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DETERMINATION OF THE THERMAL DIFFUSIVITY OF PYROTECHNIC MATERIALS

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INTRODUCTION

Thermal diffusivity studies have been initiated to better characterize developmental pyrotechnic materials. Thermal diffusivity, along with density and specific heat, can be used to calculate another important thermophysical property, namely, thermal conductivity. A literature search revealed the relatively simple method commonly known as the flash-diffusivity method. This method, with appropriate modification to accent pyrotechnic materials at elevated temperatures, was selected for these studies.

METHOD AND APPARATUS

The flash-diffusivity method is based on the transient behavior of a specimen when one side is subjected to a short thermal pulse. As the heat pulse travels through the specimen, its back surface temperature rise is recorded as a function of time. This time-temperature history is directly related to the thermal diffusivity.

Parker et al [1] derived the simple relationship:

$$\alpha = 0.139L^2/t_{1/2}$$

where: α = thermal diffusivity
L = specimen thickness
 $t_{1/2}$ = time required for back surface of specimen to reach half of the maximum temperature rise.

This relationship involves several simplifying assumptions:

- 1) The heat pulse is uniformly absorbed on the front face of an opaque specimen.
- 2) The heat pulse is of negligible time compared to the time required for heat propagation through the specimen.

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- 3) The heat flow is one dimensional from the front face to the back face.
- 4) Heat losses of the faces are negligible.
- 5) The temperature rise within the specimen is small enough to consider the thermal properties as constant.

This method offers the advantage of not being necessary to quantitatively measure the heat flowing through the specimen. Additional advantages are that small specimen requirements permit rapid attainment of equilibrium conditions as well as offering desirable safety conditions for the study of pyrotechnic materials.

The method has an accuracy of $\approx +5\%$ when values for standard materials are compared to accepted literature values. The largest error contribution is believed to be the reading of the Polaroid photograph of the time-temperature measurement.

A schematic of the thermal diffusivity apparatus is shown in Figure 1. The disc-shaped specimen is positioned inside the heater-thermocouple assembly, which allows the specimen to be supported primarily by the thermocouple, thus giving good contact. This technique works well with fragile specimens, such as pressed pyrotechnic materials. The specimen size is 6.35 mm (0.25 in.) diameter by varying thickness 0.76 to 3.17 mm (0.030 to 0.125 in.) depending on thermal diffusivity of the material under study.

Measurements are made by pulsing the front surface in ~ 1 msec with 1.5 J from an ir laser which is focused to a spot size slightly larger than the specimen. The transient temperature at the back face of the specimen is measured by a chromel-alumel thermocouple 0.10 mm (0.004 in. diam). The output voltage from the thermocouple is fed to a dc amplifier and subsequently to the Y-axis of an oscilloscope. Maximum amplification for this system is 30 μ V full scale or 0.75°C.

A single-sweep, triggered simultaneously with the laser pulse, is presented on the oscilloscope and photographed with a Polaroid camera. Shown in Figure 2 is a typical temperature-time curve. The thermal diffusivity of the specimen can be calculated from this data.

The apparatus was designed to permit measurements to be made in any desired atmosphere. For measurements at elevated temperatures, it is necessary to null the thermocouple output at any constant temperature by using a bucking voltage. This allows the amplified ΔT signal resulting from the laser pulse, to be measured.

Initial thermal diffusivity determinations were made at ambient temperatures on known materials; such as, SiO_2 , Al_2O_3 , 304 stainless steel, and ZrO_2 to demonstrate that the method was in agreement with accepted literature values [2].

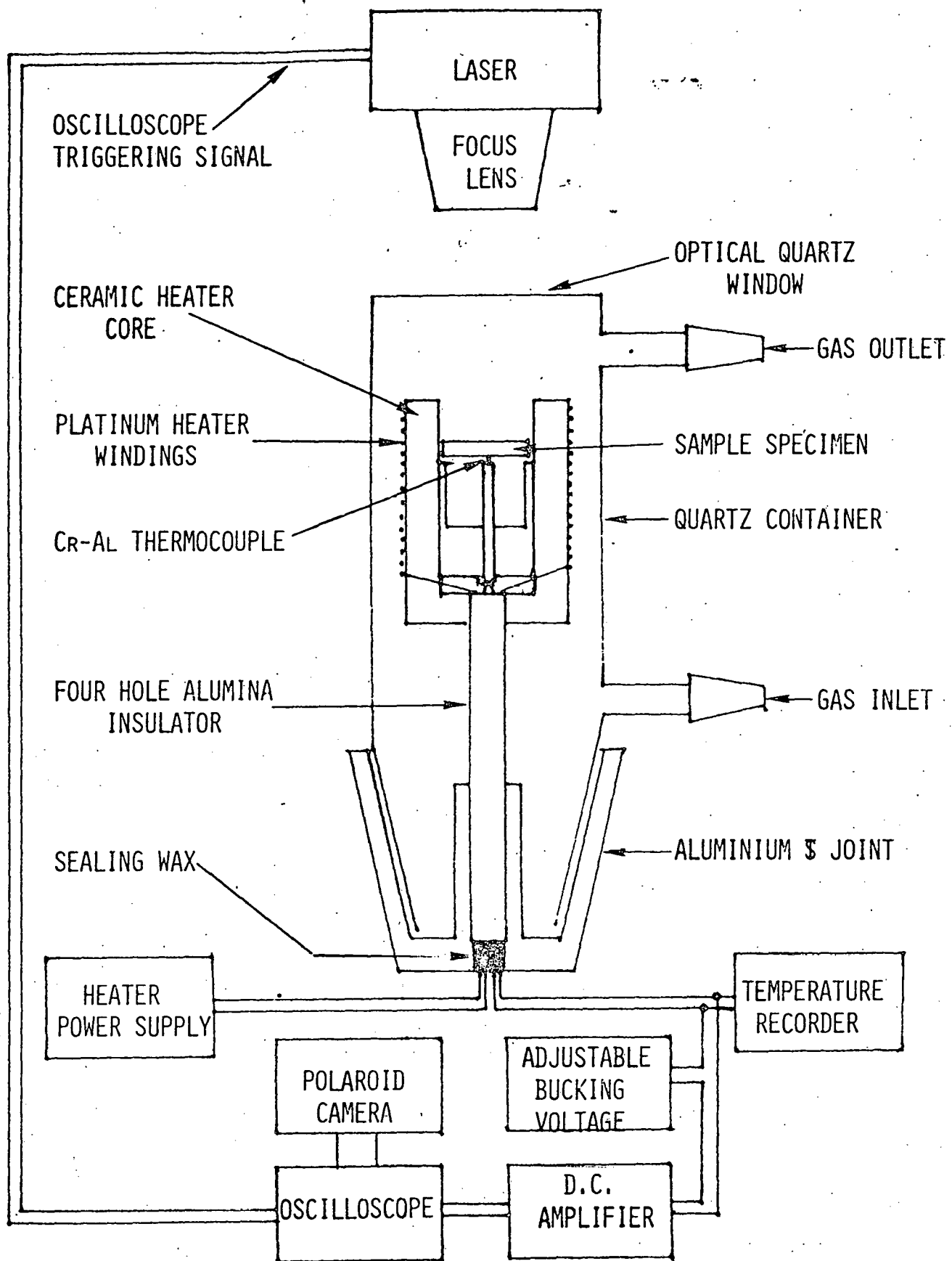


FIGURE 1 - A schematic of the thermal diffusivity apparatus.

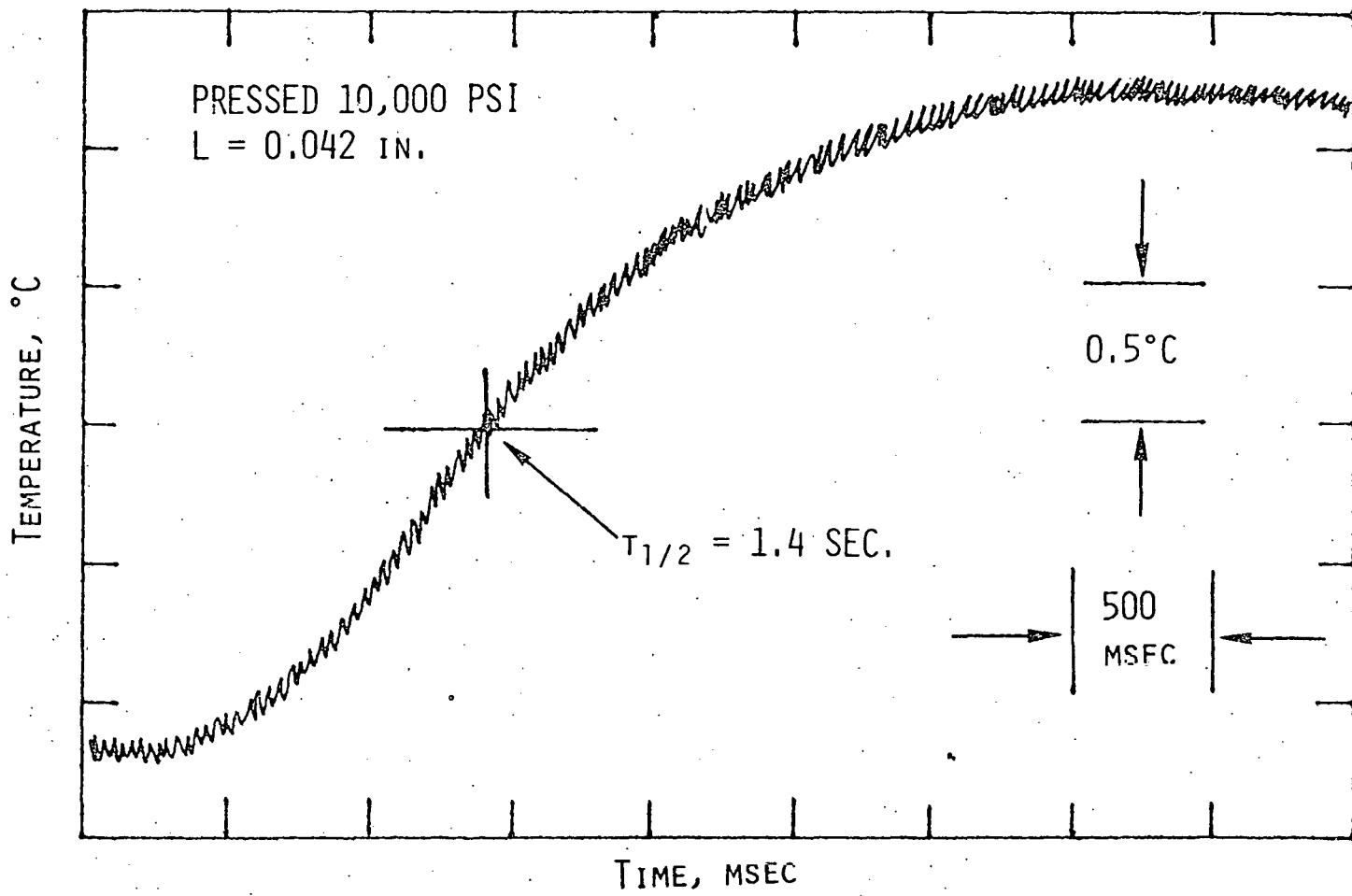


FIGURE 2 - Typical temperature-time curve for 33% TiH_{0.65}/67% KClO₄.

EXPERIMENTAL RESULTS

Several variables were investigated to determine which ones have a significant effect on the thermal diffusivity of associated pyrotechnic materials. The first study involved the thermal diffusivity measurement of $TiH_{0.675}$ as a function of temperature. This material was of particular interest since it is presently used in pyrotechnic blends, and the binary system between titanium and hydrogen exhibits a eutectoid near this composition at $319^{\circ}C$ [3]. The initial determination was made in a 95% argon-5% hydrogen atmosphere. It is apparent from results shown in Figure 3A that a significant change occurred in the vicinity of the eutectoid temperature. Also, it is evident that a degradation of the material occurred since the thermal diffusivity value at ambient temperature was not the same before and after heating. Subsequent x-ray diffraction analysis showed an increase in hydrogen content to the degree that only single phase-substoichiometric gamma-titanium hydride was evident. The complex loss of the alpha-titanium phase explains the thermal diffusivity change. These data indicate that a 95% argon-5% hydrogen atmosphere is undesirable at elevated temperatures.

Because of the overwhelming quantity of $KClO_4$, this effect was virtually undetectable in the pyrotechnic blend ($TiH_{0.65}/67\% KClO_4$), which is shown in Figure 3B.

These two determinations were repeated in an argon atmosphere, and the results are shown in Figures 4A and 4B. The contrast between Figures 3A and 4A is quite evident. It appears that the integrity of the $TiH_{0.675}$ was maintained in an argon atmosphere; however, the thermal diffusivity was found to decrease from ambient to $300^{\circ}C$, then stabilize between 300 and $400^{\circ}C$.

A comparison between the pyrotechnic blend in the two atmospheres, Figures 3B and 4B, exhibits very little difference--both decreasing in thermal diffusivity up to $300^{\circ}C$, then increasing slightly between 300 and $400^{\circ}C$.

Another variable investigated was the thermal diffusivity of $TiH_{0.675}$ as a function of density. The data are plotted in Figure 5, showing essentially a linear rise of thermal diffusivity as the density is increased. Over the density range of 2.18 to 2.37 g/cc, the thermal diffusivity increases from 39.3 to $46 \times 10^{-4} \text{ cm}^2\text{sec}^{-1}$.

A linear relationship between thermal diffusivity and density was also found to exist for $KClO_4$ and $TiH_{0.65}/67\% KClO_4$ blend materials. The $KClO_4$ thermal diffusivity increased from 12 to $16 \times 10^{-4} \text{ cm}^2\text{sec}^{-1}$ over a density range of 2.03 to 2.19 g/cc, whereas the blend exhibited only a very slight increase from 13.6 to $14 \times 10^{-4} \text{ cm}^2\text{sec}^{-1}$ when its density was increased from 2.09 to 2.28 g/cc. These data are shown in Figures 6 and 7, respectively.

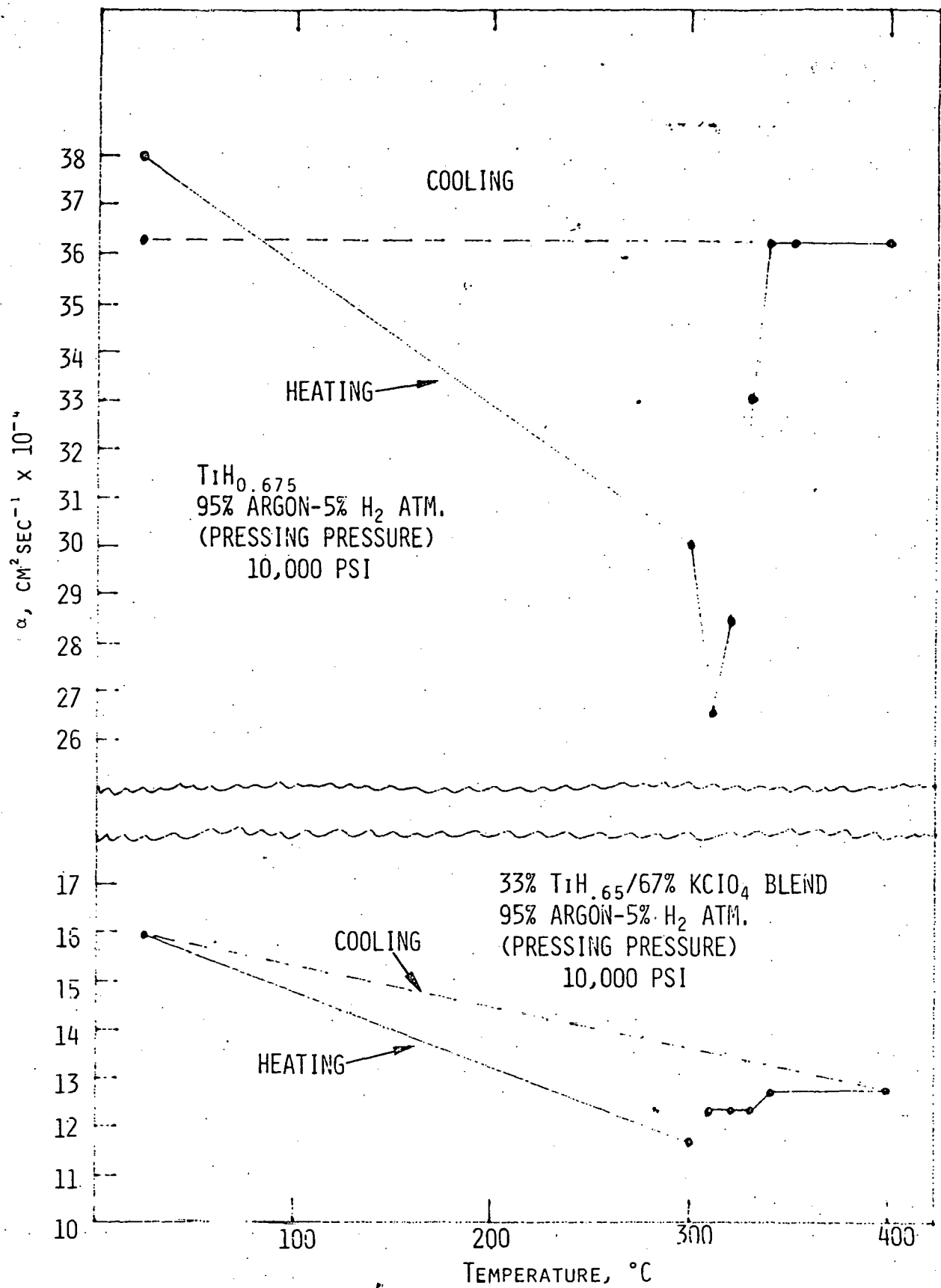


FIGURE 3A/3B - The thermal diffusivity of $TiH_{0.675}$ and 33% $TiH_{0.65}$ /67% $KClO_4$ as a function of temperature in a 95% argon-5% hydrogen atmosphere.

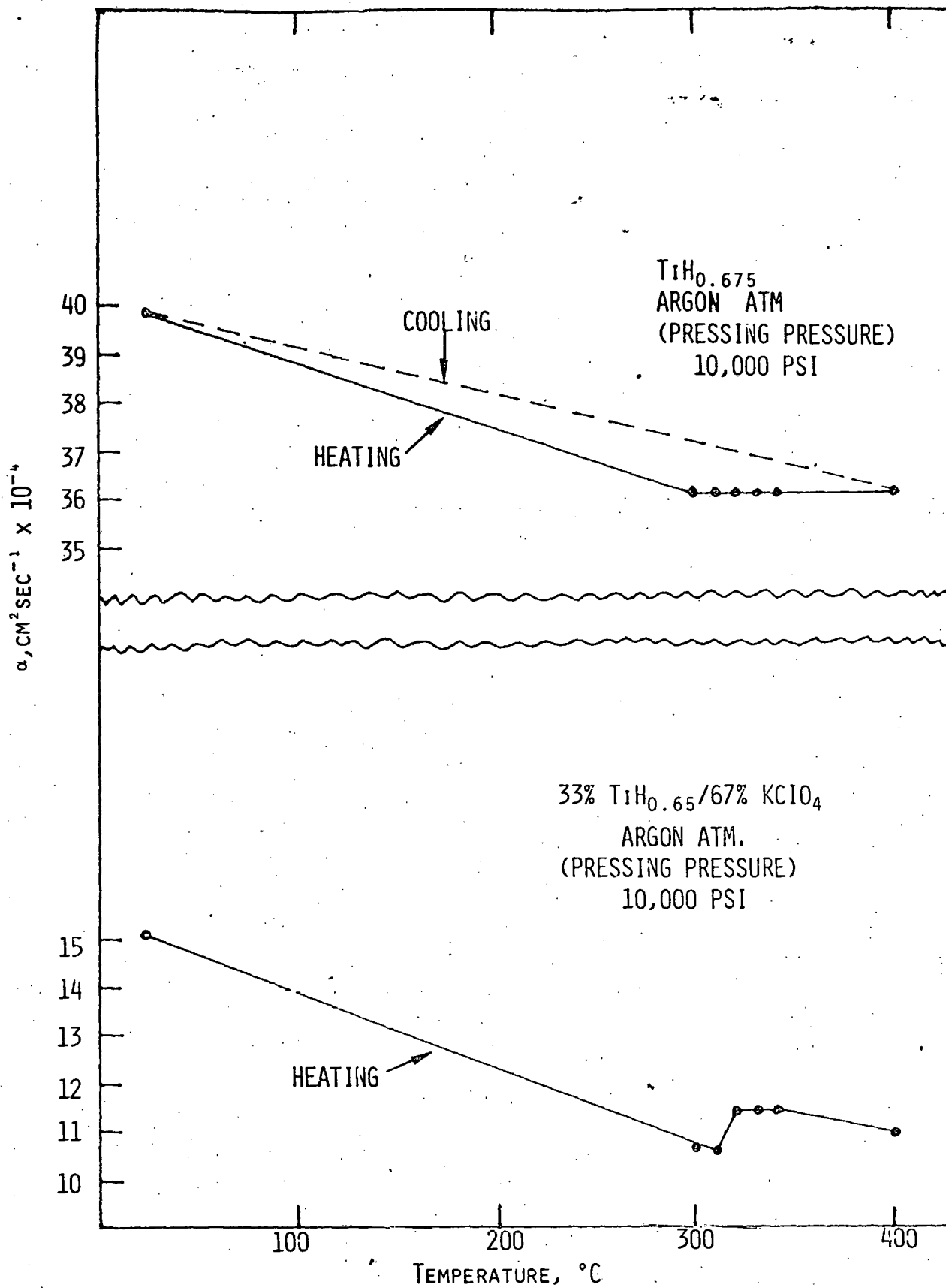


FIGURE 4A/4B - The thermal diffusivity of $TiH_{0.675}$ and 33% $TiH_{0.65}$ /67% $KClO_4$ as a function of temperature in an argon atmosphere.

FIGURE 5 - Thermal diffusivity of $TiH_{0.67}$ as a function of density.

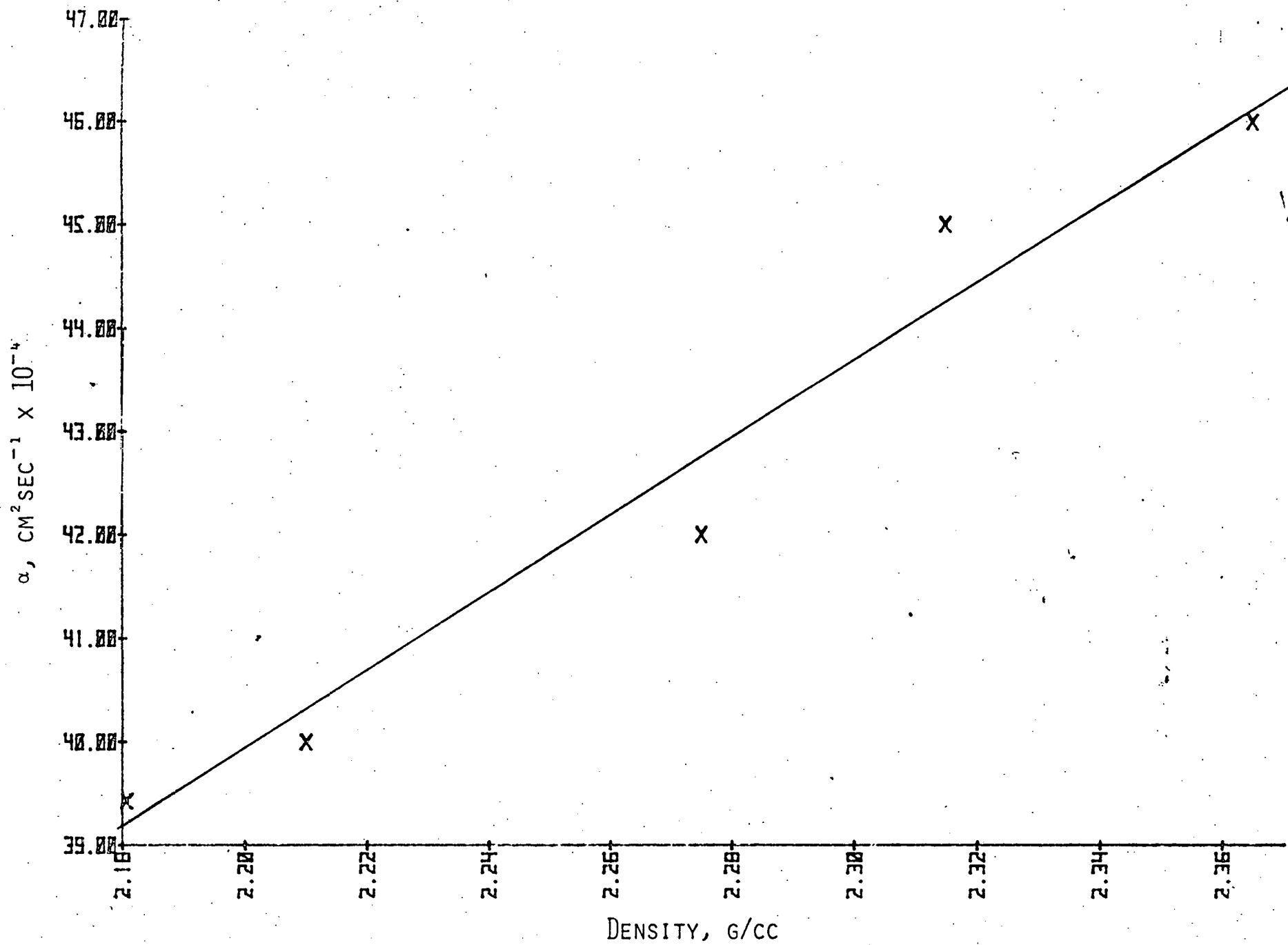
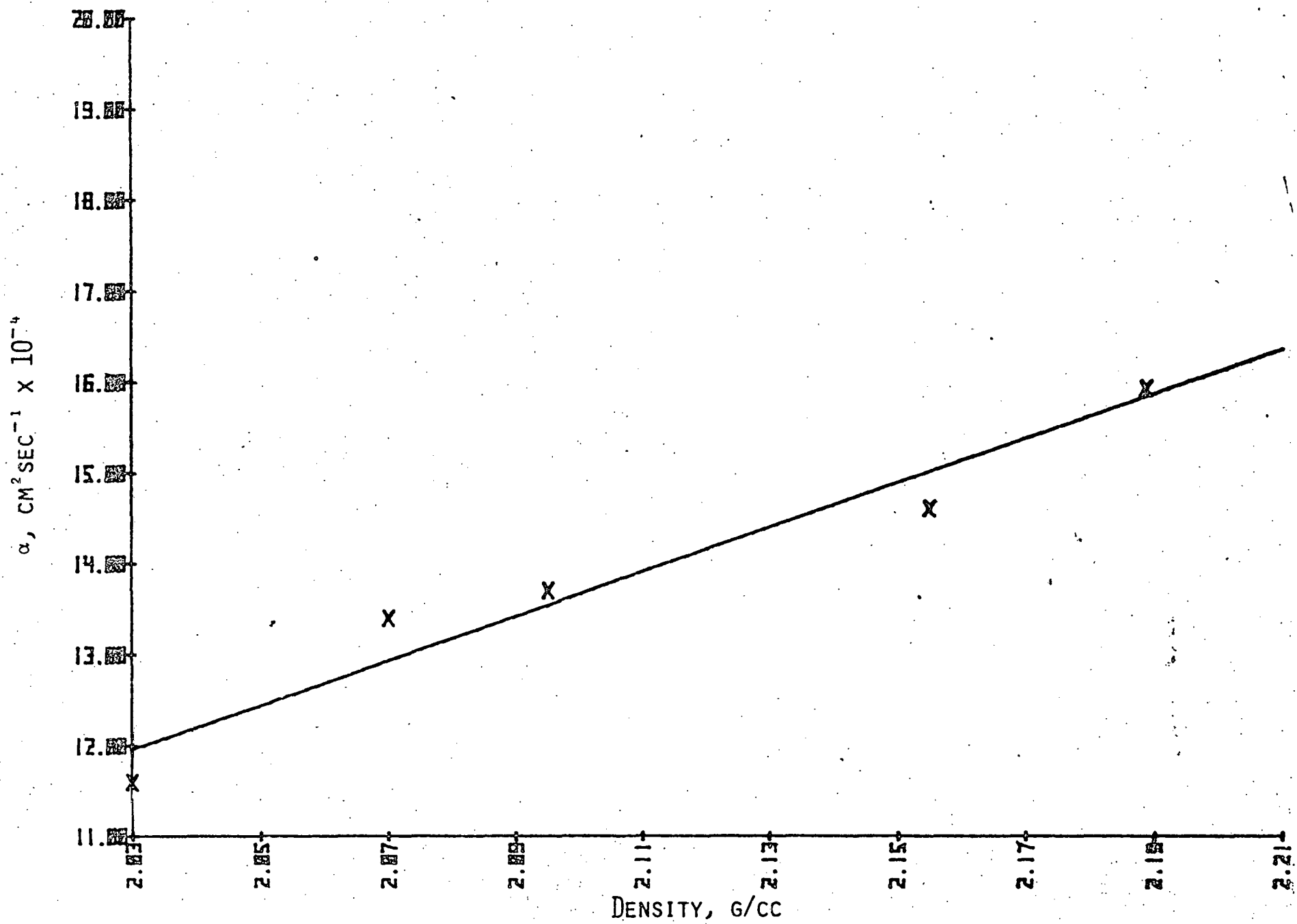


FIGURE 6 - Thermal diffusivity of $KClO_4$ as a function of density.



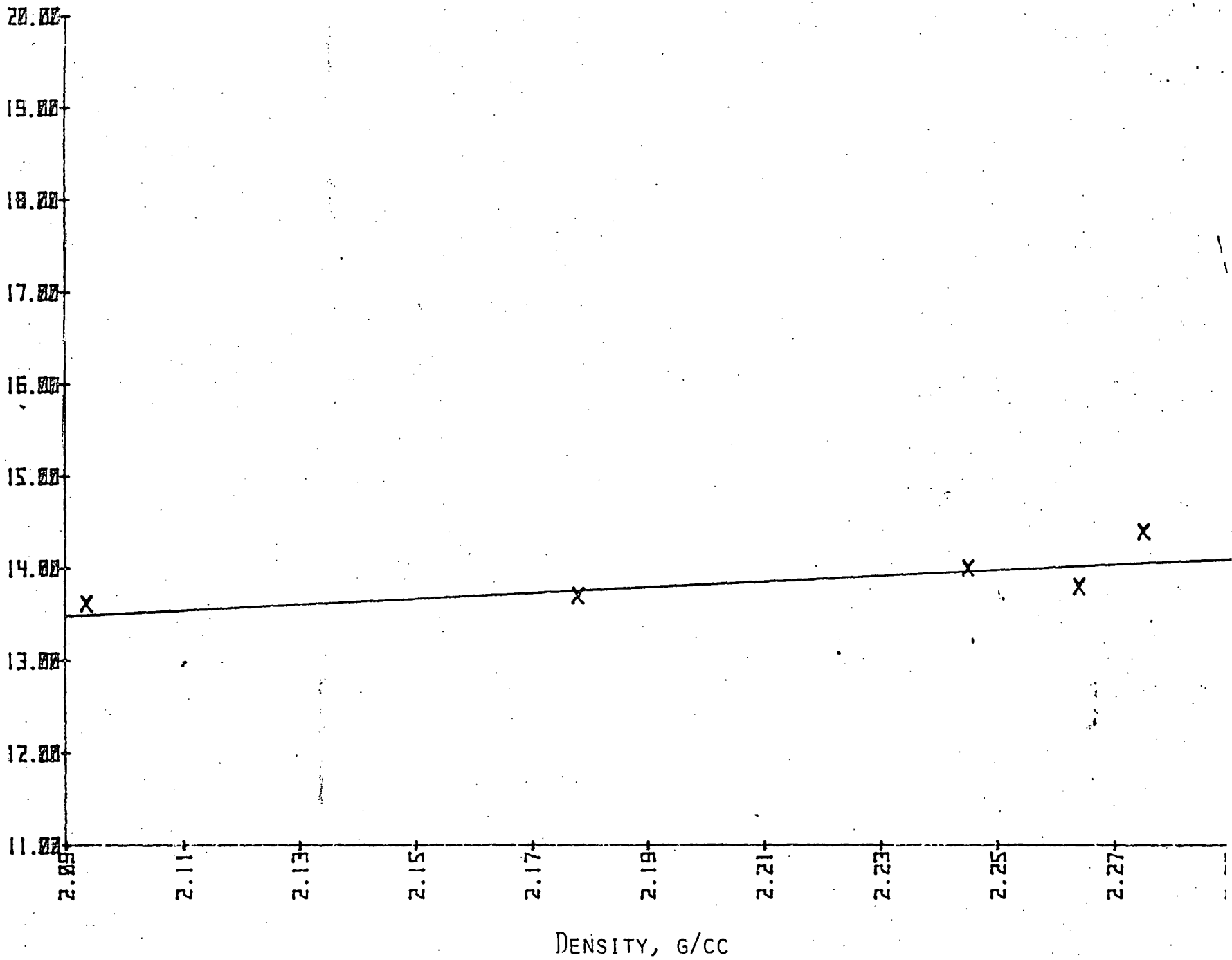


FIGURE 7 - Thermal diffusivity of 33% TiH_{0.65}/67% KClO₄ blend as a function of density.

The next experiment involved varying the $\text{TiH}_{0.65}\text{-KClO}_4$ blend ratio and measuring the thermal diffusivity. The results are that of a nonlinear curve, as shown in Figure 8. The data show the major effect of the KClO_4 ; the line just above the measured data is calculated using the mathematical model for one-dimensional composite membrane diffusion [3]. Although the calculated and the measured data do not match exactly, it is obvious that a good estimation can be obtained using this model.

The final variable investigated was the relationship between thermal diffusivity and the titanium-hydrogen ratio. Since a limited number of ratios were available, the study can only be considered cursory; however, the results indicated a linear decrease in thermal diffusivity of 40×10^{-4} to $26 \times 10^{-4} \text{ cm}^2\text{sec}^{-1}$ for samples ranging from $\text{TiH}_{0.38}$ to $\text{TiH}_{1.32}$, respectively.

SUMMARY AND CONCLUSIONS

The thermal diffusivity of $\text{TiH}_{0.675}$ was found to decrease from 40×10^{-4} to $36 \times 10^{-4} \text{ cm}^2\text{sec}^{-1}$ when heated in an argon atmosphere to 400°C . A decrease was also evident for the pyrotechnic blend of $\text{TiH}_{0.65}/67\% \text{ KClO}_4$, under similar conditions, from $15 \times 10^{-4} \text{ cm}^2\text{sec}^{-1}$ to $11 \times 10^{-4} \text{ cm}^2\text{sec}^{-1}$.

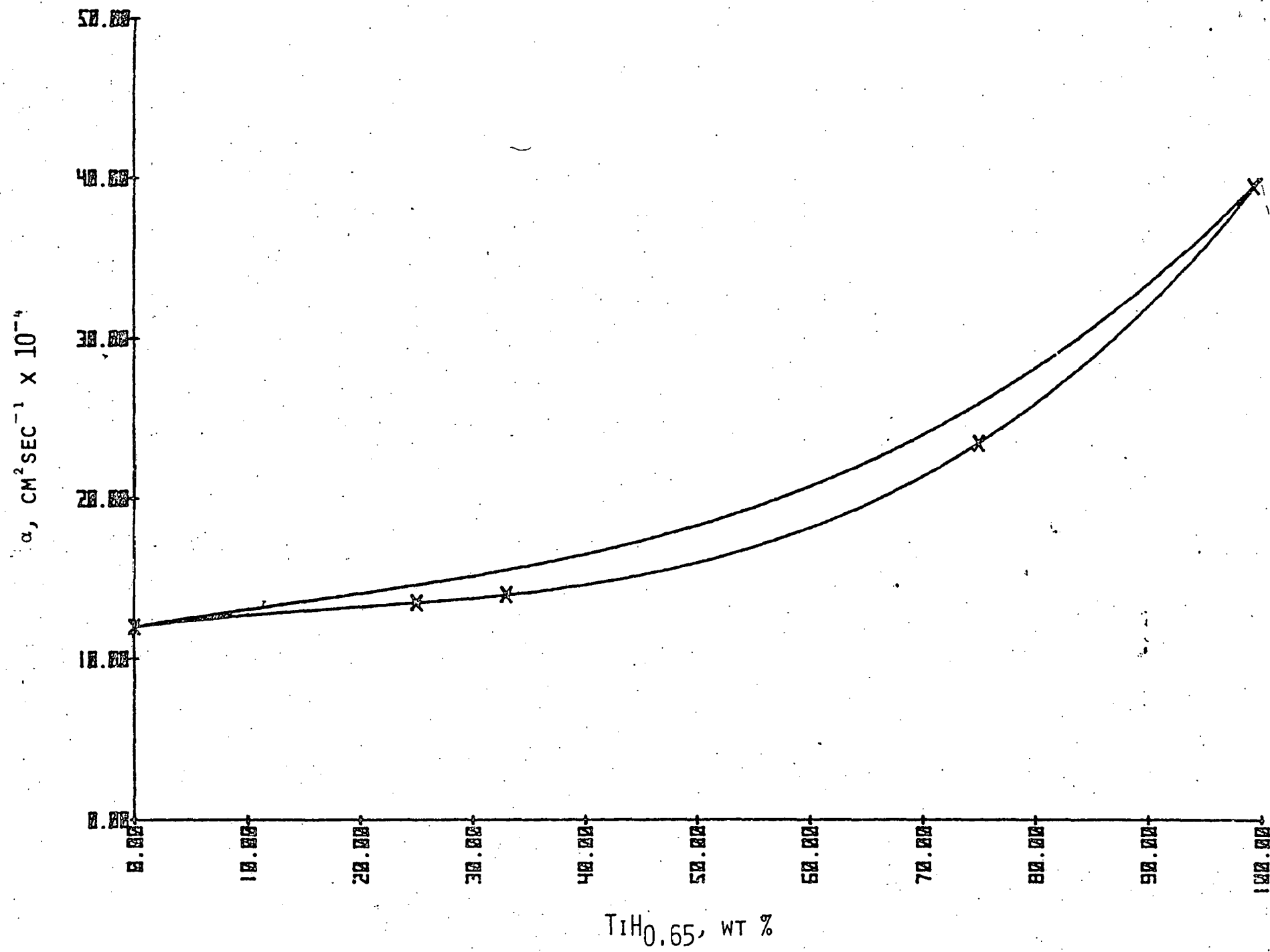
Substoichiometric titanium hydride compositions ranging from $\text{TiH}_{0.38}$ to $\text{TiH}_{1.32}$ show essentially a linear decrease in thermal diffusivity from 42×10^{-4} to $26 \times 10^{-4} \text{ cm}^2\text{sec}^{-1}$ as the hydrogen content is increased.

The effect of density on the thermal diffusivity of the hydride, $\text{TiH}_{0.65}$, which is most commonly used in pyrotechnic blends, shows a linear increase from 39.3×10^{-4} to $46 \times 10^{-4} \text{ cm}^2\text{sec}^{-1}$ for a density increase from 2.18 to 2.37 g/cc. In contrast, the blend ($\text{TiH}_{0.65}/67\% \text{ KClO}_4$) exhibits a virtual independence of density over the range of 2.09 to 2.28 g/cc, yielding a thermal diffusivity of $14 \times 10^{-4} \text{ cm}^2\text{sec}^{-1}$. These data indicate that the large quantity of KClO_4 in the blend is the controlling factor.

In addition, the study on varying the $\text{TiH}_{0.65}\text{-KClO}_4$ blend ratios showed that thermal diffusivity was affected nonlinearly, significantly favoring the influence of the KClO_4 . This relationship was also found to closely resemble the mathematical model for one-dimensional composite membrane diffusion [3].

In closing, the flash diffusivity method has proven adaptable to such fragile specimens as pressed pyrotechnic materials. It also has the added feature of small specimen requirements--which is desirable when handling pyrotechnic materials.

FIGURE 8 - $TiH_{0.65}$ - $KClO_4$ blend ratio effect on thermal diffusivity.



ACKNOWLEDGEMENTS

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