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THERMODYNAMICS OF HIGH TEMPERATURE MATERIALS

Final
~~Annual~~ Report for the Period of

1 October 1978 - 30 September 1979

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

[redacted]

AFOSR-79-0012

ABSTRACT

Heat capacity, electrical resistivity, total hemispherical emittance of carbon composite (supplied by AFML), and palladium, radiance temperature at melting point of palladium, heat of fusion of niobium measured. Electrical system of pulse interferometer for thermal expansion and system for thermal diffusivity completed.

Enthalpy measurements to 1200 K on Silicon nitride made. Analysis of silicon carbide completed and enthalpy measurements made to 770 K.

Computer codes for direct sum technique to assess effect of vibrational anhamonicity on thermodynamic functions completed and tested. Vibrational assements for two silicon fluoride bromide species completed. Direct sum programs for thermodynamic functions for several Hund's coupling cases completed.

I. HIGH-SPEED THERMOPHYSICAL MEASUREMENTS

Investigations performed during FY79 with the millisecond-resolution thermophysical measurements system are summarized in the following paragraphs.

(a) Definitive experiments were performed on a carbon-carbon composite material supplied by the AFML. The results indicated that heat capacity, electrical resistivity, and hemispherical total emittance of carbon-carbon composites can be measured in the temperature range 1500-3000 K with the present millisecond system. This will provide a unique means of accurately measuring the thermal properties of graphitic composites at high temperatures where coventional techniques fail.

(b) The heat capacity, electrical resistivity, and hemispherical total emittance of palladium were measured in the temperature range 1400 - 1800 K. The melting temperature of palladium was also measured as a confirmation of the accuracy of the measurement system, since palladium melting temperature is a secondary reference point on the Temperature Scale. A paper describing the results was prepared and submitted for publication.

(c) The data obtained by a novel dynamic technique to determine the heat of fusion of niobium have been processed. A systematic analysis of the technique and a study of all possible sources of errors have been made. A paper was prepared and was submitted for publication.

(d) The construction of the electronics for the unique pulse interferometric system (for thermal expansion measurements) was completed. The electronic system is able to count the fringes generated that result from the expanding specimens during rapid heating and store the information in a memory simultaneously with the data related to the measurements of heat capacity, electrical resistivity and thermal emittance. Extensive tests were started to determine the accuracy, precision, and reliability of the system.

(e) The optical and electronic systems to be used in the thermal diffusivity apparatus were designed and constructed. The combined optical and electronic systems will be used to detect the radiation from the back surface of the specimen when its front surface is exposed to radiation from a pulsed laser. The response characteristics are of millisecond resolution. Their partial testing were performed under simulated conditions.

II HIGH TEMPERATURE ENTHALPY MEASUREMENTS

Preliminary analysis of the high-temperature enthalpy data obtained on β-Si_3N_4 to 1200 K has shown a rather large spread (up to 10 percent) between the NBS heat-capacity results near room temperature and those available from published low-temperature studies. In addition, heat-capacity values from a JANAF correlation of publishel high-temperature heat-capacity data for Si_3N_4 differ from the NBS results by four to seven percent below 400 K, and by a similar amount from the published low-temperature measurements. These large differences may arise from systematic measuring error, from sample impurity phases or from uncertainty in the α-β phase composition of the samples. Analysis of Si_3N_4 materials on which heat-capacity data have been published show typically several percent impurities. Our sample is of 99+ percent purity. With regard to the distrubution of α and β phases in the specimens, the NBS Specimen was examined by X-ray diffraction and estimated to be 95 to 99 percent β-phase. Although it does not seem likely that there would be a significant difference between the heat capacity of the d and β phases, it is true that none of the published studies on the heat capacity of Si_3N_4 has presented evidence for adequate structural characterization.

We are re-examining the data and continuing our study of these differences. Measurements of enthalpy above 1200 K were delayed by malfunctioning and necessary for repair of our automatic optical pyrometer.

Chemical analyses of three single-crystal SiC samples for total silicon and total carbon as well as uncombined carbon have been completed and indicate samples of 99 percent purity. Three SiC specimens were encapsulated in Pt 10 Rh containers and enthalpy measurements on one specimen have been completed to 770 K.

III SPECTROSCOPIC PROGRAMS

The vibrational assignments for SiF_2Br_2 and $SiBrF_3$ have been completed.

The major effort this fiscal year has gone into the problems of the computetion of thermal functions of polyatomic molecules. In particular the effect of vibretional arhaimonia on computed third law Entropies has been explored. Computations using the direct sum/technique in our newly developed codes have been run on $B(CH_3)_3$ and $Fe(Co)_5$. The major use of this program is to assess what differences due to vibretional anhaimoniaty should be expected between computed thermal functions (using traditional harmonic oscillator rigid rotor formalism) and experimentally determined entropies. It provides the thermodynamic modeller and envaluator a mathematical method for assessing the consistency of spectroscopic and thermodynamic data. Since the utility of this program has been demonstrated with large polyatomic molecules having many vibrational modes we are confident it will find good use for the small polyatomic species (number of atoms less than 6-7) most important in high temperature systems.

The direct sum technique codes for computing thermodynamic functions of dietomic molecules has been completed for several types of Hund's couplings and are available for use by other AFOSR contractors.

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Thermodynamics of High Temperature Materials

Annual Report for the Period of

1 October 1977 - 30 September 1978

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
AFOSR-ISSA-78-0007

I. HIGH-SPEED THERMOPHYSICAL MEASUREMENTS

Summary

Investigations performed during FY 78 with the millisecond-resolution thermophysical measurements system are summarized in the following paragraphs.

(a) Preliminary experiments were performed on carbon - carbon composite specimens as a step toward establishing the feasibility of obtaining thermal data at high temperatures. The results indicated that it is possible to heat these specimens in less than one second to temperatures over 2000K with the persent millisecond-resolution pulse heating system.

(b) The processing of data on the heat capacity and electrical resistivity of graphite (POCO grade) up to 3800K was completed. With the existing capabilities which permit pressurizing the apparatus to about 200 atm. it was not possible to make observations on graphite above 3800K. This is due to the vapor pressure of graphite which is about 1 atm. at these temperatures. Attempts will be made to reach the triple point of graphite ($\sim$ 4200K) with either an apparatus capable of operating at 200 atm. or with the microsecond resolution system expected to be operational in about two years.

(c) The radiance temperatures at the melting points of vanadium and palladium were measured. Papers describing this work are in preparation.

(d) A new technique, utilizing the millisecond apparatus was developed for the measurement of the heat of fusion of refractory metals at high temperatures. Measurements were performed on niobium, a computer program was prepared and the data were partially processed.

II. SPECTROSCOPIC PROGRAMS

(a) The infrared and Raman Spectra of $SiFBr_3$ and SiF_2Br_2 have been obtained. All fundamental vibrations have been observed and assigned for each species allowing the calculation of thermodynamic functions.

(b) Informal workshops concerned with the methods used for the computation of thermodynamic functions of diatomic species have been held. As a result of these meetings held with the cooperation of NBS, JANAF and Institute for High Temperatures (Moscow) personnel, a better understanding of the needed methodology for these computations has been realized. It is believed that with the wide availability of high speed computers direct sum methods will supplant the other formalisms for these high temperature systems.

(c) A preliminary investigation of the effect of anharmonicity on the computed thermal functions of polyatomic molecules has been completed. A computer program has been written and run for $B(CH_3)_3$. In this connection the infrared and Raman spectra for $B(CH_3)_3$ have been reinvestigated leading to some changes in vibrational assignments. This allows for a direct sum calculation for all energy levels which contribute to the functions. This type approach should eventually allow one to compare measured third law entropies with those computed from vibrational frequencies and rotational constants. This program will be continued in collaboration with the JANAF group.

(d) The JANAF type tables of thermodynamic functions for species of interest to the Chemical laser community which were computed by NBS have been distributed by JANAF after suitable editorial modification.

(e) The feasibility of a new transient interferometric technique for measuring thermal expansion of metals was demonstrated. Preliminary experiments were performed on tantalum up to 2300K. Electronic components were designed and partially constructed for the pulse interferometer which will extend the measurement capability to higher temperatures, up to the melting point of the specimen. A paper describing this work is in press.

(f) Work on the thermal diffusivity apparatus was continued. New components for the furnace were designed and their fabrication was started.

Papers published in FY 78 on work performed earlier on Air Force contracts are given in the References.

III. HIGH TEMPERATURE DROP-CALORIMETRY

High-temperature investigations during FY-78 were carried out on Silicon nitride and Silicon carbide.

(a) Si_3N_4: Enthalpy measurements in the range 273 to 1173K were completed. These showed excellent precision and no evidence of phase change or decomposition. X-ray analysis of the polycrystalline sample indicated it to be mostly β-Si_3N_4 with probably less than 5 wt.% α-Si_3N_4. Qualitative spectrographic analysis indicated an impurity level no greater than 0.8 wt.%. This is consistent with quantitative analyses for total silicon and nitrogen which indicated 0.6 wt.% impurity. The enthalpy data are now being analyzed and preparations made for enthalpy measurements above 1173K in an adiabatic receiving calorimeter.

(b) SiC: Sample capsules have been fabricated for enthalpy measurements in the range 273 to 1173K. Three specimens have been submitted for elemental analyses and for free carbon content.

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