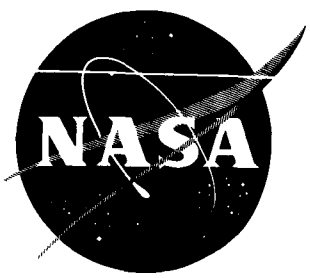


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# TECHNICAL NOTE

D-722

**TITANIUM NITRIDE: AN OXIDIZABLE COATING FOR THE  
HIGH-TEMPERATURE PROTECTION OF GRAPHITE**

By N. T. Wakelyn

Langley Research Center  
Langley Field, Va.

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**  
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HIGH-TEMPERATURE PROTECTION OF GRAPHITE

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## SUMMARY

A titanium nitride coating for graphite, prepared by the vapor-deposition process, protected test specimens for 60 seconds in a supersonic ceramic-heated air jet with a stagnation temperature of approximately  $2,250^{\circ}$  K. For the same test conditions, coated specimens showed no damage to the graphite body for the 60-second test, whereas uncoated specimens were very severely damaged after 20 seconds and were destroyed toward the end of the test. A discussion of the coating of these graphite specimens and of some of the conditions necessary for the utilization of oxidizable substances as oxidation-protective coatings for bodies facing high convective heat transfer in the atmosphere is presented.

## INTRODUCTION

Graphite has good high-temperature strength in comparison with other materials and has the characteristic that its strength increases with increasing temperature up to about  $2,750^{\circ}$  K. (See ref. 1.) However, this material is subject to severe oxidation when in the atmosphere at a temperature above about  $1,250^{\circ}$  K. If graphite could be coated with an oxidation-resistant nonporous barrier, its high-temperature properties would be more capable of utilization.

Some substances form protective scales which hinder further interaction of the base material with the atmosphere. Aluminum, for example, is a highly electropositive metal and would rapidly oxidize in air at room temperature if it were not for its forming such an adherent, protective oxide scale. Graphite, producing only gaseous oxides at the temperatures at which it rapidly reacts with oxygen, cannot form a protective scale.

Various methods of cladding, plating, and coating have been used to keep oxygen from coming into contact with materials which require oxidation protection if they are to be utilized. One of the most versatile

coating techniques is the vapor-deposition process. In this process, a gaseous compound of the coating material is flowed over the heated substrate and thermally or chemically decomposed; the coating is then precipitated upon the substrate. The coated product, its density, its thickness, and its structure can be varied by varying the flow rates, temperature, time of coating, and the relative concentrations of the reactants. The titanium nitride coatings discussed in this paper were vapor-deposited.

The purpose of this investigation is to show that graphite can be protected at elevated temperatures by a thin coating of titanium nitride and that the protection mechanism involved is analogous to that of aluminum at room temperature; that is, the surface interacts with its environment to form an oxide coat which blocks further rapid oxidation.

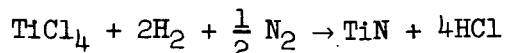
#### SYMBOLS

- $\Delta H_f^\circ$  standard enthalpy of formation, that is, increment in heat content associated with the reaction of forming the given compound from its elements, all substances involved in the reaction being in their thermodynamically stable modification at a pressure of 1 atmosphere and at the given temperature, kcal/mole; subscripts I and II indicate reaction to produce nitride and dioxide, respectively
- $\Delta F_f^\circ$  standard free energy of formation, that is, increment in free energy associated with the reaction of forming the given compound from its elements, all substances involved in the reaction being in their thermodynamically stable modification at a pressure of 1 atmosphere and at the given temperature; the free energy change is the criterion of chemical spontaneity for the constant-pressure, constant-temperature process, kcal/mole
- $\Delta H_R^\circ$  enthalpy of reaction, calculated from published  $\Delta H_f^\circ$  data, kcal/mole
- $\Delta F_R^\circ$  free energy of reaction, calculated from published  $\Delta F_f^\circ$  data, kcal/mole

#### COATING PROCEDURE

The titanium-nitride-coated graphite models were prepared by the hydrogen-reduction variation of the vapor-deposition process. (See ref. 2.) In the process described in reference 2 a gaseous mixture of

hydrogen ( $H_2$ ), nitrogen ( $N_2$ ), and titanium tetrachloride ( $TiCl_4$ ) is passed over heated graphite, and a golden-hued titanium nitride ( $TiN$ ) coating is formed on the surface of the graphite. The commercial-grade hydrogen used in the present investigation was found to contain sufficient nitrogen as an impurity to make the separate addition of nitrogen unnecessary. The reaction can be idealized as follows:



The mixing of the reactant gases was achieved by passing hydrogen through the volatile liquid, titanium tetrachloride, at room temperature. This gaseous mixture was then passed over a hemisphere-cylinder specimen (fig. 1) of AGX graphite which had been heated to approximately  $1,475^\circ K$  in a quartz-tube reaction vessel by an induction furnace. This apparatus is shown in figure 2. Argon is used to purge the system before coating.

The quality of titanium nitride formed, as judged by visual inspection, varied considerably with the particular batch of titanium tetrachloride used; thus, some modification of the operating conditions was necessary from time to time. Coating times of from 8 to 28 minutes were used, with 12 minutes producing approximately 20 milligrams of titanium nitride per square centimeter of substrate surface. The rate of hydrogen flow through the system was approximately 1.6 liters per minute.

#### TEST PROCEDURE AND RESULTS

The model presented consists of a massive graphite substrate coated with a thin film of titanium nitride of from 25.4 to 50.8 microns (1 to 2 mils) in thickness. This model is in a gaseous environment with properties such that carbon dioxide is thermodynamically preferred to unprotected graphite. The titanium nitride coating is oxidized by the environment and the resulting titanium dioxide ( $TiO_2$ ) - the rutile modification - then acts as a barrier to the oxidizing gas. This protective oxide is forming as the graphite is beginning to require protection and is formed in time to prevent serious damage.

Both titanium nitride coated and uncoated hemisphere-cylinder specimens (fig. 1) of graphite were tested in the supersonic ceramic-heated air jet described in reference 3. This free jet has a stagnation pressure of 7.14 atmospheres (105 lb/sq in. abs) and an estimated stagnation temperature of  $2,250^\circ K$ . Both a motion-picture camera and a two-color optical pyrometer were included as instrumentation in the tests. The  $TiN$  to  $TiO_2$  transformation was established by X-ray diffraction techniques.

When tested in the Mach 2 ceramic-heated jet, a coated specimen reached an equilibrium surface temperature of about  $1,700^{\circ}$  K and the surface temperature of an uncoated specimen rose from ambient to about  $2,165^{\circ}$  K, declined slightly, and then rose to about  $2,200^{\circ}$  K toward the end of the test. Figure 3 presents photographs of both coated and uncoated graphite models taken at various times in the ceramic-heated jet.

All uncoated specimens were severely damaged after 10 to 20 seconds under the test conditions and were destroyed toward the end of the test. On the basis of 20 tests in the ceramic-heated jet, it was ascertained that the minimum weight of coating to surface area required for survival of the jet test was approximately 20 milligrams of coating per square centimeter of substrate surface. Specimens with less than 20 milligrams failed at the stagnation point (not the sides), whereas specimens with 20 or more milligrams of coating per square centimeter of substrate surface survived the 60-second test without significant change, other than the transformation of the thin film of TiN to  $TiO_2$ .

Consistent with the observation of a threshold in the protection offered by a coating, based upon weight of coating per unit area, as found by the jet testing is the preliminary weight-change data taken from a resistance-heated, still-air facility. Figure 4 gives the specimen configuration and test data, in both tabular and graphical form, for the first five tests in still air of titanium-nitride-coated graphite cylinders evaluated at  $1,680^{\circ}$  K (jet test at  $1,700^{\circ}$  K) for periods of time varying from approximately 4 to 6 minutes. The data indicate positive weight changes for a test period for specimens possessing total coating weights in excess of 150 milligrams and negative weight changes for those specimens possessing less than 150 milligrams. Since the area of the coated surface of the cylindrical specimens is approximately 12 square centimeters, the threshold of protection is thus around 13 milligrams per square centimeter. The very limited nature of the still-air tests should be emphasized along with the fact that although the threshold for the jet tests was based upon readily observable changes in specimen geometry, any small negative weight change constituted failure in the preliminary still-air test.

## DISCUSSION

There are certain obvious characteristics which must be possessed by a coating system if it is going to be capable of forming a protective oxide. The Pilling and Bedworth rule (discussed in ref. 4), for example, which relates the specific volumes of metal and metal oxide to the ability of the metal to form a protective scale should hold in slightly

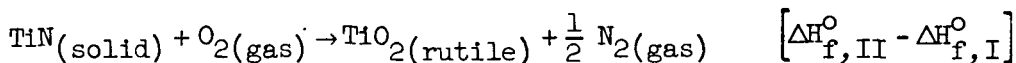
modified form for this case in which a compound of a metal is oxidized. It seems apparent that the molar volume of the oxide coating must be equal to or larger than that of the nitride coating in order to provide for the formation of a nonporous barrier. Of course, it must not be too much larger or spalling may occur. Since reference 5 gives the room-temperature density of titanium nitride as 5.24 grams per cubic centimeter and that of rutile as 4.24 grams per cubic centimeter, one can estimate a molar volume ratio of 11.8 to 18.8 or an expansion of the coating volume of approximately 1:1.6 for the transformation,  $TiN$  to  $TiO_2$ .

As it is difficult to conceive of an adherent, nonporous, oxide coating being formed while the surface is expelling gaseous substrate oxide, it appears that for highly energetic systems, especially if the substrate oxide is volatile under the reaction conditions, the formation of a protective oxide coating should proceed rapidly and in such a way that oxygen does not come into contact with the substrate. Thus, it seems reasonable to assume that the thermal expansion coefficients of the nitride coating, the oxide coating, and the substrate must be closely matched at all points in the usable temperature range in order to prevent spalling or cracking.

The thickness of the coating plays a very important part in how well it fulfills its role as a barrier to oxidation. A certain minimum thickness is necessary to provide protection; but, on the other hand, very thick coatings are more subject to thermal shocking. Kubaschewski and Hopkins (ref. 6) suggest that a  $TiO_2$  coating for titanium is unsatisfactory because of the reversion to a linear oxidation rate at high temperatures due to the cracking of the thicker oxide films, which continue to grow with time. If the titanium oxide is limited to a thin film, as by the oxidation of a thin film of titanium nitride on a nontitanium substrate, oxidation of the substrate would be governed by diffusion through the oxide barrier, rather than access of oxygen through cracks; thus, a much slower oxidation rate is established.

The enthalpy of formation of the oxide should be such that serious damage (solid-state phenomena) or melting is not incurred as a result of temperature increases produced by the process which forms the oxidation-resistant coating. The transformation of 1 mole of titanium metal into 1 mole of rutile is a fairly energetic one involving approximately -224 kcal (see ref. 5 for enthalpy of formation data for rutile and titanium nitride) of energy liberated at the surface of the substrate. (A negative enthalpy of formation designates heat evolved.) However, the heat of reaction for the transformation from the nitride is less, being of the order of -144 kcal/mole. (See fig. 5.) The following

example is presented to illustrate the calculation of the heat of reaction:



$$\Delta H_R^{\circ} = \text{Heat of reaction} = \left[ \Delta H_{f, II}^{\circ} - \Delta H_{f, I}^{\circ} \right] \approx -144 \text{ kcal/mole}$$

It should be mentioned, however, that since the amount of coating is very severely limited, the total heat from this oxidation process is negligible compared with the convective heat transfer. For a system with 20 milligrams of TiN per square centimeter of substrate surface, the oxidation will add about 47 calories input per square centimeter. Since the  $\Delta H_f^{\circ}$  data listed in reference 5 are given only to 1,500° K, some other thermodynamic data must be used in order to obtain a  $\Delta H_R^{\circ}$  valid to the temperature of the jet test. From specific heat at constant pressure data, valid from 1,000° K to 2,000° K (data for O<sub>2</sub> and N<sub>2</sub> from ref. 7; data for TiO<sub>2</sub> and TiN from ref. 8), the following expression can be derived (see fig. 5):

$$\Delta H_R^{\circ} = -145.743 + (1.87 \times 10^{-3})T - (4.2 \times 10^{-7})T^2 - (1.67 \times 10^{-11})T^3$$

The oxide formed should remain in the solid phase while the structure is threatened with oxidation and must present a surface capable of withstanding any viscous forces impressed upon it by the conditions. Although this requirement may seem obvious at first, it is possible that a coating need not be solid in order to provide the necessary protection for a substrate. It is conceivable that highly viscous liquid coatings could offer ample protection for high-altitude hypersonic vehicles. A highly viscous liquid could withstand the shear forces of a boundary layer formed from low-density air at high altitudes for finite lengths of time. In fact, the rutile coatings discussed in this paper were tested at or close to their melting points and this test involves high shear forces. Perhaps a zirconium nitride analog may offer promise for higher temperature use. The listed handbook data for the melting points of the two oxides are as follows: rutile, 1,913° K; zirconia, 2,988° K. (See ref. 9.)

Another consideration of interest in evaluating the suitability of a given coating for a particular substrate is the free energy of the reaction  $\Delta F_R^{\circ}$  between the coating and the substrate to form an oxide of the substrate. If  $\Delta F_R^{\circ}$  is positive the coating is thermodynamically preferred to the substrate oxide. The greater the value of  $\Delta F_R^{\circ}$  the more the equilibrium is displaced toward the coating plus substrate; or, in other words, the less tendency there is for the protective oxide to be reduced by the substrate. If  $\Delta F_R^{\circ}$  is negative the coating plus substrate system is less stable than the substrate oxide plus reduced-coating system. Actually, thermodynamics treats only of the position of a chemical equilibrium and not of its rate of attainment; thus, a reaction with a negative value of  $\Delta F_R^{\circ}$  may proceed so slowly as to be insignificant. However, since the rates of chemical reactions generally increase with temperature, at sufficiently high temperatures it is felt that a large positive value of  $\Delta F_R^{\circ}$  may be regarded as a necessary and sufficient condition for the coating to be stable in the presence of the substrate. Figure 6 gives some pertinent thermodynamic data for this coating system, with the data for titanium compounds from reference 5 and that for the oxides of carbon from reference 10. Of the readily apparent interactions, only the reaction to produce carbon monoxide plus titanium carbide seems probable, and that only to some slight extent at the higher temperatures.

Although the oxidation-protection mechanism presented is demonstrated for the TiN to TiO<sub>2</sub> interaction only, it appears that silicon- and boron-based coatings are also of the protective oxide type. In fact, the conditions given should apply to all nonoxide coatings (neglecting the noble metals) designed for oxidation protection.

In designing coatings for certain oxidizing environments, it is necessary to plan either for the use of oxides originally or for the eventuality of subsequent refractory oxide formation. In certain instances, use of materials such as the nitrides, silicides, borides, and carbides may be necessary (for example, for good bonding, nonporosity, etc.) but one of the species present must be able to form a usable oxide.

#### CONCLUDING REMARKS

Graphite can be protected for 60 seconds in a Mach 2 airstream with a stagnation temperature of approximately 2,250° K - conditions which would normally destroy it - by a thin coating of titanium nitride. The protective mechanism at elevated temperatures appears to be analogous to that of aluminum at room temperature, in that the surface interacts

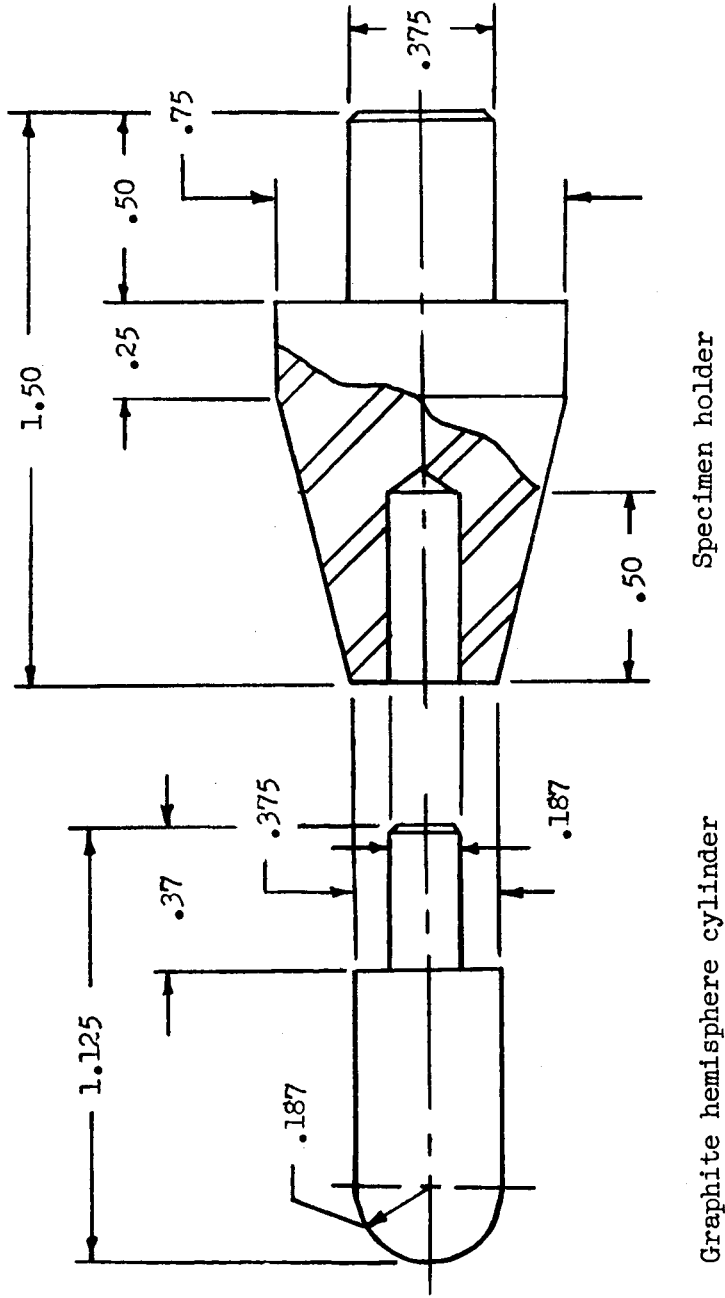


with its environment to form a protective oxide coating which blocks further rapid oxidation.

Langley Research Center,  
National Aeronautics and Space Administration,  
Langley Field, Va., December 20, 1960.

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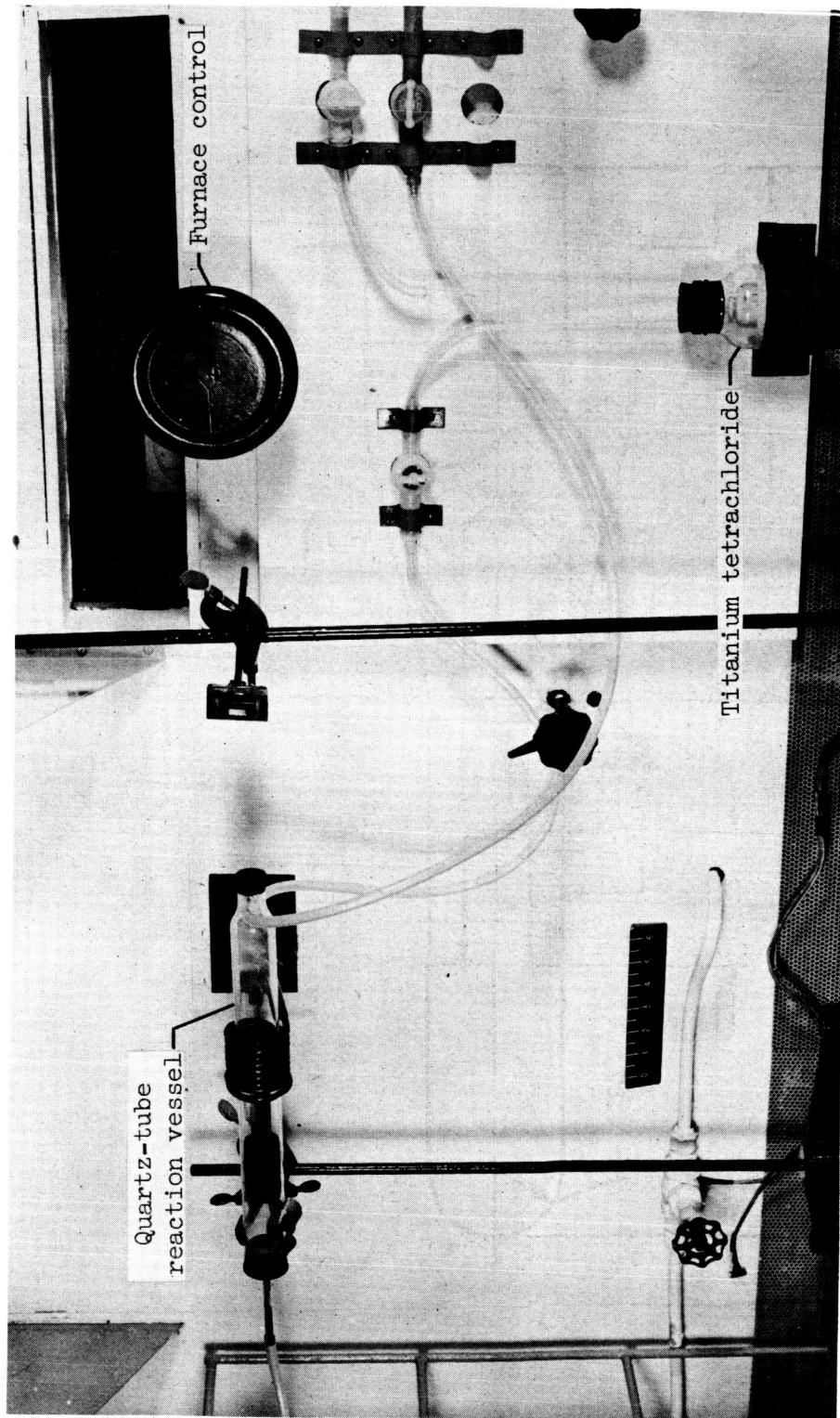
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Graphite hemisphere cylinder

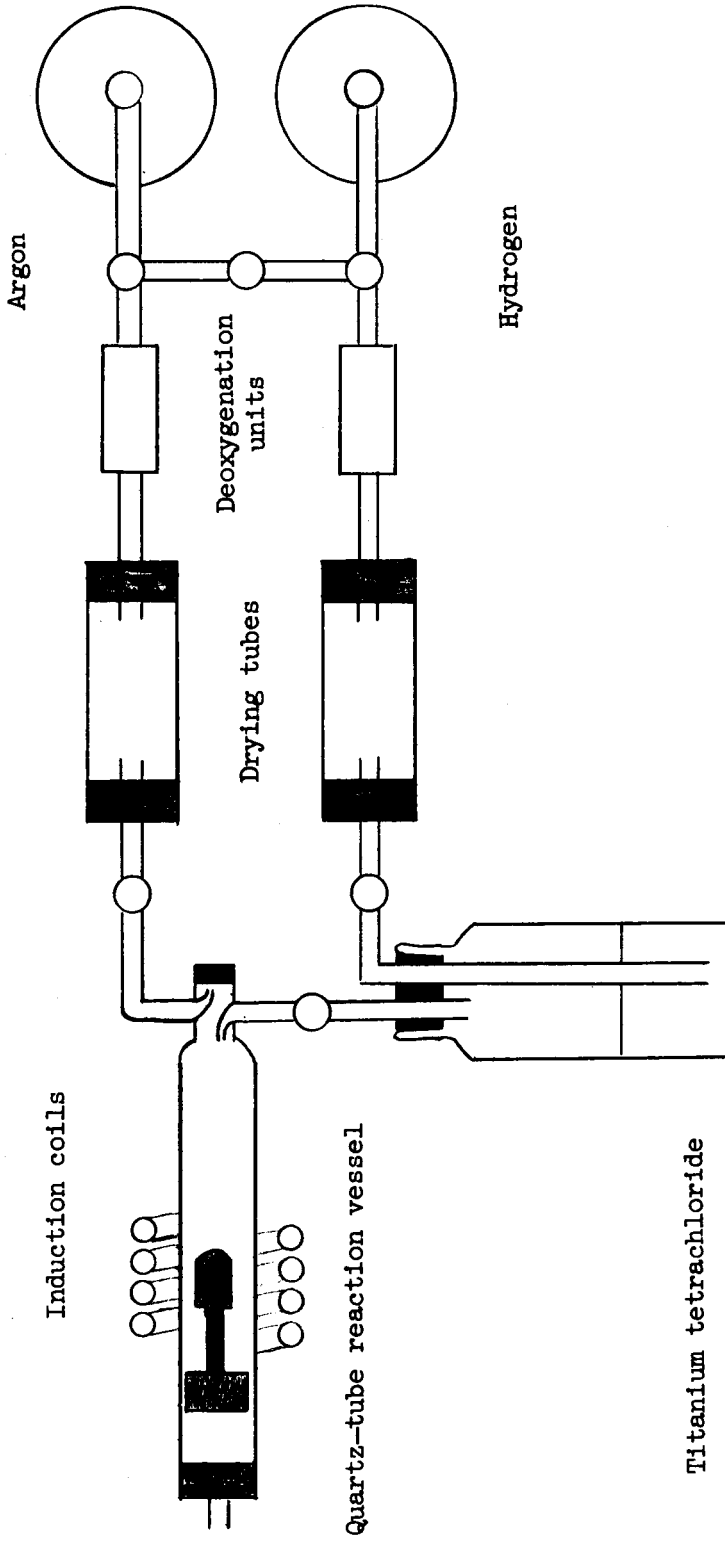
Specimen holder

Figure 1.- The test specimen. All dimensions in inches.



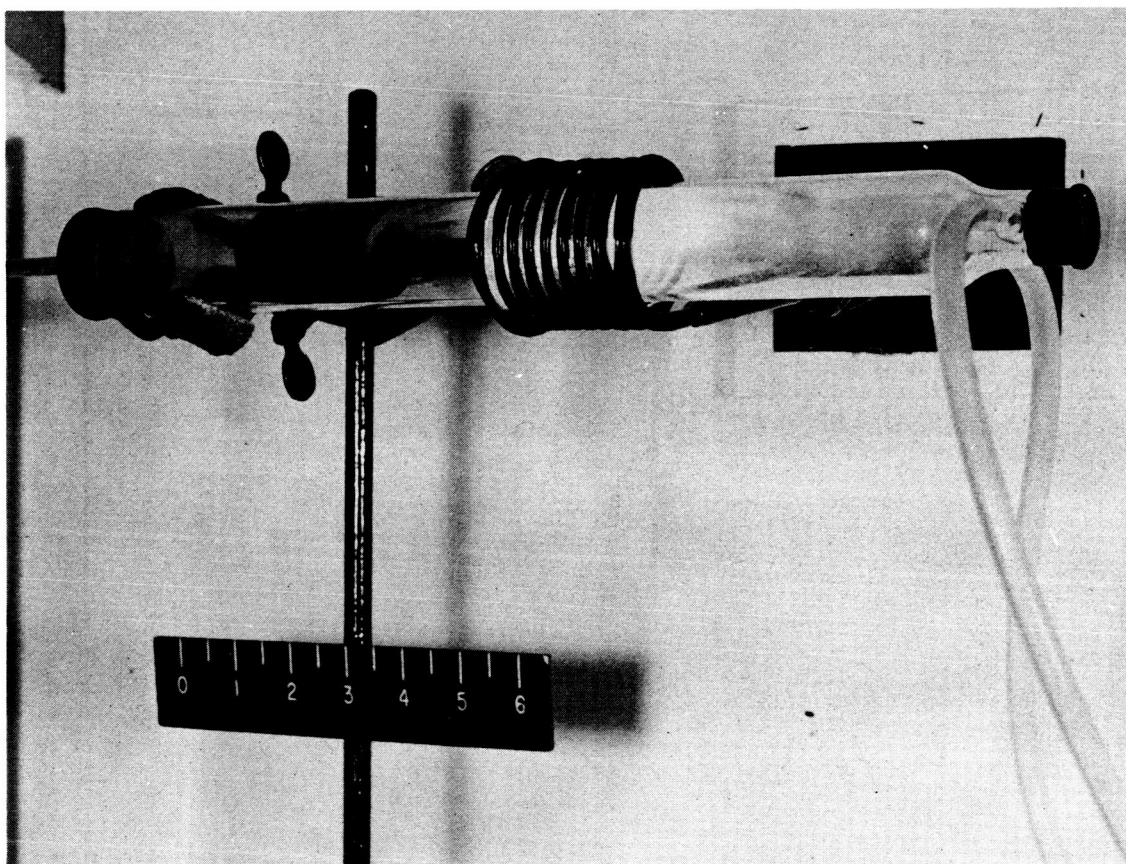
(a) General scheme. I-59-4364.1

Figure 2. - The coating facility.



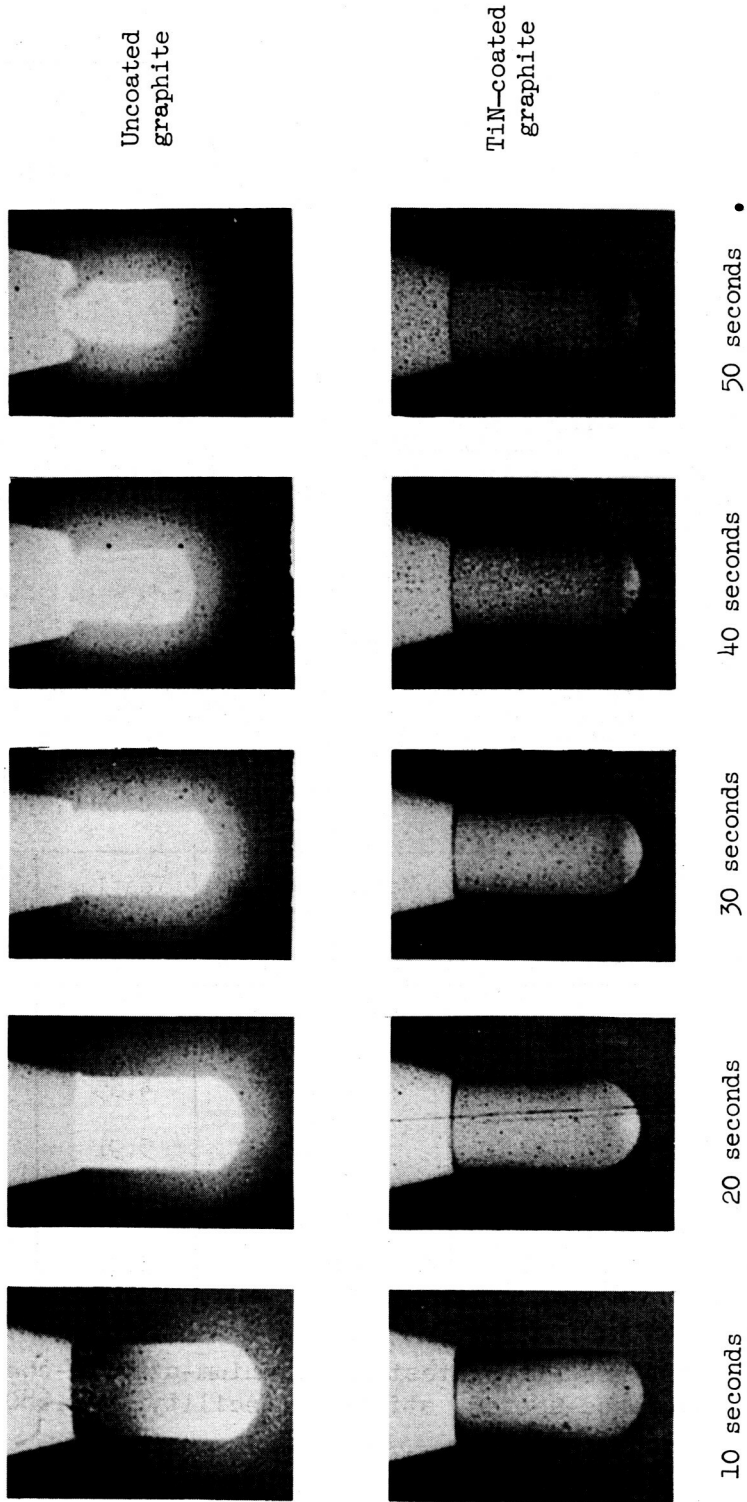
(b) Schematic diagram.

Figure 2.- Continued.



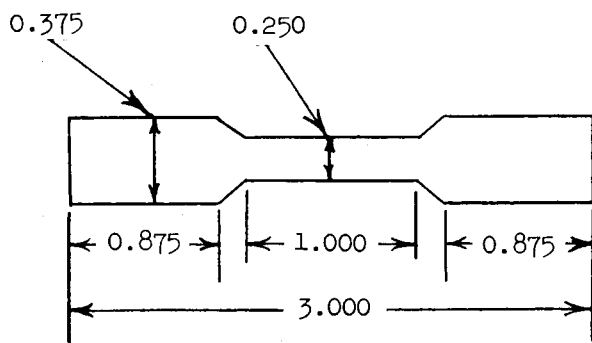
(c) The heated specimen during a coating period. L-59-4365

Figure 2.- Concluded.

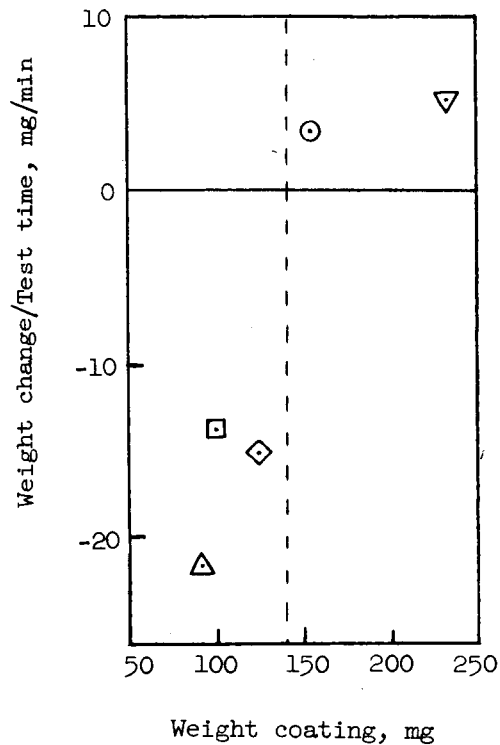


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Figure 3.- Coated and uncoated test specimens taken at various times in the ceramic-heated jet.



Dimensions are in inches



	Model	Coating weight, mg	Weight change with testing, mg	Testing time, min
○	1	154.8	13.1	3.93
□	2	99.7	-66.9	4.85
◇	3	123.8	-90.1	5.91
△	4	91.9	-108.1	5.00
▽	5	230.8	25.6	5.06

Figure 4.- Preliminary results of testing titanium-nitride-coated graphite in a resistance-heated, still-air facility at 1,680° K.



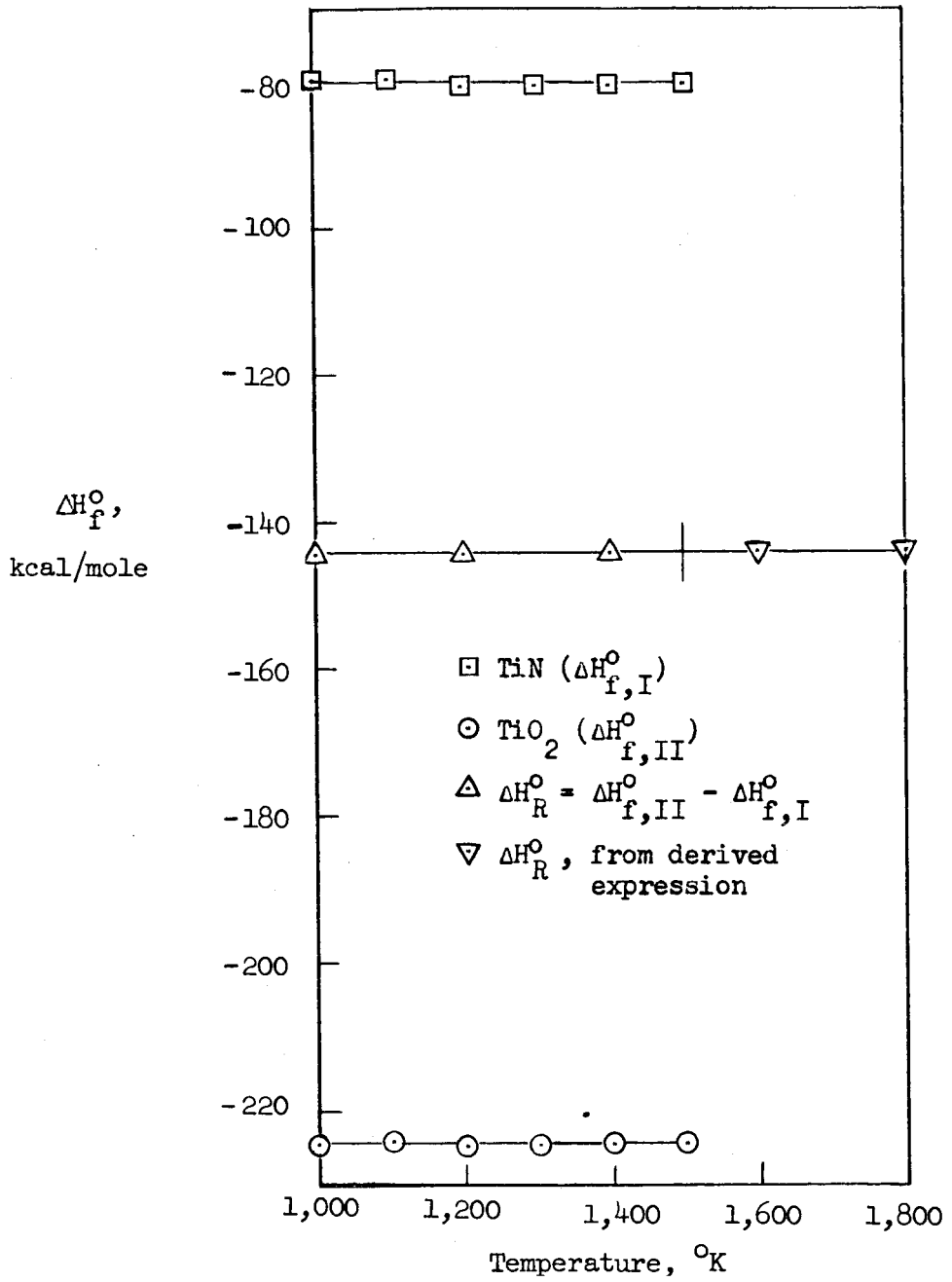


Figure 5.- Heat of reaction for the oxidation of titanium nitride to titanium dioxide plotted against absolute temperature.

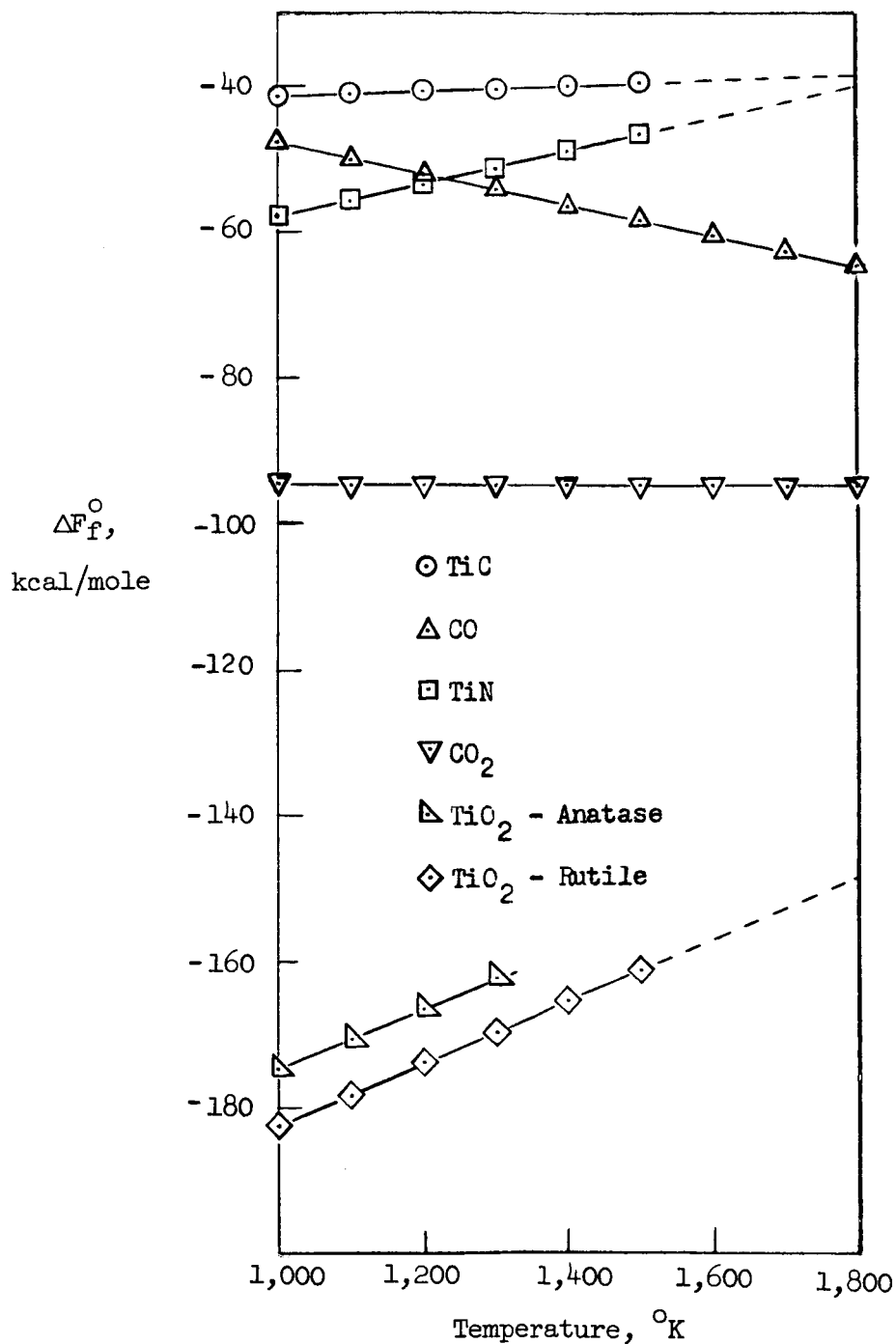


Figure 6.- Standard free energies of formation of some applicable compounds plotted against absolute temperature.