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CHEMICAL VAPOR SYNTHESIS OF NIOBIUM ALUMINIDES

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PhaseI experiments to produce thin films of various niobium aluminide compositions by chemical vapor deposition and supporting process models are described.

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CHEMICAL VAPOR SYNTHESIS OF NIOBIUM ALUMINIDES

1.0 SUMMARY OF PHASE I RESULTS

The Phase I research demonstrated that direct chemical vapor deposition of fine grained, homogeneous, high purity Nb-Al intermetallic compound thin films could be successfully performed. Deposition of the compounds Nb_3Al, Nb_2Al and $NbAl_3$ was demonstrated as was deposition of two-phase microstructures of Nb_2Al + $NbAl_3$ and the end-point composition Nb(Al).

Thermochemical process models were developed to guide the chemical vapor deposition experiments. A preliminary model for surface reaction-controlled deposition was formulated which appears to explain the observed deposition processes. A hot-wall apparatus was developed for deposition of Nb-Al intermetallic films from $NbCl_5$, AlCl (from $AlCl_3$), and H_2 gas mixtures at temperatures of 700-900^{o}C. Deposits were produced on Mo foil substrates. The intermetallic films were generally dense and fine grained with a somewhat irregular surface showing typical chemical vapor deposition growth features. Accurate analyses of residual gas content of the foils was complicated by surface contamination of the foils by condensed precursor species during cooling after deposition. Preliminary thick film deposits were produced on Mo foil substrates in a cold-wall system using the same precursor gases. The thick films possessed dense two-phase (Nb + Nb_3Al) microstructures. The microhardness of the two-phase deposits was 150-250 kg/mm^2 DPH.

The Phase I research suggests needed improvements in the process deposition rate

will be achieved using the cold-wall deposition system. Improvements in deposit homogeneity are sugggested through use of separate, temperature-controllable evaporators for each precursor species and use of higher purity inert carrier gases for the precursor species. Examination of alternative precursor species is suggested for possibly achieving reduced residual gas content in the deposited films. Finally, improved characterization techniques for the deposited films, including direct mechanical property measurements, are required.

2.0 INTRODUCTION

The objectives of this project were to produce and characterize chemically vapor deposited thin films of Nb, Al, and films corresponding to the compositions Nb_3Al, (NbAl), and $NbAl_3$ with special emphasis on $NbAl_3$. The feasibility of syntheses at both low temperature and high temperatures were studied. A high temperature synthesis method was selected for foil preparation characterization of the films was performed to permit general comparison to rapidly solidified alloys in terms of microstructure and degree of crystallinity, compositional uniformity and residual impurities. This report describes Phase I studies carried out in performance of the contract requirements.

3.0 PROCESS MODELING

3.1 Preliminary Considerations

The Nb-Al phases expected to be encountered during this study and their chemical stabilities in terms of chemical activities of the basic components have been the subject of a literature search and evaluation. There appears to be agreement

among several authors as to the phase diagram for the Nb-Al system. It is shown in Fig. 1 as reported by Lundin and Yamamoto(1). This diagram shows Nb_3Al and Nb_2Al as extended compounds and an $NbAl_3$ line compound, all stable up to greater than 1500°C. The composition (NbAl) falls in the two-phase region $Nb_{2-x}Al$-$NbAl_3$. The diagram does not indicate the solubility of Nb in Al but does indicate considerable solubility of Al in Nb. Thus the thermodynamically stable phases for the compositions to be synthesized are Nb(Al), Al(Nb), Nb_3Al, $Nb_{2-x}Al$-$NbAl_3$, and $NbAl_3$ (and perhaps two-phase systems in the immediate vicinity of $NbAl_3$.)

The stability of these phases has also been investigated. Malets(2) studied this system electrochemically. The paper has not been fully translated. However, a table in this report describes important thermodynamic quantities, both measured and estimated. What have been measured are the voltages of a concentration cell comparing the alloy with Al(s) near 900K. The 900K emfs can be reduced to Al activities at this temperature. Malets(2) also includes integral Gibbs free energy data (it is not clear how he obtained this data). The reported integral free energy data at two-phase borders is consistent with these being integral free energy data at the measured emfs. This then allows us to calculate Nb activity values. Figure 2, which is an activity diagram at 900K, has been constructed from Malets values(2) where the data allow. The dotted lines, used to fill in this diagram, are interpolated and extrapolated values and are expected to be qualitatively, if not quantitatively, correct. The points worthy of note are the low Al activity in Nb-Al solutions as compared to the Nb activity on the high Al side. Al thus appears to be bound more tightly in the intermetallic compounds than is Nb. It is also suggested that the $NbAl_3$ compound will exist over a wider range of Al activities than either the Nb_3Al or Nb_2Al compounds even though it is basically a line compound. This is probably true for

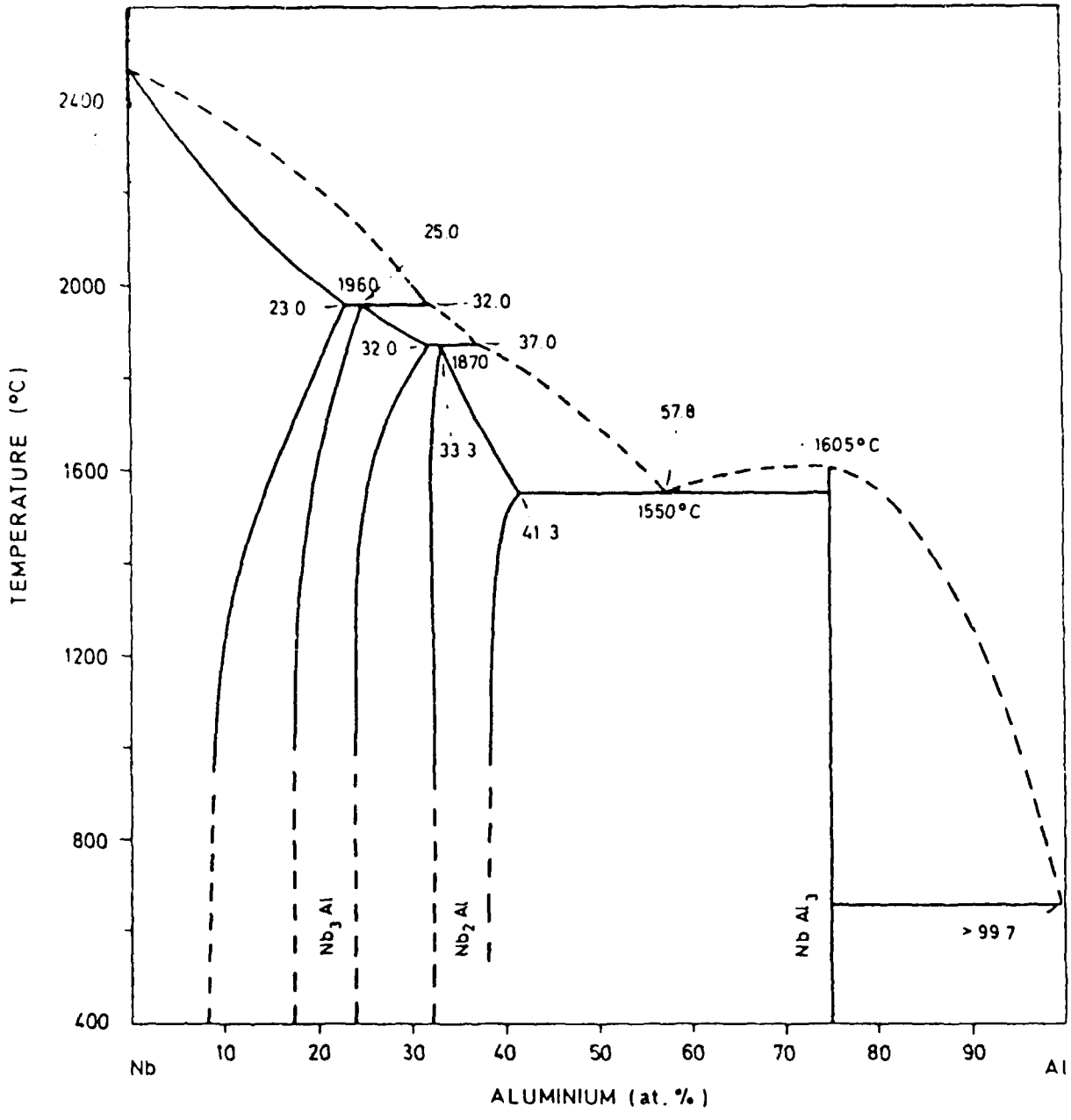
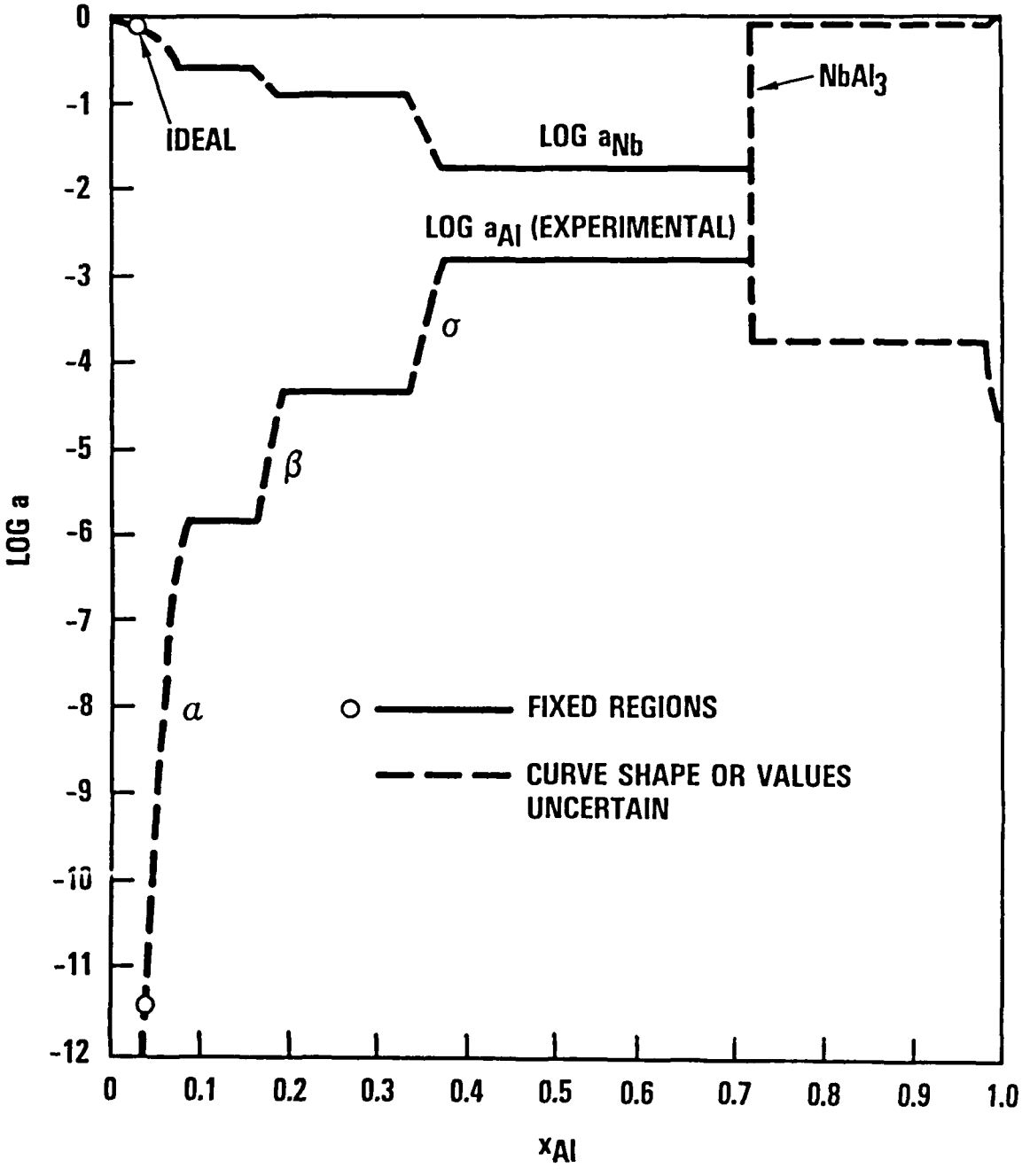


FIG. 1. Phase diagram of the system niobium-aluminium

Figure 2

Al-Nb ACTIVITY DIAGRAM ACCORDING TO MALETS' DATA (900K)



Nb activities also. Thus, something is quite special about the $NbAl_3$ compound. High temperature synthesis around $NbAl_3$ may indeed lead to $NbAl_{3+/-x}$ phase and it may be difficult to contaminate this phase with Al or $Nb_{2-x}Al$ in small amounts due to this special stability, if one is using near-equilibrium methods of film deposition.

Figure 2 can also be used to predict alloys deposited under various, close to equilibrium, coating conditions. For instance, $Nb_{0.96}Al_{0.04}$ would be deposited with an Nb activity near unity and an Al activity of 10^{-11} at 900K. That is, for a system $pAlCl_3 = 0.01$, $pH_2 = 0.1$, $pHCl = 0.01$ the Al activity is 4×10^{-12}.

Thus, Al will be codeposited while depositing Nb (from $NbCl_5$ reduction by H_2) at a concentration around 4%, but its activity would be far below that necessary to make Nb_3Al (10^{-6}). Thus, the temperature must be considerably increased or the Al activity increased using techniques other than H_2 reduction for successful codeposition.

3.2 Synthesis of Alloys and Compounds

Deposition of Al in low temperature processes has been performed using aluminum alkyls, in particular triisobutylaluminum at 250-300°C. This has been found to give a reasonably pure Al deposit. Precursors where Al is bonded to O or N do not give pure deposits. Table 1 shows several possible Al compounds where high purity deposits may occur and some of the physical properties of these Al precursor compounds important to their use as precursors for coating are also shown.

Table 1

Possible Low Temperature Precursors for Aluminum Coating

Aluminum Alkyls

Triisobutylaluminum

$(C_4H_9)_3Al$

MP 4°C

BP 73°C/5 mm.

Trimethylaluminum

$(CH_3)_3Al$

MP 0°C

BP 130°C/125 mm.

Dimethylaluminum chloride

$(CH_3)_2AlCl$

MP -50°C

BP 83°C/200mm

Low temperature, high purity Nb deposition appears to be much more limited. Table 2 shows three possible Nb precursor compounds that may deposit Nb at low temperatures. Carbonyls of Ni, Fe, Co, Mo, etc. have been used to deposit these metals. There is no pure niobium carbonyl, however. The nearest compound to a metal carbonyl is cyclopentadienylniobium carbonyl which, in principle, could release CO and cyclopentadiene by H_2 reduction. The third compound shown is a partial alkyl and might also be induced to deposit Nb by reduction techniques.

High temperature Al deposition has usually been performed by a sequence similar to that occurring in a pack cementation process where $AlCl_3(g)$ is reduced to AlCl(g) by Al(s). This reaction then reverses in the presence of an Al sink or upon lowering of the temperature. The extended equations which govern this process are shown in Table 3. Physical properties of various AlX_3 halides are shown in Table 4 for aiding the selection of the proper halide for the coating process. Note the 3HCl energies listed and compared with the AlX_3 energies. This comparison says it is difficult (at room temperature at least) to reduce an aluminum halide with H_2. This process will work but only at rather high temperatures.

In contrast, the reaction shown in Table 5 and the data shown in Table 6 for Nb are more hopeful since they are 20 kcals lower for $NbCl_5$ reduction than $AlCl_3$ reduction. The liberation of 5HCl instead of 3HCl formed helps the reduction also. The $NbCl_5$ reduction proceeds readily at about 1000K in H_2. Calculations of equilibrium pressures of HCl, $AlCl_2$, $AlCl_3$, and Al_2Cl_6 have been made under conditions representative of a coating process. These demonstrate the aluminum deposition capability of $AlCl/AlCl_2$ gas mixtures. The calculations were performed for the condition of equilibrium with Al(s,l) at various temperatures.

Table 2

Possible Low Temperature Precursors For Nb Coating

Pentadienyltetracarbonyl-niobium

$(C_5H_5)Nb(CO)_4$

MP 144-6°C

BP Sublimes

Pentadienyl trihydrido-niobium

$(C_5H_5)NbH_3$

Properties Unknown

Trimethyldichloro-niobium

$(CH_3)_3\ NbCl_2$

Known to Sublime

Table 3

High Temperature Al Coating Reactions

$$3\ AlX(g) \rightleftarrows 2\ Al(s) + AlX_3(g)$$

$$6\ AlX(g) \rightleftarrows 4\ Al(s) + Al_2X_6(g)$$

$$3\ AlX_2(g) \rightleftarrows Al(s) + 2\ AlX_3(g)$$

$$3\ AlX_2(g) \rightleftarrows 2\ Al(s) + Al_2X_6(g)$$

where X = halide

Table 4

AlX_3 Properties

X	MP(°C)	BP(°C)	ΔH_f (kcal/mole)	3HX(g) ΔH_f (kcal/3mole)
F	-	1276	-361.0	-195.4
Cl	190*	181	-168.3	-66.2
Br	98	256	-126.0	-26.0
I	191	385	-73.9	+18.9

* 2.5 atmospheres

Table 5

High Temperature Nb Coating Reaction

$$NbX_5(g)^* + 5/2\ H_2 \rightarrow Nb(s) + 5\ HX$$

where X = halide

* (lower halides, e.g. NbX_4, are also known)

Table 6

NbX_5 Properties

X	MP(°C)	BP(°C)	ΔH_f (kcal/mole)	5HX(g) ΔH_f (kcal/5mole)
F	79	234	-433.5	-325.7
Cl	203.4	242.4	-190.5	-110.3
Br	254.0	365.0	-133.0	-43.3
I	-	-	-64.6	+31.5

The data, developed from the JANAF Thermochemical Tables, are shown in Table 7. The last portion of this table is the most revealing. It shows that high capacities for depositing Al are attained by about 1200K where the AlCl pressure exceeds 10^{-2} atm. $AlCl_3$ and is approaching 10^{-1} atm. $AlCl_3$. Note that under these conditions Al_2Cl_6 is largely dissociated and does not enter into the considerations. Coating temperatures in the vicinity of 900°C are required for efficient Al deposition.

This analysis suggests the most likely way to deposit high purity Nb-Al alloys. If H_2 is used to reduce $NbCl_5$ the resultant product HCl is expected to react with Al, AlCl, or $AlCl_2$ producing H_2 and forming stable $AlCl_3$ which will reduce the Al deposition rate severely. These two coating reactions and the interfering HCl reaction are shown in Table 8. Also shown is the reaction producing intermetallics which will aid the deposition of Al as governed by the activities shown in Figure 2. It appears better to avoid H_2 reduction systems and consider AlCl(g) as the reductant for $NbCl_5$(g). Significant amounts of AlCl(g) will be used in a coating process to reduce $NbCl_5$(g) to the metal. Since codeposition of Al with Nb is desired, more AlCl will have to be present to accomplish the codeposition.

The deposition reactions for the appropriate intermetallic compounds using NbX_5(g) and AlX(g) are shown in Table 9. These equations describe the stoichiometry from both AlX and AlX_2 species and clearly demonstrate the large excess of AlX necessary to produce the various intermetallic compounds. Note for example the 7/1 ratio of AlX over NbX_5 needed to obtain $NbAl_3$(s). This effect will be quite apparent during the operation of the Al source. One will have to inject about 10 times as much $AlCl_3$ into the Al reactor as $NbCl_5$ to produce

Table 7

Aluminum Chloride Equilibria (Pressures in Atm.)

$AlCl_3 + 2Al(s,l) \rightleftarrows 3AlCl \qquad K_1 = pAlCl^3/pAlCl_3$

$2AlCl_3 + Al(s,l) \rightleftarrows 3AlCl_2 \qquad K_2 = pAlCl_2{}^3/pAlCl_3{}^2$

$2AlCl_3 \rightleftarrows Al_2Cl_6 \qquad K_3 = pAl_2Cl_6/pAlCl_3{}^2$

	Al_2Cl_6	$AlCl_3$	AlCl	$AlCl_2$			
T(K)	log K	log K	log K	log K	log K_1	log K_2	log K_3
600	99.822	48.338	9.005	26.319	-21.323	-17.707	3.146
800	71.708	35.589	7.813	20.152	-12.150	-10.722	0.530
1000	54.774	27.885	7.025	16.383	-6.810	-6.6621	-0.996
1200	43.358	22.671	6.410	13.782	-3.441	-3.996	-1.984
1400	35.208	18.939	5.954	11.910	-1.077	-2.148	-2.67

	For $pAlCl_3 = 0.1$			For $pAlCl_3 = 0.01$		
T (K)	log pAl_2Cl_6	log pAlCl	log $pAlCl_2$	log pAl_2Cl_6	log pAlCl	log pAlCl
600	1.146	-7.441	-6.569	-0.854	-7.774	-7.236
800	-1.470	-4.383	-4.241	-3.470	-4.717	-4.907
1000	-2.996	-2.603	-2.874	-4.996	-2.937	-3.540
1200	-3.984	-1.480	-1.999	-5.984	-1.814	-2.665
1400	-4.670	-0.692	-1.382	-6.670	-1.026	-2.049

Table 8

High Temperature Coating Reactions

Nb:

$NbCl_5 + 1/2H_2 \rightleftarrows NbCl_4 + HCl$

$NbCl_4 + 2H_2 \rightleftarrows Nb + 4\ HCl$

Al:

$AlCl_3 + 2\ Al \rightleftarrows 3\ AlCl$

$3\ AlCl \rightleftarrows 2\ Al + AlCl_3$

Interference Reactions:

$2\ HCl + AlCl \rightleftarrows AlCl_3 + H_2$

$3\ HCl + Al \rightleftarrows AlCl_3 + 3/2\ H_2$

Assistance Reactions

$Al + 2Nb \rightleftarrows Nb_2Al$ (or Nb_3Al, or $NbAl_3$)

Table 9

High Temperature Combined Nb-Al Coating Reactions

$$4NbX_5(g) + 13AlX(g) \rightleftarrows 2Nb_2Al(s) + 11AlX_3(g)$$

$$2NbX_5(g) + 13AlX_2(g) \rightleftarrows 2Nb_2Al + 12AlX_3(g)$$

$$3NbX_5(g) + 9AlX(g) \rightleftarrows Nb_3Al + 8AlX_3(g)$$

$$3NbX_5 + 18AlX_2(g) \rightleftarrows Nb_3Al + 17AlX_3(g)$$

$$NbX_5(g) + 7AlX(g) \rightleftarrows NbAl_3 + 4AlX_3(g)$$

$$NbX_5 + 14AlX_2(g) \rightleftarrows NbAl_3 + 11AlX_3$$

where X = halide

(Al_2X_6 also a product)

$NbAl_3$. This assumes that $pAlCl_3$ = pAlCl at the exit of the Al source as pictured in Figure 3 and that AlCl is almost absent from the coating chamber exit. The coating apparatus shown in this figure is now in operation. Note in Figure 3 that H_2 is suggested as a possible carrier gas. This is to aid in Nb deposition if the AlCl-$NbCl_5$ reaction kinetics are poor. In any case the presence of H_2 is expected to be only catalytic and not as an overall reactant and will be considered further in the next section including reaction mechanisms.

3.3 Reaction Mechanisms

The reaction of $AlCl_3$(g) with Al(s or l) to produce AlCl(g) is almost certainly a heterogeneous reaction involving (1) the adsorption of $AlCl_3$(g) on the Al surface, (2) the interaction of the $AlCl_3$(ads) with the surface Al, and (3) the desorption of AlCl(ads) from the surface to give gaseous AlCl. The formation of $AlCl_2$(g) would follow a similar route and $AlCl_2$(ads) may be an intermediate.

$$AlCl_3(g) \rightarrow AlCl_3(ads)$$

$$AlCl_3(ads) + 2Al(s \text{ or } l) \rightarrow 3AlCl(ads)$$

$$3AlCl(ads) \rightarrow 3AlCl(g)$$

The reverse reaction undoubtedly follows a similar course. A fully gaseous reaction would lead to Al(g) and this is a very energetic intermediate and thus unlikely.

These reactions seem appropriate for AlCl formation and decomposition. Reactions

Nb Al COATING PROCESS SCHEMATIC

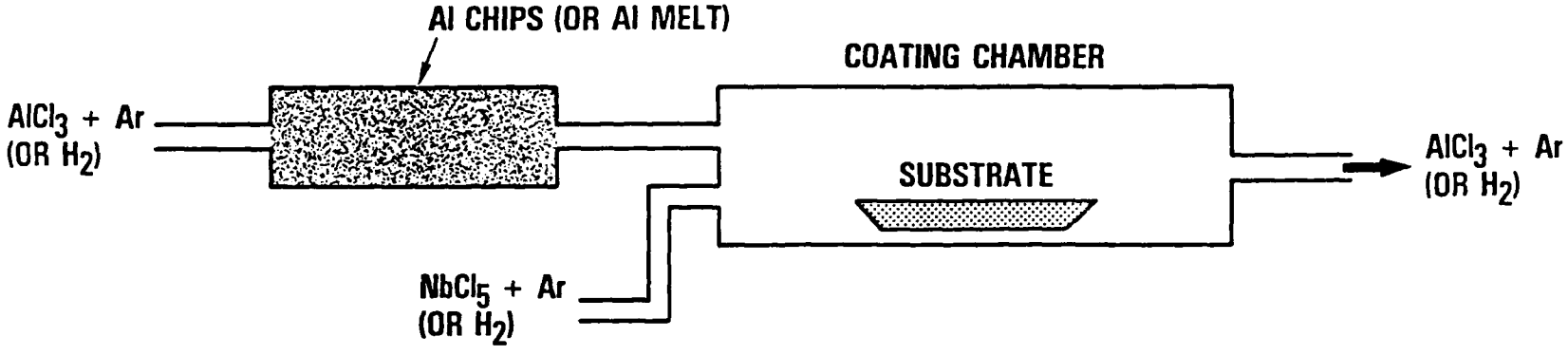


Figure 3

involving H_2 may also be important, particularly in the case of $NbCl_5$ reduction. Here again adsorbed state reactions are likely to constitute the critical path. An important step on many metal surfaces is the the adsorption and dissociation of H_2 on the surface.

$$H_2 \rightarrow H_2(ads)$$

$$H_2(ads) \rightarrow 2H(ads)$$

These adsorbed H atoms can approach adsorbed halides and extract halide ions sequentially.

$$NbCl_n(ads) + H(ads) \rightarrow NbCl_{(n-1)}(ads) + HCl(ads).$$

The adsorbed HCl can then react with adsorbed AlCl.

$$HCl(ads) + AlCl(ads) \rightarrow AlCl_2(ads) + H(ads)$$

$$HCl(ads) + AlCl_2(ads) \rightarrow AlCl_3(ads) + H(ads)$$

and the formed $AlCl_3$ vaporized according to

$$AlCl_3(ads) \rightarrow AlCl_3(g)$$

Thus H_2 may act catalytically to facilitate the reduction of $NbCl_5$ by AlCl. Indeed, what is observed experimentally is a faster rate of deposition of Nb-Al (as intermetallics) in the presence of H_2 than when using $NbCl_5(g)$ + AlCl(g)

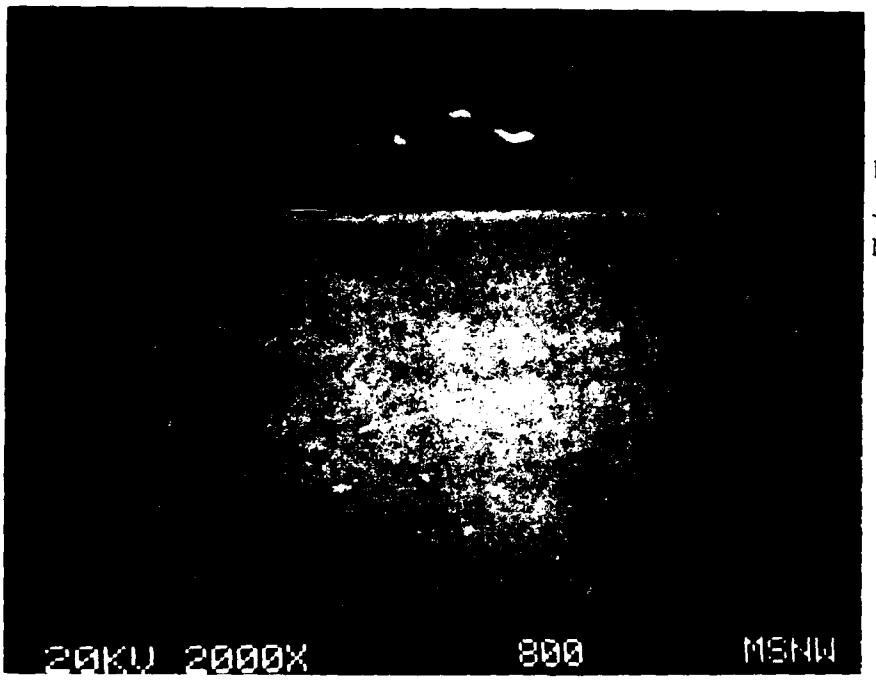
alone. Thus, the use of catalytic H_2 in Nb-Al alloy deposition appears useful in aiding the Nb reduction at least.

It should also be noted that the Nb-Al deposits do not appear to be generated as powders or dust by reduction and condensation from the gaseous state. This is another indication of adsorbed state surface reactions being rate controlling.

4.0 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Preliminary Experiments

Preliminary experiments examined low temperature deposition of pure Al from triisobutylaluminum, high temperature deposition of pure Nb from mixed $NbCl_5/H_2$ gases, and high temperature deposition of alloy compositions from mixed $NbCl_5/AlCl_3/H_2$ gases. Other preliminary experiments involved triethyl or triisobutyl aluminum in combination with $NbCl_5$ and H_2. The product deposits were powdery and nonadherent. Deposition of the pure metals was demonstrated without difficulty. The dense, adherent Nb-Al alloy coating from the $AlCl_3/NbCl_5/H_2$ experiment is shown in Figure 4. Here, the secondary electron SEM micrograph shows the coating, on a molybdenum foil substrate, to be about 5 microns thick. The coating exhibits the typical nodular appearance characteristic of CVD processes. However, because of the H_2 reduction of $AlCl_3$ deposition process used, the coating contains less than 4% Al. This is consistent with Figure 2 where the Al activity of this composition is about 10^{-11} at 900K. More Al in the deposit would not be expected unless the $AlCl_3$ is prereduced to AlCl. The apparatus shown in Figure 3 was constructed to make this correction and lead to the desired intermetallic compounds and their mixtures.



Nb Al Alloy Coating

←

Molybdenum Substrate

Figure 4. Chemically vapor deposited Nb-Al alloy film (containing 2-4 at.% Al) produced from mixed chlorides, 800°C/1 hr., on molybdenum foil substrate.

4.2 Deposition From $AlCl/NbCl_5$ Mixtures

The apparatus shown in Figure 3 was constructed to prereact the $AlCl_3$ vapor with molten Al to form AlCl. As shown in section 3.0, AlCl will reduce $NbCl_5$ to form the desired intermetallic compounds. Although this was found to be the case the product coatings were extremely thin, i.e. the deposition rate was low. It was found that the addition of H_2 gas to the $NbCl_5$/AlCl gas mixture greatly increased the deposition rate.

A total of 25 deposition runs were performed with the $NbCl_5$/AlCl gas mixtures. The deposition conditions used are summarized in Table 10. Since the apparatus shown in Figure 3 is a hot-wall device, containing a quartz tube surrounded by a clamshell resistance heater, deposition of the Nb-Al compounds occurred on the walls of the quartz tube as well as on the Mo foil substrate coupons contained within the quartz tube. Thus most coatings produced were rather thin.

Figure 5. shows a typical coating on a Mo substrate. This deposit, whose preparative parameters are identified in Table 10 as Run No. 1028, shows a duplex deposit. The thick inner coating was found to be Nb containing a minor amount of Al, while the darker outer coating was found to be approximately 50 at.% Nb and Al as shown in Figure 6. (The calculated elemental analysis corresponding to these x-ray spectra are shown following Figure 6.). Several such duplex coatings were obtained in early experiments.

One multilayer coating (Run No. 1028) where the $AlCl_3$ source temperature and inert carrier gas flow rate were increased in steps during the deposition run is shown in Figure 7. The innermost coating layer corresponded to Nb containing a

Table 10

Summary of Nb-Al Deposition Conditions Using $AlCl_3$ + $NbCl_5$ Precursors

Run No.	Temp. (°C)	Pressure (mm Hg)	A Flow (ml/min)*	H_2 Flow (ml/min)	AlCl Conversion
1014	800	100	35	100	No
1015	900	100	35	100	No
1020	900	9	40	100	No
1021	900	10	60	100	Yes
1022	900	10	50	100	Yes
1026	910	10	60	100	Yes
1027	900	10	50	100	Yes
1028	900	10	100 (in steps)	100	Yes
1228	900	12	30	50	Yes
1229	900	20	30	50	Yes
1230	900	20	100	120	Yes
0104	900	100	300	325	Yes
0105	900	400	75	250	Yes
0120	800	100	35	100	Yes
0202	800	100	35	100	Yes
0203	800	100	35	100	No
0204	900	14	130	200	Yes
0209	900	160	130	200	Yes
0217	900	650	200	350	Yes
0218	900	650	200	350	Yes
0222	900	300	200	250	Yes
0321	860	650	225	210	Yes
0323	860	730	50	170	Yes
0324	860	760	80	250	Yes
0325	860	760	100	250	Yes

*Divided between $AlCl_3$ and $NbCl_5$ source boats.

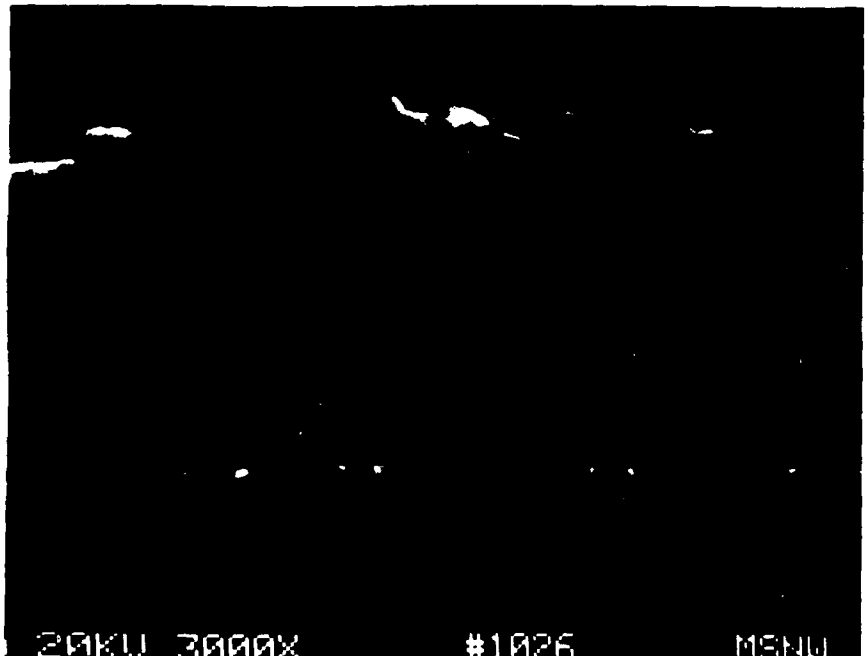


Figure 5. Cross section through chemically vapor deposited coating. Substrate material is Mo foil.

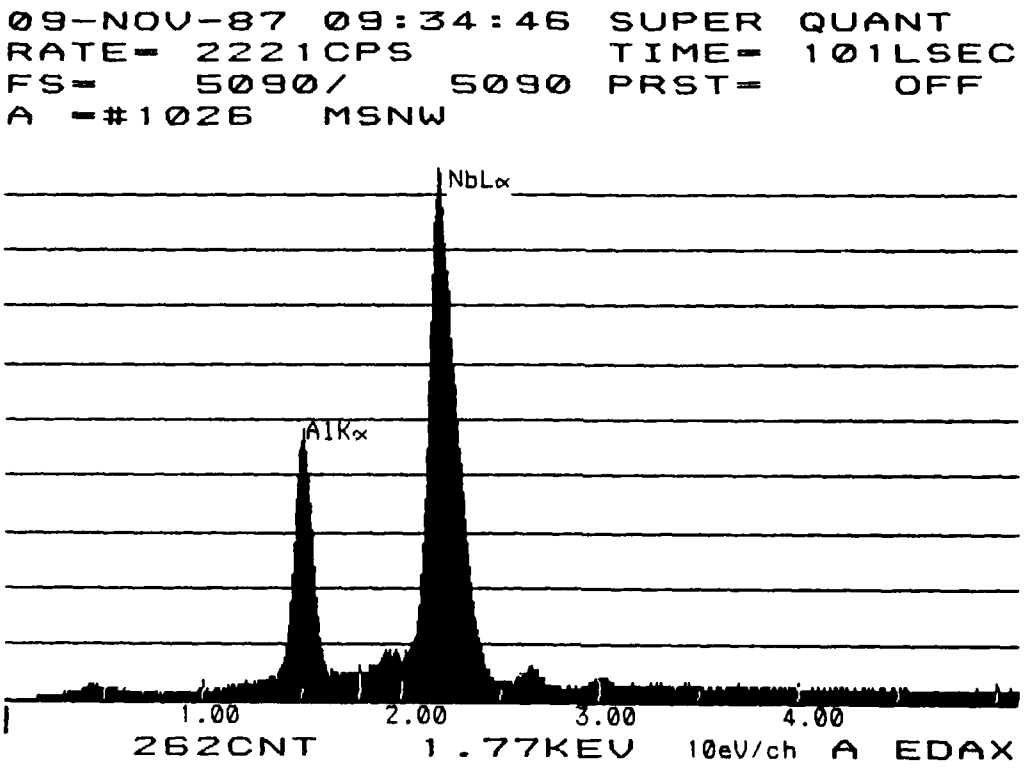


Figure 6. X-ray spectra of the outer coating shown in Figure 5.

EPIC TABLE FOR SI - 14

LINE	ENERGY	LAMBDA	REL.HT.
K A1	1.739	7.130	100.0
K B1	1.828	6.783	1.7
K ABS	1.843	6.727	0.0

INTE-%-ZAF:
LABEL = #1026 MSNW
09-NOV-87 09:32:13
101.015 LIVE SECONDS
KV= 20.0 TILT= 0. TKOFF=20.
ZAF CORRECTION

ELEM	K	Z	A	F
ALK	0.1153	1.119	0.451	1.011
NBL	0.6192	0.949	0.843	1.000

ELEM	CPS	AT % ELEM
AL K	195.7042	50.12
NB L	440.3517	49.88
TOTAL		100.00

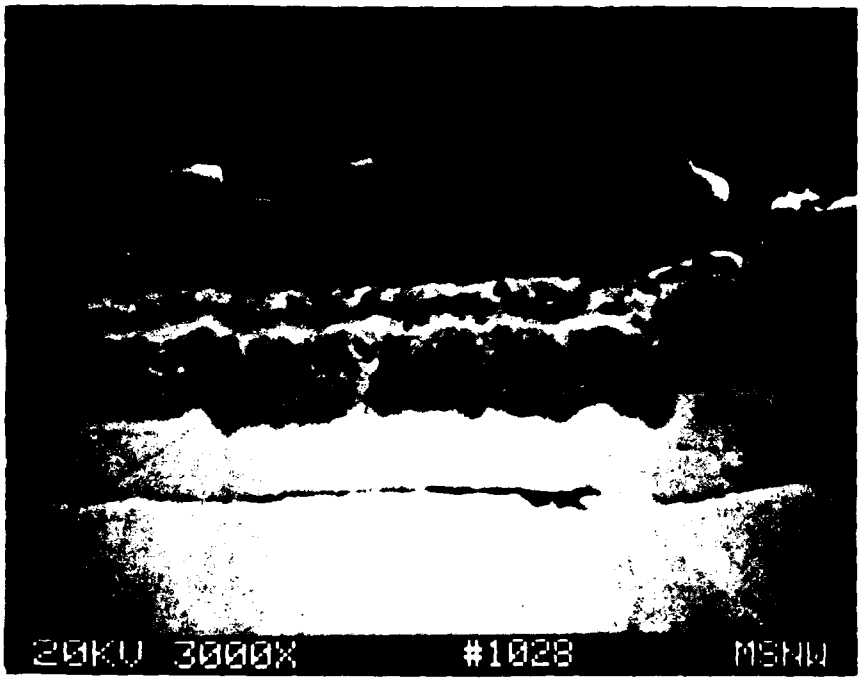


Figure 7. Cross section through chemically vapor deposited coating. Substrate material is Mo foil.

small amount of Al (ca. 1-2 at.%) as shown in Figure 8. The second coating layer corresponded approximately to Nb_3Al as shown in Figure 9 (and the table following Figure 9). The third layer corresponded closely to Nb_2Al as shown in Figure 10 and the table which follows. The fourth, or outermost, coating layer corresponded almost exactly to Al_3Nb as shown in Figure 11 and the table which follows. Note in Figure 7 that the three outer coatings contain some porosity and that the outermost coating is cracked. This presumably resulted from the higher thermal expansion coefficient expected for the higher Al content layers.

Another example of a thin product Nb-Al film from Run No. 0203 is shown in Figure 12. As shown in Figure 13, the coating composition was 60 at.% Nb-40 at.% Al which corresponds to a two-phase Nb_2Al-Al_3Nb composition. As with all Nb-Al coatings produced, no grain structure can be resolved in the as-deposited material.

4.3 Deposition of Thick Films

A cold-wall deposition apparatus was constructed which was similar to that shown schematically in Figure 3. The resistance furnace surrounding the quartz tube coating chamber in Figure 3 was removed. Copper bus bars through the end flanges were connected to a 0.5 in. x 6.0 in. Mo foil resistance heater which was maintained at 800°C while the quartz tube remained near room temperature. The resistance heated foil served as the substrate for deposition. The precursor gas mixtures used were those found earlier to produce Nb_3Al, Nb_2Al and $NbAl_3$ thin films in the hot-wall system. Deposition times of 2.0 hours were used for comparison to the earlier results. The resulting deposit thicknesses were in the range of 25-125 microns (as opposed to less than 6 microns in the hot-wall

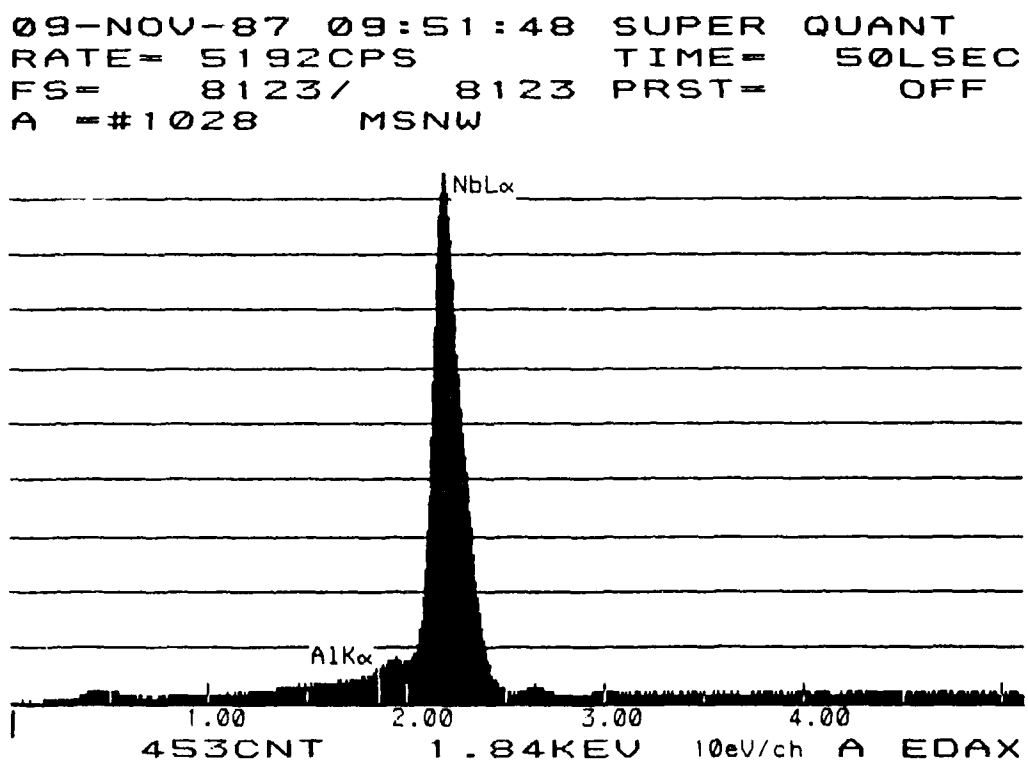


Figure 8. X-ray spectra of innermost coating shown in Figure 7.

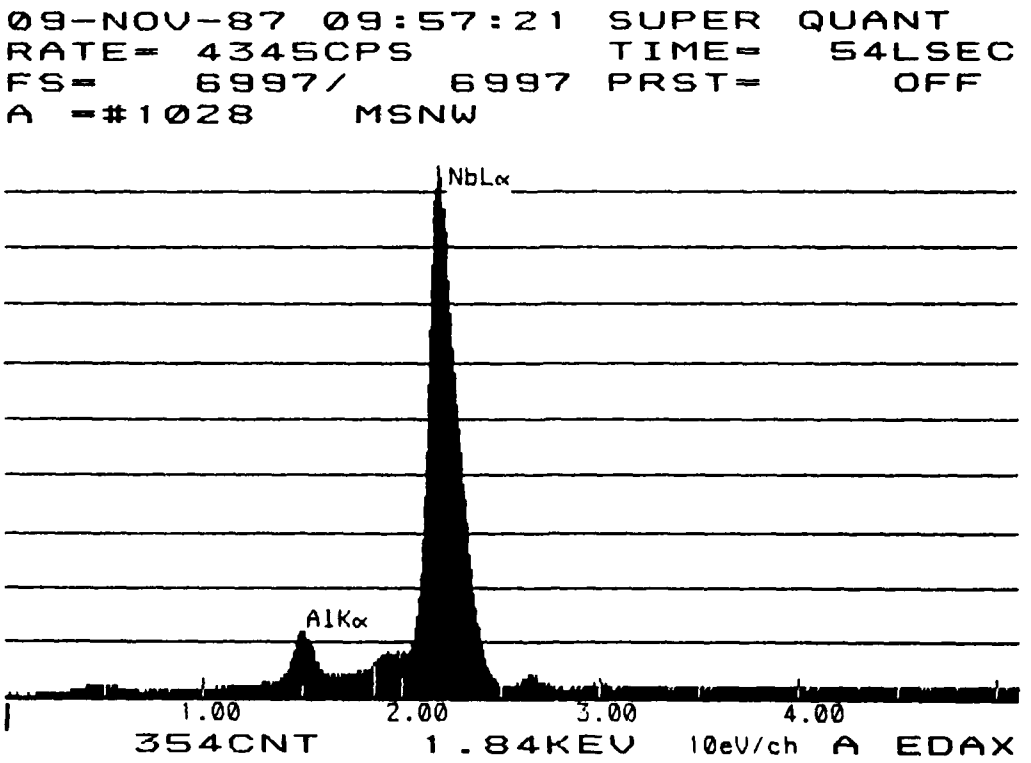


Figure 9. X-ray spectra of second layer of coating shown in Figure 7.

INTE-%-ZAF:
LABEL = #1028 MSNW
09-NOV-87 09:56:24
  54.504 LIVE SECONDS
KV= 20.0 TILT= 0. TKOFF=20.
ZAF CORRECTION

ELEM	K	Z	A	F
ALK	0.0332	1.152	0.403	1.014
NBL	0.8658	0.983	0.948	1.000

ELEM	CPS	AT % ELEM
AL K	106.1396	20.71
NB L	1160.8936	79.29
TOTAL		100.00

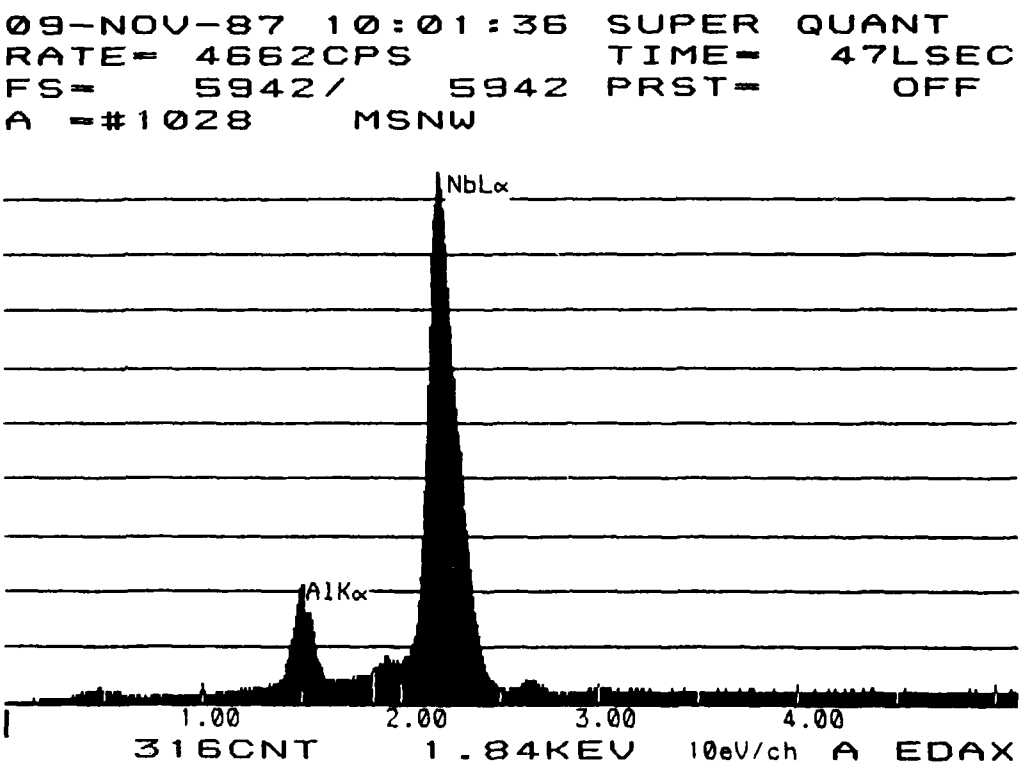


Figure 10. X-ray spectra of third layer coating shown in Figure 7.

```
INTE-%-ZAF:
LABEL = #1028    MSNW
09-NOV-87    10:01:01
   47.514  LIVE SECONDS
KV=  20.0    TILT= 0.    TKOFF=20.
            ZAF CORRECTION


 ELEM    K       Z       A       F

 ALK 0.0583 1.141 0.417 1.013
 NBL 0.7788 0.971 0.912 1.000



                          AT %
ELEM        CPS           ELEM
AL K     202.4246         32.15
NB L    1131.6876         67.85
                          ------
TOTAL                     100.00
```

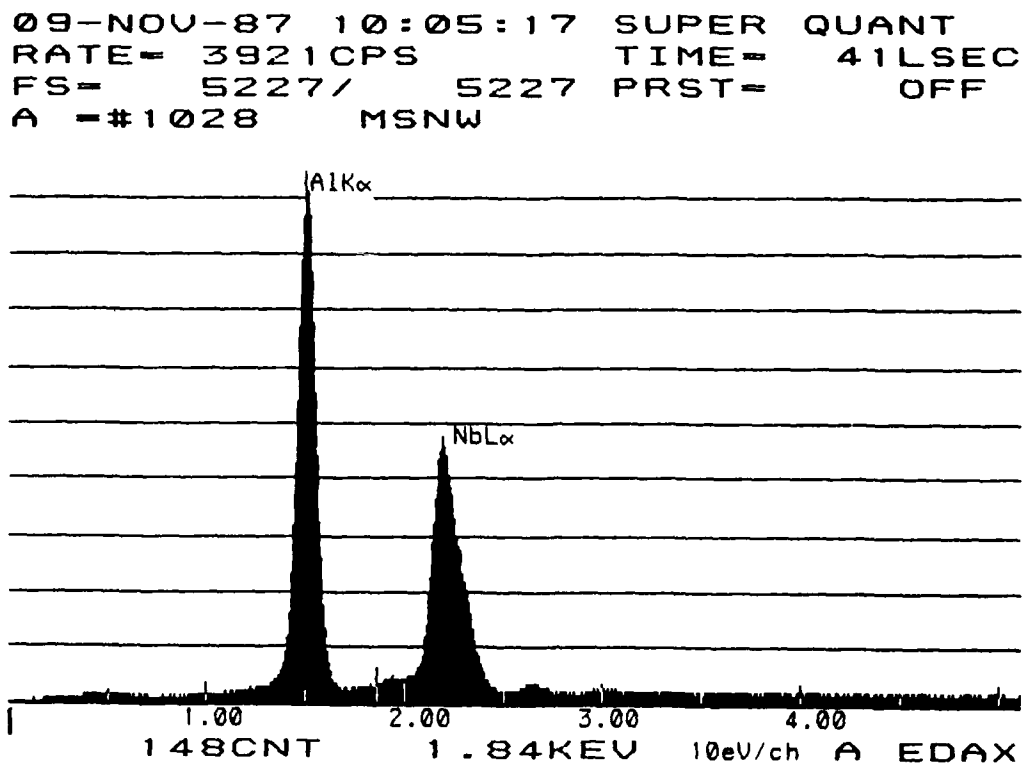


Figure 11. X-ray spectra of outermost coating shown in Figure 7.

INTE-%-ZAF:
LABEL = #1028 MSNW
09-NOV-87 10:04:44
  41.210 LIVE SECONDS
KV= 20.0 TILT= 0. TKOFF=20.
ZAF CORRECTION

ELEM	K	Z	A	F
ALK	0.2727	1.076	0.547	1.007
NBL	0.3466	0.904	0.710	1.000

ELEM	CPS	AT % ELEM
AL K	1034.3252	74.58
NB L	550.6614	25.42
TOTAL		100.00

Figure 12. Cross section through chemically vapor deposited coating. Substrate material is Mo foil.

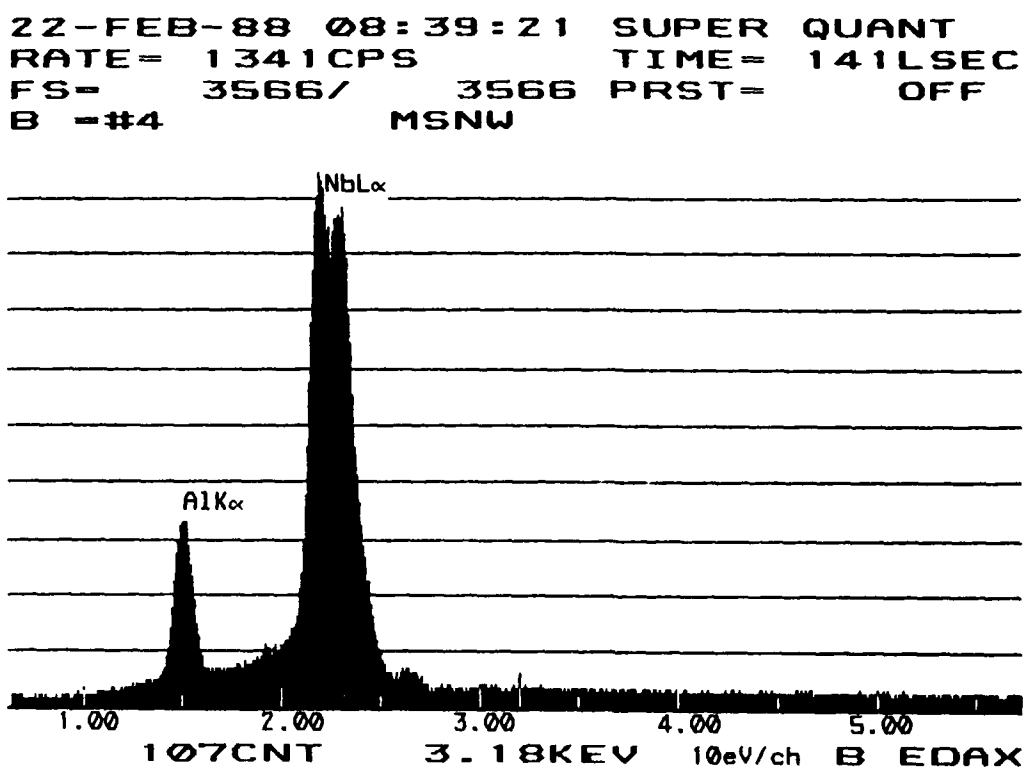


Figure 13. X-ray spectra of the coating shown in Figure 12.

INTE-%-ZAF:
LABEL = #4 MSNW
22-FEB-88 08:38:09
141.098 LIVE SECONDS
KV= 20.0 TILT= 0. TKOFF=20.
ZAF CORRECTION

ELEM	K	Z	A	F
ALK	0.0858	1.130	0.434	1.012
NBL	0.6960	0.960	0.877	1.000

ELEM	CPS	AT % ELEM
AL K	63.0554	41.90
NB L	217.7136	58.10
TOTAL		100.00

system). Thus the overall deposition rate was increased by almost an order of magnitude through use of the cold-wall system. The microstructures of these coatings and their corresponding x-ray spectra are shown in Figures 14-19. All were found to have lower than expected average Al contents which indicates that the deposition efficiency of Al in the cold-wall system was lower than observed in the hot-wall system. An increased $AlCl_3$ (and AlCl) flux would produce the desired higher Al content deposits.

These thick deposits showed varying amounts of Nb_3Al second phase which is quite apparent in the highest Al content deposit shown in Figure 18. The Nb_3Al second phase was also noted to be layered or occur in bands in the deposit.

Microhardness results on the thick film deposits are shown in Table 11. Readings were consistent for a given deposit but do not appear to correlate with the observable amount of Nb_3Al second phase.

Optimization of the composition of the thick film deposits will be continued under internal funding as will the residual gas analyses on the deposited films.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from these preliminary experiments.

1. The end point composition Nb(Al) and the intermetallic compositions Nb_3Al, Nb_2Al and Al_3Nb and mixtures of these phases can be successfully deposited as thin films from $AlCl$-$NbCl_5$ gas mixtures in a hot-wall system. The deposition rate of the films is significantly increased by the presence of H_2 and the

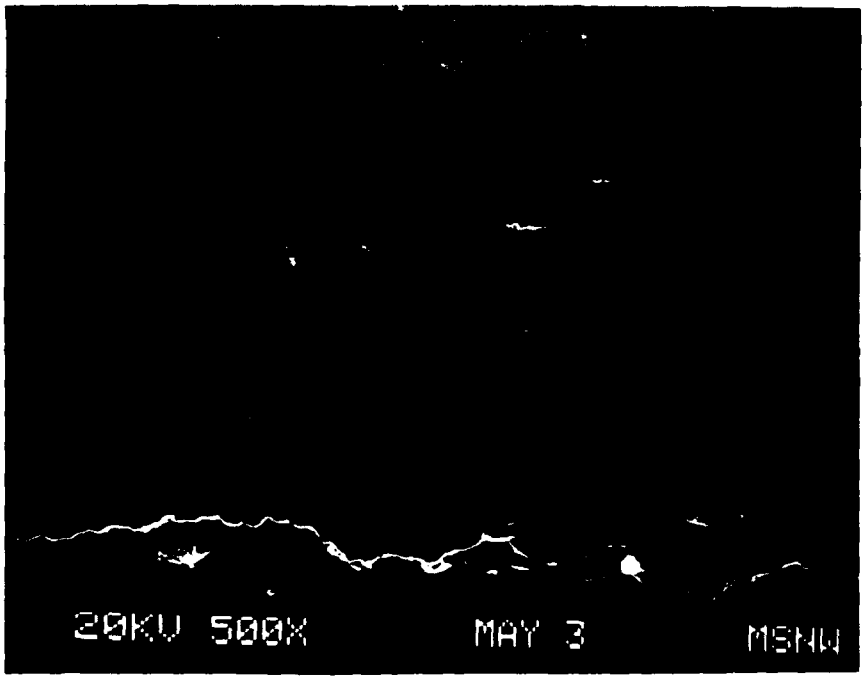


Figure 14. Cross section through chemically vapor deposited coating produced in cold-wall apparatus. Substrate material is Mo foil.

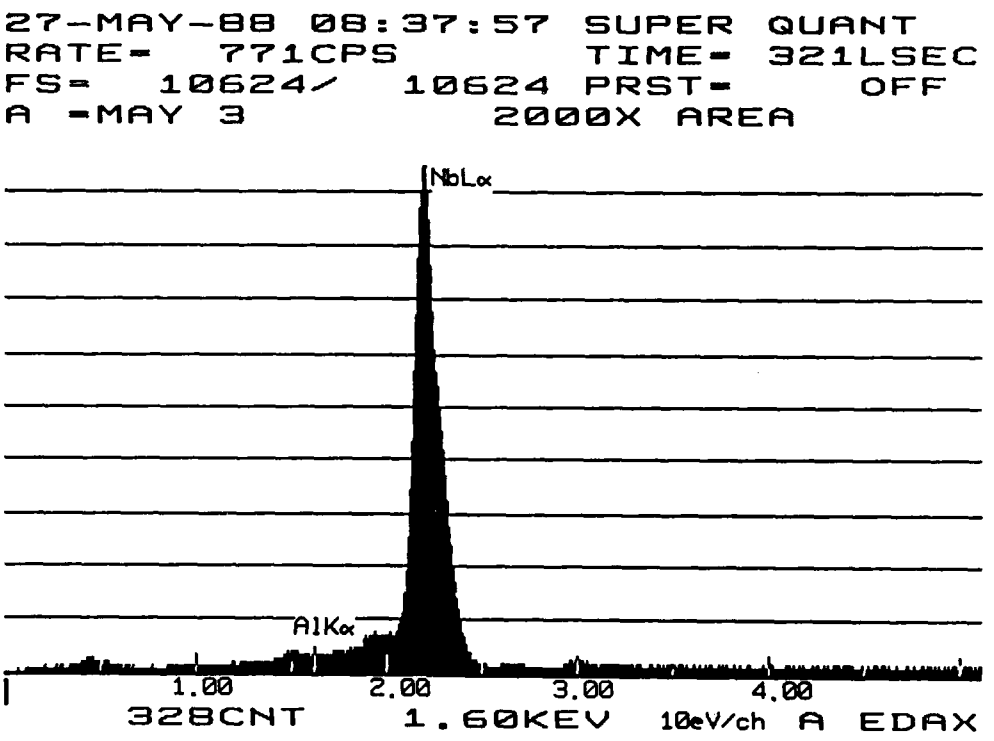


Figure 15. X-ray spectra of central portion of coating shown in Figure 14.

INTE-%-ZAF:
LABEL = MAY 3 2000X AREA
27-MAY-88 06:58:11
321.323 LIVE SECONDS
KV= 20.0 TILT= 0. TKOFF=20.
ZAF CORRECTION

ELEM	K	Z	A	F
ALK	0.0023	1.167	0.385	1.015
NBL	0.9898	0.999	0.996	1.000

ELEM	CPS	AT % ELEM
AL K	1.5903	1.72
NB L	296.3840	98.28
TOTAL		100.00

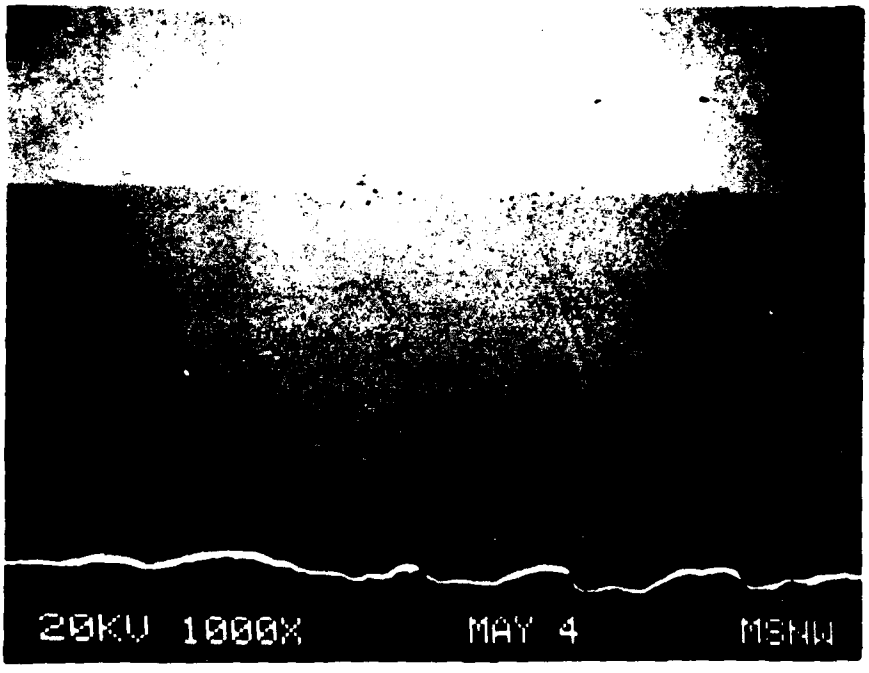


Figure 16. Cross section through chemically vapor deposited coating produced in cold-wall apparatus. Substrate material is Mo foil.

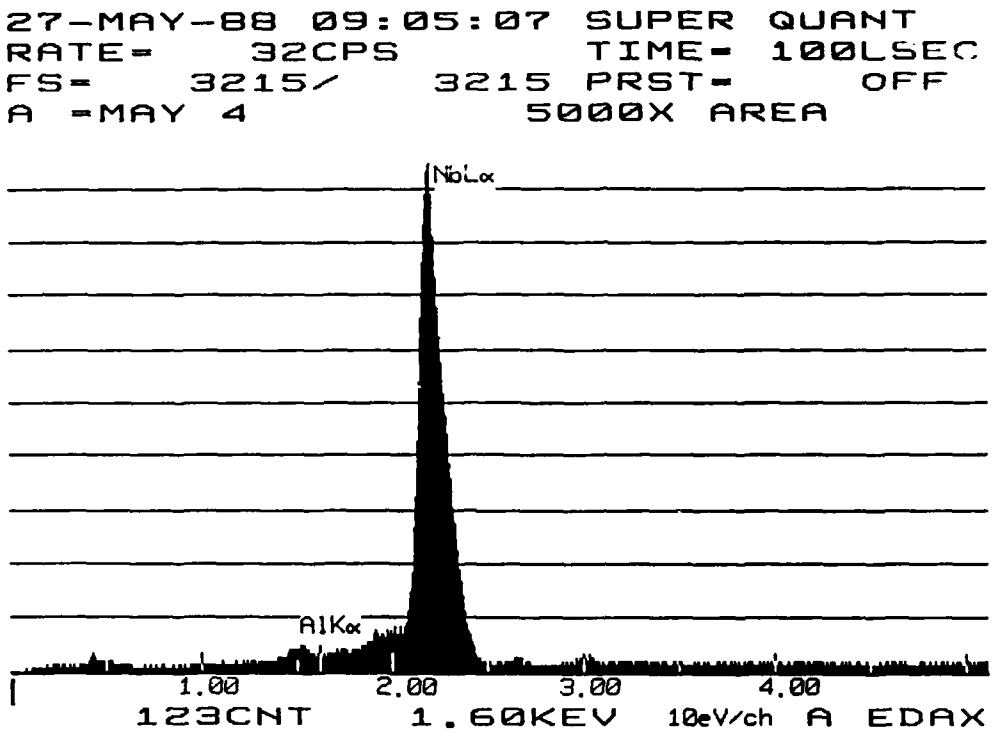


Figure 17. X-ray spectra of central portion of coating shown in Figure 16.

LABEL = MAY 4 5000X AREA
27-MAY-88 06:58:11
100.411 LIVE SECONDS
KV= 20.0 TILT= 0. TKOFF=20.
ZAF CORRECTION

ELEM	K	Z	A	F
ALK	0.0029	1.166	0.385	1.015
NBL	0.9872	0.998	0.995	1.000

ELEM	CPS	AT % ELEM
AL K	1.8325	2.17
NB L	269.1041	97.83
TOTAL		100.00

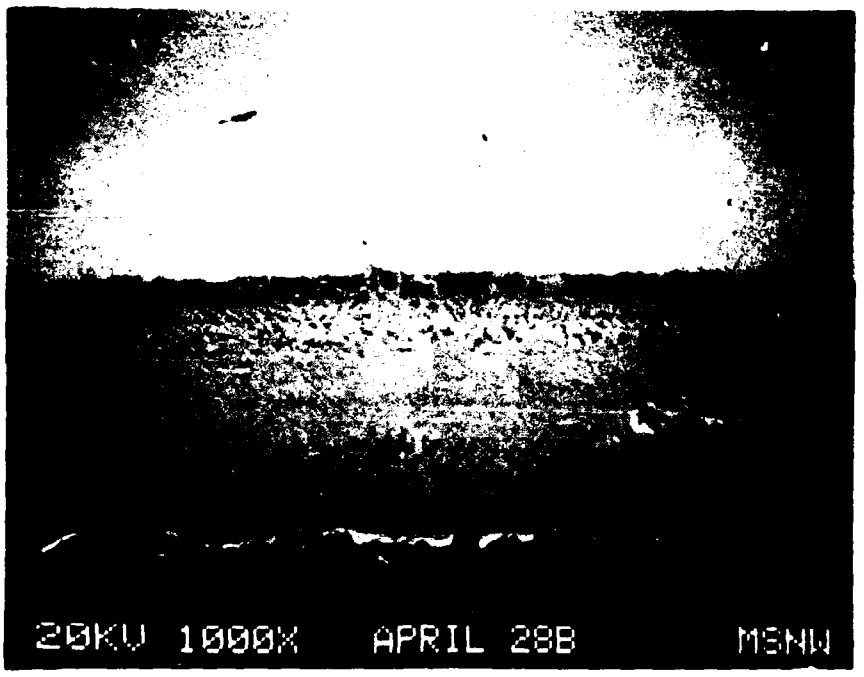


Figure 18. Cross section through chemically vapor deposited coating produced in cold-wall apparatus. Substrate material is Mo foil.

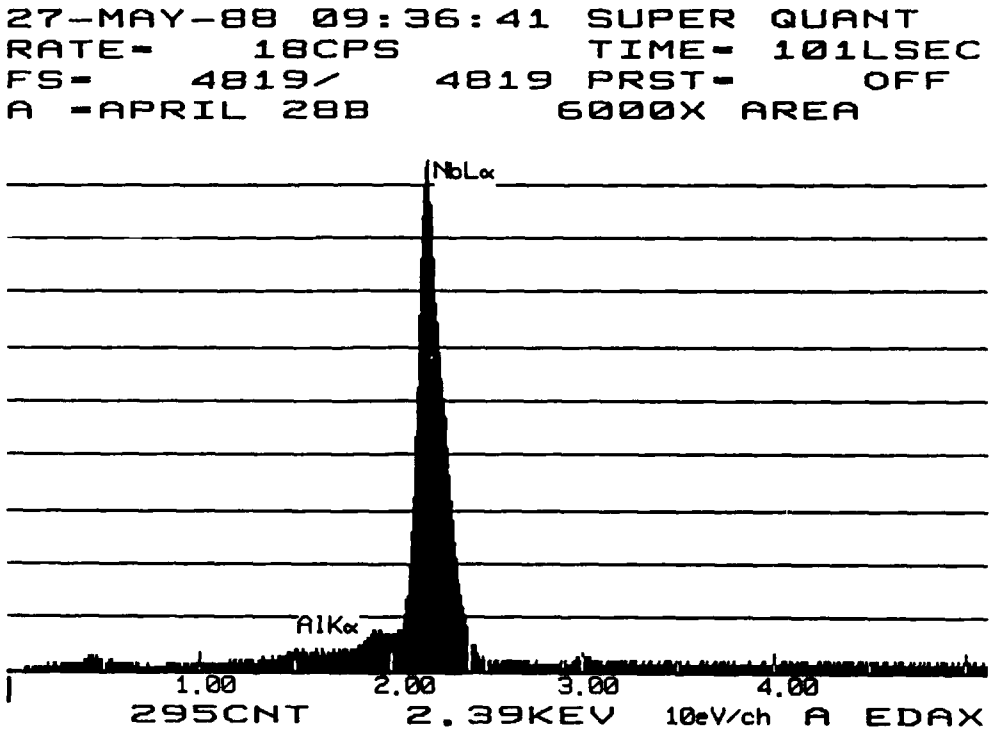


Figure 19. X-ray spectra of central portion of coating shown in Figure 18.

LABEL = APRIL 28B 6000X AREA
27-MAY-88 06:58:11
101.283 LIVE SECONDS
KV= 20.0 TILT= 0. TKOFF=20.
ZAF CORRECTION

ELEM	K	Z	A	F
ALK	0.0059	1.165	0.387	1.015
NBL	0.9745	0.997	0.990	1.000

ELEM	CPS	AT % ELEM
AL K	5.6278	4.27
NB L	407.5923	95.73
TOTAL		100.00

Table 11

Microhardness Results on Thick-Film Deposits (DPH, 50g Load)

Run No.	Microhardness, kg/mm^2
0503	169, 164, 170
0504	262, 257, 260
0428B	146, 145, 144

observed details of the process are consistent with a surface reaction-controlled process. Preliminary deposits produced in a cold-wall system were of low Al content and had an observable Nb-Nb_3Al two-phase microstructure.

2. The deposited materials are generally dense, very fine grained and homogeneous in composition if deposition process parameters are held constant during their synthesis.

3. Improved process control is required to reliably produce the desired compositions. The coating apparatus configuration should be changed to a cold-wall system to effect higher deposition rates for the product intermetallic films.

The following recommendations are offered:

1. The coating apparatus should be modified and optimized for cold-wall operation to avoid deposition on the coater tube walls and increase the deposition rate, particularly of Al, on the target substrate.

2. The coating source gas materials (Nb and Al halides) should be dispensed from independent, temperature-controlled evaporators. High purity inert carrier gases should be used.

3. Alternative precursor species, such as Nb and Al iodides, which may decompose easier and more completely than the corresponding chlorides, should be examined.

4. Detailed characterization of the deposits properties and composition should

be performed.

6.0 REFERENCES

1. C. E. Lundin and A.S. Yamamoto, Trans. Met. Soc. AIME, 236, 863, (1966).

2. G. A. Malets, Vesti. Akad. Nauk., B. SSR, Ser. Khim, Nauk. 6, 127, (1974).