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FABRICATION AND PROPERTIES OF CHEMICAL VAPOR DEPOSITED Nb LAYERS ON Al_2O_3 BODIES FOR THERMIONIC APPLICATION

by

P. FIEBELMANN

1968

Joint Nuclear Research Center
Ispra Establishment - Italy

Engineering Department
Technology

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For application in the 800 to 1100°C temperature range, brazing and diffusion bonding of Nb-plated Al_2O_3-bodies have proved feasible. Related results are also communicated.

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KEYWORDS

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NIOBIUM
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DEGASSING
IMPURITIES
ADHESION
SURFACES
THICKNESS
LAYERS
HIGH TEMPERATURE
BRAZING
DIFFUSION
BONDING
VAPORS

CONTENTS

FABRICATION AND PROPERTIES OF CHEMICAL VAPOR DEPOSITED Nb LAYERS ON Al_2O_3 BODIES FOR THERMIONIC APPLICATION(+)

INTRODUCTION

In connection with the Direct Conversion Research Programme there arose the problem of covering AL_2O_3 tubes with niobium. This was one of the problems which had to be solved before embarking on the fabrication of sandwich tubes with Nb-Al_2O_3-Nb.

1. PREPARATION OF CHEMICAL VAPOR DEPOSITED Nb LAYERS

1.1 Process

Interesting processes for applying Nb plates on ceramics are vacuum-vapor deposition and chemical-vapor deposition (CVD).

A CVD process was selected for its flexibility to adjust the deposition process to almost any kind of shape and size as well as for the possibility which it offers of co-depositing different elements.

There are a number of CVD processes for depositing Nb in existence, which for the most part are described in ref. 1 by Powell, Campbell, Gonser.

One of the reduction-type processes was considered in detail (refs. 2 and 3), where zinc reduction of niobium penta-chloride is used instead of hydrogen reduction. The deposition temperature may be as low as 500°C. The main reason for selecting this process was to achieve fine-grained deposits at a sufficiently low plating temperature, apart from practical advantages when working at lower temperatures.

The reaction proceeds as follows:

$$2\ NbCl_5 + 5\ Zn \rightarrow 5\ ZnCl_2 + 2Nb$$

The reaction takes place inside a reaction chamber, evacuated to a total pressure in the Torr range, heating the $NbCl_5$ and Zn to temperatures corresponding to the given pressure and feeding their vapors into the

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(+)Manuscript received on November 13, 1967.

chamber. $ZnCl_2$ is volatile and exhausted, whereas Nb is deposited on all surfaces inside the chamber.

For coating Al_2O_3 cylinders of about 100 mm in length and diameters up to 25 mm, a laboratory apparatus was developed and put into operation early in 1966.

1.2 Description of Apparatus

The basic components of the apparatus are outlined in Fig. 1. It consists of a vertically positioned quartz tube closed at the lower end. The upper part is sealed to a head, which itself is connected to a vacuum system. The head provides further openings for the thermocouples, the pressure gauge and a rotary feed-through for the driving spindle of the workpiece at the top. During the process the specimen is rotated and moved up and down. The course may be determined by setting end-switches.

There are three independent heating zones. The lower one is for $NbCl_5$ evaporation, the second for Zn evaporation and the upper one for providing heat to the coating chamber. The starting materials for the process, $NbCl_5$ and Zn, are placed in separate containers.

The lower end of the quartz tube contains granulated $NbCl_5$. An annular quartz chamber positioned above contains Zn granules. The annular Zn chamber is closed at the top and provides openings perpendicular to the work-piece for the Zn vapor. In this zone the Zn vapor meets the up streaming $NbCl_5$-vapor and the reaction takes place.

1.3 Depositing Conditions

Unlike what is proposed in refs. 2 and 3, total pressures lower than 1 Torr are applied. For the apparatus described, the following conditions give reproducible results:

total pressure	$10^{-1} \div 5 . 10^{-1}$ Torr
temperature of $NbCl_5$	102°C
temperature of Zn	460°C

Under such conditions the growing velocity for the layers is about 15μ/h.

It was found that the layers showed comparable quality for slight changes of the total pressure in either direction andfor adjustment of the $NbCl_5$ and Zn temperature in line with the pressure change. Higher total pressures tend to accelerate layer growth. In one case a thin-walled Nb tube was obtained instead of a deposit on the Al_2O_3 rod inserted. Increasing growing rate tends to increase surface roughness.

1.4 Preparation of Specimens

The specimens are Al_2O_3 tubes with 15 mm outside diameters and 35 mm in length or cones with similar dimensions.

In order to obtain a good adherence of the deposited layer, Al_2O_3 bodies should be carefully cleaned by one of the standard methods used in metallizing ceramics, i.e. degreasing, rinsing in HNO_3 and H_2O and firing to 1200°C in air.

1.5 Depositing Procedure

The starting and shutdown conditions have to be carefully observed. After the required pressure has been achieved, the specimen has to be heated to a temperature sufficiently high in order to avoid Zn condensation (e.g. 500°C). The Zn and the $NbCl_5$ should reach their maximum process temperatures at the same time. Operating conditions then have to be kept constant for the time the process lasts. When the temperatures are changed during the process, especially that of the Zn or $NbCl_5$, the reaction zone changes position, which almost always results in poor layer quality and uneven layer thickness.

To stop the reaction, the procedure has to be inverted. Fig. 2 shows the specimen, Zn and $NbCl_5$ temperature versus time during startup, continuous operation and shutdown at constant total pressure.

2. PROPERTIES OF DEPOSITS

All deposits were performed on high-density sintered Al_2O_3 bodies or porous plasma-sprayed Al_2O_3 layers.

2.1 Chemical Analyses

The quality and purity of the layers are conditioned largely by the cleanliness of the apparatus, the material of which it is made and the purity of the starting materials. The best results were obtained by using a quartz apparatus. Table 1 shows the chief impurities in such layers. If iron or steel crucibles are used for the evaporation of the Zn, together with Nb, traces of Fe, Ni, Cr are deposited in the order of 0.1 wt%.

After the deposition procedure, the specimens are outgassed at 1650°C for about 10 minutes prior to further application. During this heat treatment, the original Zn and Cl contents disappear completely, as shown by mass-spectrometer.

The 1 wt.% Zr content is related to a Zr impurity in the $NbCl_5$ delivered, which is used for the preparation of the specimens. This is advantageous because the metal parts which have to be connected to the layers also consist of Nb1Zr alloy.

TABLE 1

Chief Impurities in CVD-Nb Layers Fabrication by Zn Reduction of $NbCl_5$

	Zr wt%	Zn wt%	Cl wt%
prior to outgassing at 1650°C	< 1	< 0.01	< 0.05
after outgassing at 1650°C	1	-	-

2.2 Layer Thickness

Layers with thicknesses up to 35 μ have been fabricated. However, the process does not limit the thickness to this value. The movement of the specimen produces an equal layer thickness over the entire surface of the specimen. The uniformity of the layers on tube-type samples can easily be checked by directly heating them to red heat under vaccum by means of an RF generator. By reason of the fact that the specific electrical resistance varies with the layer thickness, differences become visible through different red-heat colours.

2.3 Porosity

From microscopic and fluorescence inspection it can be concluded that the layers are virtually non-porous. Sometimes pores parallel to the surface exist. Open pores from the surface to the substrate are unlikely to be found on account of the deposition procedure, in which successive layers are deposited. Tests to find out open pores are in preparation.

2.4 Surface Adherence

The surface adherence of the Nb deposits was found to be acceptable.

Nb layers deposited on ground surfaces of Al_2O_3 cones spall off when a mechanical stress 8 to 14 kg/mm^2 is applied perpendicular to the plate. For the tensile test the plated surfaces, 2 cones in every case, are joined by brazing or diffusion bonding. Table 2 shows diagrammatically the test arrangement and the results for diffusion-bonded specimens.

Fig. 3 shows a microsection of a tubular seal of low carbon steel to Al_2O_3 (Degussit Al 23 PT). From left to right are seen the steel, the brazing layer (Cu 2Ni), the Nb layer and the Al_2O_3. The Nb layer has a thickness of 2μ. In the ceramic, cracks are observed parallel to the surface, having been formed through rapid heating of the steel sleeve by radio frequency with a temperature rise of 200°C per minute, demonstrating the good surface adherence of the deposited layer.

In some cases, when the surface preparation or the various plating conditions have not been carefully complied with, layers partially spall off or tend to form bubbles during the outgassing process. The outgassing process may, therefore, be considered as a control for the layer quality.

2.5 Shear Strength

For measuring shear strength values, specimens were prepared consisting of an inner Al_2O_3 ring, to which a displaced concentric Nb ring was brazed (Cu2Ni). Under axial load, these connections show shear-strength values between 15 kg/mm^2 and 22 kg/mm^2. The results are summarized in Table 3. Higher values cannot be expected because the shear strength of the copper braze is of the same order. A fracture analysis results in 61,7% fracture in the brazing layer, 9% in the ceramic, and 29,3% between the ceramic and one of the plated layers.

2.6 Chemical Reaction Between Nb and Al_2O_3 Substrate

Deposits having a thickness in the order of a few thousand Å evaporate during outgassing between 1650°C and 1750°C at a furnace pressure of 10^{-5} Torr. Slight changes in surface roughness on unground Al_2O_3 tubes have been observed at such occasions. Strong surface reactions have never been observed. There is a change of colour from white to grey.

A calculation based on an evaporation velocity of 1.3×10^{-9} g/cm^2s for Nb (ref. 4) at 1727°C should result in the evaporation of about 15 Å in Nb layer thickness during outgassing. This was found to be in disagreement with the evaporation velocity observed, which was at least 2 orders of magnitude higher.

From a study (ref. 5) of the equilibrium interaction between Nb and Al_2O_3 between 1530°C and 1930°C, it is known that there exists a chemical reaction which increases with temperature. The predicted total pressure of the reaction products is about 2×10^{-4} Torr at 1730°C. Outgassing thin, not yet dense layers therefore seems to favour the chemical reaction by the evaporation of the reaction products, resulting in a quicker evaporation of the layer than there should be without the Nb being in contact with Al_2O_3.

3. JOINING POSSIBILITIES

The ceramic body metallized by a layer of Nb may be joined to other metallic parts by brazing or diffusion bonding. Joints performed by electron-beam welding or ultrasonic welding have not been attempted.

3.1 Brazed Bond

No particular difficulties arose during the brazing of Nb-covered ceramic parts to metallic parts. Nb layer thicknesses down to 2μ proved to be sufficient for such connections, although in many practical cases thicker layers are desirable.

3.2 Diffusion Bond

For high-temperature service, brazing materials often give rise to difficulties due to more or less rapid alloying with the metallization layer, causing a weakening or destruction of the joint. In order to eliminate the brazing material completely, a diffusion bond was made between a Nb sheet and a Nb-covered Al_2O_3 disk (SPK Masse E 37). Fig. 4 shows a micro-cross-section of such a bonding. The deposited Nb layer was 8μ thick. The bonding conditions used were 1150°C and 700 kg/cm^2 over a period of 3 hours (ref. 6).

4. PROPERTIES OF THE JOINTS

4.1 Leaktightness

Leaktightness measurements were made on 8 short-length cylindrically brazed tabular sandwiches. The specimens had a length of 10 mm and consisted of a concentric arrangement of an inside Nb tube, a Nb-covered Al_2O_3 tube and an outside Nb tube.

No leakage was found between the deposited layer and the ceramic. The samples were either vacuum-tight (6 specimens) or showed a reasonable leakage rate as a consequence of defects in the brazing layers.

4.2 Thermal Cycling Behaviour

The thermal cycling behaviour for Nb-Al_2O_3 sandwiches is very promising.

Fig. 5 shows a micro-section of the interface of a tubular Nb-to-Al_2O_3 connection brazed by Cu2Ni after 6 thermal cycles between 500°C and 1000°C. The average heating rate was 198°C/min., the cooling rate being 163°C/min. No cracks along the interfaces or in the ceramic could be detected.

5. CONCLUSIONS

The CVD process considered is suitable for covering Al_2O_3 bodies with Nb layers having a good surface adherence. For the fabrication of metal ceramic sandwiches the process is of interest, as it is possible to effect diffusion bondings between the Nb sheet and the deposited layers.

Furthermore, the examinationshave shown that the chemical vapour deposition of Nb on Al_2O_3 results in layers having a quality comparable with a good standard metallization.

6. ACKNOWLEDGMENT

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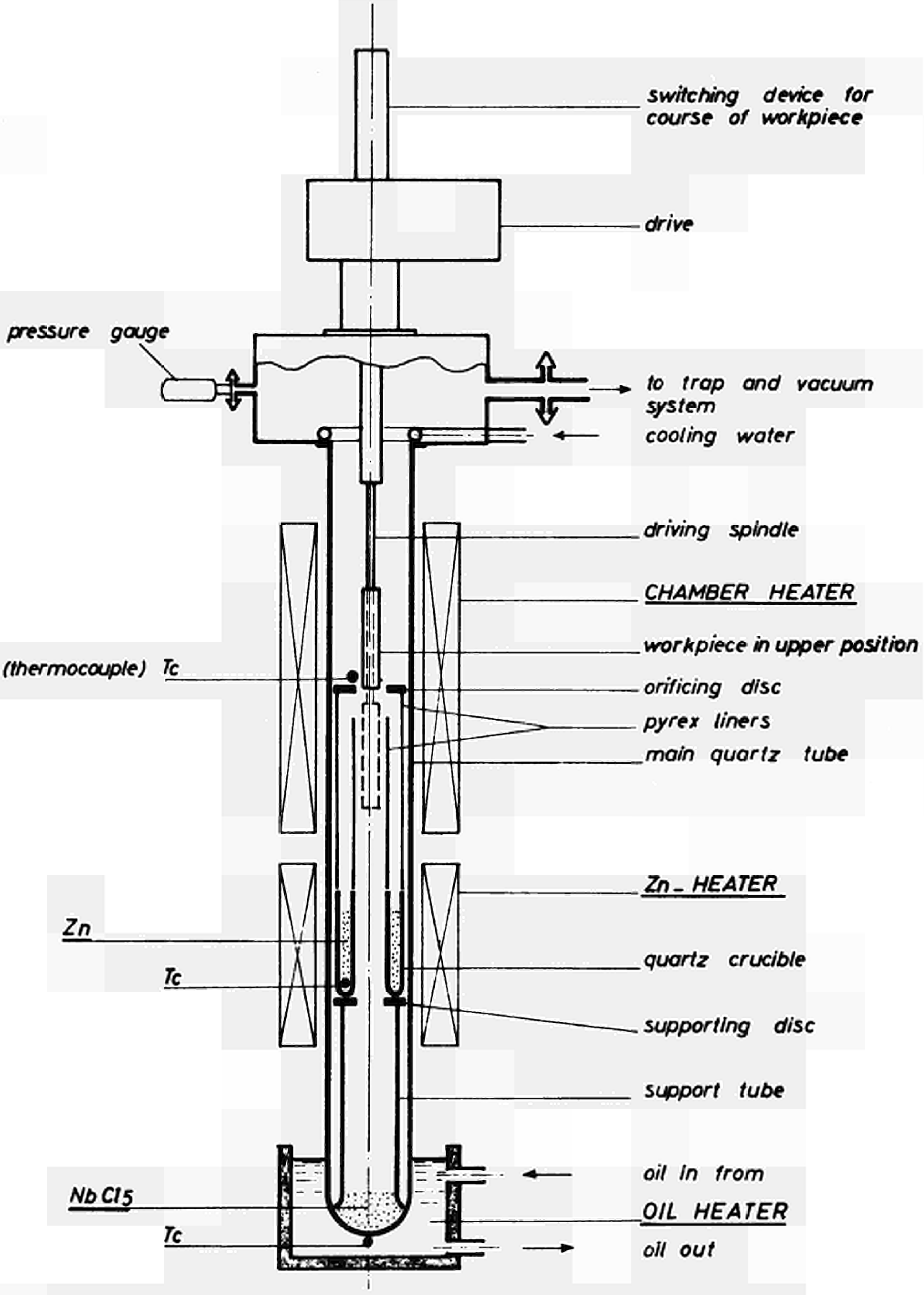

Fig. 1 APPARATUS FOR CHEMICAL VAPOR DEPOSITION OF Nb BY Zn-REDUCTION OF $NbCl_5$

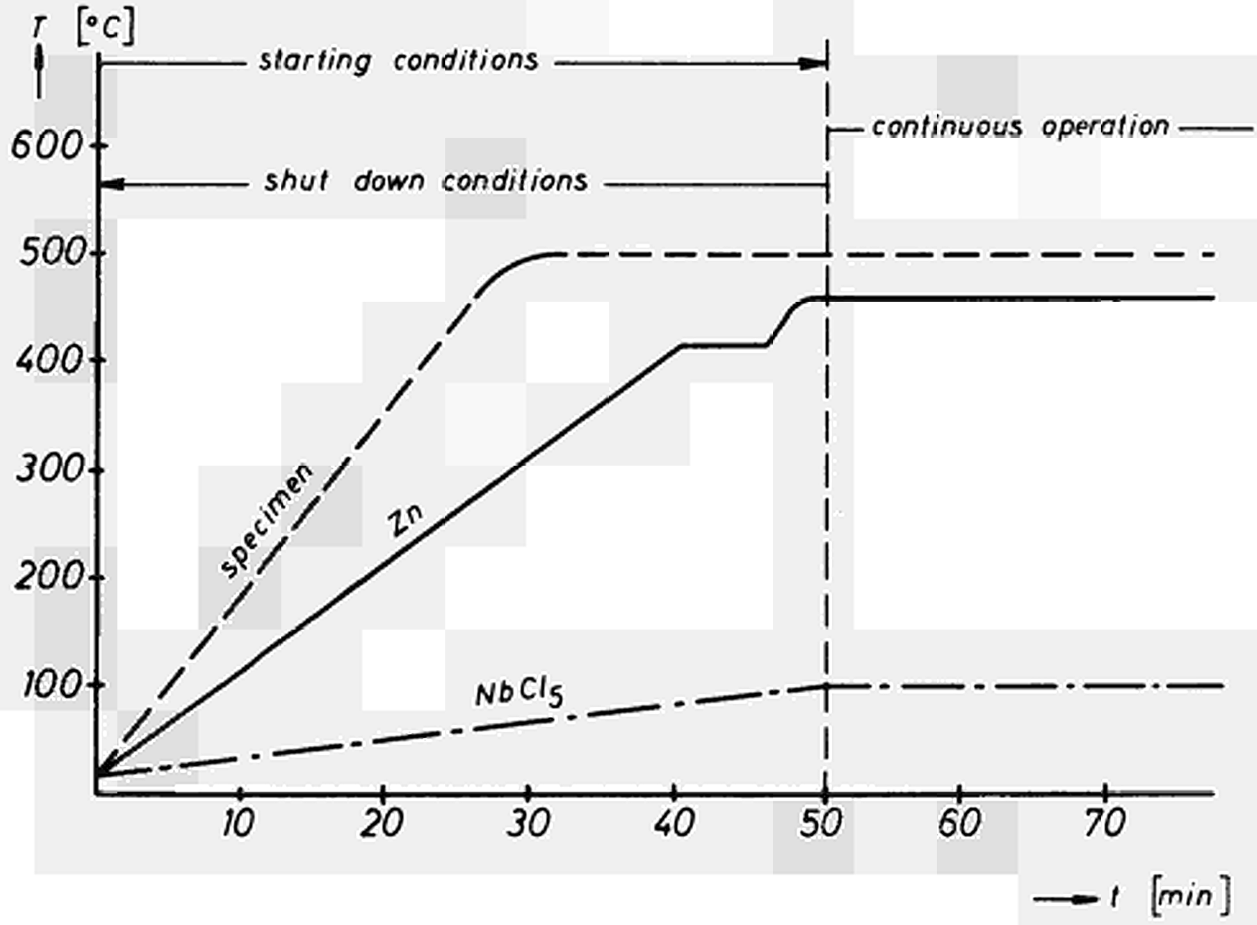

Fig. 2 TEMPERATURE CONDITIONS FOR CHEMICAL VAPOR DEPOSITION OF Nb BY Zn-REDUCTION OF $NbCl_5$ AT CONSTANT TOTAL PRESSURE

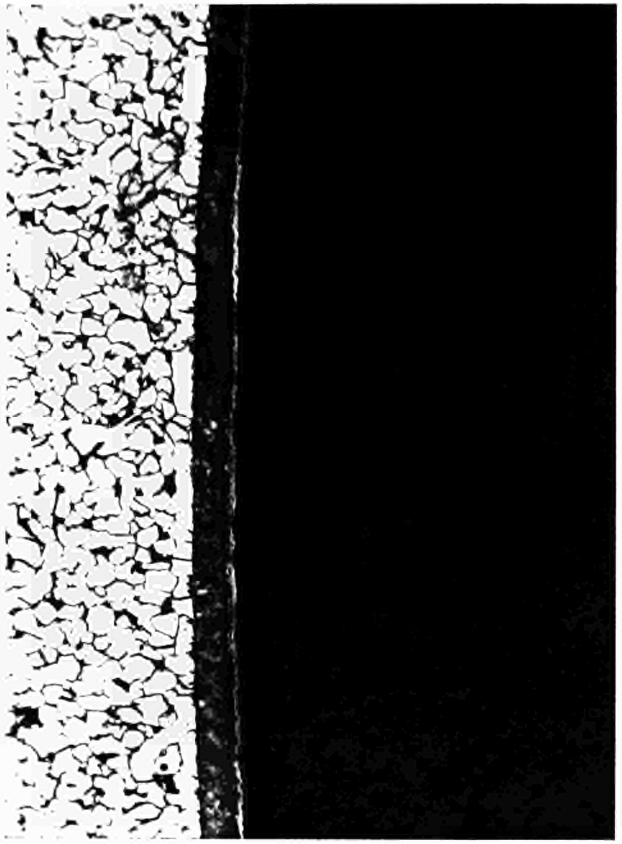

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FIG. 3

Cu2Ni-Brazed Low-Carbon-Steel Bond
To A CVD Nb Layer On Al_2O_3 After Rapid Heating

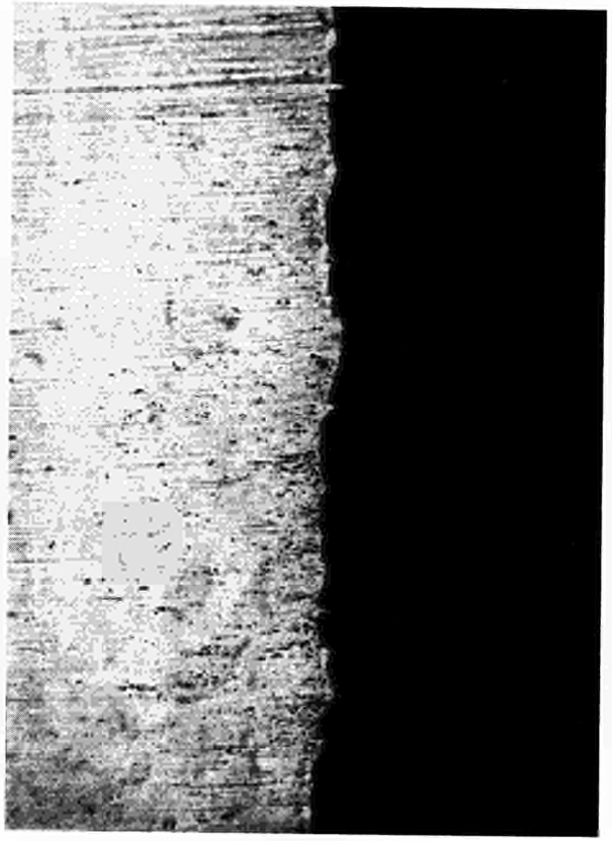

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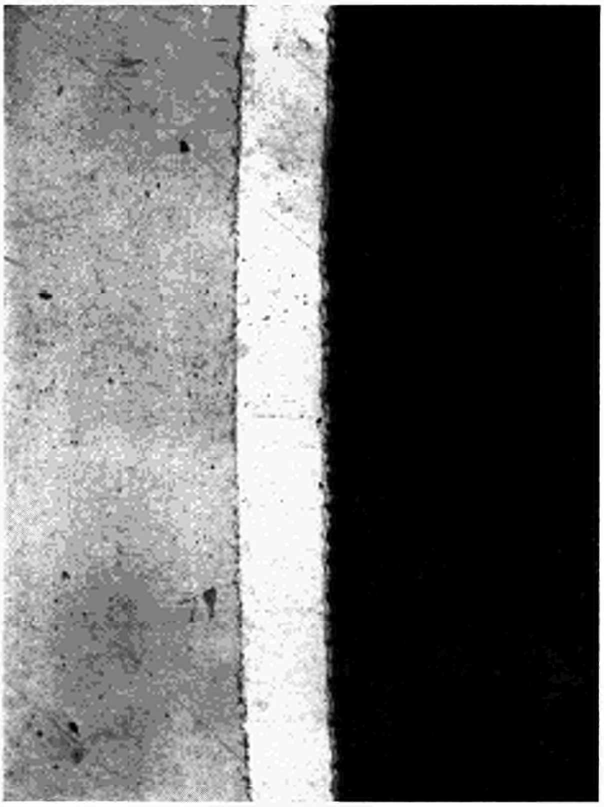
FIG. 4

Nb Self-Bond Between A Nb Sheet
And A CVD Nb Layer On High-Purity, High-Density Al_2O_3



200 ×

FIG. 5

Cu2Ni-Brazed Nb Bond To A CVD Nb Layer On Al_2O_3
After thermal Cycling Between 500 and 1000°C

TABLE 2

SURFACE ADHERENCE MEASUREMENTS ON CVD Nb LAYERS DEPOSITED ON GROUND AL_2O_3 SPK E 37 "CONES"

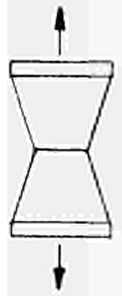
Test Arrangement	Deposition Run	Nb Layer Thicknesses (μ)	Bond	Rupture Strength kg/mm^2	Observation Main Fracture Location
	V 51	35/35	Diffusion Bond	8, 3	Between Nb Layer and AL_2O_3
	V 51	35/35	Diffusion Bond	14, 1	Between Nb Layer and AL_2O_3
	V 52	30/35	Diffusion Bond	12, 5	Between Nb Layer and AL_2O_3
	V 53	28/28	Diffusion Bond	11, 9	Between Nb Layer and AL_2O_3
	V 53	28/26	Diffusion Bond	9, 2	Between Nb Layer and AL_2O_3
	V 55	25/25	Diffusion Bond	10, 6	Between Nb Layer and AL_2O_3
	V 55	25/26	Diffusion Bond	11, 2	Between Nb Layer and AL_2O_3

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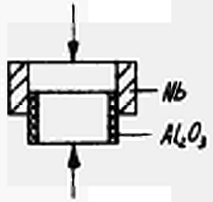
TABLE 3

SHEAR STRENGTH MEASUREMENTS ON CVD Nb LAYERS DEPOSITED ON NOT GROUND AL_2O_3 DEGUSSIT AL 23 PT TUBES

Test Arrangement	Deposition Run	Nb Layer Thickness (μm)	Bond	Shear Strength kg/mm^2	Observation Main Fracture Location
	V 19	22	Cu 2Ni Brazed	17	Between Nb Layer/AL_2O_3
	V 19	22	Cu 2Ni Brazed	16,1	Between Nb Layer/Brazing Layer
	V 19	22	Cu 2Ni Brazed	21,7	Between Nb Layer/Brazing Layer
	V 19	22	Cu 2Ni Brazed	22	Between Nb Layer/AL_2O_3
	V 46	16	Cu 2Ni Brazed	17,5	Brazing Layer
	V 46	16	Cu 2Ni Brazed	18,1	Brazing Layer
	V 46	16	Cu 2Ni Brazed	15	50% Between Nb Layer/AL_2O_3
	V 48	20	Cu 2Ni Brazed	20,7	Brazing Layer; AL_2O_3
	V 48	20	Cu 2Ni Brazed	17,7	Brazing Layer

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> Alfred Nobel

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