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The Coating of Metals with Titanium Diboride by Chemical Vapor Deposition

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ABSTRACT

This study is an experimental investigation of the chemical vapor deposition of titanium diboride on metallic substrates by the hydrogen reduction of $TiCl_4$ and BCl_3 at temperatures between 850°C and 1100°C. Kovar, tantalum, and several stainless steels were found to be suitable substrates since they could withstand the deposition temperature, had adequate resistance to HCl, a by-product of the deposition reaction, and had thermal expansion coefficients sufficiently close to that of TiB_2 ($\leq 10 \times 10^{-6}/^{\circ}C$). The TiB_2 coatings produced were 68.2% Ti and thus near stoichiometry and had very low impurity content. They had Knoop hardnesses averaging 3300 kg/mm^2 and exhibited extraordinary erosion resistance.

MASTER

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DISCLAIMER

INTRODUCTION

Titanium diboride is a very stable, high melting point refractory. It has a high thermal conductivity, low thermal expansion, and as a result, good resistance to thermal stresses. In this respect, it is superior to most oxides and carbides.[1] It is an extremely hard material, and its hardness is not as temperature-dependent as most other refractories.[2] It has good chemical resistance, particularly at high temperatures, and is unaffected by most acids, molten metals, and nonbasic slags and salts.[3]. It has better oxidation resistance than the carbides and nitrides. Table I summarizes its properties and compares them with those of other refractory materials.[4,5,6,7]

Not only are these properties of considerable scientific interest, but they also make titanium diboride a promising candidate for many engineering applications where conditions of erosion, corrosion, and high temperature are found. Because of its refractory nature, however, high purity, dense TiB_2 is difficult to prepare. The common preparation processes are listed in Table II.[5,8] The major drawbacks of these processes are the need for very high temperature in most cases and the production of impure materials which may lead to considerable degradation of the properties. In addition, with the exception of the fused salt electrolysis, these processes do not easily lend themselves to the formation of coatings.

High purity coatings may be achieved by another process--chemical vapor deposition (CVD). The reactions leading to the CVD of TiB_2 were investigated as far back as 1931 by Moers[9] and more recently, by Walther[10] and several others.[11,12,13,14] These investigations were generally limited to the formation of powder or the coating of graphite in the temperature range of 1250° to 1800°C. At these temperatures the use of metal substrates is severely restricted, since most common alloys would either melt or undergo excessive grain growth or other damage. To broaden the potential of TiB_2 coatings, it is essential to develop a process that does not require such high temperatures and is compatible with metal substrates.

This study was then designed with these objectives: (1) the investigation of the CVD of TiB_2 at temperatures below 1200°C, (2) the systematic investigation of potentially compatible metal substrates, (3) the analysis of the physical properties of the TiB_2 coating and their relationship with the CVD parameters.

Thermodynamic Considerations

The chlorides of boron and titanium are generally considered more suitable than the other halides for CVD of TiB_2.[11,12,13,14] The gaseous synthesis of TiB_2 is according to the reaction:

$$TiCl_4 + 2\ BCl_3 + 5\ H_2 \rightarrow TiB_2 + 10\ HCl \qquad (1)$$

It is also necessary to consider the formation of the respective metals by hydrogen reduction:

$$TiCl_4 + 2\ H_2 \rightarrow Ti + 4\ HCl \qquad (2)$$

$$BCl_3 + 3/2\ H_2 \rightarrow B + 3\ HCl \qquad (3)$$

The free energy changes for these three reactions are illustrated in Fig. 1.[13,15,16] For reaction (1), these changes become negative at approximately 925°C; for reaction (2), above 2700°C; and for reaction (3), above approximately 1200°C (although values in the literature are not in complete agreement). It is therefore likely that below 1200°C reaction (1) would be dominant and the formation of free titanium may be reasonably ruled out. The CVD process is also governed to a large extent by kinetic factors, and the thermodynamic predictions must be viewed accordingly.[17]

EXPERIMENTAL

CVD Apparatus and Process

The CVD apparatus is shown schematically in Fig. 2. The sample was heated inductively in a fused silica reactor. In the case of nonmagnetic materials, a steel susceptor was used as the sample support. A Pt -10% Rh thermocouple sheathed in a fused silica tube was placed in contact with the sample. The temperature was controlled to ± 10°C. Great care was taken to exclude air from the reactor since some of the metals used, tantalum in particular, have great affinity for oxygen.

The gases were fed to the reactor through mass flowmeters. Argon was supplied from a liquid Ar tank and was passed through a gettering furnace before entering the reactor to maintain an impurity level of less than 0.1 ppm of O_2 and H_2O. The impurity level of hydrogen was maintained at less than 0.5 ppm by passing it through a heated Pd diffusion element.

BCl_3 was supplied directly from a cylinder with the following impurity analysis: Si < 10 ppm, $Cl_2 < 100$ ppm, $CoCl_2 < 900$ ppm. $TiCl_4$ was metered into the reactor after passing through a vaporizer at 150°C. The $TiCl_4$ had the following analysis: Fe < 1 ppm, Si < 20 ppm, Sn < 100 ppm. The $TiCl_4$ line was heated to 135°C to prevent clogging.

The reactor was evacuated to less than 0.01 torr. It was then backfilled and flushed with hydrogen. The sample was heated to the desired deposition temperature and the hydrogen flow was maintained for 20 minutes to clean the sample surface of any residual contamination. The reactive gas mixture was then introduced and maintained for 1.5 hours. The sample was cooled to room temperatures in flowing argon.

Substrates

The substrates used in this study included Ni, Ta, Kovar, and Types 304 and 446 stainless steel. Properties of these materials are listed in Table III. The Ta and Kovar samples were approximately 5 x 1.25 x 0.3 cm and all other specimens were disks 2.5 cm in diameter and 0.6 cm thick. Surface preparation consisted of ultrasonic cleaning with isopropyl alcohol, a light abrasion, and a second ultrasonic cleaning. The sample was then placed in the reactor without delay.

Parametric Study

In addition to the evaluation of the substrates listed above, the following deposition parameters were investigated:

1. Temperature of deposition from 850°C to 1150°C.
2. Gas ratio: the flow of $TiCl_4$ and BCl_3 was maintained constant at the stoichiometric ratio of 12 ml/m to 24 ml/m, respectively. Three hydrogen flows were investigated: 360 ml/m, 800 ml/m, and 7200 ml/m.

Hardness and Erosion Tests

The samples were cross-sectioned and polished through 1 μm diamond paste using standard metallographic techniques. Microhardness tests on the coating edge were then conducted using a Knoop indenter with a 100 gm load.

Erosion tests were conducted on the coatings with an S.S. White Model C "Airbrasive" unit. 50 µm Al_2O_3 was used as the abrasive and the impingement angle was 45°. Several additional materials were eroded as standards for comparison of relative erosion resistance. These include a WC 15% Co sintered carbide and Types 304 and 316 stainless steel. Tests were run at room temperature in air with 20% R.H. Specimens were eroded for a total of 25 minutes. During the test each specimen was periodically weighed to determine weight loss. Ultrasonic cleaning in acetone preceded every weighing. Weighing repeatability was ± 0.0001 gm.

RESULTS AND DISCUSSION

CVD Conditions

Table IV summarizes the CVD conditions used in this study. In low flow condition (molar ratio $H_2/[TiCl_4+2\ BCl_3]$ ~10 for a total flow of 396 ml/m), deposition was accompanied by the formation of vapor, particularly in the vicinity of the heated sample, and a powdery purple deposit was formed on the reactor wall. This would indicate a certain amount of gas phase nucleation, which is to be expected when gas velocity is low, and the gases may be heated to reaction temperature before coming in contact with the heated substrate.[18] Partial decomposition of $TiCl_4$ also occurs to form the purple solid $TiCl_3$. Under these conditions the HCl formed as a product of reaction (1) remains in relatively high concentration near the surface of the substrate and reacts with it if the temperature is sufficiently high. This temperature appears to be 950°C for 446 stainless steel, 1000°C for 304 stainless steel, 1050°C for Kovar, and 1100°C for nickel. Tantalum was unaffected at any temperature.

At the high total gas flow (7236 ml/m), there was less vapor and less powdery deposit on the reactor wall. Because of the high gas velocity, vapor phase nucleation was less likely than at low gas flow; furthermore, HCl was swept away in the gas stream as soon as it formed. The various substrates still suffered HCl attack (with the exception of tantalum), but the upper temperature limit where attack begins was 50 to 100°C higher than at low gas flow. These results are in general agreement with experimental results reported in the literature.[19,20] Chromium is more readily attacked by HCl than either iron, nickel, or cobalt, which explains why 446 stainless steel (27% Cr) is more readily attacked than 304 (18% Cr).

Effect of CVD Conditions on Deposition Rate

Table IV shows the effects of deposition temperature on the rate of deposition of the TiB_2 coating. At 850°C, the rate is relatively slow; it increases to 1000°C and appears to remain constant above 1000°C. The total gas flow also has an effect on the rate of deposition, although to a lesser degree than the temperature. At low gas flow (396 ml/m), the rate is approximately 50% higher than at the high total gas flow (7236 ml/m). It should be pointed out that the flow of BCl_3 and $TiCl_4$ always remains constant and only the flow of H_2 varies. These results are in agreement with previous studies.[11,13]

Substrate Requirements

The CVD of TiB_2 places limitations on the type of metal substrate that can be used. The metals must meet three prerequisites: ability to withstand the deposition temperature, resistance to HCl attack, and low thermal expansion. Low melting point metals are not suitable, and of the steels, those that do not go through a phase transformation below the deposition temperature are more desirable.

Of the materials listed in Table III, only Ta, Kovar, and 446 stainless steel proved suitable.* Nickel was marginal and generally yielded cracked or spalled coating. Type 304 stainless steel yielded highly-cracked coatings.

There is a direct relationship between the respective coefficient of thermal expansions of TiB_2 and the substrate and the residual strain in the coating. When the ratio of the two coefficients is essentially one, as with Kovar and tantalum (Table III), the coating does not crack on cooling due to thermal stresses. With 446 stainless steel, the ratio is slightly higher, yet not enough to generate significant stress, and the coating is also free of cracks. With nickel, the ratio is approximately 2 to 1 and the coating shows a network of small cracks. With 304 stainless steel, the ratio is 3 to 1, spalling and cracking is severe during cooling and further spalling

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* Note: Low carbon steel (1018) was successfully coated late in the study at 800°C.

occurs when the sample is scratched or machined. As expected, these effects resulting from thermal expansion differences become less pronounced as the deposition temperature is lowered.

Coating Composition and Morphology

The TiB_2 coatings produced are very pure. Electron microprobe analysis showed a Ti content of 68.2 ± 1.3 wt%, the balance being B (by difference). Emission spectroscopy showed a very low level of impurities (Table V). These composition results are in excellent agreement with the stoichiometric composition of TiB_2 which is 68.8 wt% Ti.

X-ray diffraction analysis yielded lattice parameters of a = 3.0283 ± .0009 Å and c = 3.2292 ± .001 Å. These values are in excellent agreement with those reported in the literature.[5,7,24,25] Both x-ray and SEM analysis indicate a very small crystallite size on the order of 50 - 300 Å with the larger sizes corresponding to higher deposition temperatures.

The morphology of the coatings changed strongly with deposition temperature. At temperatures above 1000°C, the coatings consisted of a coarse nodular structure with rodlike appendages (Figs. 3a, 4a). Below 1000°C, the coatings were smoother and no rodlike structures were present (Fig. 3b). A TiB_2 coating deposited at 850°C on 446 stainless steel was reflective and lacked a nodular structure.

Hardness and Erosion Resistance

Microhardness of hard materials such as TiB_2 is a difficult quantity to measure. It varies widely with indentor load and usually a range of values can be found in the literature.[26] In this study, Knoop hardness of the TiB_2 ranged from 3722 kg/mm^2 for a 77 μm coating deposited at 850°C on Type 446 stainless steel to 2724 kg/mm^2 for a 25 μm coating deposited at 1050°C on Kovar. Cracking of the thinner coatings no doubt leads to spuriously low hardness values. The typical average hardness of 2300 - 3300 kg/mm^2 agrees well with the measurements of other investigators. (Table I).

Under severe erosion conditions, TiB_2 coatings on Kovar had weight losses averaging 10^{-2} times that of a WC-15% Co alloy. Most of these weight losses were in the initial stages of erosion when the abrasive removed loosely bound TiB_2 nodules. The 1100 and 1050°C coatings on Kovar failed early in erosion. These coatings were not adherent due to HCl attack as discussed previously. The 900, 950, and 1000°C coatings showed outstanding erosion resistance. The initial high weight loss of the 950°C sample shown in Fig. 4 occurred during fracturing in an area away from the erosion area.

CONCLUSIONS

This study demonstrated conclusively that an extremely hard, erosion-resistant, dense and adherent coating of TiB_2 can be applied on metal substrates by chemical vapor deposition at temperatures as low as 850°C (and possibly lower). The choice of substrate is limited by the requirements of resistance to the HCl attack, the ability to withstand the deposition temperature, and having a thermal expansion close to that of TiB_2. In this study, Kovar, tantalum, and Type 446 stainless steel were successfully coated and, undoubtedly, other substrate should also be satisfactory, such as molybdenum, tungsten, and some carbides and oxides. It is also very possible that TiB_2 can be deposited on low carbon steels and tool steels, as indicated by preliminary experiments.

Thus, with its unique erosion-corrosion resistance and its ability to be applied on a wide variety of metals, it appears that chemically vapor-deposited TiB_2 is an excellent candidate for a wide variety of engineering applications.

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PROPERTIES OF SELECTED REFRACTORY MATERIALS

Table I - (Ref. 4,5,6,7)

Material	Melting Point °C	Density G/cm^3	Thermal Conductivity cal/cm sec°K	Thermal Expansion ppm °C	Vickers Hardness kg/mm^2 (2)	Oxidation Threshold in air °C
B_4C	2450	3.52		4.5	3700	900
WC	2776	15.77	0.07	5.0	2400	700
SiC	2250 dissociation	3.21	0.10	5 to 7	3500	1000
Al_2O_3	2050	4.0	0.07	8.0	2100	1950
TiC	3067	4.92	0.05	7.4	3200	800
TiN	2949	5.39	0.046	9.4	2000	1200
TiB_2	3000$^{(1)}$	4.52	0.058	5.6 - 6.6	3400	1400

NOTE: (1) There is considerable discrepancy in the value of the melting point from 2600°C to 3230°C.

(2) Reference 26 for the hardness #2, except TiN (Ref. 4).

Table II

PREPARATION PROCESSES OF TiB_2

Process	Temperature °C	Purity
Direct union of the elements	1300 to 2050	90 - 98%
Reduction of oxide with boron	1400	Unreduced oxide present
Hot pressing	> 2000	Impurities in powder mixture
Fused salt electrolysis	1000	Carbon and bath impurities
Electrodeposition from the oxide	900 - 1100	Metallic impurities

Table III

PROPERTIES OF SUBSTRATES FOR TiB_2 DEPOSITION

Material	Composition %	Density g/cm^3	Melting Point ^oC	Thermal Expansion	Reaction with HCl
Stainless Steel Type 304	C 0.08-0.020 Cr 17-19 Ni 8-10 Mn < 2	7.93	1375	16.2 to 19.9	Attacked above 370°C
Stainless Steel Type 446	Cr 25 Ni < 0.5 Mn < 2	7.38	1450	9.5	Attacked above 370°C
Kovar	Ni 28 Co 18 Fe 54	8.2	1450	6.2	Attacked at elevated temperatur
Tantalum	-	16.6	2977	6.5	Not attacked
Nickel	-	8.9	1455	13.3	Attacked above 540°C
Chromium	-	7.1	1903	6.8	Attacked
Iron	-	7.86	1535	10.0	Dissolved in dilute HCl[20]
TiB_2	-	4.52	3000	5.6 to 6.6	Not attacked[7]

Table IV

EFFECT OF CVD ON DEPOSITION RATE OF TiB_2 COATING

Total Flow ml/m(1)	Deposition Temperature °C	Deposition Rate $g/cm^2/hr \times 10^{-3}$ On Kovar	On Tantalum
396	900	14.4	9.0
-	950	21.2	21.2
-	1000	35.7	22.1
-	1050	43.3	40.2
836	850	12.2	8.5
-	900	19.0	11.7
-	950	25.0	15.6
-	1000	33.4	33.4
-	1050	33.9	31.6
7236	850	10.8	8.1
-	900	14.0	10.3
-	950	26.2	17.6
-	1000	24.4	26.2
-	1050	25.7	22.1
-	1100	27.5	27.5

NOTE: Flows of $TiCl_4$ and BCl_3 remain constant at 12 and 24 ml/m respectively.

Table V

COMPOSITION OF TiB_2 COATING

Composition (Electron Microprobe)

Ti	68.2% ± 1.37
B	Balance

Impurities (Emission Spectroscopy)

Cr	< 100 ppm
Ca	< 100 ppm
Al	none detected
Cu	none detected
Fe	< 100 ppm
Mg	none detected
Si	< 100 ppm

Lattice Parameters (X-ray Diffraction)

$a = 3.0283$ Å ± 0.0009

$c = 3.2292$ Å ± 0.001

$Lc \sim 300$ Å (at $T_D = 1100^\circ C$)

$Lc < 300$ Å (at $T_D = 900^\circ C$)

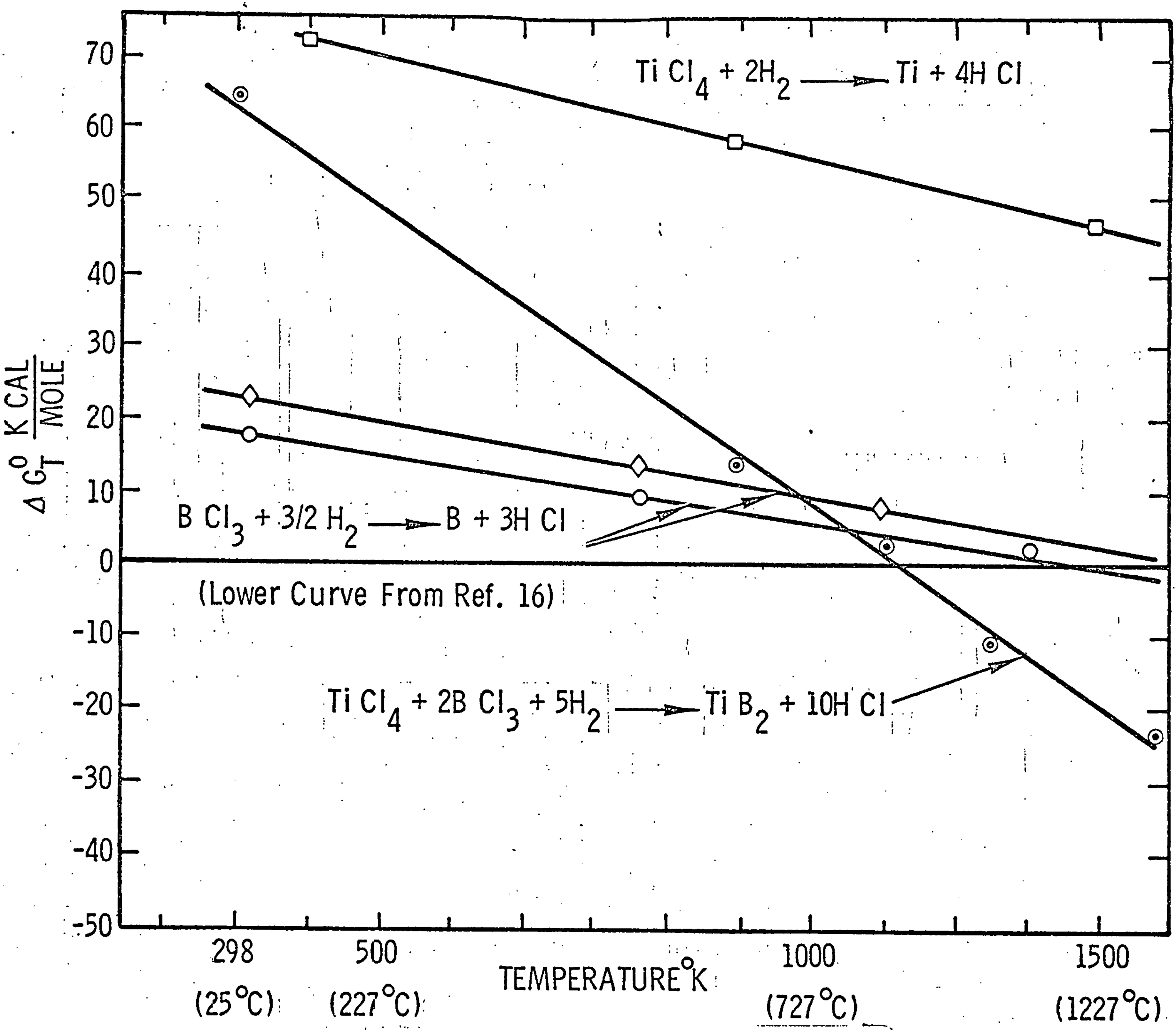

Fig. 1 - Calculated changes of free energy of formation of titanium, boron, and TiB_2 by the hydrogen reduction of the chlorides. (REF. 13, 15, 16)

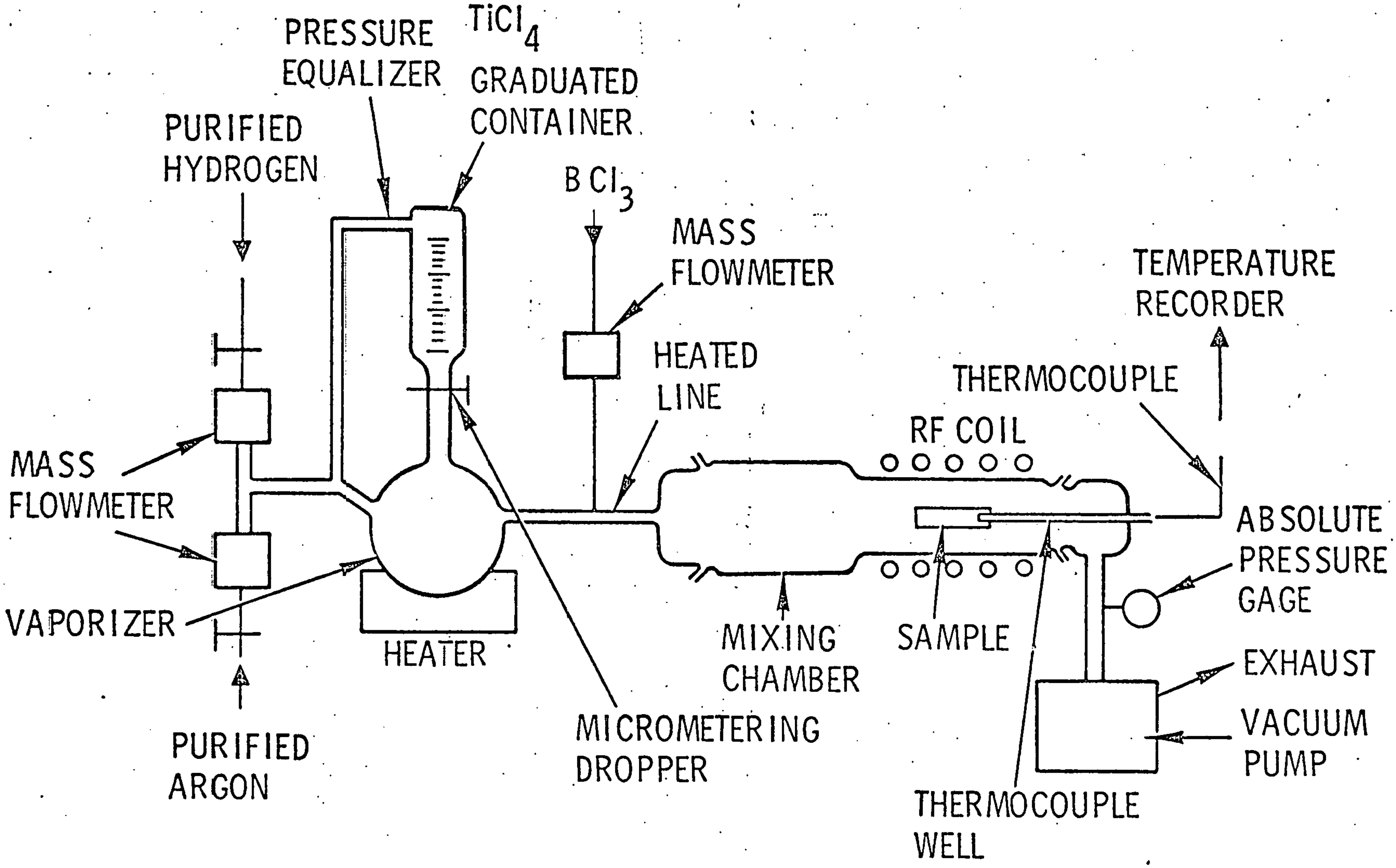

Fig. 2 - Schematic of CVD Apparatus

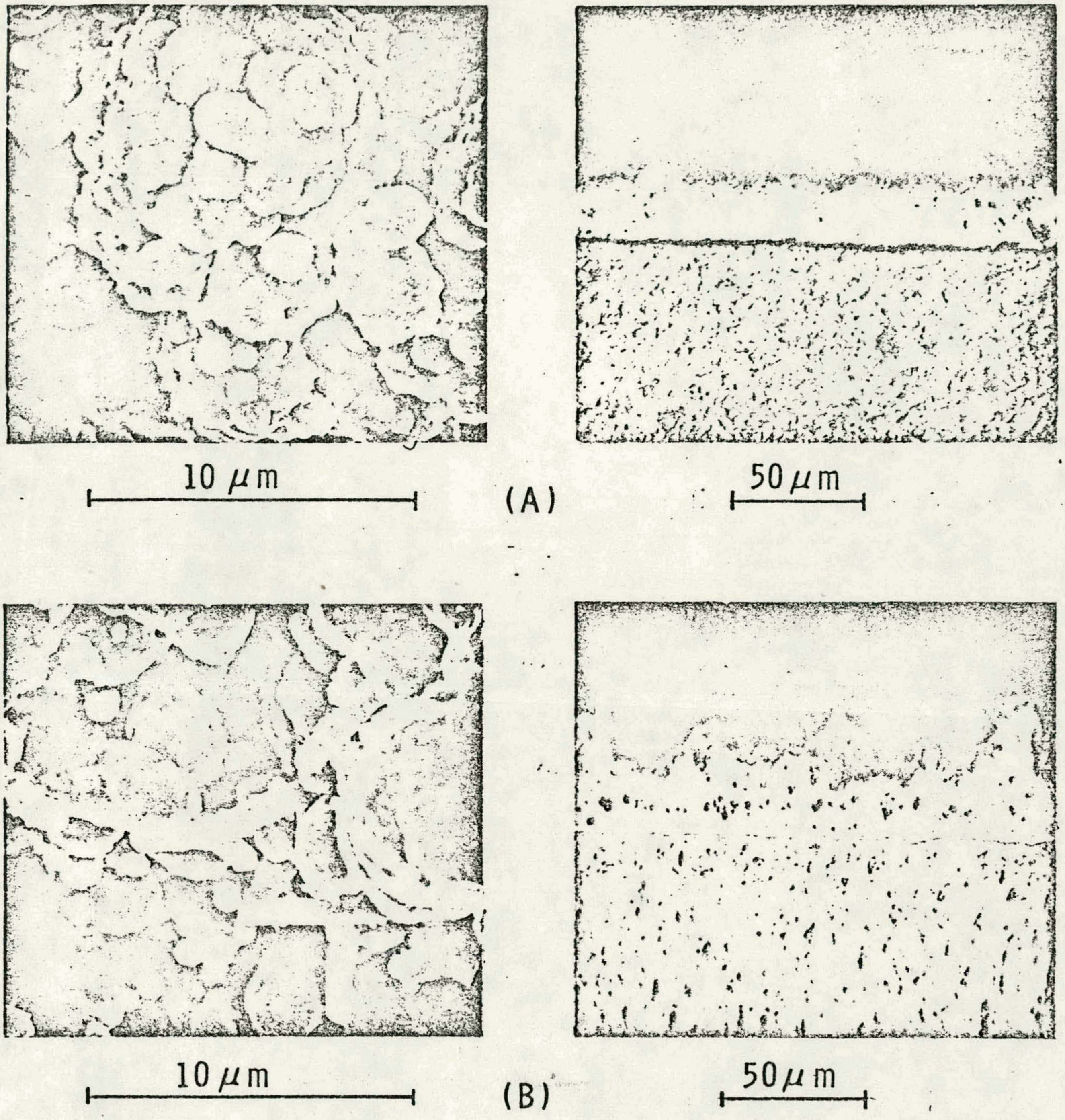

Fig. 3 - Photomicrographs of TiB_2 coatings
deposited on Kovar. Deposition
temperatures are (a) 1000°C
(b) 950°C

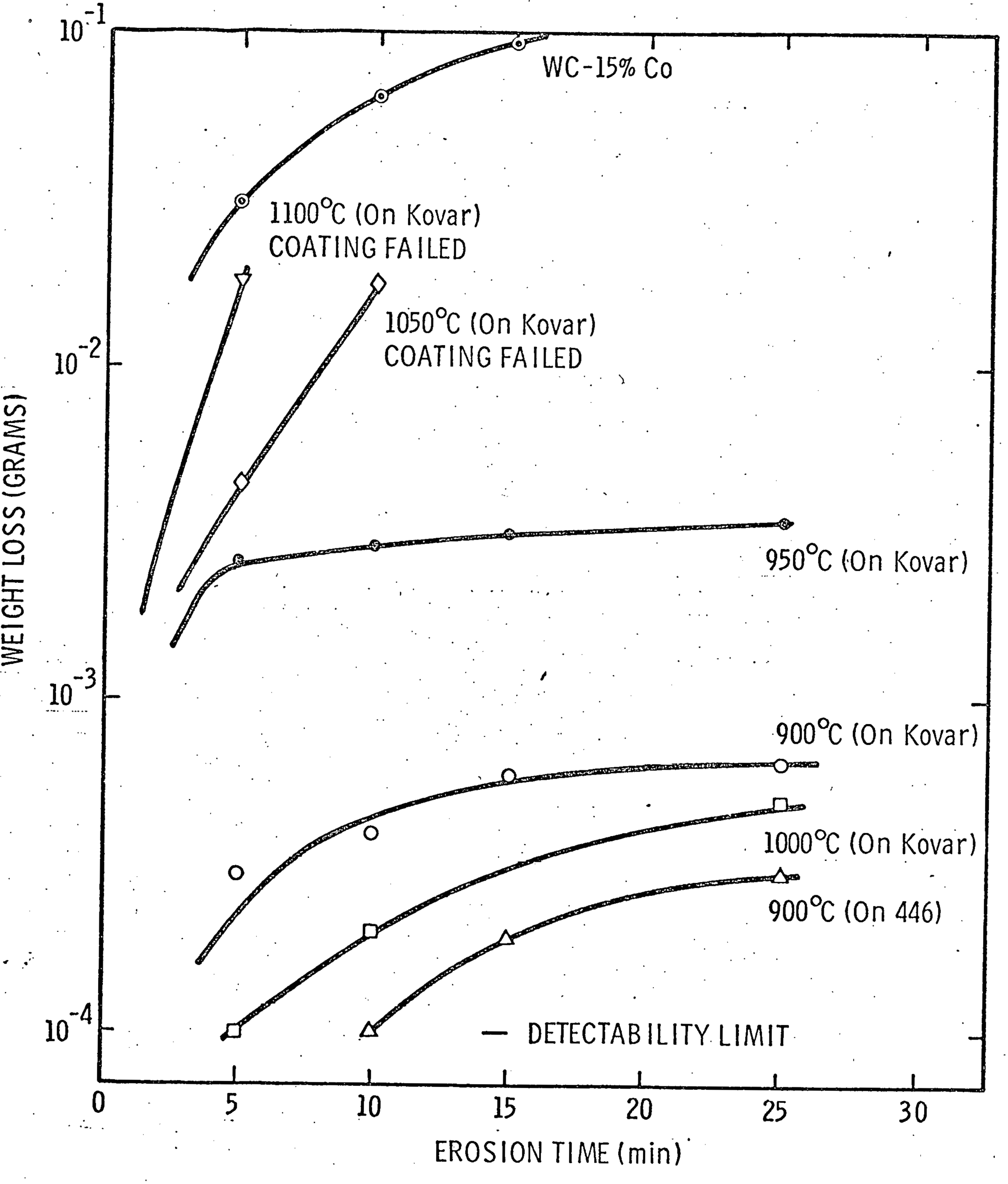

Fig. 4 - Erosion of TiB_2 coatings as a function of deposition temperature.

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