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REPORT ON DENTAL RESEARCH
AT THE
NATIONAL BUREAU OF STANDARDS

Progress Report
July 1 to December 31, 1968

The dental research program at the National Bureau of Standards is carried on in cooperation with the Council on Dental Research of the American Dental Association; the National Institute for Dental Research; the Dental Research Division of the U. S. Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

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NBS Report 9986	Crystal Structure Transformations in VPt Produced by Plastic Deformation at Room Temperature.
NBS Report 10024	Adsorption Theory Interpretation of Ca^{45} and P^{32} Exchange with Hydroxyapatite.

REPORT ON DENTAL RESEARCH at the NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

Dental research at the National Bureau of Standards during the half year ending December 31, 1968 included investigations of a wide range of materials used in restorative dentistry as well as studies of mineralized tissues and related compounds. The research program is supported by the Council on Dental Research of the American Dental Association, the Collaborative Research Office of the National Institute of Dental Research, the Dental Research Division of the U. S. Army Medical Research and Development Command, the Dental Sciences Division of the U. S. Air Force School of Aerospace Medicine, and the Veterans Administration. In the summaries below of work in progress, sponsors of various projects are identified. However, since most of the projects are closely related both technically and administratively, reports on all projects are presented for the information of all sponsors. Detailed reports issued during the period on some phases of the research are listed below and are appended to this report.

2. REPORTS ISSUED

NBS Report 9879	An Evaluation of a Gallium-Palladium-Tin Alloy for Restorative Dentistry.
NBS Report 9983	A Filled Cold-Curing Acrylic Resin as a Splinting Material.
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NBS Report 9986	Crystal Structure Transformations in VPt Produced by Plastic Deformation at Room Temperature.
NBS Report 10024	Adsorption Theory Interpretation of Ca^{45} and P^{32} Exchange with Hydroxyapatite.

3. PAPERS PUBLISHED

Brauer, G. M.; McLaughlin, R., and Huget, E. F. Aluminum Oxide as a reinforcing agent for zinc oxide-eugenol-O-ethoxybenzoic acid cements. J. Dent. Res., 47:622 July-Aug. 1968.

Oglesby, P. L.; Dickson, G.; Rodriquez, M. L.; Davenport, R.M., and Sweeney, W. T. Viscoelastic behavior of dental amalgam. J. Res. NBS (Chem. Eng. and Instr.) 72C:203 July-Sept. 1968.

Dickson, G.; Oglesby, P., and Davenport, R. The steady-state creep behavior of dental amalgam. J. Res. NBS (Chem. Eng. and Instr.) 72C:215 July-Sept. 1968.

Huget, E. F., and Brauer, G. M. Reactivity of the components of tooth structure. J. Colloid & Interface Sci., 27:714 Aug. 1968.

Bowen, R. L.; Paffenbarger, G. C., and Mullineaux, A. L. A laboratory and clinical comparison of silicate cements and a direct-filling resin with and without fused silica: A progress report. J. Pros. Dent. 20:426 Nov. 1968.

Moreno, E. C.; Gregory, T. M., and Brown, W. E. Preparation and solubility of hydroxyapatite. J. Res. NBS (Physics and Chem.) 72A:773-782, Nov.-Dec. 1968.

Gardner, Jr., T. V.; Dickson, G., and Kumpula, J. W. Application of diffraction gratings to measurement of strain of dental materials. J. Dent. Res. 47:1104-1110, Nov.-Dec. 1968.

Eick, J. D. and Hegdahl, T. Segregation in dental gold casting alloys. J. Dent. Res. 47:1118-1127, Nov.-Dec. 1968.

4. WORK IN PROGRESS

4.1. Crystallography of Calcium Carbonates and Calcium Phosphates

Sponsor: NIDR, ADA

In general, two classes of compounds are of primary interest in mineralization phenomena - the calcium phosphates and the calcium carbonates. Our objectives are to increase the understanding of how the ions are arranged in ideal structures so as to provide a basis for models describing chemical reactions such as dissolution, crystallization and the incorporation of carbonate, fluoride and other impurities in bone mineral.

$Ca_4Mg_5(PO_4)_6$: The structure has been determined up to the point of final refinement. Because of the unusually large number of data collected to solve this structure, the computer programs had to be modified and tested. The structure is known well enough at this stage (agreement between calculated and measured structure factors is quite good, R = 0.08) to draw the following conclusions:

1. The composition has been reported both as $Ca_{4.5}Mg_{4.5}(PO_4)_6$ and as $Ca_4Mg_5(PO_4)_6$, and has been indicated to have a small range of variability. The structure shows that one of the cation sites can contain either Ca or Mg, apparently in a random distribution. The formula should therefore be written $Ca_{3.5}Mg_{4.5}(Ca, Mg)(PO_4)_6$. In our crystal it appears that the variable site was about equally filled with Ca and Mg, thus yielding an empirical formula $Ca_{4.5}Mg_{4.5}(PO_4)_6$. After the final refinement, the characteristics of this site will be compared with those of the other Ca and Mg sites in an attempt to understand why one site behaves so differently.
2. When the model of the structure is viewed along [201], an unexpected degree of pseudo-symmetry is observed. When the difference between Ca and Mg and relatively small shifts in the positions of the atoms are ignored, an approximate three-fold inversion axis can be seen parallel to [201] and a basic pseudo-cell can be defined with the dimensions a′ = 8.68 (along [101]), b′ = 9.99 (along [010]), and c′ = 14.88 Å (along [201]). This cell has pronounced orthohexagonal character.

When this cell is compared with that of glaserite, $NaK_3(SO_4)_2$, a definite relationship between the two structures can be seen. The structure of glaserite consists of two kinds of columns, one entirely made up of cations and one with cations and anions alternating. In the $Ca_{3.5}\,Mg_{4.5}(Ca,Mg)(PO_4)_6$ structure, similar columns are present parallel to c'. The cation columns are essentially the same as in glaserite, but every other cation site is vacant in the anion-cation columns. This unexpected relationship between these two compounds provides new insight into structural relationships among calcium phosphates. Glaserite is known to be closely related to $CaK_3H(PO_4)_2$ and $CaKPO_4$, and has a formal structural relationship to hydroxyapatite. Glaserite has a cation-toanion ratio of 12/6; the cation-vacancy mechanism in the calcium magnesium phosphate makes it possible to extend the structural relationship between glaserite and hydroxyapatite to a salt with a cation-to-anion ratio (9/6) lower than that (10/6) in hydroxyapatite.

3. One of the main objectives in our study of $Ca_{3.5}\,Mg_{4.5}(Ca,Mg)(PO_4)_6$ is to find relationships between it and the two better known tricalcium phosphates, $\beta\text{-}Ca_3(PO_4)2$, and $\beta\text{-}Ca_3(PO_4)_2$, neither of which has a known structure. The dimensions of the pseudo-orthohexagonal cell strongly suggest that there are relationships between it and the

two tricalcium phosphates. For example, whitlockite is known to have a prominent pseudo-repeat in its structure of $\underline{c}'/4$ (i.e., 3.72 Å). The $\underline{a}$ unit cell dimension of whitlockite, 10.43 Å, is quite similar in length to the $\underline{b}'$ axis of $Ca_{3.5}Mg_{4.5}(Ca,Mg)(PO_4)_6$, 9.99 Å. The dimensions of the pseudo-orthorhombic cell of α-$Ca_3(PO_4)_2$, $\underline{a}$ = 15.22, $\underline{b}$ = 20.71, and $\underline{c}$ = 9.11 Å, are also similar to those of the pseudo-orthohexagonal cell of $Ca_{3.5}Mg_{4.5}(Ca,Mg)(PO_4)_6$. It now appears that no two of these compounds are iosstructural, but it is likely that they will share important structural features.

Computer Programming for Crystal-Structure Analysis: Extensive use of computers is necessary in all stages of crystal-structure analysis. The computer programs are constantly being improved and adapted to new situations. For this reason, a considerable amount of time is spent in developing and revising programs.

The results of a crystal-structure determination are most conveniently expressed in the form of a diagram which shows both the positions of the atoms and their thermal vibrations in the form of ellipsoids. Such a program, "The Oak Ridge Thermal Ellipsoid Program," has been adapted to the output of programs used at the NBS for the earlier stages of calculation, and is now being used to draw diagrams to accompany manuscripts submitted for publication.

A computer program recently written by W. R. Busing of Oak Ridge National Laboratory has been tested in the calculation of the lattice energies and concomitant parameters of $Na_2CO_3 \cdot H_2O$.

The program uses least squares methods to calculate new parameters from initial estimates. The present conclusion is that least squares refinements in which the parameters are all equally weighted do not refine to the minimum energy. A new version with provision for weighting has been received and will be used in further tests.

One of the difficulties with the x-ray analysis of the structures of crystals containing hydrogen is that the hydrogen positions are systematically too close to their bonded atoms. Computer programs have been written to impose an idealized water geometry on the approximate water geometry obtained in the determinations of crystal structures of hydrate salts and to place a hydrogen in a realistic position with a reasonable X-O-H bond angle and O-H distance for hydrogens on such groups as PO_4 groups. In this way it is possible to obtain a more realistic set of hydrogen positions and to test the rationality of a proposed hydrogen bonding scheme.

Petrographic Study of Pineal Calcifications. Concentrically micro banded spherite calcifications, calcospherites, are a common occurrence in the pineal gland, early dentine, aortic walls and elsewhere. Since the calcospherite is essentially the sole form of calcification in pineal gland parenchyma,, these calcifications are good subjects for the characterization of the calcospherite form.

The mineral phase present in pineal calcifications has been identified with x-rays by earlier workers to be hydroxyapitite. Acid treatment evolves CO_2 and the possibility of a carbonate apatite has been suggested. The present study employed optical and electron microscopic techniques, x-ray, thermogravimetry, electron probe and chemical analysis. A carbonate hydroxyapatite is confirmed as being the predominant mineral phase present. While this work will be subsequently submitted as a detailed report, the following conclusions can be given at this time: (1) Bovine and human calcifications occur as concentrically microlaminate bodies in which protein-rich (collagen or keratin) zones alternate with apatite-rich zones. (2) Apatite crystallites commonly are approximately 200-220 Å wide. These crystallites have preferred orientation of the C-axis perpendicular to the micro laminae. (3) These calcifications appear to be mineralogically similar to enamel.

4.2. Solubilities of Calcium Phosphates

Sponsor: ADA, NIDR

Previous reports have described the results of solubility studies on the dicalcium phosphates, $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$, which are now completed, and similar studies on hydroxyapatite, $Ca_5OH(PO_4)_3$, and whitlockite, β-$Ca_3(PO_4)_2$, which are still in progress. Solubility measurements on hydroxyapatite at 37°C were described in the previous report. Similar measurements (from undersaturation) at 5°, 15° and 25°C have now been completed. Some of these data remain to be processed. The present values for the solubility constants are 3.20×10^{-59}, 2.74×10^{-59}, 2.60×10^{-59} and 2.12×10^{-59} for 5°, 15°, 25° and 37°C. A log K_{SP} vs 1/T plot of these data defines a straight line but the standard enthalpy and entropy of dissolution derived from this plot differed from those obtained from calorimetric data by more than the expected experimental errors. The reason for this difference is being investigated.

During the present report period processing of the solubility data on whitlockite at 25°C was completed and measurements were extended to 5°C and 15°C. The solubility constant at 25°C is 1.38×10^{-29}; the data at 5° and 15°C are still being processed but they already indicate that whitlockite has a negative thermal coefficient of solubility as predicted in the previous report. The data at 25°C permitted calculation of the formation constant for the ion pair $[CaHPO_4]^0$ which was found to be in good agreement with the constants derived from the solubility data on $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$. The metastability of whitlockite is such that a similar test of the formation constant for the ion pair $[CaH_2PO_4]^+$ could not be made.

We have now made solubility studies on four preparations of hydroxyapatite.

1. Hydroxyapatite prepared by titrating $Ca(OH)_2$ with H_3PO_4, and stabilizing by extraction and by boiling for a period of 10 days: These are the results described above, and comprise the most extensive series of solubility measurements made on a single preparation of hydroxyapatite.
2. Hydroxyapatite prepared as above by Dr. Avnimelech in connection with his surface studies: The solubility product of this material was subject to a relatively large error, within which the two sets of measurements are in agreement.
3. Hydroxyapatite precipitated slowly and then heated in steam at 1000°C: Contrary to expectations based on the fact that the particle size of this material was significantly larger than either of the above two, its solubility product was greater by almost an order of magnitude ($K_{sp}(25°C) = 2.60 \times 10^{-59}$ vs 3.73×10^{-58} for the steam-heated material). The difference was attributed to the heat treatment which may have introduced extra free energy into the crystals through lattice defects or some other mechanism.
4. Hydroxyapatite heated in air at 1000°C: This material had an apparent solubility product 10^3 times as great as the steam heated material. This difference was attributed to the fact that under the conditions of heating, the hydroxyapatite is known to be unstable and

> will tend to form whitlockite and tetracalcium phosphate, $Ca_4O(PO_4)_2$. It is believed that when the air heated material is returned to an aqueous solution for the solubility measurements, these products reform hydroxyapatite, but in such a poorly crystallized form that it yields an unusually large solubility product.

The ability to detect differences in the free energies of various hydroxyapatite preparations through solubility measurements, if valid, constitutes a valuable means for the study of one of the most basic properties. We cannot, however, rule out the possibility that some of the differences must be attributed to systematic errors arising from variations in the experimental conditions of the varioussets of solubility measurements. Two types of experiments will be used to study this phenomenon: (1) The solubilities of hydroxyapatites prepared in different ways, or exposed to various thermal treatments, will be measured simultaneously. (2) Solubility measurements will be made in which equilibrium is approached from conditions of supersaturation. In each of the four studies on hydroxyapatite described above, equilibrium was approached only from undersaturation. Equilibrium was approached from both directions in the studies with the dicalcium phosphates, thus added considerably to the veracity of the results.

Our initial attempt to approach equilibrium by passing a supersaturated solution through a column of hydroxyapatite defined an isotherm which we now know corresponds to that of whitlockite. Apparently, the precipitation reaction within the column resulted in the formation of whitlockite instead of hydroxyapatite. More recent experiments, in which batches of hydroxyapatite were rotated for longer times in a thermostatic bath, yielded points which fell fairly close to the hydroxyapatite isotherm, but they represented solubilities which are believed to be significantly different from those obtained from undersaturation. We are investigating whether this apparently greater solubility relates to a property of the hydroxyapatite formed in the equilibration process or to the formation during this process of a small amount of a metastable calcium phosphate.

To further the studies on hydroxyapatite, a new method of preparation was developed which is based on the hydrolysis of $\alpha\text{-Ca}_3(\text{PO}_4)_2$. The hydroxyapatite crystals obtained in this way appear to be the largest (up to 50µm) yet obtained in a synthesis carried out at atmospheric pressure. One of the advantages of this method is its simplicity since it involves direct hydrolysis of an easily prepared material, $\alpha\text{-Ca}_3(\text{PO}_4)_2$, in boiling water. Although the crystals derived in this way are well formed, voids paralleling the c axis are common. In this respect they resemble crystals grown in hydrothermal bombs. This suggests that the growth mechanisms in the two procedures are similar. In common with so many other methods for the preparation of hydroxyapatite, the infrared spectra of these crystals show some contamination by acid calcium phosphates. It is believed that, under the conditions of preparation, octacalcium phosphate is the only acid calcium phosphate more insoluble than $\alpha\text{-Ca}_3(\text{PO}_4)_2$.

Preliminary solubility measurements on hydroxyapatite prepared in this way indicate that it has an unusually high solubility. Investigations are continuing to learn if this relates to an inherent instability of the hydroxyapatite prepared in this way, or whether it is caused by a contaminant.

The same technique is being used to synthesize fluorapatite, $\text{CA}_5\text{F}(\text{PO}_4)_3$ which is to be used in solubility studies. This material should have advantages over material prepared at high temperatures, the method most commonly used up to now, because of the possibility that fluorapatite prepared at a high temperature may not be representative of material formed under physiological conditions.

Thermodynamic Properties of Calcium Phosphates. The solubility constants for the various calcium phosphates can be used to calculate their standard free energies of dissolution. When these are combined with cryogenic and thermal data, it then should be possible to calculate standard free energies, enthalpies and entropies of formation. There are, however, inconsistencies in the data in the literature caused by experimental errors, variations in the experimental conditions, and the use of ill-defined materials. Attempts are being made to reduce the errors in the standard thermodynamic quantities and to make a self consistent set of data for the calcium phosphates by using solubility data. Such a set was reported at the NBS Symposium on Structural Properties of Hydroxyapatite and Related Compounds. The need for more precise heats of dissolution data is recognized, however, and we are making plans to obtain such data experimentally.

The effect of temperature on the solubilities of the dicalcium phosphates showed an unexpected behavior. While the solubility product constant of $CaHPO_4$ decreased monotonically with temperature (i.e., increased linearly with 1/T), the constant for $CaHPO_4 \cdot 2H_2O$ showed a maximum at about 25°C. Initially, we thought the behavior of $CaHPO_4 \cdot 2H_2O$ related to phenomena occurring in the solution, but the contrasting behavior of the two salts pointed to the properties of the solid phases as the source of difference in temperature dependence. Calculations were made, therefore, of the temperature dependence of solubility for the two salts using heat capacity data. It was found that $CaHPO_4 \cdot 2H_2O$ should have a maximum in the solubility product constant near where it was found experimentally; $CaHPO_4$ also shows a theoretical maximum, but at a very low temperature (~ -70°C), thus explaining why the solubility constant decreases monotonically in the range 5° to 37°C.

Ionization of HF: In a test of the reliability of the fluoride electrode for use in solubility measurements, a discrepancy was found between calculated and measured activities of the fluoride ion. The experimental conditions were such that this could not be explained by inadequacies in the calculation of ionic activities. After a series of experiments, it was concluded that the discrepancies had to be attributed to errors in the reported values for the dissociation constants of HF and HF_2. In view of the importance of the fluoride ion in the prevention of caries, a study of these dissociation constants was initiated. The experimental work on about 100 solutions has been completed, the data are being processed, and the indications are that they will yield improved values for the dissociation constants.

Diffusion in Calcium Phosphate Solutions: In a previous report, we described the plans to use a diaphragm-type diffusion cell containing a thin cellulose membrane. Trials with this cell, however, showed that the thickness of the unstirred solution layer adjacent to the membrane was comparable in magnitudeto the thickness of the membrane, so that relatively small variations in solution compositions or experimental conditions would have large effects on the diffusion rates. Metal membranes should be unaffected by formation of electrostatic charges on surfaces, but trials with a thin silver membrane indicated that it was chemically unstable as shown by its accumulation of P^{32} and Ca^{45} radioactivity during the experiments. A new, thicker, diaphragm of sintored platinum has been obtained and it appears to be free of the above difficulties.

4.3. Study of Dentinal and Enamel Surfaces from Sorption Isotherms

Sponsor: NIDR

Little information is available regarding the presence and relative abundance of acidic and basic functional groups at the surface of dentin and enamel. During this period a study was initiated to determine quantitatively the presence of those sites that are accessible to CO_2 or NH_3. These gases were selected since they are likely to react chemically with acid or basic groups present in dental collagen. Initially, the adsorption isotherms at temperatures in the vicinity of the respective boiling points of the adsorbates will be determined and from these data the isosteric heats of adsorption will be obtained. It is hoped that results of this investigation will yield valuable information with respect to the surface composition of odontic powders.

Because of the molecular interaction and finite size of the molecules at the temperature of the experiment, correction terms for the non-ideal behavior of the gases must be applied to obtain the exact amount of gas adsorbed on the surface of the substrate. A literature search indicated that tables containing these correction terms are out-dated and incomplete. Therefore, more accurate methods for calculating and comparing non-ideal gas correction terms for use in this type of work were developed and a manuscript summarizing the results of this investigation was prepared for publication.

A cryostat was designed and built to obtain adsorption data at different temperatures within ± 0.5°C. The final design consisted of a liquid nitrogen heat sink to which excess heat was conducted thermally. A solid copper rod bent into an inverted U-tube with appropriate radiating vanes cooled the adsorption vessel sufficiently so that additional heat was required to sustain a desired temperature. The other arm of the thermal conductor was immersed in a Dewar surrounding the sample. The Dewar contained a low freezing pt liquid such as trichlorethylene (or toluene) in the stirrer, thermocouple, heater, etc. For controlling the temperature at the desired cryogenic setting, a hand-wound heater enclosed in a glass tube was used. The temperature regulator was responsive to changes in resistance of a temperature-sensing probe. A 5000-ohm carbon composition resistor had a sufficiently high temperature coefficient of resistance to make it sufficiently sensitive to function satisfactorily for this purpose.

The first series of experiments were performed on anorganic teeth in order to obtain a control (free of collagen) with which to compare the results that will later be obtained with dentin and enamel. Using CO_2 as the adsorbate at dry ice temperature, it was found necessary to pre-condition the sample by purging in helium at 110°C for several hours. Before this pre-treatment had been done, the isotherms of samples degassed at room temperature showed significantly lower adsorption and were not reproducible. Subsequent evacuations at room temperature between successive adsorption experiments gave reasonably reproducible isotherms.

Preliminary findings indicated isosteric heats of adsorption decreasing to a constant vlue of about 4 kilocalories per mole as surface coverage increased to about 0.7 of a monolayer.

Besides this investigation, work on two papers "Adsorption Theory Interpretation of Ca^{45} and P^{32} Exchange with Hydroxyapatite" and an "Empirical Method for Optimizing the Number of Terms of a Fitted Power Series" was completed. The manuscripts of these studies were written up and are being reviewed.

4.4. Mechanical Behavior of Skin

Sponsor: NIDR

Using rat skin as a model system for the mechanical behavior of the mucous membrane of the oral cavity, preliminary stress-strain determinations have been carried out on adult rat skin (500 gm male rats). The elastic behavior was found to be the predominant phenomenon over short time intervals being in the approximate ratio of 5/1 in relation to the time dependent phenomenon for time intervals less than 5 minutes. The elastic behavior was found to be nonlinear in its behavior which is in agreement with other workers who ran conventional stress-strain curves at a given strain rate. However, their stress-strain data, unlike ours, contained some viscoelastic contribution, as well as elastic. This viscoelastic contribution has nearly been eliminated from our data, but with its elimination, nonlinearity is still observed. The work of R. D. Harkness and coworkers described the stress-strain behavior of skin by a power function, while V. Wright and coworkers described their stress-strain data by means of an exponential function. With the nearly complete elimination of the viscoelastic contribution in our determination, we found that exponential description is more closely representative than the power function description, but the data obtained thus far indicate that neither description is representative. The elastic behavior of stomach skin was found to be readily distinguishable from that of back skin on the same animal.

4.5. Thermal Expansion of Tooth Structure

Sponsor: USAF, VA, NIDR

Investigations of the thermal expansion of human tooth enamel and dentin are being undertaken because of the importance of this property in the stability of restorations in teeth. This is of particular importance in regard to the adhesive restorative materials which are the objective of numerous studies in this and other laboratories. Differences between the thermal expansion of tooth and restorative materials will tend to separate the restoration from the tooth surface. If adhesion is maintained, thermal expansion differences may tend to cause fracture in tooth or restoration if the viscoelastic characteristics of the materials do not accommodate the thermally produced dimensional changes.

The determination of accurate thermal expansion values is complicated by the small size of the specimens that can be obtained from natural teeth. Results obtained in the present study have verified the wide variability previously found in the expansion of dentin. Present objectives are to determine if these variations can be related to differences between teeth, effects of orientation, the viscoelastic characteristics of dentin, variations in the contributions of the organic and inorganic portion of the material to the expansion of the composite, or to other factors.

4.6. Metallurgy

Sponsor: ADA, USAF, VA, NIDR

The objective of our metallurgical research program is to provide information which can be used either directly or indirectly to develop new alloys for dentistry or to modify present alloys in order to obtain an enhancement of such properties as strength, ductility, and ease of fabrication. In developing new or improved alloys, the metallurgist is greatly assisted by a knowledge of the relevant phase diagrams which summarize graphically the structure of a given alloy system as a function of temperature and composition. Phase diagrams are readily available for many base-metal alloy systems since many of these alloys are widely used in industrial applications. Alloys of the noble metals, however, find only limited industrial use although they are widely used in dentistry where cost is not a major deterrent. Phase diagrams for noble metal alloys are, therefore, frequently unavailable or unreliable, thus severely retarding the use of noble metals in alloy combinations with each other or in combination with base metals.

In order to promote a more favorable consideration of the many desirable properties imparted by the use of the noble metals, we have undertaken a systematic exploration of binary phase diagrams in which a noble metal is combined with various base metals. During the past six months, we have continued to prepare alloys spanning the entire range of composition in the binary systems Cr-Pt, V-Pt, Cr-Ir, and Cr-Rh. These alloys are being subjected to extensive heat-treatment at various temperatures, followed by a metallographic examination of their microstructures and analysis by x-ray diffraction and electron microprobe methods.

Despite experimental difficulties in maintaining high purity in these alloys, we have succeeded in establishing the general outline of the binary phase diagrams for the systems Cr-Pt and V-Pt and are now engaged in determining the exact temperatures and compositions at which critical structure transformations occur.

The Cr-Pt system contains only one intermediate phase having the approximate formula $Cr_{79}Pt_{21}$ and a composition range of several percent. Chromium is extensively soluble in platinum and initially increases its melting temperature to a maximum in the vicinity of 30 atomic percent chromium followed by a gradual decrease in liquidus and solidus temperatures at higher chromium contents. Atomic ordering analagous to that which occurs in the copper-gold system is observed over a wide range of compositions and is associated with ferromagnetic behavior.

The V-Pt system contains four intermediate phases at the approximate compositions VPt_3, VPt_2, VPt, and V_3Pt with the latter phase being stable over a rather extensive composition range on both sides of the "ideal" composition. The phase VPt is of particular interest since its behavior may lead to important developments in regard to desirable mechanical properties. Its crystal structure can be viewed as an orthorhombic distortion of the ordered tetragonal CuAu type structure which is responsible for the hardening of dental gold alloys. The phase VPt forms by means of an ordering reaction from the platinum solid solution at a rather high temperature (not yet determined, but believed to be about 1500°C). When the phase VPt is subjected to severe deformation at room temperature, its crystal structure changes to that of either the CuAu type or to that of a disordered face-centered cubic structure depending on the extent of cold-working. These structures are apparently metastable since strain-annealing results in a transformation to the original orthorhombic structure. When alloys such as $V_{43}Pt_{57}$ are annealed in the two-phase region between the face-centered cubic platinum solid solution and the phase VPt, one obtains ribbons of the phase VPt in the face-centered cubic solid solution matrix phase. Such a structure suggests possible strengthening by means of the well-known "whisker" or "fibre-reinforcement" mechanisms. In addition, since the phase VPt transforms as a result of cold-work to the usually ductile face-centered cubic structure, one might expect a possible enhancement of ductility as a result of cold-working contrary to conventional behavior. Confirmation of such behavior must await a comprehensive investigation of the mechanical properties of these alloys, but such an investigation is beyond the scope of our present phase-diagram studies.

In order to complete our work on these alloy systems, we will need to study the observed transformations using dilatometric (thermal expansion) and thermal analysis techniques. This requires specialized equipment for measuring transformation temperatures while maintaining sample composition and purity. It appears that it may be necessary to contract for such work in other laboratories since the necessary equipment is not now available at the National Bureau of Standards.

4.7. Adhesion to Dentine and Enamel Surfaces

Sponsor: USA

A study of potential adhesive liners that bond to tooth structure and plastic restorative materials has been initiated. One aspect of this work is the synthesis of tailor-made molecules that may be capable of bonding to tooth surface and at the same time are compatible with the well-accepted dental resins. The bonding between bovine enamel or dentin and a commercial cold-curing poly(methyl methacrylate) restorative resin was determined for a series of these newly synthesized compounds. Treatment of enamel with 10% solutions of (1) equimolar condensation product of 2-hydroxyethyl methacrylate and tetrahydrofurane-2,3,4,5-tetracarboxylic acid (HEM-THFTC), (2) partially polymerized 4-hydroxy-3-methoxystyrene, (3) N-phenylglycine-glycidyl methacrylate (NPG-GMA), and (4) methacrylate chromic chloride (Volan L) in acetone, increased significantly the adhesive properties when the materials were stored in a 100% relative humidity environment. However, when stored in water at 37°C for 24 hours, the bond strength was decreased markedly. Failures were always of an adhesive nature. Pretreatment of the surface with transition metal chloride did not improve bonding. None of the compounds studied adhered to dentinal surfaces. No bonding was obtained with trans-isoeugenol, 4-hydroxy-3-methoxystyrene and its methacrylate ester, 4-hydroxy-3,5-dinitrostyrene, allylphosphonic acid and its hydroxyethyl methacrylate ester and N-allylimino-N,N-dimethylene diphosphoric acid.

Another study dealt with treating enamel and dentinal surfaces with inorganic compounds, especially halides, and determining the bond strength of the tooth surface acrylic resin interphase. In this test, the enamel surface was cleaned with a 5% aqueous solution of tetrahydrofurane,2,3,4,5-tetracarboxylic acid (THFTC) by swabbing for 15 seconds. After rinsing with water, the surface was dried and wetted with 4N NaOH and excess base was wiped off after 15 seconds. A 5 to 10% aqueous solution of the salt was applied and excess was removed after 15 seconds. The cold curing resin was then applied and the samples immersed in water at 37°C for 20 hours. Treatment of the enamel surfaces with many halide solutions increased the adhesion. For instance, treatment with $FcCl_3 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$ and ammonium vanadate gave tensile strength of $29^{\pm 3}$ kg/cm^2,

40 ± 3 kg/cm^2 and 29 ± 12 kg/cm^3, respectively, compared to 5 ± 2 kg/cm^2 for untreated teeth. The tensile adhesion of $AlCl_3$ treated enamel surfaces was dependent on the restorative used, decreased on substituting 1N NaOH or 10% Na_2CO_3 for the 4N NaOH, and decreased with decreasing pH of the aqueous solution in which the assembly was stored prior to the adhesion test. Unfortunately, the bond strength became negligible on storage in water for 30 days. Dentinal surfaces did not adhere to the acrylic restorative. With 10% ammonium vanadate solutions, pretreatment of the enamel with 1.5 N NaOH, wiping off excess precipitate, and acidification with 0.5 N HCl gave optimum results. Tensile adhesion values varied little with the pH of the aqueous solution (4.8 to 9.5) in which the test specimens were stored.

4.8. Development of an Adhesive Restorative Material

Sponsor: ADA, USAF, VA, NIDR

With the objective of improving the quality and sophistication of dental materials, the development of an adhesive restorative material was further pursued. The material under investigation, depending on the physical, chemical and biological properties that can be realized, will have applications in preventative as well as restorative dentistry.

This composite material utilizes (1) a maximal amount of particulate reinforcing filler together with (2) a minimal amount of cross-linking, polymerizable organic resin. An organofunctional silane coupling agent (3) promotes bonding at the filler-polymer interfaces. A surface-active comonomer (4) improves bonding at the interface between the composite material and the tooth surface.

With regard to the reinforcing fillers for the restorative material, a manuscript has been accepted for publication (February 1969) by the Journal of Dental Research covering our development of a special barium fluoride glass. It has been informally reported that three dental manufacturers have sought this glass from an industrial glass manufacturer, one company placing an order for 1000 pounds of it. We have just developed a similar x-ray-opaque glass that is free of fluoride, since fluoride undesirably raises the thermal expansion of the glass (from about 3.8 to about 7.3 ppm/°C).

The crosslinking, dimethacrylate monomer system has been described in a manuscript that is now being prepared for submission to a journal. The rapid polymerization of this resin is accomplished with an amine-peroxide initiator system. In the past six months, work was continued in investigating the effect of moderately high molecular weight alkyl substituents on the properties of aromatic amine accelerators. Compounds under investigation which have been synthesized are N-dodecyl-N-methyl-*p*-toluidine, N-dodecyl-N-methyl-*sym*-*m*-xylidine and N,N-dimethyl-*p*-dodecylaniline. These compounds were compared for ability to accelerate polymerization and remain color stable (in specimens incorporating them) during exposure to a sunlamp for 24 hours.

They were compared also to their corresponding lower-molecular-weight homologs N,N-dimethyl-*p*-toluidine and N,N-dimethyl-*sym*-*m*-xylidine. N,N-dimethyl-*p*-*t*-butylaniline containing a tertiary alkyl substituent on the aromatic ring was also synthesized. This compound was needed to investigate the effect of alkyl ring substituents not possessing hydrogen atoms alpha to the benzene ring. The initial color and the color stability of specimens prepared with this amine compared favorably with those prepared with the others. The results suggest that a higher-molecular-weight homolog of this compound should be synthesized and evaluated.

The commercially-available organofunctional silane coupling agents appear to be satisfactory for this application. However, there was suggestive evidence that silica surfaces formed at high temperature need to be "re-hydroxylated" to get the best silane surface treatment. Since the filler-resin interface is of such great importance to the properties of particulate composites, this should be studied further.

The most emphasis has been placed on perfecting the surface-active comonomer or adhesion-promoting primer system. The major problem under attack is the lack of understanding of why the stability of the formulations during storage is unpredictable. Efforts were made to understand the mechanism of instability and to formulate stable solutions of the adhesion promoting coupling agent, NPG-GMA (the adduct of N-phenylglycine and glycidyl methacrylate). Special emphasis was given to the synthesis and evaluation of surface-active methacrylate monomers analogous to NPG-GMA, but with modifications that (1) lower the solubility parameter (allowing solubility in liquid dimethacrylate monomers), and (2) elucidate the factors involved in storage stability in the liquid state. Approximately one-third of the 15 syntheses to these ends were considered successful.

During the last six months, three additional composite restorative materials, "Adaptic" (Johnson & Johnson), "Blendant" (Kerr) and "DFR" (Surgident), have been placed on the market by dental manufacturers. These, as were two previously available materials, "Addent" (3M Co.) and "Dakor" (Caulk), have been based on, and result from, the research done in this project. A very modest clinical comparison is planned to evaluate the value of X-ray opacity for diagnostic and prognostic procedures.

4.9. Composite Resin Material for Temporary Posterior Restorations

Sponsor: USA

The physical properties of a resin-silica composite material developed for use as a temporary posterior restorative material have been investigated. It is intended that this material withstand the forces of mastication for at least two years, be radio opaque so that it is possible to distinguish between the material and remaining or recurring caries and that it exhibit minimal pupal irritations. Ease of manipulation and minimal cavity preparation are also desired. Esthetic properties are of secondary importance. The formulation is based on a liquid ternary eutectic of isomeric phthalate esters of 2 hydroxyethyl methacrylates and a resin filler consisting of irregular particles of vitreous silica and an x-ray opaque glass.

The material can be spatulated on a slab in one and one-quarter minutes at a ratio of 1.35g of powder to 0.4 ml of liquid. Setting time is five minutes, and a maximum temperature rise of 5 to 7°C is observed between 4 and 6 minutes after the beginning of mix. Shrinkage on setting was found to be approximately 0.4%.

Tensile strength of the composite at 5000 to 6000 psi is near that of dental amalgam, while the compressive strength at 25,000 to 30,000 psi is approximately one-half that of amalgam. Thermal expansion is approximately 30 to 35 parts per million per °C between 25 and 60°C.

Water sorption of the composite is considerably below the maximum ADA specification limit for denture base resin. Water solubility is low in comparison to silicate cement.

Radio opacity is sufficient for distinguishing between the cement and caries. Color stability is good. Optical opacity is near or above the maximum specification limit for silicate cement.

Properties of the material appear to be adequate for temporary posterior restorations. Clinical evaluation is needed before routine use can be recommended.

4.10. Zinc Oxide-Eugenol Type Restorative Materials

Sponsor: USAF, VA, USA

The investigation to develop clinically improved temporary restorative materials with good tissue tolerance was continued. During this period, emphasis was placed on reducing the in vitro solubility of these materials and studying the effect of different polymeric fillers as reinforcing agents. Formulations containing bentonite-coated rosin have higher compressive strength, but higher solubility, than those containing hydrogenated rosin. Substitution of poly(ethyl methacrylate), polyacetal or butadiene-styrene-acrylonitrile terpolymer for the methyl methacrylate copolymer powder lowered the tensile strength. However, formulations containing polycarbonate powders as reinforcing agents look promising. Coating the surface of aluminum oxide with a polymer film instead of the incorporation of polymer powder in the formulation does not improve the physical properties of the resulting cement. A nine-month clinical study of a limited number of restorations, including those subject to heavy occlusal stresses, showed no sign of wear during this period of observation.

4.11. Rapidly Fabricated Surgical Splint

Sponsor: USA

The investigation of suitable compositions for development of a rapid splint for fractures of the mandible and alveolar fractures has been completed. Best results were obtained using 50% methyl methacrylate copolymer, 50% $CaCO_3$ powder and a liquid consisting of methyl methacrylate containing 0.2% N,N-dimethyl-p-toluidine. If a hardening time of less than 10 minutes is desired, 0.2% of benzoyl peroxide can be added to the powder. The material has been used successfully in a variety of applications by the U. S. Army here and abroad. A detailed report describing the results of this investigation is appended.

4.12. Grafting of Polymers to Hard and Soft Tissues

Sponsor: USA

A graft copolymer is comprised of a high molecular weight backbone to which a second polymer is attached at intervals along the chain. This chemical modification will alter the properties of the substrate according to the type of monomer unit selected as a graft. Grafting procedures produce surface modifications of natural and synthetic polymers and yield tailor-made products with preselected physical and chemical properties. If successful, grafting may offer an attractive technique of bonding chemically to collageneous surfaces such as dentin.

An extensive review of the literature indicates that much progress has been made during the last two years in the grafting of long chain polymeric compounds to natural products, including fibrous proteins such as wool or corium collagen. Thus, it appears feasible that chemical pretreatment of hard and soft tissues may facilitate the grafting of polymerizable monomers to such tissues.

Detailed information of the optimum conditions under which vinyl monomers such as acrylonitrile or methacrylate esters can be grafted to collagenous surfaces in an environment which could be duplicated clinically are not available. Thus, initial investigations utilize a model system: finely divided purified collagen suspended in water, acrylonitrile monomer and ceric ammonium nitrate as redox initiator. Since collagen contains alcoholic groups such as hydroxyproline, hydroxylysine, serine and threonine, the presence of free radicals on the backbone initiates polymerization at these sites to produce a graft copolymer.

$$\mathrm{Ce^{IV}} + \sim\mathrm{RCH_2OH} \rightleftharpoons \text{Ceric alcohol complex}$$

$$\downarrow$$

$$\mathrm{Ce^{III}} + \mathrm{H^+} \sim\mathrm{R\dot{C}HOH}$$

free radical

The resulting product is then washed with water to remove acrylonitrile monomer and extracted with dimethylformamide to dissolve any polyacrylonitrile. Definitive identification of grafts onto the collagen surface using multiple total reflectance infra-red techniques awaits the receipt of a 25 reflection attenuated total reflectance equipment ordered recently. If the graft sites cannot be characterized by this technique, "labelled" monomers, such as chloroacrylonitrile or 2-chloroethyl methacrylate, will be employed as grafting agents.

4.13. Clinical Research

Sponsor: ADA, USAF, VA, NIDR

Methods were formulated for clinical evaluation of direct filling materials developed in the laboratory. Scales of reference for grading surface texture or roughness, lack of marginal flushness, marginal notch or crevice and other qualities of restorations were prepared. Composite restorations, 50 with and 50 without the NPG-GMA coupling agent, have been placed and will be observed to see if there is a discernible difference in serviceability.

Investigations of the effectiveness of radio opacifying agents in direct filling and denture base resins are in progress. The effects of the radio opacifying agents on mechanical and optical properties and other characteristics of the materials are also being studied.

4.14. Specification and Advisory Activities

Sponsor: ADA, NIDR, USAF, VA

Although the Dental Research Section conducts very little research oriented directly toward specification development, members of the staff, through activity on various committees and otherwise, contribute significantly to the formulation of national and international specifications for dental materials. Members of the staff are active on 11 of the 14 subcommittees formulating new or revised specifications for the American Dental Association, serving as chairmen of 3 and secretaries of 7 of the committees. In addition, members of the staff hold the chairmanships of the Specifications Committee of the Dental Materials Group of the International Association for Dental Research; the United States of America Standards Institute Committee for the International Organization for Standardization Committee for Dentistry; and the Commission on Dental Materials, Instruments, Equipment and Therapeutics of the Federation Dentaire Internationale.

Advisory and consultative activities included lectures to dental groups in this country and abroad, review of numerous papers for publication in research journals and reviews of grant applications including site visits for the National Institute of Dental Research.