NATIONAL BUREAU OF STANDARDS REPORT

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to Government Agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. A major portion of the Bureau's work is performed for other Government Agencies, particularly the Department of Defense and the Atomic Energy Commission. The scope of activities is suggested by the listing of divisions and sections on the inside of the back cover.

Reports and Publications

The results of the Bureau's work take the form of either actual equipment and devices or published papers and reports. Reports are issued to the sponsoring agency of a particular project or program. Published papers appear either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau itself publishes three monthly periodicals, available from the Government Printing Office: The Journal of Research, which presents complete papers reporting technical investigations; the Technical News Bulletin, which presents summary and preliminary reports on work in progress; and Basic Radio Propagation Predictions, which provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: The Applied Mathematics Series, Circulars, Handbooks, Building Materials and Structures Reports, and Miscellaneous Publications.

Information on the Bureau's publications can be found in NBS Circular 460, Publications of the National Bureau of Standards ($1.25) and its Supplement ($0.75), available from the Superintendent of Documents, Government Printing Office, Washington 25, D. C.

Inquiries regarding the Bureau's reports should be addressed to the Office of Technical Information, National Bureau of Standards, Washington 25, D. C.

MINERAL PRODUCTS DIVISION

(Division 9)

Sections

0900-11-0914 The Chemistry of Portland Cement F. Ordway

NBS and Portland Cement Association

Objectives. To study the fundamental physical chemistry of calcium silicate systems related to portland cement: To obtain experimental data extending our knowledge of such systems, and to find theoretical interpretations yielding general correlation of the facts observed; to develop new experimental techniques if needed for obtaining the required data; to relate the results when possible with the burning of portland cement clinker and the hardening of concrete, for improved understanding of these processes and ultimately for the advancement of their technologies.

Importance of the Project. The portland cement industry is large, and its product is vital to many parts of the nation's economy. Fundamental research on the physical chemistry of silicates at high temperatures and in hydrous systems, of the type done in this project, is of potential importance to many other fields of industry, and of science as well.

This research project has been carried on by the Portland Cement Association Fellowship since 1924. It has done pioneering work on the formulas of the major cement clinker constituents, the measurement of heats of hydration, the application of spectrography and X-ray diffraction to cement analysis, and the development of new tools and approaches to phase equilibrium research at high temperatures. Almost all cement manufacture is now receiving the benefits of some of these developments.

Activity Summary. This is a continuing project. During the year the work has been concentrated in the fields of high-temperature phase equilibria and X-ray crystallography. The study of the quaternary system CaO-$2CaO \cdot SiO_2$-$12CaO \cdot 7Al_2O_3$-$2CaO \cdot Fe_2O_3$ was continued. The techniques of quenching, differential thermal analysis, and microscopic and X-ray examination are being used for the determination of solid-liquid equilibria involving the $2CaO \cdot Fe_2O_3$ solid solution phase, which had been previously determined in the ternary boundary system lacking silica.

The high-temperature centrifuge used to study the senary system K_2O-Na_2O-CaO-Al_2O_3-Fe_2O_3-SiO_2 was rebuilt and considerably improved, particularly by the provision of forced-air

cooling for the metal shaft to which the ceramic rotor is attached. The determination of the course of crystallization for selected mixtures in the composition range of practical cement clinkers is continuing.

The study of X-ray diffraction intensities for calcium hydroxide was used as a test of a newly procured microdensitometer, with special modifications for single-crystal X-ray diffraction patterns. The development of optimum techniques for applying this instrument to X-ray diffraction promises to increase greatly the precision obtainable by film methods.

The previous study of the $2CaO \cdot Fe_2O_3$ solid solution in the ternary system suggested the possibility that structural changes occur within the composition range previously thought to represent complete solid solution without change of phase. This question is being further studied by single-crystal X-ray diffraction methods. Crystals of a composition approximating $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ are being studied.

Publications incidental to the program included:

"Differential Thermal Analysis Above 1200°C," by T.F.Newkirk (submitted to J. Amer. Ceram. Soc.)

"The Pseudo-Ternary System Calcium Oxide-Monocalcium Aluminate ($CaO \cdot Al_2O_3$)-Dicalcium Ferrite ($2CaO \cdot Fe_2O_3$)," by T.F. Newkirk and R.D. Thwaite. (Manuscript being reviewed preparatory to publication in the NBS J. of Research)

"Hydration of Tricalcium Silicate," by Max Swerdlow, H.F. McMurdie, and Francis A. Heckman, (published by the Royal Microscopical Society in "Proceedings of International Conference on Electron Microscopy held at London, July,1954").

Plans for Fiscal Year 1958. The studies of phase equilibria and crystal structure will be continued. In addition, a study of the physical chemistry of hydrous calcium silicate systems will be started, with emphasis on the determination of the activities of ionic species in calcium silicate solutions, and their effect on the equilibria and rates of formation of the hydrous silicates.

0900-11-0946 Structure of Barium Titanate A.D.Franklin

NBS

Objectives. To conduct a basic investigation of the relation between the fundamental structure and the ferroelectric properties of barium titanate and related materials.

Importance of the Project. Many of the ferroelectric properties, like those of ferromagnetic materials, are "structure-sensitive", in that they depend strongly on such non-basic properties of the specimen as the grain size, impurity content, distribution of internal strains, lattice defects, etc. It is important for our understanding of ferroelectricity to study these effects. At the same time. valuable tools for the exploration of these non-basic properties will be developed.

The ferroelectric oxides, of which barium titanate may be considered to be the prototype, have found wide application as dielectrics in capacitors, as accelerometers, as memory devices for electronic computers, as transducers in ultrasonic generators, and in many other devices. Many problems in the application of these materials remain, however, and the potentialities of as yet unexplored new materials of this type are great. From a practical standpoint also, increased understanding of the behavior of these materials is important.

Activity Summary. A number of specimens of $BaTiO_3$ were prepared by calcination of pure barium titanium oxalate; and the shapes of the X-ray diffraction peaks studied as a function of the calcining temperature. Low temperatures resulted in small crystallites and broad diffraction peaks. In addition, these small crystallites showed a more nearly cubic structure than large-crystal $BaTiO_3$. The calcining temperatures were found to be above the temperature at which all chemical reaction involved in decomposition of the oxalate is complete. The variations in structure found for different calcining temperatures therefore reflect changes (recrystallization, grain growth, etc.) taking place in the $BaTiO_3$ rather than changes in the degree of decomposition.

Attempts to analyze the peak shapes in detail revealed several problems, of which one was outstanding. Some of the most interesting peaks overlap, so that their detailed

0900-11-0946 - (continued)

analysis required that they first be separated. A Fourier series method was developed by which this separation can be accomplished in certain cases. This method was reported in a paper by A.D. Franklin and B.F. Canty, "Separation of the $\alpha_1 - \alpha_2$ Doublet of X-ray Diffraction Lines", Bull. Am. Phys. Soc., Ser II, 2, 132 (1957) (presented at the American Physical Society Meeting in March, 1957, in Philadelphia). A detailed version of this paper has been submitted to the Journal of Applied Physics.

A review of the literature on ferroelectricity for the calendar year 1956 was prepared by A.D. Franklin and K.A. King and will appear as Chapter XI, "Ferroelectric and Piezoelectric Materials" in the Digest of the Literature on Dielectrics for 1956, published by the Conference on Electrical Insulation of the National Research Council.

Plans for Fiscal Year 1958. Previous work has indicated a need for the highest precision possible in the X-ray diffraction data. It is planned to incorporate pulse-height analyzer into the equipment in order to increase the precision. The theoretical study of the Fourier series method of resolving overlapping peaks will be continued in order to try to make the method more general. Analysis of the diffraction peaks of the pure $BaTiO_3$ described above will be carried out to separate crystal size, strain, and stacking fault effects; and to study these as functions of the decomposition variables.

0900-40-0999 Consultative and Advisory Services — I.C. Schoonover

NBS

Objectives. To provide consulting services on a wide variety of ceramics problems of interest to government agencies, industry, and the public.

Importance of the Project. The National Bureau of Standards has, in areas within its competence, responsibility for providing advisory and consulting assistance to other govern-

0900-40-0999 - (continued)

ment agencies. The Mineral Products Division implements this responsibility in the general field of non-metallic minerals through its staff of specialized scientists and engineers.

Activity Summary. There has been a growing attention to problems of higher-temperature, and to materials for use in atomic power plants, resulting in consultations, frequently of a classified type, regarding ordnance and military aircraft. This is in addition to a continuance of requests on rather routine uses of ceramics in industry and government.

0900-30-4447 Acceptance Testing of Ceramic Materials I.C. Schoonover

Various

Objectives. To test ceramic materials for compliance with the technical requirements of Federal or Departmental Specifications.

Importance of the Project. The Federal Government is a large purchaser of ceramic materials. Since a very substantial cost is involved in the erection of structures and in other fabrication from these materials, acceptance testing assumes a major importance in a number of cases. This is particularly true in the use of refractories for boilers, incinerators, and similar installations; therefore most of the testing work under this project is concerned with refractory materials.

Activity Summary. The material submitted for acceptance testing required the assignment of one employee for approximately one-third man-year to this project. A total of 150 tests were performed on 22 samples.

0900-11-4461 Aging of Ceramic Dielectrics A.D. Franklin

Diamond Ordnance Fuze Laboratory

Objectives. (Task 1) To conduct a basic investigation of factors involved in the aging (the change in dielectric and piezoelectric properties with time) of some types of ceramic dielectrics with the aim of controlling and reducing the loss in dielectric constant (K) per decade of time. (Task 2) To explore the method of preparation of ceramic bodies with composition $Pb(Zr_{0.55}Ti_{0.45})O_3$ and determine the effect of preparation variables on the properties of these bodies. (Task 3) To develop methods of preparing titanates and related materials containing controlled amounts of impurities.

Importance of the Project. (Task 1) When a ceramic dielectric is cooled to room temperature from some temperature above its Curie point, there will occur a change in capacitance (used in calculating dielectric constant K) in some nonlinear relation to time. For dependable service in electronic devices, it is essential that this change in K reach a limiting value in relatively short time. It is important, therefore, to establish those chemical and physical properties which determine the relation of change in K with time, in order that dielectrics of stable characteristics may be developed.

Task (2) Ceramic piezoelectric transducers have a large potential application in ultrasonics, as accelerometers, and specialized electronic equipment (delay lines, transformers, etc.). Currently, formulations based on $BaTiO_3$ are most widely used. These are limited by the relatively low Curie point near 120°C, above which the desirable properties disappear. Recent work in this Division revealed another composition, $Pb(Zr_{0.55}Ti_{0.45})O_3$ with piezoelectric properties equivalent to those of $BaTiO_3$, but with considerably higher Curie point. However, fabrication of this new material is difficult due to the volatility of PbO. In order to take advantage of the greater temperature range inherent in the new material, methods for firing the ceramic bodies must be found, and the variation to be expected in the electrical properties explored.

0900-11-4461 - (continued)

(Task 3) The electrical properties of these materials are very sensitive to the presence of impurities. In order to understand how these effects come about, it is necessary to have specimens in which the impurity content is rigidly controlled.

Activity Summary. (Task 1, Aging) A dielectric relaxation occurring at low frequencies was observed and studied in pure $BaTiO_3$ ceramic. The data was found to fit one of the empirical equations that has been found to fit dielectric relaxation data in liquids. This work was reported in a paper by S. Marzullo and A.D. Franklin, "Low-Frequency Loss in Ceramic Barium Titanate", presented at the Bedford Springs meeting of the American Ceramic Society. A technique was developed for the representation of dielectric data in terms of a complex conductivity rather than the usually used complex dielectric constant. This was reported in a paper by F. Grant, "Use of Complex Conductivity in the Representation of Dielectric Phenomena", Bull. Am. Phys. Soc. Ser II, 2, 131 (1957), presented at the March meeting of the American Physical Society in Philadelphia. A more detailed version has been submitted for publication in the Journal of Chemical Physics.

Initial studies indicated that the dielectric properties of ceramic $BaTiO_3$ may be sensitive to the sizes of the grains in the ceramic body. A sedimentation column was constructed and some pure $BaTiO_3$ powder has been fractionated in order to produce powders with narrow distributions of particle size. These will be used to study the grain size effect in ceramic $BaTiO_3$.

(Task 2, Preparation of $Pb[Zr_{0.55}Ti_{0.45}]O_3$ Ceramic Bodies). A firing technique for these bodies was developed that kept the weight loss (due to volatilization of PbO) to about 0.5%. It was found that commercially available crucibles of MgO and Al_2O_3 were suitable as containers, provided they were pure and dense. This task is complete except for an evaluation of the reproducibility of the electrical properties of the bodies made using the technique developed here.

(Task 3, Controlled Impurities). This task has just been started. There are no activities to report.

0900-11-4461 - (continued)

Plans for Fiscal Year 1958. (Task 1, Aging). In order to characterize the low-frequency relaxation observed in $BaTiO_3$ ceramics, the equipment for measuring dielectric constant and loss will be extended to provide measurements at frequencies as low as 0.1 cycle per second. Attempts will be made to determine the mechanism producing this relaxation by studying the effects of electrodes, impurities, heat treatment, etc. Aging in $BaTiO_3$ ceramic will be studied as a function of frequency. Fractionation of $BaTiO_3$ powders will be completed and ceramics prepared from the fractions. These will be studied as to grain size distribution and electrical characteristics after firing.

(Task 2, Preparation of $Pb[Zr_{0.55}Ti_{0.45}]O_3$). During the work on the development of a firing technique a large number of specimens were produced. The dielectric and piezoelectric properties of some of these will be measured in order to determine the reproducibility of the specimens produced by our technique. When this has been done, this task will be completed.

(Task 3, Controlled Impurities). Initial work will be directed toward making TiO_2 with MnO_2 as an impurity. The method chosen for this preparation is coprecipitation of the oxalates followed by calcination to the oxides. First the preparation of pure TiO_2 will be studied as influenced by the temperatures of precipitation and calcination, etc. The crystal size and the tendency for crystals to agglomerate will be determined using X-ray line-broadening and surface area measurements, and microscopic examination. Then the preparation of the mixed oxides will be considered. The concentration limits of solid solution will be determined, and the influence of the impurity on the structure and properties studied.

0900-11-4475 Leakage in Titanates A.D. Franklin

U.S. Atomic Energy Commission

Objectives. To investigate the fundamental mechanism of electrical conduction in the ferroelectric oxides such as $BaTiO_3$, $Pb(Ti\text{-}Zr)O_2$, etc.

0900-11-4475 - (continued)

Importance of the Project. The ferroelectric oxides, in both ceramic and single-crystal form, have found wide application in many electronic devices. In these applications, it is usually desirable to keep the conductivity low. This is particularly true at higher temperatures. At present, for instance, the usable upper temperature limit for piezoelectric devices is about 100°C, near the Curie point of $BaTiO_3$. Recently, however, a new material of formula $Pb(Zr_{0.55}Ti_{0.45})O_3$ has been found with a considerably higher Curie point, and therefore a higher potential limiting temperature. This higher temperature range cannot yet be used, however, due to the excessive electrical conductivity that appears at the higher temperatures. In order to control this conductivity, a thorough and fundamental understanding of the mechanism of conductivity is required.

Activity Summary. Sensitive equipment for the measurement of the dc conductivity of titanate specimens as a function of temperature and atmosphere was set up. Measurements on $BaTiO_3$ single crystals revealed some interesting effects. Transient currents with decay times of days were observed. (P.H. Fang, "Electrical Conductivity of $BaTiO_3$ Single Crystals", Bull. Am. Phys. Soc., Ser II, 2, 23 [1957]). The conductivity of $BaTiO_3$ crystals containing small amounts of cerium or vanadium were much greater than those of crystals without deliberate additions. Furthermore, drastic changes in the magnitudes and temperature coefficients of conductivity in these impure crystals occurred at the ferroelectric transitions. This work requires the use of single-domain crystals. These are usually obtained by converting multi-domain crystals into single-domain form at the ferroelectric Curie point at 120°C. During this work it was found that domain conversion could also be accomplished at the tetragonal-orthorhombic transition. This result has been incorporated into a paper to be published.

Some theoretical work on methods of representing dielectric data was also done, and presented in a paper by P.H. Fang, "Relation Between Complex Conductivity and Complex Permittivity", Bull. Am. Phys.Soc., Ser. II, 2, 132 (1957).

0900-11-4475 - (continued)

Plans for Fiscal Year 1958. The past year's work has shown that conductivity phenomena are very complicated for specimens in the ferroelectric state. It is planned therefore to concentrate on $BaTiO_3$ above the Curie point and on the closely-related but non-ferroelectric $SrTiO_3$. The effect of added impurities, particularly vanadium and defects in the oxygen lattice, will be studied. By using conductivity, thermopower, and possibly Hall effect measurements, it is hoped to determine the number, signs, and mobilities of the charge carriers; to relate these to the impurity content; and to explore the energy band structure associated with conductivity.

0901-11-0942 Engineering Properties of Ceramics — J.B. Wachtman, Jr. H.S. Parker

NBS

Objectives. To devise methods and equipment for, and to determine the properties of, ceramics.

Importance of the Project. Progress and advancement in the use and development of any material have been based upon a backlog of information on the chemical and physical properties of that material. This backlog does not exist for systems of ceramics, nor is it available even for the more common ceramic materials over extended temperature ranges. Until such accumulations of information can be obtained, particularly the engineering properties, the utilization of ceramics in high-temperature applications such as rockets, jet aircraft, nuclear-powered units, and others cannot be effectively accomplished. However, before such systematic studies can be launched, both the methods and the equipment must be developed for these physical property determinations.

Activity Summary. An apparatus for the measurement of dynamic elastic properties of ceramics in the range 1000°C to 1700°C was designed and constructed in collaboration with project 0901-11-4416. This apparatus consists of a furnace of special design which permits a rod- or bar-shaped specimen to be heated while it is simultaneously caused to vibrate and the amplitude of its vibration is measured. The specimen is suspended horizontally from two fine wires. One of these wires is connected to a driver and is used to excite the vibrations; the other wire is connected to a crystal pickup and is used to measure the amplitude of vibration. The furnace is heated by a cage of 12 parallel tungsten wires spaced on a 1-inch circle with the specimen in the center. This heater is surrounded with radiation shields and a water-cooled shell with provision for the free passage of the specimen support wires through the top. This entire assembly is placed into a bell jar and operated in vacuo.

This apparatus, together with the auxiliary electronic equipment for supplying the driving voltage and detecting the pickup signal, was used to determine the resonant frequencies of flexural vibrations of ceramic specimens up to a

0901-11-0942 (continued)

temperature of 1700°C. From these measurements, Young's modulus as a function of temperature can be calculated.

Plans for Fiscal Year 1958. It is intended to modify the apparatus described above to extend its temperature range to 2000°C and to adapt this apparatus or design another for the measurement of internal friction at high temperatures.

0901-11-4400 Properties of Ceramics at Elevated Temperatures — H.S. Parker

U. S. Atomic Energy Commission

Objectives. To increase the understanding of the interrelationship of the physical properties of ceramic oxides and of the mechanisms and parameters which influence these properties and to evaluate these mechanical properties for a wide variety of ceramics as a function of temperature.

Importance of the Project: Ceramic materials have great potentialities in a wide variety of applications because of their nuclear, thermal, and structural characteristics. However, as progress in nuclear and high-temperature technology is made, the demands on materials are becoming more and more stringent. An increased understanding of the factors affecting material properties is essential for the continued improvement and development of materials required to meet these demands. In addition, during the course of the study, much data of immediate interest to the sponsor and others interested in reactor design are obtained. The project emphasis is reviewed annually to meet both current and future needs. Certain members of the project staff act as consultants to the Division of Research, US AEC, particularly with regard to the equilibrium relations of oxide systems containing UO_2 as one component. Although the work itself is not classified, the application of the data is, in general, classified.

0901-11-4400 (continued)

Activity Summary. This is a continuing program in the sense that the basic objective, the determination of fundamental information on the high-temperature properties of ceramic-type materials of interest to the sponsor, remains the same. However, the emphasis may be changed, either to meet the needs of the sponsor or as indicated by the results of previous phases of the investigation. During the current year, this project has proposed and provided some verification for an expression relating the brittle strength of polycrystalline materials to their porosity and grain size. A detailed report of this phase of the work is being prepared for publication in the Journal of the American Ceramic Society. A second phase of the work has studied the strength-related properties of four varieties of chemically-prepared UO_2. This has provided information on the flexural strength of this type of UO_2 at both room and elevated temperatures and in addition has shown the effect of minor additives on strength and porosity. A paper describing the results is currently in preparation. The third phase of this project has been concerned with the determination of elastic constants by sonic methods for a wide variety of ceramic materials. It has been shown by statistical analysis that the sonically-determined elastic properties yield a more efficient evaluation of merit of groups or lots of ceramic specimens than do measurements of their bulk densities. The elastic properties are preferred over bulk densities in the comparison of various fabrication methods. Some of the temperature dependence of the elastic properties of oxide-type materials have been determined. Some cermets, bonded-carbides, and intermetallics have been evaluated by room-temperature sonic tests before and after oxidation at various temperatures.

Plans for Fiscal Year 1958. During the next year, plans have been made to demonstrate the applicability of the proposed expression relating strength-porosity-grain size to other brittle ceramics and to attempt to incorporate the contact area between grains in the proposed expression. The possibility of using electrical resistivity and optical methods to measure or represent the contact area will be investigated. In addition, the determination of the elastic constants of approximately 35 ceramic-type materials as a function of temperature will be determined. A paper will be prepared which will report on the room-temperature elastic constants of these materials and the statistical evaluation of the forming methods employed. The internal friction of many of these materials as a function of temperature will also be determined.

0901-11-4416 Mechanism of Deformation in Polycrystalline Ceramics J.B. Wachtman,Jr.

Wright Air Development Center

Objectives. To study polycrystalline (glass-free) ceramic specimens for the purpose of interpreting their deformation behavior in the light of single-crystal behavior and, ultimate, of improving their serviceability at high temperatures.

Importance of the Project. Ceramic bodies have been regarded as being brittle at low temperatures and viscous at high temperatures. However, preliminary results have shown that single-crystal ceramics are plastic at high temperatures rather than viscous. It is important, therefore, to understand the nature of both deformation and failure in ceramic materials because there is an urgent need for materials that can deliver dependable service under severe conditions of mechanical and thermal stress at temperatures above the useful ranges of most metals and their alloys. The study is essentially fundamental but with broad objectives.

Activity Summary. This is a continuing project. Results of the measurements of creep properties of single-crystal ceramic oxides have been summarized in the Journal of the American Ceramic Society, 37 (7), 291 (1954), in the ASTM Bulletin, No. 211, 38 (1956), and in two papers accepted for publication in the Journal of the American Ceramic Society and in the Transactions of the ASM. Results of the measurements of creep properties of polycrystalline ceramic oxides are being prepared for circulation as a Wright Air Development Center Technical Report. During the past year, emphasis was shifted from static measurements of creep and modulus of rupture to dynamic measurements of elastic moduli and internal friction. Young's modulus of single-crystal aluminum oxide was measured up to a temperature of 1700°C and was found to depend linearly on temperature in this range. Young's modulus of polycrystalline aluminum oxide was measured up to 1300°C and was found to depend linearly on temperature up to 950°C, at which temperature relaxation, apparently caused by grain-boundary slip, began. The temperature dependence of Young's modulus of other ceramics was measured in the range room temperature to 1200°C to determine where grain-boundary relaxation began. Materials

0901-11-4416 (continued)

investigated included magnesia, thoria, stabilized zirconia, spinel, mullite, and silicon carbide. All showed relaxation beginning somewhere in the range 800° to 1300°C. The internal friction of aluminum oxide and magnesium oxide was measured as a function of temperature and strong peaks were found to accompany relaxation of Young's modulus.

Plans for Fiscal Year 1958. It is planned to use the present apparatus and techniques to survey the temperature dependence of Young's modulus up to the temperature where grain-boundary slip causes relaxation for as many ceramic oxides, borides, carbides, and cermets as can be obtained in suitable specimen sizes. It is hoped to make a fundamental study of grain-boundary properties by improving the accuracy of measurement of internal friction sufficiently to permit determination of energies of activation for grain-boundary slip and by studying the effect of impurities on Young's modulus and internal friction.

0901-11-4468 The Mechanism of Plasticity W. C. Ormsby
0901-11-0947

The Edward Orton Jr. Ceramic Foundation
NBS

Objectives. To obtain a scientific understanding of the physical and chemical properties of matter determining plastic behavior in clay-water systems. Involved is a fundamental explanation of plasticity and a method for its measurement.

Importance of the Project. Clays, partially because of their plastic nature, are the most widely used of all raw materials in the making of ceramic objects (approximately two billion dollars' worth of ceramic products are produced annually in this country). The so-called "plastic materials" are distinctly different in their behavior from viscous substances, and a scientific understanding of what

0901-11-4468
0901-11-0947 (continued)

plastic behavior is, and of the properties of matter determining, controlling, and measuring it, has not been developed. Mechanization of the ceramic industry is dependent upon the "workability" of clay, and can be fully realized only through an adequate understanding of "plastic" behavior. Furthermore, this dependence will become more acute, and scientific knowledge a virtual necessity, as the natural resources of the most desirable clays are exhausted; and scientific information will be required to so treat lower-quality clays that their plasticity will supply the desired workability.

Activity Summary. This is a continuing project. Detailed studies of the mineralogical, chemical and physical properties of several clays have been completed. On the basis of the results obtained, a single clay has been chosen and is being carefully fractionated into monodisperse fractions. The rheological properties (viscous behavior of dilute clay-water suspensions and deformation behavior of clay-water "pastes") of these fractions will be determined. Apparatus for the determination of these properties is being designed.

An evaluation of purification methods; i.e., electrodialysis and ion-exchange resins, has indicated that the latter is to be preferred. This technique will be used in converting fractionated samples to the homoionic condition prior to testing.

Plans for Fiscal Year 1958. The fractionation of clay will be continued until sizeable quantities of a wide range of particle-size fractions have been accumulated. These samples will be converted to a homoionic condition with the aid of ion-exchange resins.

The study of the viscous and "plastic" behavior of the fractionated clay will be undertaken with special emphasis on the effect of systematic variations in particle size and surface area. Later, tests may be designed to study the effect of various types of exchangeable ions and dispersion media.

0902-11-0901 Chemical Properties of Glass-Forming Systems - Donald Hubbard

NBS

Objectives. To conduct basic investigations on the chemical properties of a number of glass-forming systems. Included will be the reactions of glass with other materials, such as water and aqueous solutions. The bahaviour of glass as an electrolyte will be studied.

Importance of the Project. Any fundamental study of the structure of glass will be more complete if it includes the nature of the reaction of glass with other materials, as well as the changes that take place in the glass itself. The reactions that take place between glass and aqueous solutions and the interchange of ions between the glass and the solution yield valuable information on the structure of glass itself. The behavior of glass as an electrolyte should furnish valuable information on the energy relations between the various atoms or ions in glass and should indicate whether these ions will migrate under the influence of an electric current as single atoms or whether the movement will also include large groups corresponding to hydrated ions in aqueous solutions. Although the project is designed primarily to yield information of value in the basic study of the structure of glass, the findings should be of almost immediate practical use.

Activity Summary. Samples of arsenic sulfide glass from Commercial and NBS sources were investigated for hygroscopicity, chemical durability, hydrogen electrode function (pH response), expansivity, elastic moduli, modulus of rupture, hardness, thermal shock, spectral transmittance and indices of refraction.

In an effort to obtain a better understanding of the destructive reaction that often occurs when certain natural aggregates are used with high alkali contents, eleven natural and synthetic aggregates were studied by several methods, such as expansion bar tests, chemical durability, hygroscopicity, electrical surface resistance, and heterogeneous equilibria.

Interferometric methods were developed to demonstrate the dimensional changes caused by reactive aggregates, the extensive dimensional changes caused by wetting and drying of hydrated cement, the inbibiting effect of calcium ions

0902-11-0901 (continued)

on the alkali-aggregate reaction, and anomalous chemical durability phenomena.

The excessive chemical reactivity of the surface of solutions compared with that of the bulk volume was investigated. Experiments were completed by which a direct comparison of the difference in the surface activity compared with the bulk-volume of buffer solutions over the range pH_2 to $pH_{11.8}$ could be made using Corning 015 glass as the indicator. For a buffer at pH_7 the surface activity corresponded to a hydrogen ion activity of $pH_{9.45}$. The apparent concentration differential between the surface and bulk-volume falls off sharply for buffers of increased pH_1 amounting to only 0.22 pH units for the buffer at $pH_{11.8}$.

In a special investigation typical specimens of Australite (tektite) glass were studied for such properties as expansivity, annealing temperature, chemical durability over an extended pH range, hygroscopicity, electrode pH response, heterogeneous equilibria at the liquid-solid interface, and spectral transmittance to ultraviolet, visible, and infra-red radiation. The results obtained on this glass, supposedly of extra-terrestrial origin, have been compared with similar data obtained on obsidian glass from Yellowstone Park, and some present-day industrial, optical, and natural glasses. The comparison showed the Australite specimens to be distinctly different from the obsidian, the optical glasses and the industrial glasses.

Plans for Fiscal Year 1958 - The major effort for the fiscal year 1957-58 will be devoted to a study of the sources of the non-migratable ionic charges developed by Portland and High-alumina cements during hydration.

During the same period the ionic nature of surfaces (treated and untreated) of silicate materials (natural and experimental) used as aggregates in concrete will be under observation.

0902-11-0902 Physical Properties of Glasses and Glass-Forming Systems — A.B. Bestul

NBS

Objectives. To conduct basic investigations on glasses and glass forming systems both to increase the fund of experimental information in this field and to analyze this information and correlate with existing data in order to increase the theoretical understanding of the constitution of glass.

Importance of the Project. Modern theories of the constitution of glass begin with the pioneer work of Zachariasen and Warren, about 20 years ago. However, it has been found that the structure postulated by Zachariasen, though very fruitful, is not adequate to explain many of the known phenomena characteristic of glasses. Considerable theoretical work has been done in recent years in attempts to amend and modify Zachariasen's theory to account for the experimental data. However, the picture is still incomplete and much work, experimental and theoretical, needs to be done before a major breakthrough in the impasse in which science now finds itself with respect to the molecular structure of the vitreous state can be effected. Because of the complexity of glass structure, in contrast to the regular structure of crystals, it is often important to work with very simple glasses so that the changes in physical properties with changes in composition, temperature, or heat treatment can be interpreted on the basis of the spacing and the energy relations between the atoms and groups. The reason why various physical properties change with change in composition is of practical as well as theoretical importance. When this is better understoon, it should be possible to design a glass with specified properties without the costly process of making a large number of experimental melts. In a like manner, a knowledge of the structure of glasses would enable one to predict more closely how various properties will change with temperature and heat treatment.

Activity Summary. 1) The dependence of viscosity on temperature for several inorganic glasses has been analyzed in terms of the Williams-Landel-Ferry equation expressing this dependence for different types of glasses in a limited temperature region above the glass transformation temperature in terms of two universal constants and the glass transformation temperature. Directions have been detected in which modification of the equation is necessary for inorganic glasses or high transformation temperatures. 2) Investigation of the correspondence between elastic and other properties as functions of heat treatment, previously limited to rate annealing, have been extended to different types of heat treatment. An apparatus has been constructed for the measurement of dynamic elastic

0902-11-0902 (continued)

properties of glasses at temperatures below room temperature. 3) Preliminary vapor pressure measurements have been made by transpiration techniques on vitreous arsenic trisulfide at temperatures between 120° and 180°C, which is just below its glass transformation temperature. A Knudsen effusion cell for vapor pressure measurements has been constructed.

Plans for Fiscal Year 1958.

TASK I. Temperature Dependence of Viscosity and Elastic Modulus. - Modifications indicated in the Williams-Landel-Ferry equation when applied to inorganic glasses or high glass transformation temperatures will be examined. The temperature coefficient of elastic modulus will be analyzed in terms of the energy and the entropy contributions to the modulus.

TASK II. Dynamic Mechanical Measurements. - Measurements of dynamic elastic moduli of glasses will be extended to as low temperatures as possible. The relation between the change with heat treatment of elastic modulus as compared with density or refractive index will be determined for several dozen different inorganic oxide glasses.

TASK III. Excess Entropy of Glass. - Vapor pressures of several glasses and the molecularly similar crystals will be determined at temperatures just below their glass transformation temperature by transpiration techniques and by Knudsen effusion techniques. Differences between entropies of vaporization for glass and crystal will be determined from the results. Calorimetric apparatus will be constructed for the determination of the residual entropy of glasses at absolute zero temperature.

0902-20-0948 Standard Glasses A. Napolitano

NBS

Objectives. To obtain a number of glasses that can be used for calibrating instruments and comparing results between laboratories. The glass will be of two classes (1) standard glasses, representative of important commercial types that can be used for calibration and standardization of instruments. (2) High purity simple glasses containing one, two or three components that can be used in comparing results between laboratories, especially studies of structure and constitution.

0902-20-0948 (continued)

Importance of Project. There has been a strong demand from research laboratories for glasses that can be used for calibrating instruments such as those used for measuring viscosity and surface tension of glasses at elevated temperatures. No adequate standards for this work are available at this time. There is also a need for a series of simple glasses that can be used by a number of laboratories in studies of properties that can yield information on structure and constitution of glass. The correlation of results between laboratories when they have included one or more of these standard glasses in their studies will be much more meaningful than when each laboratory works on its own samples.

Activity Summary. The project was started late in the fiscal year. The time so far has been devoted to designing and building equipment that will be used in measuring viscosity and surface tension. Orders have been placed for a lot of soda-lime-silica glass of a high degree of homogeneity which will be used for the first sample.

Plans for Fiscal Year 1958.

1. Obtain a lot of soda-lime-silica glass and make measurements (chemical analyses, index of refraction and density) to determine suitable homogeneity for standard sample work.

2. Design and build rotating cylinder type viscometer for use at temperatures up to 1450°C.

3. Build apparatus for measuring viscosity by fiber elongation method.

4. Build apparatus for measuring surface tension of glass at high temperatures.

5. Determine viscosity and surface tension of a soda-lime-silica glass and start measurements on one other type.

0902-11-0949 High Temperature Viscosity and Surface Tension — A.B. Bestul

NBS

Objectives. To develop techniques and instrumentation for the measurement of viscosity and surface tension of glass-forming and other liquids at temperatures above 1500°C where such measurements are as yet practically unknown.

Importance of Project. Technological practice and scientific interest are relentlessly advancing to higher and higher temperatures. Two material properties which are necessarily concerned in this advance are viscosity and surface tension. Knowledge of these properties is particularly important for melts of inorganic materials often of a glass-forming nature. Pertinent experimental data is almost totally lacking at temperatures above 1500°C. Well-known technological efforts are already being hampered by this lack at present and will inevitably be more and more seriously hampered as time goes on if the data is not made available. It is therefore of a high degree of importance that the means of obtaining this data come into being as soon as possible.

Activity Summary. 1) A prototype viscometer of the oscillating cup design has been partially constructed for room temperature measurements to investigate this viscometric technique. 2) By the informal cooperation of the Wright Air Development Center the corrosive effect of boron trioxide up to 2100°C was examined for molybdenum, tungsten and tantalum. Their resistance decreased in the above order. 3) The quantitative determination of water content in boron trioxide at temperatures up to 1400°C has been investigated using infrared spectrometric techniques and pyrolysis followed by the reduction of water to hydrogen by uranium for measurement.

Plans for Fiscal Year 1958.

TASK I. All the activities reported in the above section will be continued.

TASK II. Measurement of Viscosity of Boron Trioxide at Temperatures above 1500°C. - In anticipation of the successful development of the oscillating cup viscometer for the present application it is planned to obtain viscosity values for a boron trioxide system of known water content up to temperatures as high as can be accomodated with the viscometer developed.

0902-11-0949 (continued)

TASK III. Ultrasonic Measurement of Viscosity. - The possibility of viscosity measurements at high temperatures by ultrasonic techniques, probably using a modification of the commercially available Ultraviscoson instrument will be thoroughly investigated.

TASK IV. Surface Tension Measurements. - General techniques and specific designs for the measurement of surface tension at high temperatures will be explored with the goal of selecting one or more for intensive development effort.

0902-20-4405 Optical Glass Technology E.H. Hamilton

Air Force

Objectives.

(a) To develop an heat-resisting optical glass to be used in supersonic aircraft which encounter high skin temperatures.

(b) To continue the survey and summarizing of classified and unclassified literature dealing with the effects of high energy radiation on optical materials.

Importance of the Project. In view of the rapid progress being made in neuclear power plants and supersonic aircraft research, new applications of glass are being studied. Improvements in the physical, chemical and optical properties of old and new glasses are needed to fulfill these new requirements.

Activity Summary. Development of a heat resistant glass. The work on heat resistant glasses was directed toward the development of glasses with low coefficients of thermal expansion. A large number of compositions were melted which contained SiO_2, B_2O_3, CaO, Al_2O_3 and Na_2O as the principal constituents. None of these melts produced low expansion glasses that could be melted at temperatures below 1500°C. The possibility of producing low expansion glasses with melting temperatures above 1550°C was indicated.

0902-20-4405 (continued)

The investigation of zinc borosilicate and zinc magnesium borosilicate glasses has produced glasses with coefficients of expansion of 5 x 10^{-6} and 6.1 to 6.4 x 10^{-6} respectively. Glasses, containing as principal constituents SiO_2, B_2O_3, MgO, and Al_2O_3 in the approximate proportions found in tourmaline minerals, have been made with coefficients of expansions between 4.3 and 4.9 x 10^{-6}.

The study of the elastic properties of the glasses of the various types both at room and elevated temperatures has been undertaken. Determinations have been made on several glasses at elevated temperatures.

Radiation Resistant Glasses. The survey of the classified and unclassified literature on the effects of high energy radiation on optical materials was completed. A report, including recommendations for future work, has been completed and approved by the Air Force.

Plans for Fiscal Year 1958. 1. Development of Heat Resistant Glasses. The melting of zinc borosilicate glasses and tourmaline type glasses will be continued and directed toward the development of glasses with low coefficients of expansion. Li_2O, MgO, Al_2O_3 and other oxides will be introduced into the glasses and their effect upon the thermal expansion and other properties such as elastic moduli, refractive index, melting temperatures, sag point, chemical durability, etc. will be determined.

2. Literature Survey of Effect of High Energy Radiation on Optical Materials. The survey of the classified and unclassified literature on the subject will be continued and reports issued from time to time to keep this survey current.

0902-20-4407 Development of Special Optical Glasses G.W. Cleek

Navy, Bureau of Ordnance

Objectives. To develop new optical glasses for use in the near-infrared. Suitable glasses are needed for the following purposes: (1) as a material for making refracting type optical elements, (2) as a window material, (3) as envelope or substrate material for the production of detector cells. It is also necessary to study and develop the techniques required to make and fabricate the glasses into usable shapes of the required quality.

Importance of the Project. Glasses having special optical and physical properties are needed to meet the requirements of new fire control and other optical instruments being developed by the Armed Services. The sponsor has indicated an urgent need for a variety of glasses having, along with other special properties, good transmittances in the near infrared. In addition to meeting a need of the defense effort, this work is a contribution to the general field of glass technology, in that it is extending the knowledge of the oxides that may be used as components of glasses, and by the correlation of the physical properties of the glasses as a function of chemical composition gives information as to the contribution of each oxide to the physical properties of the resulting glasses.

Activity Summary. Considerable effort during the year was devoted to improving the durability of the calcium aluminate glasses. These glasses transmit very well in the wavelength range from 3.5 to 5.0 microns, but are readily attacked when exposed to moist atmospheres. Substantial progress has been made in this effort. Composition changes have produced glasses which are more resistive to attack by moisture, by a factor of ten, than the original glass. In addition, it was found that treatment of the polished glass surface with hydrofluoric acid produces an iridescent surface film which further reduces the attack. In fact, the improved glass samples treated with hydrofluoric acid showed no detectable attack after exposures of 72 hours to an atmosphere of nearly 100% relative humidity at 50°C.

Other glass-forming systems investigated include binary glasses consisting of TeO_2 and another oxide, such as BaO, Al_2O_3, PbO, and WO_3. These glasses have a refractive index, n_D, about 2.0 and fairly good transmittance in the near infrared. However, we were not able to cool them without crystalline inclusions in melts larger than 500 g.

0902-20-4407 (continued)

Investigations have also determined the glass-forming areas in the $BaO-La_2O_3-SiO_2$ and $BaO-Ta_2O_5-SiO_2$ systems. Certain compositions in these systems are very stable as glasses and promise to serve as base compositions for further substitutions. It has been found that fluorides can be introduced into these glasses in appreciable amounts and that they improve the transmittance considerably in the wavelength region from 3 to 4 microns.

Except for the TeO_2 glasses, most of the glasses investigated have deformation temperatures about 800°C, linear coefficients of expansion of 8 or 9 x 10^{-6} and liquidus temperatures below 1425°C.

Plans for Fiscal Year 1958. The tasks for Fiscal Year 1958 are:

TASK I. To develop glasses that will provide the optical designer with a greater range of refractive indices and dispersions at wavelengths in the infrared. In addition, the glasses should possess other physical properties, such as high transmittance at these wavelengths and good chemical durability.

TASK II. To develop glasses for use as a window material in the infrared. For this use the glasses should have a refractive index as low as possible and a high deformation temperature.

TASK III. To develop glasses for use as an envelope or substrate material for the production of detector cells. The glasses should have good infrared transmittance, a high deformation temperature and no adverse effect or reaction with the sensitive films.

TASK IV. To study the physical properties of ternary glasses that are made in the development of glasses for the above uses. In addition to the properties normally determined to evaluate the experimental glasses for use as an infrared material, it is proposed that other properties, such as the transmittance of thin films in the infrared and the dielectric constant, be measured insofar as facilities are available. These measurements possibly will lead to a clearer understanding of the structure of glass and thus aid in enabling one to predict the properties to be found in a glass of a given composition.

TASK V. To supply limited amounts of the glasses developed to the sponsor for testing purposes, and if the demand warrants, to supply the necessary information and assist commercial producers in the initial production of any of the glasses.

0902-40-4408 Developing Process for Making Special Optical Glass — A. Napolitano

Navy, Bur. of Ordnance

Objectives. To develop glass compositions, procedures, and equipment for melting high quality optical glasses with desired optical and physical properties in platinum pots. To develop procedures for the fabrication of the glasses into optical elements. To furnish small quantities of special optical glasses for military purposes to the Department of the Navy and to other government departments when it cannot be obtained from other sources. Much of the glass is used for prototype instruments.

Importance of Project. For many years the National Bureau of Standards, as an integral part of its program on optical glass, had operated a pilot plant production facility to supply the needs of the Navy, Bureau of Ordnance. With the rapid development of new methods of making optical glass that could be used economically for either ophthalmic glass or precision optical glass, the commercial facilities of the country seem adequate to meet the military needs. For this reason the Bureau of Ordnance and the National Bureau of Standards felt that it was no longer necessary to maintain a cadre of optical glass works in a government facility and the project was terminated at the end of Fiscal Year 1957.

Activity Summary. During the Fiscal Year 1957 approximately 3,000 lbs of optical glass was made and delivered to the Naval Gun Factory. Included were a number of large special shapes. Steps were taken to help the Naval Gun Factory start procurement of glass from commercial producers.

Plans for Fiscal Year 1958. Completed.

0902-20-4464 Glass Fibers — W. Capps

Navy

Objectives. To investigate the factors which produce effects on fiber formation and on properties of glass fibers, particularly their elastic properties.

0902-20-4464 (continued)

Importance of the Project. Because of the magnitude of the commercial and military effort to develop high-speed aircraft and weapons, there is a corresponding need for the development of lightweight, strong, dimensionally stable structural material which will withstand high temperatures. Glass fiber-reinforced materials presently available do not have the required stiffness for many applications. The Navy Department has requested NBS to investigate the possibility of developing a glass composition from which fibers can be made having a Young's modulus twice that of ordinary glass and withstanding temperatures at least 100°C higher than commercial fibers. Success in this work would ensure a considerable improvement in the performance of certain fiber-reinforced composites.

Activity Summary. This project was officially completed on November 30, 1956 and thus lasted only five months of this fiscal year. During this period the two major accomplishments were (1) the increasing of the ease of making fibers from high modulus glasses and (2) the development of a means of coating rapidly moving glass fibers with aluminum immediately after their formation from molten glass.

This method of coating was satisfactory for single fibers but would not lend itself to multiple strand production. It was believed that the glass development, which we were well suited to handle, was successfully completed but that the metals part of the program was outside of scope of the original project. For that reason the whole project was considered completed at the end of it's second year.

Plans for Fiscal Year 1958. Completed.

0902-40-4465 Optical Glass Bank F.W. Glaze

Air Force

Objectives. To obtain and maintain a reserve supply of optical glass of known properties as a source of glass for experimental or prototype instruments when the glasses are not immediately available from commercial firms. The supply would be operated as a "bank" from which instrument manufacturers would draw glass as needed and replace it, when available, from commercial sources.

0902-40-4465 (continued)

Importance of the Project. The Air Force, and contractors working on new designs for the Air Force, have on many occasions had difficulty in obtaining glass for experimental or prototype work. At times the delay in obtaining small amounts of glass or the initial delivery on larger amounts has been many months. In an attempt to minimize this delay, the Air Force has proposed the establishment of a glass "bank" to take care of these small but highly important needs. It is not proposed that this "bank" should ever be sufficiently large to take care of production runs on instruments, except perhaps for the first few to be made. The increased use of "continuous tanks" for melting optical glass has accentuated the problem of obtaining rapid delivery of small quantities of glass, since long production runs of a single type of glass are required for economical reasons.

Activity Summary. Six blanks were loaned out during the year, four of which have been returned. At present, there are a total of seven blanks on loan (five from the previous year).

The following glass has been received for deposit in the "Bank": (1) From Hayward Scientific Glass Corporation, seven types, gross weight 1785 pounds; (2) From Bell & Howell, two types, gross weight 168 pounds.

A purchase order for eight types of six blanks each has been issued on Fish-Shurman to round out the stock of glass on deposit in the "Bank".

Also, 59 of the 70 boxes of glass received from Bausch & Lomb Optical Company and all of the nine boxes received from Hayward Scientific Glass Corporation and the two boxes received from Bell & Howell have been inspected.

Plans for Fiscal Year 1958. The inspection of the remaining glass received from Bausch & Lomb Optical Company is to be completed. At the completion of the inspection, the storage of the glass is to be rearranged for ease of access, and to make room for the glass now on order.

With the discontinuation of the pilot Optical Glass Plant at this Bureau, any large blanks or large chunks of rough glass of suitable quality will be transferred to the "Bank".

Also, as soon as the inspection of the Bausch & Lomb glass is completed and the glass now on order is received, a new catalog of the glass available for loan will be issued.

0902-12-4471 Properties of Glasses at Elevated Temperatures — M.J. Kerper

Air Force

Objectives. To develop suitable methods and apparatus for determining the mechanical properties of glass at temperatures ranging from room to the strain temperature; and to determine the mechanical properties of some representative glasses.

Importance of Project. In recent years, there has been an increased interest in transparent inorganic glasses for applications where high temperatures will be encountered (cockpit covers, navigation lights, etc., on high speed aircraft). Data on the mechanical properties of glasses, particularly at temperatures near the strain point, are meager and often inadequate to permit sound engineering design. Furthermore, suitable methods for obtaining such data are not always available and need to be developed. The development of such methods and the obtaining of basic data over a wide range of temperatures is important to the entire glass producing industry for use on presently available glasses, as well as in connection with the development of new and improved glasses for high temperature applications.

Activity Summary. Tests have been made on a commercial plate glass to determine the effect of temperature on the modulus of rupture, the effect of cutting the specimens by different laboratories on the modulus of rupture, and the effect of surface abrasion on the modulus of rupture. Measurements of the smooth (mirror) portion of the fracture surface have been made in an attempt to correlate the size of these surfaces with strength and to see if they vary with temperature. Additional stress-rupture and creep assemblies have been constructed and the preliminary work on stress-rupture and creep has been completed.

Plans for Fiscal Year 1958. The modulus of rupture and the modulus of elasticity of several commercially available glasses that are candidates for aircraft glazing will be determined at temperatures ranging up to the strain temperature. Measurements of the internal stress will be made of the heat treated glass before and after exposure to elevated temperatures to determine the effect of temperature on internal stress. Dynamic measurements of the modulus of elasticity and Poisson's ratio will also be determined before and after exposure to elevated temperatures to determine the effect of temperature on these properties. The mirror portion of the fracture surface will be measured on all broken specimens. Stress-rupture and creep tests will be conducted all during the year.

0903-12-0903 Physical Properties of Refractory Materials L.E. Mong

NBS

Objectives. To investigate the physical properties of refractory materials for the purpose of obtaining data that will be useful in revising existing standards, including Federal specifications or forming the basis for the technical requirements of new specifications for such materials. To study the physical and chemical changes which occur when the various refractory ingredients of pyrometric cones are heat treated.

Importance of the Project. New refractory products are continually being developed by industry, improvements made in existing ones, and new applications found for these products. In order to keep abreast of such developments, both from the standpoint of current Federal specifications and the inauguration of new ones, a knowledge of the properties of the products under service conditions is highly desirable. There is a dearth of information on the properties of refractory castables. The principle engineering test for refractories is the establishment for a material the pyrometric cone equivalent (P.C.E.). The ASTM test for PCE does not specify the furnace to be used but merely insists on neutral or oxidizing atmosphere. It has been established that the furnace atmosphere to a high degree determines the PCE. It is essential that evaluation of the various commercial and laboratory furnaces be made to assist ASTM in specifying a furnace. This study has a theoretical background in the study of the influence of atmosphere on liquid formation in these silicate compositions.

Activity Summary. During the past year the mineralogical changes in refractory castables on heat treatment have been studied and reported. In addition, differential thermal analyses and thermal length changes were carried out. A comparison of four furnaces - electric, two commercial gas fuel furnaces and a special controlled atmosphere laboratory furnace for determination of PCE is under way.

0903-12-0903 - (continued)

Plans for Fiscal Year 1958. The work on castables will be completed and will include data on a high purity cement recently made available. The furnace evaluation for PCE will be continued so that a report to ASTM can be made.

0903-11-0904 Phase Equilibrium of Inorganic Non-Metallic Systems — S. Zerfoss

NBS

Objectives. (1) To study heterogeneous equilibrium in inorganic non-metallic systems. (2) To prepare phase diagrams of such systems. (3) To devise new methods for presenting data on multicomponent systems. (4) To explore the possibility of calculating phase equilibrium relations from thermodynamic data.

Importance of the Project. The subject of heterogeneous equilibrium in inorganic non-metallic systems is one which is basic to all of the many branches of the ceramic industry. By studying a number of selected compositions in a system and applying the principles of the phase rule and of phase diagrams to the data obtained, generalizations can be drawn which can be applied to all compositions in the system to give a phase equilibrium diagram of the system or its equivalent. Such information is essential to a complete understanding of the behavior of ceramic products during firing and is most valuable as a source of information for the development of new products.

Activity Summary. There are three longtime programs under way in this project. (1) Constitutional study of immiscibility. Crystal chemistry principles were applied to the quantitative interpretation of immiscibility in binary and ternary oxide systems. Using ionic radii and one of two structural types, two methods were developed for calculating extent of immiscibility. A density method gave agreement with experimental results to within about

0903-11-0904 (continued)

5 mol.%. An oxygen volume method gave agreement within about 2 mol.%. These concepts are applied to structure of glass. (2) The system MgO-GeO_2 is under study as the first of a series of systems paralleling the silicate diagrams. (3) Several members of the perovskite family (ABO_3) of compounds have been synthesized and their X-ray structure is being examined.

Plans for Fiscal Year 1958. These three programs are long term and will be continued. They are reported as the various steps are completed.

0903-11-0945 Chemical Reactions of Inorganic Materials at High Temperature — S. Zerfoss, R.F. Walker

NBS

Objectives. To provide basic information on the physical and chemical properties, reactivity, and stability of inorganic materials at elevated temperatures.

Importance of the Project. The temperature level of operation of modern power plants, engines, etc. and the temperature of fabrication of many ceramic components for modern industrial equipment are constantly being raised. It is common knowledge that design of rockets which will operate at high Mach values is seriously limited by lack of suitable high-temperature materials. The temperature requirements for rockets, jet engines, etc. which are of greatest interest are already out of range of most metals. For this reason there has been a renewed interest in inorganic materials such as oxides, silicides, etc., either as protective coatings for metals or as construction components which are to be subjected to high temperatures under oxidizing conditions.

Numerous articles have appeared in recent scientific periodicals pointing out the inadequacy of our knowledge of the properties and behavior of materials at high temperature. For example in a recent issue of Chemical and Engineering News, Willard F. Libby, Commissioner AEC, in discussing

0903-11-0945 (continued)

the need for work in this area stated, "It is not possible to predict with any reliability the relative volatilities, thermodynamic free energies or even molecular species of compounds which are likely to result from a given mixture of elements heated at temperatures between 500° and 1000°C or above."

There is a need for data on the melting points, phase equilibria, stability, mechanism of reaction with other materials, and volatility under a variety of conditions of oxide and non-oxide materials. This need was further emphasized at a recent National Symposium at Berkeley, California, "High Temperature -- A Tool for the Future," attended by 650 scientists and engineers.

Activity Summary. Volatility of Inorganic Substances. The general operational characteristics of the high temperature vacuum microbalance were determined, and such improvements made as were necessary for its routine use. The balance has been used to study the amount of material volatilizing into a vacuum from single crystal of alumina of known surface area. Using an assumed molecular weight for the vaporizing species, the data obtained have been used to determine the vapor pressure curve for alumina in the range 1000-1350°C.

Some preliminary experiments on the effect of water vapor on the volatilization of alumina at high temperatures were completed. At 800°C water vapor was not found to have a very profound effect on the rate of volatility. However, at a temperature a little above its melting point (2050°C), alumina in the presence of water vapor volatilized at such a rate that the molten material appeared to first boil, then freeze as it drew upon its own heat to maintain the volatilization process. The experiments at the very high temperatures were done with the solar furnace, and indicate that after attention to the temperature measurement problem, the solar furnace should prove to be a useful tool in the study of volatility phenomena at high temperature.

A study of the inversion of cristobalite using a highly purified silica source showed that the well known anomalies disappeared for silica heat-treated above 1500°C. Below 1500°C the cristobalite had lower varying inversion temperatures probably because of a disordered structure as revealed by X-ray examination.

0903-11-0945 (continued)

Experiments on the reaction of platinum and aluminum oxide are continued. Numerous side reactions, principally the adsorption of oxygen by platinum will have to be evaluated before continuing the study.

Plans for Fiscal Year 1958. Work on the vaporization processes of inorganic solids will be materially assisted by the new 50 KW induction heater just installed. With this heater the vapor pressure of Al_2O_3 can be studied from 1350°C to the melting point. Influence of water vapor on the vaporization will be continued, using the microbalance and in the solar furnace. The work on cristobalite will be completed and submitted for publication.

The solar furnace will be explored as to the feasibility of zone purification and single crystal growth.

0903-20-4428 Properties of Concrete at Elevated Temperatures W.L. Pendergast

Navy, Bureau of Yards and Docks

Objectives. Study the mechanism responsible for spalling and failure of concrete when exposed to intense thermal shock.

Importance of the Project. Concrete aprons used by jet aircraft were often observed to deteriorate rapidly, even explosively, as a result of the extreme thermal shock occurring both during the warm-up and take-off periods. While it was generally assumed that the water content of the concrete was an important factor in deterioration of concretes subjected to severe thermal shock, it was not known whether both bound and unbound water were involved or what effect such factors as mode of preparation, type of aggregate, porosity, etc., would have on the amount of water retained. Such information needs to be obtained in order to design new concrete formulae with improved thermal stability.

0903-20-4428 (continued)

Activity Summary. Data were obtained which indicate that the primary cause of spalling of concretes when subjected to rapid thermal shock is related to the total amount of unbound water present in the concrete. Additional data were obtained on the rate and amount of water that is absorbed by concretes as a function of the mode of preparation, type of aggregate employed and porosity of the hardened mass. Wide variations in both the rate and amount of water absorbed and returned was observed depending on the type of aggregate used. The available pore space or degree of consolidation in the aggregate is the dominant factor in the selection of a proper aggregate. Measurements completed on the water vapor pressure developed in neat cement when heated rapidly, giving results approximating those of the Steam Tables.

Plans for Fiscal Year 1958. The immediate goal is to fix the dried conditions or water content limit for failure under test. The role of the aggregate as to water holding capacity etc. will continue to be studied. A study of the mechanism by which water vapor travels through the concrete will continue.

0903-20-4431 Investigation of Stress-Rupture and Short-Time Creep of Cermets M.J. Kerper

Watertown Arsenal

Objectives. To develop apparatus and test methods for evaluating stress-rupture and creep properties of cermets, intermetallics, and related refractory materials at extremely high temperatures in various gases.

Importance of the Project. The necessity of increasing the temperature to which rocket parts are subjected in order to improve efficiency has intensified the search for materials having greater refractoriness and has extended the operating temperatures to a region where their mechanical properties are not known. Currently, the lack of data for these properties introduces uncertainty in the design and engineering

0903-20-4431 (continued)

of these high-temperature parts, causing failures in the performance of the weapon. Such failures make the missile unsafe and ineffective. This project has been proposed to develop methods of test which yield reliable data for the design of such parts. The test methods could also be employed for other high-temperature applications of cermets.

Activity Summary. This project was discontinued during the year and the only activity was the preparation of the final report.

0904-11-0908 Ceramic to Metal Interactions

W.N.Harrison
J.R.Crandall
J.C.Richmond
D.G.Moore

NBS

Objectives. To study the fundamentals controlling the behavior of inorganic materials in the fused or vitreous state, including especially their interactions with metals when applied as coatings or when the two types of materials are brought in close contact for other purposes.

Importance of the Project. The expanding use of inorganic (ceramic) coatings (Manufacturers' cost of porcelain enameled parts was 440 million dollars in 1954, representing retail value of finished appliances of 1 1/2 to 2 billion dollars), along with the extended utilization of ceramic coatings for military purposes (jet engines, rockets, and atomic energy power plants), has introduced a whole new series of problems in this general field, which will require a more basic approach to their solution. For example, the mechanism by which ceramic-metal interactions affect the high-temperature properties of coated alloys is only partially understood, and better comprehension is needed because of the extensive current and potential use of ceramic coatings to improve the usefulness of metals and heat-resisting alloys at high temperatures. In the high-temperature applications, basic data on such properties as ionic diffusion and permeability to gases, as well as a knowledge of other general properties as a function of composition and temperature, are also badly needed. Further, in many applications chemical stability is the reason for the choice of these materials; thus the study of surface chemistry of such vitreous materials, and the mechanisms controlling their chemical durability, are matters of considerable technological importance. Along with fundamental studies of this type, new and adequate methods must be developed for evaluating the behavior of such coatings in the new fields in which they are being used.

Activity Summary: Analysis of the data taken during a fifteen-year weather-exposure test of porcelain enameled steel panels was completed, and a manuscript describing the study was released for publication as a BMS report. The industry considered this work, on which two previous reports had been published, of such importance that the Porcelain Enamel Institute requested the Bureau to establish it on a continuing

0904-11-0908 (continued)

basis, and agreed to have the laboratory and field work handled by their Research Associate, under Bureau supervision. Specimens of recently developed enamels have been exposed in this newly extended program, which also provides for a wider variety of climatic conditions, as well as for continued exposure of some of the original panels.

A paper giving the results of color-difference evaluations for porcelain enameled specimens was prepared and released for publication. It contained an analysis of visual estimates made by over 30 individuals in 8 different laboratories. These results will be compared with several types of instrumental measurements, and will be useful in the establishment of a standard color-difference test.

Analysis of extensive field service and laboratory data, taken over periods of five to seven years on porcelain enameled fixtures, was continued. Also experimental laboratory tests were made in effort to develop methods of test that would give better correlation with service results than existing tests do, and that would be suitable for adoption as standards.

Plans for Fiscal Year 1958. The following work is planned: (1) The correlation of laboratory test results with 5-year service data will be continued, and the results prepared for publication.

(2) The study of weathering of porcelain enamels will be continued; this involves return to the Bureau for inspection and subsequent re-installation of a considerable variety of specimens at exposure sites that are widely dispersed for access to different climatic conditions. It also involves further development work on a laboratory test for the weather resistance of certain recently introduced types of enamels for which existing tests are not adequate.

(3) Development of a laboratory test for resistance of porcelain enameled steel chalk boards to deterioration in service will go forward in the Porcelain Enamel Institute Research Associateship, under supervision of NBS personnel.

0904-11-0908 (continued)

(4) Study of the mechanism of adhesion between ceramics and metals. This activity, added as a task under this project by conversion from a sponsored program, will involve a basic approach, calling for selected ceramic and metallic materials of high purity, on which contact angle at high temperatures can be measured, work of adhesion computed, and actual adhesiveness experimentally determined. Synthetic, single crystals of sapphire (Al_2O_3) and purified gold will be among the materials used in the study.

0904-11-4412 Ceramic Coatings for Aircraft Parts — D.G. Moore, A.G.Eubanks

National Advisory Committee for Aeronautics

Objectives. To develop surface coatings capable of reducing the temperature of airframes in supersonic flight; also, to obtain spectral emissivity data on the developed coatings for comparison with data on various aluminum and high-temperature alloys.

Importance of the Project. At high Mach numbers, aerodynamic heating in aircraft and missiles becomes a serious problem. In addition to the necessity for fabricating the airframe from alloys of high strategic index in order to insure structural stability at the high operating temperatures, components inside the structure must be thermally protected. If coatings could be prepared that would bring about a decrease in the alloy skin temperature of the airframe, either by improving the emissivity characteristics or by providing thermal insulation, one of the following benefits should result: (a) savings in structural material and in internal insulation costs could be realized, (b) more severe operating conditions could be tolerated.

Activity Summary. The design and testing of thermally insulating ceramic coatings that can be matured at relatively low temperatures, for possible use on air frames, was continued during the year. The term "insulating" as used here pertains to all means of minimizing the temperature of the

0904-11-4412 (continued)

substrate, whether by low thermal conduction, high reflectance, or high emittance. Since the latter two properties are complementary under suitable conditions, only one need be measured; spectral emittance determinations were made on various materials, both metal and ceramic. Also an apparatus adapted to the determination of thermal conductivity of thin ceramic coatings at high temperatures was completed, and conductivity measurements were made on a number of experimental coatings. A report on the spectral emissivity of a specific specimen-type of silicon carbide, to be used as a reference standard in emittance determinations, was released for publication.

Plans for Fiscal Year 1958. (1) Emphasis will be placed upon the development of configurations for metallic reinforcement of bond between insulating ceramic coatings and the alloy substrates. Types of insulating coatings to be studied include those having dispersed particles of materials with high melting points in binders such as sodium silicate, aluminum phosphate, and calcium aluminate.

(2) Appropriate materials for use in ceramic insulating coatings will be studied with particular reference to their spectral emittance characteristics. Materials of the refractory type to be studied are exemplified by alumina, thoria, and zirconia.

(3) Thermal conductivity measurements on selected coatings and coating materials will be made on specimens of thickness simulating expected application conditions.

0904-20-4458 High Temperature Strain Gage J.W.Pitts, D.G.Moore

Navy; Air Force

Objectives. To develop an electrical resistance type strain gage that will measure static strain at temperatures as high as 1500°F and be suitable for use in analyzing stresses in aircraft structures and other parts operating at elevated temperatures.

0904-20-4458 (continued)

Importance of the Project. Aerodynamic heating of aircraft and missiles becomes serious at high Mach numbers. Thermal gradients result from this heating and these gradients create stress concentration in the structural parts. If the design of the parts is to be sound the magnitude of these stresses must be evaluated. The preferred method of obtaining such an evaluation is through use of an electrical resistance strain gage. The SF-4 gages, which use organic binders, are unsuitable at temperatures above 250°F. A rugged, reliable ceramic type gage is definitely needed. Such a gage would not only be valuable in designing safer high-speed aircraft structures, but it would also be extremely useful in analyzing stresses in aircraft structures, but it would also be extremely useful in analyzing stresses in aircraft engines, rocket motors, and nuclear reactors.

Activity Summary. At the beginning of the year a high-temperature gage had been developed which represented a significant advance over the gages available at the outset of the work; a batch of 1,000 such gages had been used in stress-analysis work on aircraft structural members at elevated temperatures, and a modification of it was going into commercial production. Its imperfections included a tendency to drift in calibration at elevated temperatures, and a lack of sufficient reproducibility from gage to gage. Its upper temperature limit for useful results was about 800°F. During the year major emphasis was placed upon isolating the factors or components causing the deficiencies in performance. It was shown that one source of error could be imperfections in the junction between the filament wires and the component alloy foil. One way of reducing the incidence of such imperfections was to enlarge the filaments at the point of attachment by electrodeposition. However, after designing and constructing test apparatus for the purpose, it was found experimentally that available filament wires were inhomogeneous, as indicated by observed thermoelectric effects at high temperatures. Further, it was observed that the change in strain-resistance ratio of the filament wires with time at elevated temperatures took place whether the wires were in air or in an inert gas; hence, an internal, temperature-dependent reaction in the alloy was considered responsible for the shift in "gage-factor".

0904-20-4458 (continued)

Plans for Fiscal Year 1958. The development of better alloys for filament wires will be carried on in another laboratory, and our work will emphasize the design of ceramic cements that will have appropriate electrical resistance, rigidity, thermal expansivity, and adhesiveness at temperatures beyond 800°F. In addition, the attempt will be made to circumvent the principal defects of available filament alloys by gage design and selection. Thus filaments of various compositions and origins will be tested for uniformity of temperature-coefficient of resistance, and assigned to classes, each having acceptable limits of variation. The incorporation of a thermocouple with the gage will be studied; ideally the emf of the thermocouple would automatically compensate for the temperature dependency of the strain-resistance ratio in the filament. In practice, even calibration curves will be helpful.

0904-20-4462 Development and Evaluation of Materials for Fuel Metering Valves — J.R. Cuthill

Department of the Navy
Bureau of Aeronautics

Objectives. To find a satisfactory material for aircraft fuel valves to meet specified temperature, pressure, corrosion resistance, hardness, and other requirements. This end may involve development work on materials such as ceramics, cermets, ceramic coatings, surface-treated metals, and alloys. It further involves development of evaluation methods and their use on experimental and commercially available materials, to determine the degree of compliance with specified technical requirements.

Importance of the Project. Operating difficulties are encountered at present in fuel-control valves of gas turbine engines as a result of the lack of resistance to salt-water corrosion of the metals from which the valves are fabricated. Because these valves are installed in jet aircraft engines, any change detrimental to their operating efficiency can result in disaster to the plane.

0904-20-4462 (continued)

Activity Summary. Specimens of approximately 10 additional materials have been prepared and evaluated during the year. Evaluation was by means of coefficient of static friction determinations before and after corrosion tests, as well as by visual examination and by hardness determinations.

The corrosion tests were of two types: the standard salt-spray test, and an autoclave test in which the specimens were immersed in a 20-percent salt solution (the same concentration as used in the salt-spray test). The autoclave tests were conducted at 500°F and 1000 psi in an apparatus constructed especially for these tests.

Many of the materials tested excelled in one or more of the required properties, and a few materials met all of the requirements, although fabrication of valves from some of these materials probably would be somewhat more difficult than from the presently used materials. Early in the investigation nitrided titanium appeared to meet all of the physical-property and corrosion-resistance requirements, and also to have the advantage of light weight and ease of fabrication. Therefore a considerable portion of the effort during the year was expended on studying the effects of selected variables in the nitriding of titanium, including the effect of certain alloying elements. The work indicated that the alloy additions which promote an improved nitride case structure may not show the best corrosion resistance. It was also found that there are appreciable differences in corrosion resistance between different nitrided alloys under the test conditions employed.

Plans for Fiscal Year 1958. This investigation will be transferred from Division 9 to Division 8 at the beginning of Fiscal 1958 because the investigation of various materials, including ceramic and cermet compositions, indicated that the most promising for the purpose were certain types of metals or alloys, as typified by nitrided titanium.

0904-11-4469 Chemical Processes and Reactions at High Temperatures

W.N.Harrison
H.B.Kirkpatrick
J.Shumaker

Air Research and Development Command

Objectives. To provide basic information on the physical properties and chemical reactivities of inorganic materials subjected to high temperatures.

Importance of the Project. The temperature level of operation of modern power plants, engines, etc., and the temperatures of many of the components for modern industrial equipment are constantly being raised. The temperature requirements for rockets, ram jets, etc., which are of greatest interest, are already almost out of the range of most metals. For this reason, there has been an increasing interest in inorganic materials, such as the oxides, silicides, borides, nitrides, etc., either as protective coatings for metals or as construction components which are to be subjected to high temperatures under oxidizing conditions. Little is known, however, of the fundamental chemistry of these materials in the temperature ranges at which they are likely to be used.

Activity Summary. (1) Construction and assembly of experimental apparatus for studies of high-current arcs was completed and preliminary determinations of temperature profiles in arc plasma, with argon atmosphere and tungsten electrodes, were made. In mid-year the work was temporarily transferred to the Institute for Experimental Physics of the University of Kiel, in order to benefit from their extensive experience in the study of temperatures and compositions of arc plasma. There, experiments have been performed with constriction-stabilized arcs. These have dealt with the determination of oxygen-transition probabilities, the reduction of powdered metallic oxides in hydrogen arcs, and the determination of temperature and composition profiles in nitrogen arcs.

(2) Some of the apparatus used in studying the early stages of niobium oxidation was revised and rebuilt to improve its effectiveness. Observations were made which, if confirmed, could have important implications. These involve (a) the fine structure of the parabolic curves relating weight gain to time at fixed temperature, and (b) the parabolic-to-linear transformation of the oxidation rate. Microscopic

0904-11-4469 (continued)

examination has revealed color patterns that are indicative of varying oxide film thickness which is associated with the orientation of individual crystals in the specimen. Electron diffraction patterns have been obtained for various stages of the transformation zone from one regime of oxidation rates to the other.

Plans for Fiscal Year 1958. (1) For a part of the year arc studies will be continued at the University of Kiel, aimed primarily at perfecting details of experimental technique and of calibration methods for relating the transition probabilities of known gases to temperatures. Upon return of the investigator to NBS laboratories, apparatus will be assembled to incorporate constriction-stabilization for the arc plasmas. This equipment will be used in studies of chemical reactions in arc plasmas involving either oxide reduction in hydrogen arcs or the chemical and thermodynamic states of oxide vapors in inert atmosphere arcs.

(2) Additional oxidation-rate measurements will be made at various pressures and temperatures, using niobium metal with different kinds of surface preparation. Other experiments will be carried out to establish whether the linear discontinuities in the weight-gain curves are reproducible and, if so, to discover their cause. Additional electron-diffraction and electron-microscope studies will be made of the parabolic-linear rate transformation to further elucidate the reason for this behavior. It is also planned to begin a study of the anomalous temperature dependency of the oxidation rate of niobium in the temperature range 600°-800°C.

0904-11-4470 Ceramic-Metal Bonding D.G. Moore

Navy, Bureau of Aeronautics

Objectives. To investigate reactions in simple ceramic-metal systems and to relate these reactions to the sealing behavior of different metals and alloys to crystalline ceramic bodies.

0904-11-4470 (continued)

Importance of the Project. Crystalline ceramic bodies such as alumina and forsterite have greater strength, lower dielectric loss, and higher softening temperatures than glass. Therefore, the possible use of such bodies as a replacement for glass envelopes in special types of electronic tubes is receiving serious attention. Experimental tubes have already been prepared with ceramic envelopes that have given excellent performance but until better and cheaper methods are devised for forming vacuum-tight ceramic-to-metal bonds, tubes of this type cannot be considered for mass production operations. One reason for the difficulties with the seals is a lack of knowledge as to the basic bonding mechanisms. The goal of the present work is to learn more about these mechanisms and, by so doing, to place the sealing of ceramics to metals on a firm scientific basis.

Activity Summary. A furnace was constructed for melting pellets of gold of the spectroscopic purity on optically polished discs of single crystal sapphire, periclase, and fused silica. Melting was done under various partial pressures of oxygen. After cooling to room temperature, the bond strengths were determined by measuring the force required to shear the pellets from the ceramic materials. The bond strength when measured in this way was found to be a function of the oxygen pressure.

A second piece of equipment was constructed for measuring the contact angle and surface tension of molten gold by the Sessile drop method. Exploratory experiments have indicated satisfactory operation.

Plans for Fiscal Year 1958. This work is not to be continued as a separate project but will, if practicable, be included as a phase of work done on "expense funds" because of the importance of learning more about the fundamentals governing the adhesion between ceramics and metals.

0904-12-4472 Surface and Subsurface Oxidation of Experimental Alloys

J.C.Richmond
H.R.Thornton

Wright Air Development Center

Objectives. To evaluate the type and extent of surface and subsurface oxidation of high-temperature alloys, especially newly developed ones, as they are submitted by the sponsor.

Importance of the Project. The oxidation resistance of new high-temperature alloys is a property of paramount importance in determining their suitability for use under oxidizing conditions at elevated temperatures. Deterioration of physical properties as a result of the oxidation of uncoated alloys at high temperatures can occur through the gradual loss of thickness, due to surface scaling. Even when surface oxidation occurs only to a minor extent, subsurface oxidation can cause marked deterioration of strength and other physical properties. In addition, with some alloys, especially when tested under load, there is a tendency for certain elements to diffuse to the surface,where they are preferentially oxidized, thus altering the composition and the properties of the remaining alloy. Information on the oxidation behavior of the alloys submitted by the sponsor will be important not only because it affects the usefulness of the uncoated alloys under oxidizing conditions at elevated temperatures, but also because of its bearing upon the application of protective coatings and upon the reactions that occur between alloys and coatings at high temperatures.

Activity Summary. By means of techniques that were worked out for use in evaluating the degree of protection afforded to alloys by ceramic coatings of specially designed compositions, a number of experimental alloys submitted by the sponsor were studied to determine their oxidation resistance under specified conditions of temperature and load, in air. Both surface and internal oxidation were evaluated. According to the sponsor's request, the alloys were tested in the "as-received" condition. It was found, however, that supposedly replicate specimens varied noticeably in surface condition, a factor which had a significant effect upon the oxidation behavior. A conference of representatives of the sponsor, the suppliers, and NBS was held. Preferred procedures, taking account of this factor, were agreed upon. The first topical report (concerning a single alloy) was sent to the sponsor, and three others have been written and edited for release.

0904-12-4472 - (continued)

Plans for Fiscal Year 1958. It is anticipated that this project can be completed during the year, provided the alloy suppliers make the specimens available on schedule. As was done for previously evaluated alloys, the specimens will be heated in air at specified loads and temperatures for 100 hours. Several different temperatures and stress levels are to be used for each alloy. Metallographic sections will be made of each tested specimen; both external oxidation and total depth of "stringer" penetration will be evaluated by procedures developed in this laboratory.

0904-11-4477 Thermal Properties of Ceramic Coating Materials — J.C.Richmond, W.N.Harrison

Army Ordnance

Objectives. To obtain characteristic constants for thermal properties of ceramic materials over a wide temperature range, with emphasis on the constants that govern emission and reflection of radiant energy; secondarily, to use acquired information in designing prototypes of hetergoeneous systems having required thermal properties.

Importance of the Project. Among the thermal properties of ceramic materials at high temperatures for which little or no data are available, emission and reflection characteristics are the most urgently needed. The energy absorbed and emitted by external or internal components of airborne vehicles, manned or unmanned, especially at supersonic velocities or very high altitudes, can have an important influence upon the maximum temperatures reached by structural members, and hence upon the limits of operating conditions. Further, the variation in absorptance and emittance with the wave length of the radiant energy has a significant bearing upon the suitability of a given material for a specific application. The urgent need for information on the spectral emission characteristics of inorganic coatings and potential coating materials, especially in the temperature range from about 900°F up to nearly the melting poonts of refractory materials, has become well recognized by design engineers, but there is a critical scarcity of data on the spectral emittance of materials at high temperatures.

0904-11-4477 (continued)

Other thermal properties such as electrical resistivity and thermal shock resistance are of recognized importance, but the current phase of the work will give top priority to the determination of emission and reflection characteristics.

Activity Summary. This project was activated during the last quarter of the fiscal year. Apparatus has been installed for making emittance measurements, and is being augmented to permit tests on specimens at high temperatures and over a much wider range of wave lengths of radiant energy. Conferences have been held in Washington and in several outside laboratories regarding the state of present knowledge and the most urgent needs of the sponsor, as well as to discuss elsewhere unconventional equipment accessories that may have application to one or another phase of this study.

Plans for Fiscal Year 1958. The assembly of all required equipment for high-temperature emittance measurements will be completed as soon as procurement processes will permit. Emittance determinations on potential coating materials of most immediate interest, such as alumina, zirconia, thoria and graphite, will be made as soon as the necessary accessories can be installed. Since emittance and reflectance are complementary under appropriate conditions, it is planned to design or select equipment for measuring the reflectance of specimens over a wide temperature range, thereby minimizing sources of error that are inherent in direct emittance measurements under certain conditions. Pending the installation of the remainder of equipment needed for emittance measurements, the facilities of other laboratories will be utilized to obtain room-temperature reflectance measurements in, and moderately beyond, the visible range of radiant energy, thus furnishing data of value at the earliest practicable date.

Physical Properties of Concreting Materials

0906-12-0910 B. E. Foster

NBS

Objectives. To provide basic information leading to a better understanding of the effects of environmental factors upon the performance of concrete and to relate the physical properties of concretes and their ingredients to performance.

Importance of the Project. Approximately $700,000,000 worth of portland cement is used annually in the United States. By the time this cement is incorporated in concrete, a several-fold increase in cost is involved. Some of this concrete fails to give satisfactory service, with a consequent large economic loss. The mechanisms responsible for several types of disintegration are partially understood, but needed is additional fundamental information on the properties of concrete and concrete aggregates, as well as additional developments of techniques to measure these properties.

Activity Summary. The automatic strain-temperature scanner and recorder mentioned in the previous report did not possess all of the features contracted for and required for the tests planned. A newly engineered instrument, with the desired features, was finally furnished by the manufacturer as a replacement. After some modifications, the instrument was placed in service in January and experiments have been made with six concrete specimens in which strain gages and thermocouples were imbedded.

A report on results obtained by subjecting 6 types of concrete to 4 types of laboratory freezing and thawing cycles was accepted for publication by the ASTM and will appear in the 1956 Proceedings. Most of the data obtained from a similar investigation involving 13 laboratories and 22 laboratory-cycles, participated in and coordinated by the NBS staff, were received during the year. Reports on two phases of this investigation, relative abilities of the various laboratory-cycles to distinguish between concretes of different durabilities, and an attempt to correlate moisture loss during test with durability factors obtained in different laboratories were prepared and presented at the Highway Research Board meeting in January. Members of the staff organized and presided over the meeting of the HRB committee on Durability of Concrete, Physical Aspects, as well as the Off-the-Record Session sponsored by that committee.

0906-12-0910 (continued)

Plans for Fiscal Year 1958. Five of the portland cements found in a previous NBS investigation to yield quite durable concrete without the use of entrained air, and five cements found to produce low-durability concrete will be the subject of a series of tests which it is hoped will answer the question of why these groups of cement behave differently. These tests will utilize embedded strain gages to measure volume changes during freezing. They will also include tests on concretes containing entrained air.

Large cylinders with embedded SR-4 strain gages and thermocouples will be frozen and thawed under differing conditions to study the strain and temperature distribution.

Coordination of and participation in the preparation of the final report on the Highway Research Board Cooperative Test Program on Freezing and Thawing will be completed.

Chemical Properties of Cementing Materials

0906-11-0923

E. T. Carlson
C. M. Hunt

NBS

Objectives. To provide basic information leading to a better understanding of the mechanism of hardening of cement and related materials, and of the reactions attending the deterioration of these materials under various conditions of use.

Importance of the Project. Cementing materials, including portland and other cements, lime, plaster, and the aggregates employed therewith, are used in great quantities in the construction of highways, dams, and nearly all types of buildings. Portland cement production in the United States alone amounts to about 50 million tons a year. Occasionally these materials fall short of standard performance in service, and considerable economic loss results from deterioration of concrete, mortar, and plaster. In many cases the causes of failure are not entirely understood, perhaps because of imperfect knowledge of the reactions that normally occur during, and subsequent to, hardening. The various cements

0906-11-0923 (continued)

and plasters have in common the property of reacting chemically with water, thereby hardening and developing strength. Much is already known, in an empirical way, about the relation between chemical and physical properties and performance in service, but it is increasingly evident that more fundamental knowledge is required.

Activity Summary. In a general program of surface and sorption studies of cements and cement compounds, the following studies are essentially completed: surface changes taking place in cement subsequent to hydration; some factors affecting the magnitude of the surface of hydrated cement as determined by nitrogen and water vapor adsorption; vacuum drying characteristics of hydrated cement. The effect of carbon dioxide on subsequent hydration of unhydrated portland cement has been studied. The carbonation of hydrated cement, as influenced by water content and age, has also been investigated. A physico-chemical study of the destructive alkali-aggregate reaction in concrete was completed, as was an experimental study of the pressure developed by such a reaction. In a further study of the mechanism of the reaction some preliminary observations of ionic charges on hydrated cements were described. These observations led to a similar study of separate cement constituents, which is not yet finished. A hypothesis was offered for the observed increase activity at the surface of certain solutions used in the aggregate studies. An investigation of the hydration of aluminous cements and its relation to the phase equilibria in the system lime-alumina-water has been completed. A study of phase equilibria in the same system at 1°C is under way, and the general areas of stability have been determined. The literature on the chemistry of supersulfated cements has been reviewed, and a few thermochemical determinations have been made on cements of this type. A thermochemical study of lime-silica-water pastes has been completed. Heat-of-solution determinations have been made on a number of samples of calcium sulfoaluminate and its dehydration products. A study has been made of a number of methods of determining uncombined calcium hydroxide in lime-pozzolan-water pastes.

0906-11-0923 (continued)

Plans for Fiscal Year 1958. (1) Effect of admixtures on the hydration rates of cement compounds. (2) Effect of admixtures on the hydration rate and colloidal structure of hydrated cement. (3) Surface properties of the hydration products of cement compounds. (4) Infra-red studies of hydrating cement compounds. (5) Microscopic studies of the diffusion of sodium and calcium ions into aggregates. (6) Studies to identify the source of the ionic charges developed by cements during hydration. (7) Expansion studies on a series of soda-silica, potash-silica, and lithia-silica glasses used as aggregates in mortar bars. (8) A study of the ionic charges exhibited by freshly broken aggregate surfaces. (9) Studies of the durability of decorative aggregates in relation to the alkali aggregate reaction. (10) Study of phase equilibria in the system lime-alumina-water at 1°C. (11) A study of the calcium sulfoaluminates and other closely related compounds. (12) Studies of hydrothermal reactions of certain cement constituents. (13) Determination of heats of formation and hydration of various materials, including hydrated calcium silicates, the alkali-bearing constituents of portland cement, the strontium aluminates, and magnesium oxysulfate. (14) Continuation of the study of activity of pozzolans.

0906-30-4415 Cement Reference Laboratory J.R. Dise

American Society for Testing Materials; Corps of Engineers; Bureau of Public Roads; NBS

Objectives. To standardize and improve the testing of portland cement in laboratories throughout the country, and to assist in the refinement of cement testing methods.

Importance of the Project. The NBS carries on a large cement testing program, and in connection therewith, does work on the development and refinement of test methods. The tests are somewhat empirical in nature and, for this reason, comparable test results between laboratories are obtainable only

0906-30-4415 (continued)

through standardization of equipment and techniques. The work of this project is an important contribution in this respect. Also, the data resulting from these activities is used extensively by technical groups concerned with the development of test equipment and procedures.

Activity Summary. As part of its Eleventh Inspection Tour among cement testing laboratories of the United States, the Cement Reference Laboratory inspected cement testing equipment and test procedures in 71 laboratories, and 132 written confirmatory reports covering these inspections were prepared and distributed. Two special investigations undertaken led to the development of two new field inspection procedures which have increased the scope of many inspections. In a continuation of the Comparative Test Program, 224 chemical and 268 physical test samples of cement were sent out, and more than 1000 reports covering the results of these tests were prepared and distributed. A total of 78 samples of the standard mixture used in checking of 10-inch flow tables were mailed, and a new supply of the powdered silica for this mixture was ground. A narrative history covering the first 25 years of CRL operation was prepared. Vigorous participation in the activities of technical committees was continued, with all of the technical secretarial work of ASTM Committee C-1 on Cement being performed.

Plans for Fiscal Year 1958. It is anticipated that the rate of inspection of laboratories will be essentially as outlined above. The importance of the Comparative Test Program is increasing rapidly, and the potential of this service will be further developed. Some attention will be given to the use of photographic techniques for instruction in correct testing procedures. Plans will be formulated for the extension of the inspection service to cover concrete testing laboratories.

0906-30-4433 Acceptance Testing, Cement D. N. Evans

Various Government Agencies

Objectives. To make acceptance tests on portland cement used by the various Federal agencies throughout the United States.

0906-30-4433 (continued)

Importance of the Project. Most of the projects for which cement is tested are of a permanent nature (large dams, air fields, etc.), and the cement-acceptance program prevents difficulties with the concrete resulting from the use of sub-standard cement.

Activity Summary. This project has been in continuous operation for over 40 years. Currently, samples representing approximately 11 million barrels of cement per year are being tested in laboratories in San Francisco, California; Seattle, Washington; Denver, Colorado; Allentown, Pennsylvania; and Washington, D. C. A mobile cement testing laboratory has been placed in operation at Duluth, Minnesota for the construction season. A statistical testing plan was put into effect which is expected to reduce the cost of testing to some extent. Measurements have been continued on the behavior of cements and concrete under prolonged outdoor exposure. Studies have been made to develop transverse strength tests and a nondestructive sonic test for cements.

Plans for Fiscal Year 1958. It is expected that the work in this project will be at a slightly higher volume.

The volume of testing is somewhat seasonal. During slack periods, work will also be accomplished on development of test methods, both physical and chemical, and on cooperative test programs with other laboratories.

0906-30-4444 Miscellaneous Testing D. N. Evans

Various Government Agencies

Objectives. To make tests, both acceptance and of other types, on a variety of materials, such as hardened and fresh concrete, concrete aggregates, soils (engineering properties), bituminous aggregates, filter trickling media, floor hardeners, integral concrete admixtures, and spelters.

0906-30-4444 (continued)

Importance of the Project. The information obtained from this project enables the various Federal agencies to control the quality of concrete and other materials going into Federal construction in the D. C. Area. It furnishes information on soils required in engineering designs. It contributes to the determination of the causes of failure in performance of unsatisfactory concretes.

Activity Summary. This is a continuing project, with the major portion of the work being accomplished in the Washington, D. C. laboratory, although a few tests each year are made in the Seattle and San Francisco cement-testing laboratories.

Plans for Fiscal Year 1958. It is expected that the work load and emphasis will remain essentially the same.

0906-20-4473 Chemical and Physical Properties of Dolomitic Limes — B.E. Foster, R.A. Clevenger

National Lime Association

Objectives. To provide information leading to a better understanding of the mechanism of the dimensional changes of dolomitic lime hydrates.

Importance of the Project. Partially hydrated dolomitic lime is used in large quantities in mortars for masonry construction. There is some question relative to the expansion and resulting deterioration of such mortars. An autoclave test has been proposed for determining the potential expansion of lime, but a controversy exists relative to the correlation of the laboratory tests and field experience. Walls are subjected to slow carbonation and to different structural loads, and creep or adjustment may take place in the mortar, which would not occur in the high-temperature steam laboratory test. Also, the nature of the hydration products and type of crystal growth may be different at the two temperatures. Before an adequate Federal specification for hydrated lime can be prepared, it will be necessary to obtain measurements of

0906-20-4473 (continued)

Dimensional changes under different exposures of masonry walls constructed of limes of different expansive characteristics as determined by the autoclave test, and to obtain fundamental information on the nature of the hydration products under various conditions.

Activity Summary. Preparations were made to construct 60 small brick walls in which various combinations including 6 different limes, 2 mortar mixes, 2 loading conditions, 2 types of brick, and 2 types of exposure will be included. A 20" strain gage for measuring the dimensional changes in the walls, bronze inserts, and the beams and springs required to load the walls were procured. Sample walls have been constructed. A room in which half of the walls can be subjected alternately to wetting and drying has been prepared. To obtain information needed to choose the 6 limes for incorporation in the walls, 26 samples from as many sources were obtained and tested. Based on these tests, 11 were tentatively selected for further test and from which the final 6 will be chosen.

Many specifications limit the amount of the unhydrated MgO in type S lime. The chemical analysis from which the unhydrated MgO is calculated is lengthy and subject to errors. A method was developed which is rapid, permitting a number of determinations in one day, and which appears to have satisfactory reproducibility. The tests consist of drying the sample of lime in CO_2-free atmosphere at 120°C and, after weighing, exposing the sample to high pressure steam to completely hydrate the magnesia, then redrying in the CO_2-free atmosphere and reweighing. A paper describing the test was prepared and delivered at an ASTM meeting in June.

Plans for Fiscal Year 1958. The 60 walls mentioned above will be built, and their dimensional changes followed. In the preliminary tests of the 26 limes noted above several showed anamolous relations between unhydrated MgO content and autoclave expansion. An explanation of this behavior will be sought.

0907-11-0917 Properties of Crystalline Solids H.E.Kissinger

NBS

Objectives. To study in detail the polymorphism, mechanism of phase change, and thermal stability of inorganic crystalline solids, and the effect of structural changes on the physical-chemical properties of the material.

Importance of the Project. The development of new methods and improved materials is often hampered by inadequate knowledge of the properties of the substances involved. When the process includes the thermal decomposition or melting of a crystalline solid, it is important to know the mechanism by which this change takes place, the crystalline form of any solid products, and the temperatures of the reactions which occur. This information, while often available for end-members of solid-solution series, is usually sketchy for intermediate compositions.

The clay minerals in particular are subject to variations in composition and in physical-chemical properties. These minerals are important in ceramic industries, in petroleum production, and in agriculture. The correlation of composition, structure, and properties of these materials is at present under study by many investigators, and much work remains to be done before the clay minerals are fully understood.

Activity Summary. A study of the effect of controlled changes in the composition on the physical-chemical properties of synthetic clay minerals has been continued. Clays have been synthesized in which Mg^{++} has been substituted for Al^{+++} in controlled amounts. The change in unit cell dimensions with composition has been studied. The results, while not yet conclusive, appear to confirm the results of similar studies by others on natural mineral samples.

The thermal decomposition of natural montmorillonite clay saturated with various cations has been studied. For some cations the decomposition reaction is of markedly different character, a difference that can not be readily explained by the presence of the exchangeable cation external to the crystal lattice. The magnitude of this effect varies with the length of time the clay is in contact with the saturating salt solution. The possibility that some of the structural ions are also exchanged is suggested. Evidence that such an exchange may

0907-11-0917 (continued)

take place has been reported by others. A further study now underway, was begun to clarify this aspect of the problem.

Plans for Fiscal Year 1958. Work on the clay minerals will be continued. The kinetics of thermal decomposition of the synthetic clays will be investigated. Exchange of the structural cations in montmorillonite with ions in external contact will be studied further, the extent and type of the exchange reaction to be determined by X-ray diffraction methods, chemical analysis and cation-exchange capacity measurements. The effect of temperature and concentration of the salt solution will be examined in an attempt to determine the mechanism of the phenomenon.

The present automatic recording balance will be redesigned and rebuilt to permit decomposition reactions to be studied in vacuum. A new, more sensitive furnace temperature controller will be installed to replace the present outmoded controller.

0907-40-0921 Standard X-ray Diffraction Patterns for Chemical Analysis — H. E. Swanson

NBS

Objectives. To accumulate data for standard X-ray diffraction patterns for use in identification of inorganic crystalline phases, to revise existing diffraction data, and to develope improved methods of producing such patterns.

Importance of the Project. In 1939 the A.S.T.M. issued a card file of X-ray diffraction data. This file, with its later supplements, serves chemists as an index to known inorganic crystalline structures. The Joint Committee on Chemical Analysis by Powder Diffraction Methods has established a fellowship at NBS to improve and to keep current the card file. Monthly reports, including additional precise patterns of compounds and a review of the literature relating to each, are published and distributed to this committee sponsored by the American Society for Testing Materials, the American Crystallographic Association, the Institute of Physics, and the National Association of Corrosion Engineers.

0907-40-0921 (continued)

Activity Summary. This is a continuing project. During the past year the data on about 60 compounds were reported. Current study is concerned with possible residual cell size change on several types of compounds with hydrothermal treatment. An attempt is also being made to reduce background in powder pattern recordings, using either pulse height discrimination or crystal monachromatization. Volume 6 of Circular 539 was published and Volume 7 sent to the printers. The fellowship now has two full time employees and two parttime employees.

Plans for Fiscal Year 1958. Approximately 70 compounds will be studied and reported on this year. Volume 8 will be published and Volume 9 will be prepared.

0907-11-0944 Determination of Crystal Structure by X-ray Diffraction — Stanley Block

NBS

Objectives. To determine the coordination principles and crystal chemistry of the borates, and phosphates.

Importance of the Project. Very little is known of the crystal chemistry of the borates. In spite of the very great importance of structural investigations in borate chemistry, no systematic study has yet been made of the crystallography of borates. Similar considerations apply to the inorganic phosphates.

Activity Summary. The structures of $BaHPO_4$ and the triclinic form of magnesium pyroborate ($Mg_2B_2O_5$) were determined. $Mg_2B_2O_5$ was incorrectly identified in the literature as MgB_2O_4 and also an incorrect structure was postulated. Three-dimensional data was obtained and Fourier projections were prepared in order to deduce the correct parameters for all the atoms. For the first time, accurate coordinates for the boron atom in a pyroborate group were determined.

0907-11-0944 (continued)

The crystal structure investigation of $BaHPO_4$ has been completed and the paper accepted for publication in the NBS Journal of Research.

Data was also obtained in order to study the structures of ZnB_2O_4, $LiBO_2$ and the monoclinic form of $Mg_2B_2O_5$.

Plans for Fiscal Year 1958. The prescence of an IBM 704 computer at the Bureau of Standards makes possible a least squares refinement of the atomic coordinates of triclinic magnesium pyroborate. If hand computations were used, approximately two months would be required for one least squares cycle. The IBM 704 can perform several such cycles in one hour. Therefore refined atomic parameters for triclinic magnesium pyroborate will be obtained and accurate bond distances and angles will be computed.

The work on the triclinic form indicates that the structure of the monoclinic form should be investigated. This will be done by Fourier and structure factor calculations. Also, work on the crystal structures of ZnB_2O_4 and $LiBO_2$ will be carried out.

0907-11-4420 Phase Relationships at High Temperatures and Pressures — A. Van Valkenburg

NBS

Objectives. 1. To study reversible and stable transformations at high pressures and temperatures, 2. To study (a) the properties of pure materials under high pressures and temperatures, and (b) the properties of new stable materials formed as a result of high pressures and temperatures, 3. To study the infra-red spectral shift of materials under high compression.

Importance of the Project. It is well known that pressure favors the formation of compounds having greater densities and the work of recent investigators has shown that some

0907-11-4420 (continued)

compounds with "open" atomic structures such as quartz (SiO_2), analcite ($NaAlSi_2O_6 \cdot H_2O$), carbon (C), etc. can be transformed into dense compounds under conditions of high pressures and temperatures. It is important that systematic studies be made of compounds with "open" structures to determine the possibility of reversible and stable transformations that may occur. It is also important to define the transformation ranges and the limits of stability of these new materials. The properties of the new dense materials that have been formed are uniquely different from those of the parent material and in general they are more stable physically, thermally, and chemically.

The infrared spectrum is used to determine the interatomic motions in molecules and the force constants and bond energies etc. can be derived from infrared data. It is known that pressure and temperature changes the atomic environment and consequently produces shifts in the infrared spectrum. The direction and magnitude of these shifts may be used to evaluate the influence of neighboring molecules on the bond energies. An evaluation of the perterbations produced by neighboring molecules is one of the most important unsolved problems in the physics of condensed phases.

Activity Summary. During the past year preliminary studies were made on the role of water as a minerializer in the synthesis of coesite, the new dense form of silica. Beryl ($3BeO.Al_2O_3 \cdot 6SiO_2$) has been synthesized and its stability limits have been determined on both natural and synthetic beryl. A new infra-red pressure cell has been developed from a type II diamond capable of attaining pressures up to 30,000 atmospheres and transmitting up to 20 microns in the infra-red band.

Plans for Fiscal Year 1958. Cordierite ($2MgO.2Al_2O_3 \cdot 5SiO_2$), which is isostructural with beryl and has a low coefficient of thermal expansion, will be synthesized in its purest form. Both natural and synthetic corderite will be investigated for the possible existence of transitions at elevated pressures and temperatures. Other iso structural minerals related to beryl and corderite will be studied. Infrared measurements at pressures up to 30,000 atmospheres will be made on various forms of silica such as quartz, cristobalite, tridymite, and coesite to determine the changes in bond energies between constituent ions.

0907-11-4466 Crystal Chemistry of Boron-Containing Compounds

Stanley Block

Navy, Bureau of Aeronautics

Objectives. To determine the crystal structure of boron-containing compounds which are liquid at room temperature and to study the structure of compounds in the boron-oxygen system.

Importance of the Project. The boron compounds are of great interest chemically and industrially. The structures of B_7O and $(BO)_n$ are unknown and only a tentative structure for B_2O_3 has been presented. The structural relationship of these compounds must be known before other properties, such as thermodynamic values can be evaluated.

Activity Summary. Before the structure of the liquid boron-containing compounds can be determined by X-ray diffraction techniques, single crystals must be grown. Equipment to grow such crystals at low temperatures on a Buerger Precession camera has been designed and assembled. B_2O_3 and B_7O are available only as crystalline powders and larger crystals must be grown for single crystal investigations. Attempts have already been made to grow crystals of B_2O_3 in a hydrothermal bomb and crystals of B_7O in a hot wire apparatus. At the present time $(BO)_n$ is available only in the amorphous state.

Plans for Fiscal Year 1958. The period of major experimental instrumental development is completed. With the low temperature apparatus now available, it is hoped to obtain single crystals of the liquid boron-containing compounds. The cell parameter will be defined and diffraction data for a complete structural investigation will be obtained.

Other techniques will be utilized to grow larger crystals of B_7O and B_2O_3. For B_2O_3, an interesting and promising approach is the growth of crystals from solutions in organic solvents.

0907-11-4476 Structure of Solids Containing Free Radicals — H. S. Peiser

Department of Defense

Objectives. To record and interpret diffraction maxima from polycrystalline solids deposited at very low temperatures from gases or vapours subjected to physical treatments favouring the formation of free radicals.

Importance of the Project. So great is the tendency of most of the molecularly simple free radicals to combine with each other that they cannot be obtained in a pure crystalline form. One can reasonably hope only to demonstrate lattice distortions of ordinary solids with occluded free radicals. The study of the corresponding perturbations of the X-ray diffraction patterns may lead to new fundamental information not at present obtainable by other experimental techniques and to another semi-quantitative determination of free-radical concentrations. Some free-radical species may be crystallized at around the boiling point of liquid helium. In favourable cases their full atomic structure including bond angles and distances can be derived. This type of information would add to fundamental knowledge on the chemical bonds and reaction mechanisms.

Activity Summary. In collaboration with Arthur D. Little Inc. a liquid-helium dewar for X-ray diffractometry has been designed, built and tested. It is judged to be broadly adequate for the very challenging experimental tasks in hand.

Plans for Fiscal Year 1958. To record and interpret a wide variety of low-temperature structures related to the free-radical programme.

0907-11-4478 Silver Iodide Particles H. Kissinger

Weather Bureau

Objectives. To provide basic information on the crystallographic nature of the silver iodide particles used in weather control experiments.

Importance of the Project. Experiments with silver iodide seeding techniques indicate that it is possible to control the discharge of atmospheric electricity. Millions of acres of woodland are destroyed yearly by forest fires, many of which are caused by lightning. With properly placed and properly operated silver iodide generators it may be possible to prevent many of these fires.

The ability of silver iodide to nucleate ice crystals is decreased after a time which varies inversely with the mean particle size. Also, ice crystals nucleated with a freshly formed silver iodide particle appear to have a different morphology than those nucleated by "aged" nuclei. The information concerning the nucleation and decay of nuclei is largely empirical, and to date is not satisfactorily explained by theory.

Silver iodide can exist at room temperature in either of two crystalline phases, one hexagonal, the other cubic. Above 150°C. another cubic form is stable. In seeding experiments the particles are very small, of the order of 100 to 500 Angstrom units in diameter. One gram of AgI yields roughly 10^{17} particles. With particles of these dimensions, a proportionately large increment of surface energy is present. The effect of this surface energy on the crystalline phase of the AgI nuclei is not known.

Activity Summary. This project has been in existance but a few weeks. A silver iodide generator of the type used in lightning prevention experiments has been secured and placed in operation. Preliminary literature review has revealed that the crystal structure of the high temperature phase of AgI is open to question, and preliminary work on this topic has been begun.

Plans for Fiscal Year 1958. The crystal structure and morphology of the AgI nuclei will be examined carefully and an attempt made to explain the properties of these particles in nucleating ice crystals from saturated water vapor. The

0907-11-4478 (continued)

electron microscope will be used to study particle morphology. Electron diffraction and x-ray diffraction will be used in crystal structure studies. Techniques of sampling and sample preparation have been partly worked out.

U. S. DEPARTMENT OF COMMERCE
Sinclair Weeks, *Secretary*

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its headquarters in Washington, D. C., and its major field laboratories in Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant reports and publications, appears on the inside front cover of this report.

WASHINGTON, D. C.

Electricity and Electronics. Resistance and Reactance. Electron Tubes. Electrical Instruments. Magnetic Measurements. Dielectrics. Engineering Electronics. Electronic Instrumentation. Electrochemistry.

Optics and Metrology. Photometry and Colorimetry. Optical Instruments. Photographic Technology. Length. Engineering Metrology.

Heat and Power. Temperature Physics. Thermodynamics. Cryogenic Physics. Rheology and Lubrication. Engine Fuels.

Atomic and Radiation Physics. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Nuclear Physics. Radioactivity. X-rays. Betatron. Nucleonic Instrumentation. Radiological Equipment. AEC Radiation Instruments.

Chemistry. Organic Coatings. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Gas Chemistry. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

Mechanics. Sound. Mechanical Instruments. Fluid Mechanics. Engineering Mechanics. Mass and Scale. Capacity, Density, and Fluid Meters. Combustion Controls.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Organic Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics.

Mineral Products. Engineering Ceramics. Glass. Refractories. Enameled Metals. Concreting Materials. Constitution and Microstructure.

Building Technology. Structural Engineering. Fire Protection. Heating and Air Conditioning. Floor, Roof, and Wall Coverings. Codes and Specifications.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics.

Data Processing Systems. SEAC Engineering Group. Components and Techniques. Digital Circuitry. Digital Systems. Analogue Systems. Application Engineering.

• Office of Basic Instrumentation

• Office of Weights and Measures

BOULDER, COLORADO

Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

Radio Propagation Physics. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Sun-Earth Relationships.

Radio Propagation Engineering. Data Reduction Instrumentation. Modulation Systems. Navigation Systems. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Radio Systems Application Engineering.

Radio Standards. Radio Frequencies. Microwave Frequencies. High Frequency Electrical Standards. Radio Broadcast Service. High Frequency Impedance Standards. Calibration Center. Microwave Physics. Microwave Circuit Standards.


NBS