m/hr}$. In this case, the layer is composed of a solid solution Nb-Zn (Zn: 8% wt, Cu: 2% wt). On the other hand, this method makes it possible to work at a lower temperature (520°C), which is an asset both on a technical and on an economical point of view.

1. INTRODUCTION - THERMODYNAMIC STUDY

Although the means to obtain niobium from its chlorides -either through the reduction by hydrogen or through metal reducers such as sodium or magnesium- has been known since the beginning of the century, hardly any study has been carried out on the coating of this metal [1-5]. We therefore concentrated first on how to obtain such a coating, using the chemical vapor deposition technique (CVD) on iron or copper substrates, and then carried out the experiment. For this purpose, we have used the pentachloride of niobium (NbCl_5) reduction either by hydrogen or by vapor of zinc (CVD-Zn).

So as to determine the best conditions for deposit, we have beforehand taken into account all the different gaseous chemical species and condensed phases that were likely to take part in the process. Our thermodynamic study aimed at finding the minimum of the total Gibbs free energy of the system, the mass transport in the gas phase being taken into consideration. This was made possible by the computerised programme GEMINI 2, which was set up after Ericksson's works [6-7]. Based on the different components that are introduced and/or are likely to form, this programme allowed us to determine the components of the system when it is in a state of thermodynamic balance. The conditions on which we built our study for both processes are listed in table 1. The conclusions we reached, grounded on this major study [8], are described below.

	Substrates (moles)	Temp. sub. $^\circ\text{C}$.	Pressure (atm)	H_2 (moles)	NbCl_5 (moles)	Zinc (moles)
Hydrogen red.	Cu, Fe (0 $\rightarrow$ 20)	650 - 950	1	2, 2.5, 5, 10, 20	1	
Vapor Zinc red.	Cu (0 $\rightarrow$ 20)	520 - 700	0.013		1	0.5, 1, 2, 2.5, 5

Tab. 1 : Operating condition of interest in the thermodynamical study.

1.1 Reduction by hydrogen

As far as this process is concerned, the thermodynamic study shows that the percentage of deposited niobium is directly linked to the quantity of hydrogen used in the reaction. For a H_2/NbCl_5 rate superior or equal to 20 and for temperatures superior to 750°C , the reduction reaction equilibrium is total (Fig. 1). The copper substrate plays no part at all in the reduction process. Conversely, the iron substrate does to a large extent, especially in cases when the amount of hydrogen is low and the temperature is high, i.e. superior to 800°C (Fig. 2).

Figure 1 : Variation of % Niobium versus equilibrium temperature for different $H_2/NbCl_5$ ratio (none substrate)

Figure 2 : Variation of % Niobium versus equilibrium temperature for a ratio $H_2/NbCl_5 = 2.5$ (Iron substrate)

Figure 3 : Variation of % Niobium and Niobium compounds versus equilibrium temperature for a $Zn/NbCl_5$ ratio = 2 (Copper substrate.)

1.2 Reduction by vapor of zinc

The thermodynamic study of the reduction of NbCl_5 by vapors of zinc was carried out for copper substrates only. The result showed that when Zn/NbCl_5 ratio are inferior to 2, zinc leads to the forming of NbCl_4 and NbCl_3 subchlorides. Niobium starts forming only when the ratio is superior to 2 (Fig. 3). For niobium to be the only metal to form, the rate must be superior to 5.

2. EXPERIMENTAL SETTING

The experimental setting for the 2 processes under study consists of 4 parts, : (i) a distribution system which controls flows and purifies gases (Ar , H_2); (ii) a reaction chamber making it possible to reheat the sample in hydrogen, also enabling an interaction between the metallic surface and the gaseous phase of a variable duration as well as fast cooling; (iii) a heating system making it possible to heat the samples and NbCl_5 ; (iiii) a gas outlet device, [8].

The main difference between the two processes lies in the design of the reactor chamber in which the chemical reactions are carried out (Fig. 4 - 5).

Figure 4 : Experimental set up of the hydrogen reduction reactor

- 1- Ni-Cr thermocouple
- 2- Gaz outlet
- 3- I.R. heater
- 4- Gaz inlet (H_2)
- 5- NbCl_5 evaporator
- 6- Substrate and susceptor
- 7- RF coil

Figure. 5 : Experimental set up of the vapor of zinc reduction reactor

- 1- I.R. heater
- 2- Ni-Cr thermocouple
- 3- Gaz inlet (Ar)
- 4- Gaz inlet (Ar)
- 5- Gaz outlet
- 6- NbCl_5 evaporator
- 7- Zinc evaporator
- 8- Resistance heating
- 9- Substrate

3. EXPERIMENTAL RESULTS AND ANALYSIS

3.1 Nature of the resulting coatings

3.1.1 Reduction by hydrogen

The first minutes of the reaction caused by the interaction of the gaseous phase and the substrates usually tell a lot about the shape and the size of the nuclei, the impact on the state of the surface, etc... This is the reason why a study on mechanically and chemically-polished substrates has been carried out. The observation of the iron (or copper) surface with SEM after 20 minutes of treatment, showed the existence of egg-shaped niobium nuclei with no preferential orientation, (Fig. 6). Yet, some grains being more coated than others, it became obvious that the crystallographic orientation of the underlying iron grains had an influence on nucleation. No special influence on the state of the surface (such as polishing scratches or impurities) was noticed. This "preferential" growth is probably linked to the fact that the distance between the 000 and the $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ niobium atoms ($2.85_3 \text{ \AA}$) and the 000 and 100 iron atoms ($2.86_6 \text{ \AA}$) are very close, which makes a similarly high atomic direction for both structures.

For treatments over 30 minutes, the substrate surface is totally covered by a bright, rough and adherent deposit. No microcracking is visible under the light microscope, even in cases of foldings close to 90° .

Figures 7 and 8 show the appearance of coating on copper and iron substrates, based on a metallographic cross section. On both substrates, a separate adherent layer, with no apparent flaws, was noticed. As far as the iron substrate is concerned, when the $H_2/NbCl_5$ rate is low, a very thin second layer of $NbFe_2$ is visible, bearing all the characteristics of the iron substrate (Fig. 9).

3.1.2 Reduction by vapor of zinc

The coating formed on copper samples treated with CVD Zn is more complex. It is made of three layers set out as follows: an outside layer of niobium made up of 8%wt zinc and 2% wt copper, a second layer of brass β underneath and a third layer of solid solution made up of Cu 62% wt, Zn 38% wt, (Fig. 10).

3.2 Kinetics of deposits

Whichever the technique used, the kinetics of deposits vary according to the different parameters, whose nature and scope of study are written down in table 2.

	Temp. subst (°C)	Temp. $NbCl_5$ (°C)	Temp. Zn (°C)	Pressure (atm)	H_2 (l/h)	Ar (l/h)	Duration (min)
Hydrogen reduction	800-950	110-170		1	4, 8.5, 12		30 - 120
Reduction vapor Zn	520 - 800	130 -170	503	0.013		1 - 5	30 - 180

Tab 2 : Range of each parameter in the experimental planning

3.2.1 Reduction by hydrogen

Figures 11 and 12 show, for the different temperatures, the variation in the thickness of deposits on iron and copper substrates, according to the duration of the treatment. The said variation is linear when the copper substrate is concerned and parabolic for the iron substrate. For a given duration of treatment, the thickness of the deposit increases with the temperature for both substrates (Fig 13).

The linear kinetics noticed in the case of copper substrate show that the only limits to the deposit mechanism are interface reactions and the mass fluxes in the reactor. As shown in the thermodynamic study, the substrate does not interfere. On the contrary, when the iron substrate is concerned, the parabolic kinetics first observed indicate that the limits to the deposit mechanism are due to diffusion phenomena. As shown in the thermodynamic study, for temperatures inferior to 850°C , iron plays a part in the forming of niobium subchlorides. The niobium used up in the formation process of subchlorides does not play a part in the forming of the coating. Under the same conditions, the quantity of deposited niobium is therefore smaller than that which is deposited on copper. It is even possible to obtain the only $NbFe$ compound.

For temperatures superior to 850°C , iron also plays a role in heterogeneous reactions, but helps, in this case, the forming of the deposit. This positive influence decreases as the treatment goes on, (the iron activity being lessened because of the very forming of the coating). Kinetics are then closer to the observations made on copper.

The apparent activation energies (E_a) of global reduction reactions calculated, for both substrates, on the basis of Arrhenius representation, bear the following values: $E_a(\text{Fe}) = 123 \text{ kJ/mole}$ for deposits on iron, $E_a(\text{Cu}) = 39 \text{ kJ/mole}$ for deposits on copper

3.2.2 Reduction by vapor of zinc

In this case, the kinetics study proved (i) the existence of a maximum heating temperature for $NbCl_5$ (145°C), which leads to a maximum thickness of deposits (Fig. 14) and (ii) a linear variation of coating depending on the duration of the treatment (Fig. 15). The linear kinetics being proved, it can be concluded that surface reactions are what essentially controls the global mechanism. For $NbCl_5$ temperatures inferior to 140°C , the quantity of $NbCl_5$ in the gaseous phase is low compared to the quantity of zinc. The chloride is entirely reduced and the niobium coating thickness increases with the heating temperature of $NbCl_5$.

As the thermodynamic study proved it, for temperatures beyond 150°C , the yield of the reduction reaction of $NbCl_5$ into niobium decreases, to the benefit of the reduction reactions of $NbCl_5$ into subchlorides,

Figure 6 : Scanning electron micrographs of the surface of iron substrate after CVD treatment a) 10 min b) 20 min
Nucleation of niobium, influence of the cristalline oriantation.

Figure 7 : Micrograph of the cross section of niobium coating on iron substrate (Hydrogen reduction process)

Figure 8 : Micrograph of the cross section of niobium coating on copper substrate (Hydrogen reduction process)

Figure 9 : Micrograph of the cross section of niobium coating on iron substrate (hydrogen reduction process)
Distribution profile of Nb and Fe at the interface coating/substrate level

Figure 10 : Micrograph of the cross section of niobium coating on copper substrate (Vapor of zinc reduction process)
Distribution profile of Nb, Cu and Zn at the interface coating/substrate level

Figure 11 : Variation of the thickness of niobium coating layer on copper substrate versus duration of treatment
(Ts =Temp. substrate, H₂ flow rate = 8.5 l/h, Temp. NbCl₅ = 140 °C)

Figure 12 : Variation of the thickness of niobium coating layer on iron substrate versus duration of treatment
(Ts =Temp. substrate, H₂ flow rate = 8.5 l/h, Temp. NbCl₅ = 140 °C)

Figure 13 : Variation of the thickness of niobium coating layer on iron substrate versus duration of treatment
(d=H₂ flow rate, Duration of treatment = 1 h, Temp. NbCl₅ = 140 °C)

Figure 14 : Variation of the thickness of niobium coating layer on copper substrate versus NbCl_5 temperature
(d = Argon flow rate, Temp.substrate = 520 $^\circ\text{C}$)

Figure 15 : Variation of the thickness of niobium coating layer on copper substrate versus growth time
(T_s = Temp. substrate, Temp. NbCl_5 = 145 $^\circ\text{C}$)

Figure 16 : Variation of the thickness of niobium coating layer on copper substrate versus the temperature of the substrate
(t = duration of treatment, Temp. NbCl_5 = 145 $^\circ\text{C}$)

which leads to a smaller deposited quantity of niobium. Besides, the decreasing in the deposited thickness of niobium when the substrate temperature increases is once again in accordance with the thermodynamic study, (Fig.16) The apparent activation energies (E_a) of global reduction reactions by vapor of zinc, calculated on the basis of Arrhenius representation, bear the following values: $E_a(\text{Cu}) = -46 \text{ kJ/mole}$

Conclusion : On the one hand, this theoretical and experimental study shows that the reduction of niobium NbCl_5 chloride by hydrogen, both on copper and iron substrates, is only possible for temperatures superior to 700°C . On the other hand, the use of the vapor of zinc as a reducer leads to the formation of coating under much cooler temperatures (520°C), which is of great interest when the substrate cannot bear high temperatures. Yet, it should be noted that the use of zinc as a reducer causes a less thick coating, which, besides, is not pure niobium anymore. Whatever the process used is, an electrochemical characterization of the resulting coatings proved their good resistance against humid corrosion, in sulfuric or nitric acid media and in room temperature. This characterization is just as good, if not better, than that of pure niobium, and definitely better than that of iron or copper substrates, [9]

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