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THE PREPARATION AND PROPERTIES OF REFRACTORY URANIUM COMPOUNDS

by

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INTRODUCTION

The need for improved reactor operating efficiencies has stimulated research in refractory uranium compounds other than oxides for use as nuclear fuels. The general material characteristics desired include, high melting point, high uranium atom density, freedom from phase transformation due to temperature or irradiation, low neutron cross section, high thermal conductivity, radiation stability and fission gas retention at high temperature and long burnup.

Representative of the materials most likely to exhibit these characteristics are the carbides, sulfides, nitrides, phosphides, aluminides, borides, and berylides of uranium, plutonium, and thorium. For the most part these materials are in the early stages of scientific investigation and the selection and evaluation of the most useful materials is impeded by a general lack of knowledge of physical and mechanical properties. In addition, many of these materials of interest are available only in laboratory quantities and the production of large quantities of high purity compounds is a major problem in research and development programs.

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Available data indicate that uranium compounds of the types indicated exhibit physical properties intermediate between uranium metal and uranium dioxide. Thus these compounds all have potential use as nuclear power fuels; however, this discussion will be limited to studies carried out at Argonne National Laboratory on preparation, sintering, and properties of uranium monocarbide and the monosulfides of uranium and thorium.

Uranium Monocarbide

In the United States, a considerable research effort is being directed toward the evaluation and use of uranium monocarbide as nuclear fuel material. At the present stage of evaluation this material appears promising in that it has a higher uranium atom density and thermal conductivity than uranium dioxide while the melting point is comparable to that of UO_2. Irradiation testing is incomplete, but preliminary results indicate resistance to radiation damage. The carbide is not compatible with oxygen or water and some cladding metals but suitable coolants and claddings are available.

At the present time, some of the major problems associated with the utilization of uranium carbide are in the areas of production of quantity lots of stoichiometric material and in fabrication of high density shapes from the monocarbide without sacrifice of properties.

Many techniques have been applied to the synthesis of uranium monocarbide, such as: (1) uranium-organic gas reactions, (2) solid state reaction of uranium oxide and carbon, and (3) arc melting of uranium with carbon. In all of these methods there is difficulty in producing single phase monocarbide of uniform composition.

Recently the Argonne Chemical Engineering Division has reported a method of synthesizing refractory compounds in liquid metals[1] and this method is being used for the preparation of material for fabrication and sintering studies. In this method, uranium is dissolved in a suitable liquid metal such as zinc-12 weight per cent magnesium and carbon is added to the melt and the melt stirred. The compound formed precipitates from the solution and some sort of phase transfer is used to remove the bulk of the metal after reaction. The compound is isolated by volatilization of the remaining solvent metals. The only carbide compound detectable by x-ray analysis of the recovered powder is uranium monocarbide. The major impurities in the product are free carbon, oxygen, zinc and magnesium. Metal impurities are easily removed and progress is being made in reduction of carbon and oxygen contamination.

Fabrication evaluation of monocarbide formed by various precipitation techniques was carried out using cold pressing and sintering techniques. Particle size of the material was reduced to 5 to 10 microns by dry ball milling. Powders were mixed with binders such as 3% napthelene dissolved in trichloroethylene, granulated, and fabricated into cylinders by pressing at 30,000 psi. All operations were carried out in argon. Binders were removed in vacuum after which the temperature was increased over four hours to 1750°C and held constant for two hours. The sintered bulk densities resulting from this treatment are shown in Table I for several powdered materials.

TABLE I

Sintering Results for Various Powder Preparations

Powder Identification	Product Analysis C/U	Wt %	Sintered Density (% Theoretical)
1	1.28	0.90	80.0
2	1.15	1.53	82.5
3	1.19	0.79	85.0
4	1.27	1.17	81.5
5	1.21	0.83	84.0
6	2.1	-	51.5

There appears to be some correlation between sintered density and the combined contents of free carbon and oxygen. The highest bulk density resulted from powder No. 2 which had the lowest carbon and oxygen content and the lowest density resulted from the material having a great excess of carbon (powder 6). It appears that the presence of oxygen and uncombined carbon contribute to lowering sintered densities in several ways: (1) the presence of uncombined carbon lowers the pressed density of the compact, (2) the reaction of carbon with oxygen and UC during sintering results in voids in the compact, and (3) the reaction of oxygen with the carbon and/or UC results in gas evolution which increases the difficulty of sintering to a dense specimen. The surfaces of these sintered specimens were good, but cross sections showed coarse voids with internal channels connected to porosity near the surface.

In order to obtain a better understanding of the sintering behavior of these materials continuous measurements were made of the shrinkage of compacts heated in a vacuum dilatometer at a rate of 38°C per 10 minutes. The test specimens were made by isostatically pressing 5 to 10 microns powders to densities of 7.8 gm/cc and 8.2 gm/cc.

The results of sintering two materials of different carbon to uranium atomic ratios are shown in Figure 1. For both materials, shrinkage began at approximately 750°C and increased gradually until 1150°C where a rapid rate was encountered. This region of shrinkage was accompanied by gas evolution and the system pressure changed from less than 5.0×10^{-5}mm to greater than 5.0×10^{-4}mm at 1200°C. Above 1200°C the pressure began to decrease and returned to the 10^{-5}mm range at 1450°C. At this temperature densification was essentially completed. The sintered densities resulting from this treatment were 80.6% theoretical for the material having a C/U ratio of 1.17 and 85.0% theoretical for the material having a C/U ratio of 1.07. Although the linear shrinkages were divergent, the ultimate volume shrinkage for both materials was 33 ± 1%. The differences in shrinkage may be accounted for by the differences in pressed density of the starting specimens.

The gas evolution accompanying shrinkage is thought to be the reaction of oxygen with either carbon and/or UC to form CO. It is also probable that carbon reacted with UC to form UC_2 since the sintered pellets were found to contain some UC_2 which was not present prior to sintering.

It appears that the presence of oxygen and free carbon in the uranium monocarbide promote the sintering reaction but at the same time prevent the attainment of high sintered density due to the evolution of gas and the creation of voids by the free carbon reaction. Results of the sintering studies indicate that in order to obtain high sintered densities the oxygen contamination must be lowered to about 0.1% and the carbon to uranium ratio to about 1.05. A slight excess of carbon is desirable to decrease the possibility of cladding reactions and to inhibit the release of free uranium.

The preparation and evaluation of the monocarbide formed by the precipitation technique are still in the preliminary stages. Results to date indicate that contamination can be controlled to a desirable level and the material shows promise for use in fabricating high density shapes by press and sinter techniques.

Uranium and Thorium Monosulfide

Uranium monosulfide has become of interest as a potential nuclear fuel since it has a cubic (NaCl) structure stable to its melting point of 2460°C[2], a uranium density comparable to UO_2, and is reported to have semimetallic properties[3]. Thorium monosulfide is reported to be isomorphous with uranium monosulfide and somewhat more refractory and stable[3] and thus solid solutions might result in improved properties and would be of interest as breeder-type nuclear fuels.

The preparation of the monosulfides has been carried out in a two stage process involving a gas-solid reaction followed by a high temperature homogenization treatment. In the first stage, reactive metal powder is formed by hydriding turnings (at 250°C for U and 200°C to 500°C for Th) and decomposing the hydride (at 550°C for U and 750°C for Th) using up to three cycles to produce a fine powder. Measured volumes of H_2S, corresponding to the stoichiometric equivalent of sulfur, were reacted with the powdered metal (at 400°C to 550°C for U and 700°C for Th) resulting in a mixture of disulfide, free metal, and some residual hydride. In the second stage, this product is crushed to minus 100 mesh particle size and heat treated in vacuum or in an inert atmosphere at 1700°C to 1800°C for US and 1800°C to 1900°C for ThS. Using this procedure materials containing up to 99.8% monosulfide phase were produced.

After the sulfide has been homogenized it may be handled in air without oxidation except for operations which produce excessive heat, such as crushing. Fabrication of the material is readily carried out using standard press-and-sinter techniques. Binder additions may be made as aqueous solutions since the sulfides are relatively inert, even to boiling water. The sulfides have also been extruded using a vacuum extruder and a conventional Methocel-Superloid aqueous binder system.

Sintering of uranium monosulfide may be carried out in argon or in vacuum and the type of sintering reaction depends upon the atmosphere. Oxygen impurity was the greatest single factor in the sintering reaction. In vacuum, solid-phase sintering prevailed and all oxygen contamination was found in the microstructure as discrete particles of UO_2. When sintering was done in argon, liquid phase sintering occurred at an accelerated rate. The mechanism appeared to be that oxygen contamination entered into a UOS phase which formed a liquid eutectic with US at about 1750°C.

Thorium monosulfide differed from uranium monosulfide in that oxygen was retained in the oxysulfide phase in vacuum as well as argon. A liquid eutectic was formed between ThOS and ThS at about 1950°C resulting in rapid liquid phase sintering to densities as high as 98% theoretical.

The sintering behavior of uranium monosulfide processed in vacuum is shown in Figure 2. For each homogenization temperature, the sintered density reached a maximum at 1800°C to 1900°C and decreased slightly at higher temperature. Sintered density increased with homogenization temperature to a maximum of 86% theoretical. Final sulfur to uranium ratios for the monosulfide phase varied from 0.96 to 1.00. Contamination in materials homogenized at 1600°C and below was determined to be UOS while that in materials homogenized at higher temperatures was predominately UO_2.

Prolonged sintering time was found to be of questionable value in vacuum processing. Increasing time at 1800°C from 1 hour to 14 hours resulted in an increase in theoretical density from 85.7% to 89.0%. Prolonged heating resulted in a weight loss of 18.5% and the primary evaporating species was found to be US. Results of volatility measurements during sintering are shown in Figure 3. Volatile losses from uranium monosulfide become appreciable above 1800°C and thorium monosulfide has somewhat lower volatility. Precise measurement by Cater at ANL have shown that US has a lower vapor pressure than UO_2.

The sintering behavior of US in argon, where a liquid phase is formed, is shown in Figure 4. Densities resulting from sintering in argon were appreciably higher and weight losses were lower. It may be seen that, for fine particled material, sintering above 1800°C has little effect on the resulting density. Higher temperatures serve mainly to increase the grain size with some consolidation of pores.

Vacuum processed material is difficult to densify, but it can be made to very high purity. At somewhat of a sacrifice in purity, liquid-phase sintering in argon appears to be the only way to achieve high density compacts at present. Indications are that the melting point of US is not greatly affected by the presence of a small amount of liquid phase but this phase may be undesirable for some uses of the material.

Although no attempt was made to establish an equilibrium diagram, a continous series of solid solutions, closely approximately Vegard's Law, was formed between US and ThS sintered in vacuum for one hour at 2050°C. Continuous solid solutions were formed as low as 1805°C but sintering conditions definitely were not equilibrium.

A summary of monosulfide structures resulting from the various treatments is shown in Figure 5. Section (a) shows a structure typical of vacuum sintered US in which the discrete gray particles are UO_2. Argon sintered US, shown in (b), exhibits a gray intergranular phase which has been identified as UOS. The polished section of high density ThS (d) shows the oxysulfide phase on grain boundaries and also precipitated on certain crystal planes, probably the (111). It has been established that ThOS does not breakdown at temperatures up to 2100°C in vacuum. The solid solution material (C) shows a structure intermediate between the end members.

Etched samples of uranium monosulfide (10:1 H_2O_2 - H_2SO_4) have shown a Widmanstatten-like structure. This structure has been found to be due to etching out of UC precipitated on (111) planes of US. Chemical analysis established a carbon contamination of 100-300 ppm in the US. This type of etching was not found in ThS or in solid solutions of US-ThS.

In order to characterize the monosulfides several physical properties were evaluated. The oxidation behavior of the sulfides was determined by differential thermal analysis. Shown in Figure 6 are representative D.T.A. curves for US and ThS in dynamic air. Uranium monosulfide undergoes a three step oxidation in the range of 360°C to 370°C which is an ignition. The phase resulting from ignition is U_3O_8. Thorium monosulfide ignites between 460°C-510°C in a two stage reaction and the ultimate phase is ThO_2. Solid solutions showed intermediate ignition temperatures but the relationship was non-linear.

Compatibility with metals was determined by immersing a sandwich of US discs and metal discs in NaK at 800°C for 14 days. Polished sections showed no reaction with NaK, Type 304 stainless steel, vanadium, and niobium; however, there was a reaction with zirconium. No reaction with tungsten sintering crucibles has been noted to 2100°C. Compatibility tests with boiling water showed only a slight surface stain after eight hours exposure. Dilute HNO_3 or H_2SO_4 slowly attack the sulfides at room temperature but HCl has no effect. Preliminary results indicate the sulfides are stable in hydrogen to at least 850°C.

The monosulfides were found to have several metallic characteristics. Sintered sulfides have a definite metallic sheen and, although somewhat brittle, shown a fair degree of machineability. High density pellets have been drilled through, turned, and faced on a lathe and smoothly filed. Centerless grinding has been carried out with normal cooling procedures. The monosulfides are soft and show Vicker's hardness of 165 to 270. The electrical resistivities are metallic in nature and are approximately $200 \mu\Omega$-cm for US and $20 \mu\Omega$-cm for ThS for materials above 90% theoretical density.

The thermal expansion coefficients have been determined to 1000°C and are approximately the same as the equivalent oxides (13.1×10^{-6} for US and 10.1×10^{-6} for ThS).

The lattice parameter of US was found to vary from 5.4875Å to 5.4910Å for material have S/U ratios from 0.96 to 1.03. The best value for pure, stoichiometric US was $a_o = 5.4905 \pm .0005$Å which results in a theoretical density of 10.84 gm/cc. Thorium monosulfide has been found to have a lattice parameter of $a_o = 5.685$Å.

Only preliminary thermal conductivity data is available. One measurement made on US at 75°C shows a value approximately 40% greater than UO_2 at the same temperature (0.11 watts/cm-°C). This is considerably lower than expected and further testing is in progress.

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SHRINKAGE VERSUS LINEARLY RISING TEMPERATURE
FOR TWO URANIUM MONOCARBIDES

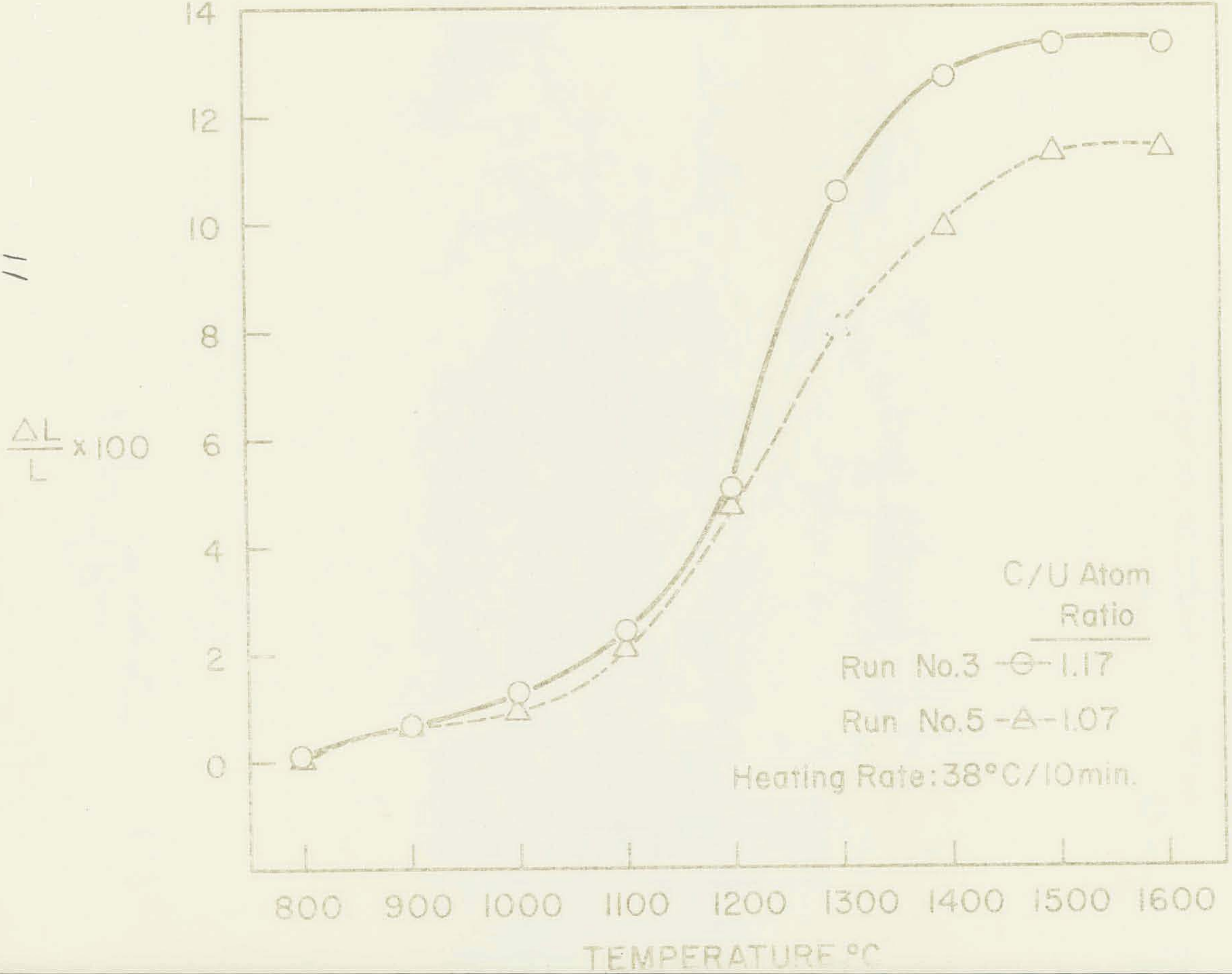


Figure 1

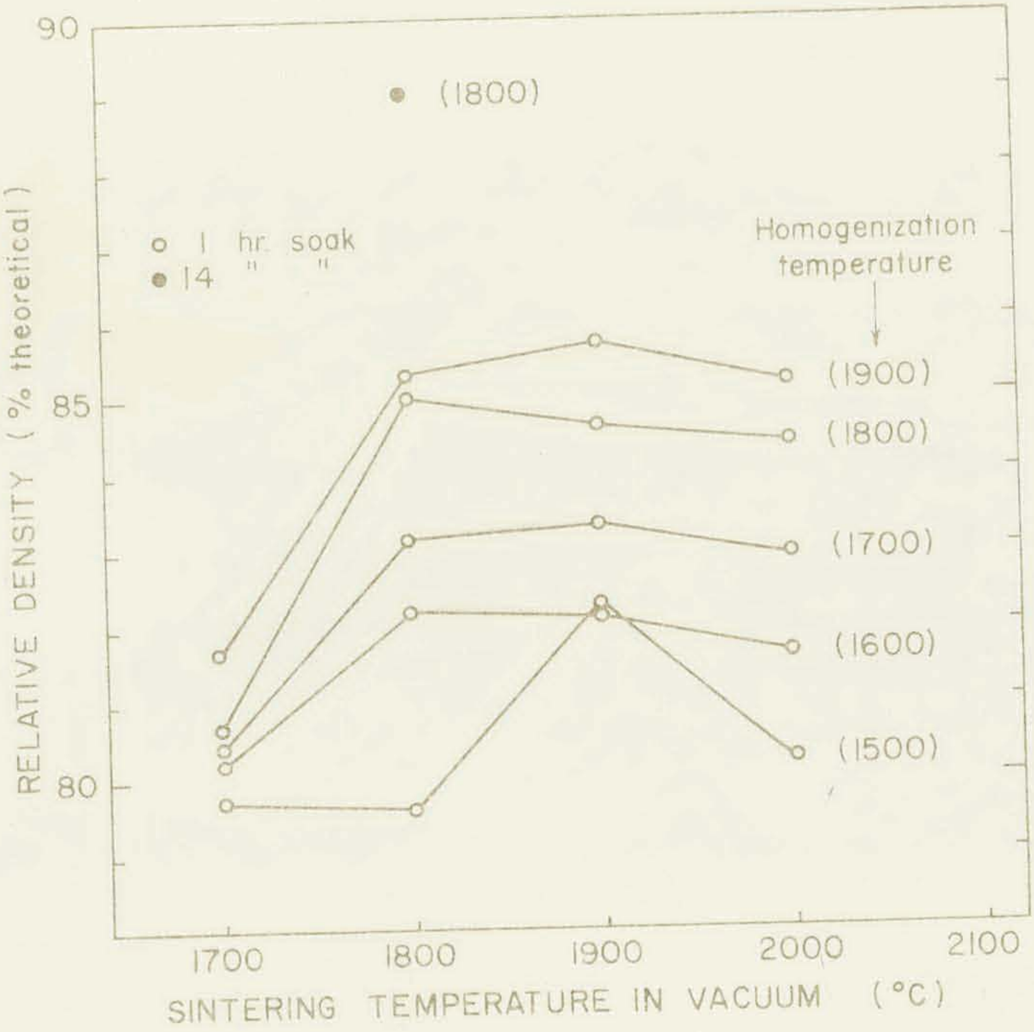
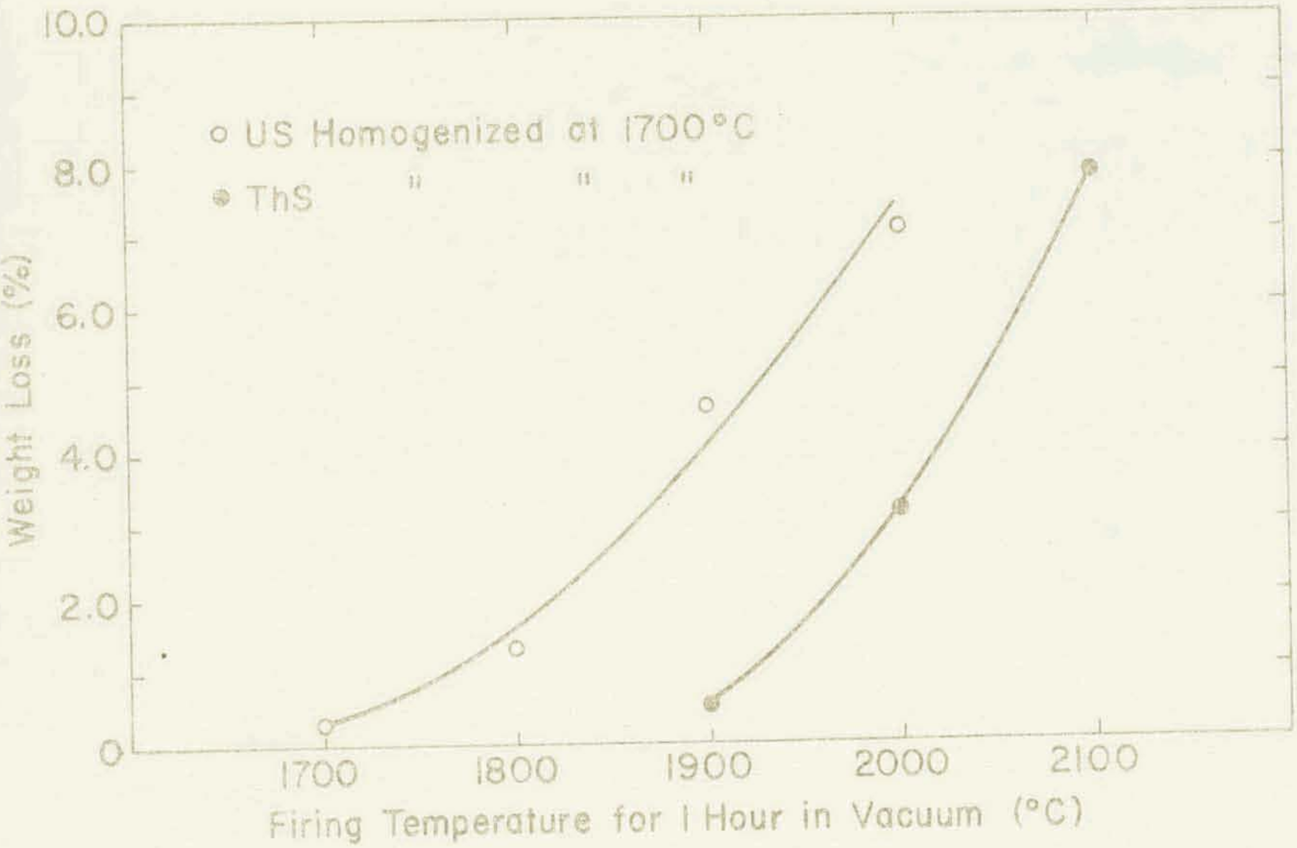


Fig. 2. Solid-phase sintering study for material of 98-99 wt % US phase.

Figure 3.

EFFECT OF FIRING TEMPERATURE
ON THE VOLATILITY OF US AND ThS



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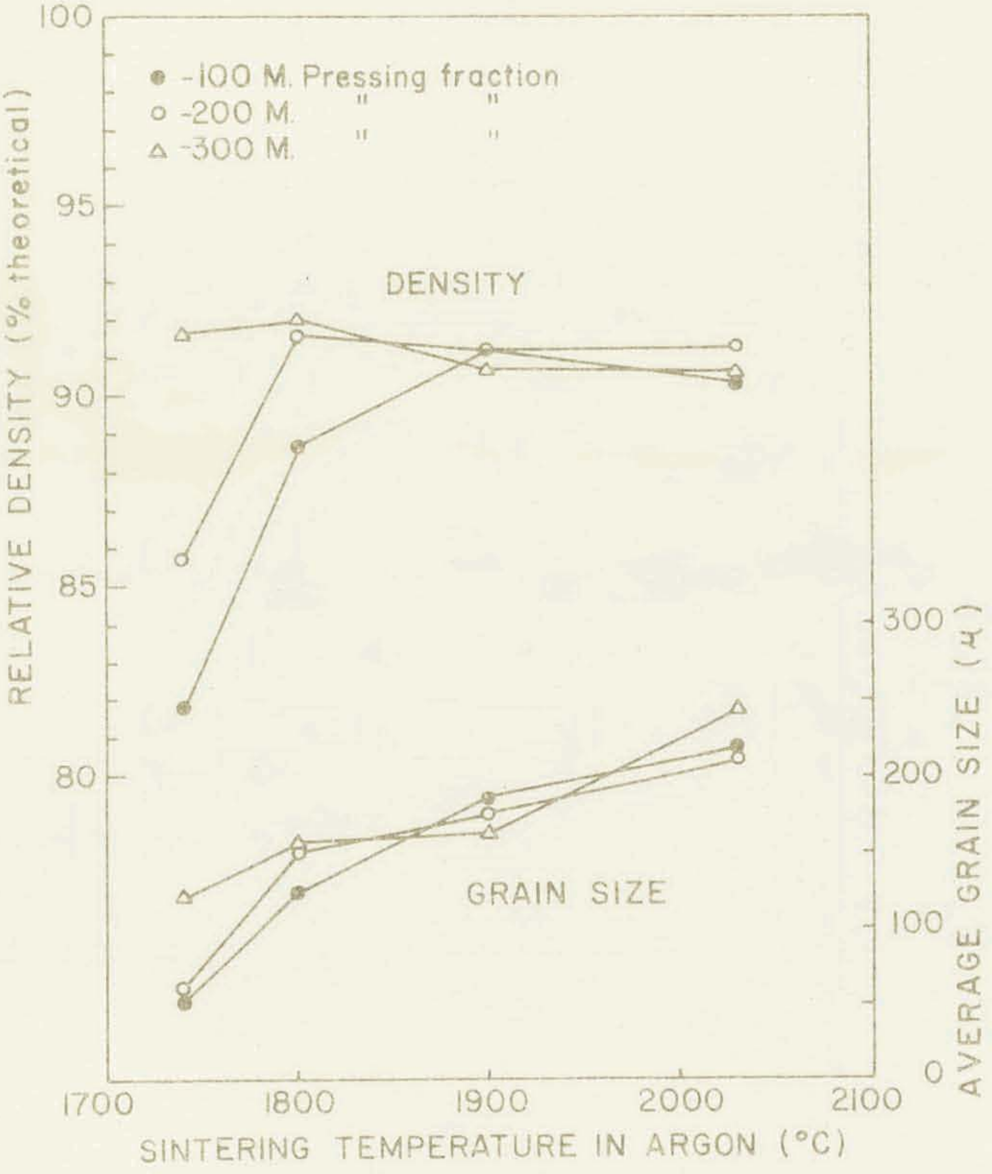

Fig. 4. Liquid-phase sintering study for material of 98-99 wt% US phase. (Soak time-4.5 hours.)

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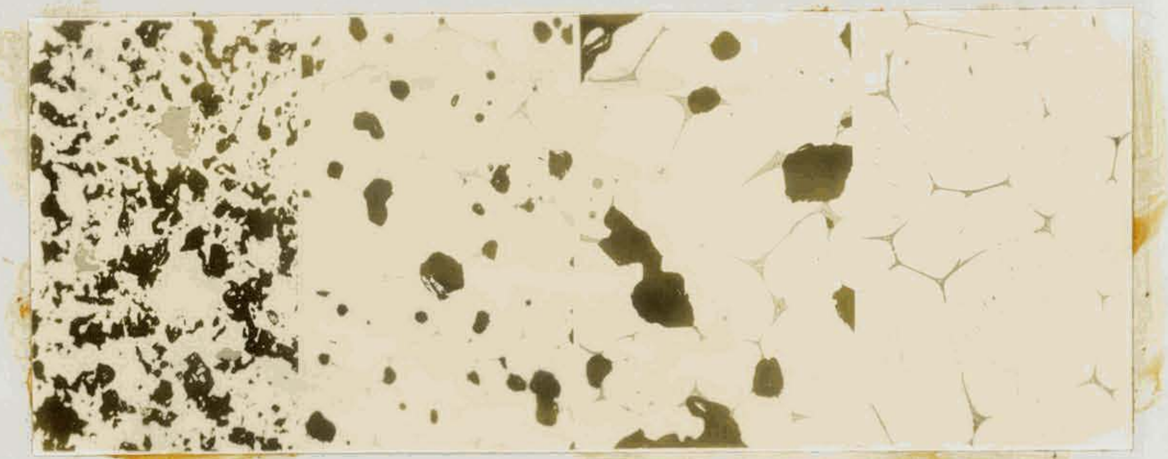
Figure 5



(a) (b) (c) (d)

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(a) US, solid-phase sintered in vacuum at 1800°C, 84% T.D.

(b) US, liquid-phase sintered in argon at 1800°C, 92% T.D.

(c) $U_{0.5}Th_{0.5}S$, sintered in vacuum at 2050°C, 73% T.D.

(d) ThS, sintered in vacuum at 2100°C, 98% T.D.

Fig 6

16

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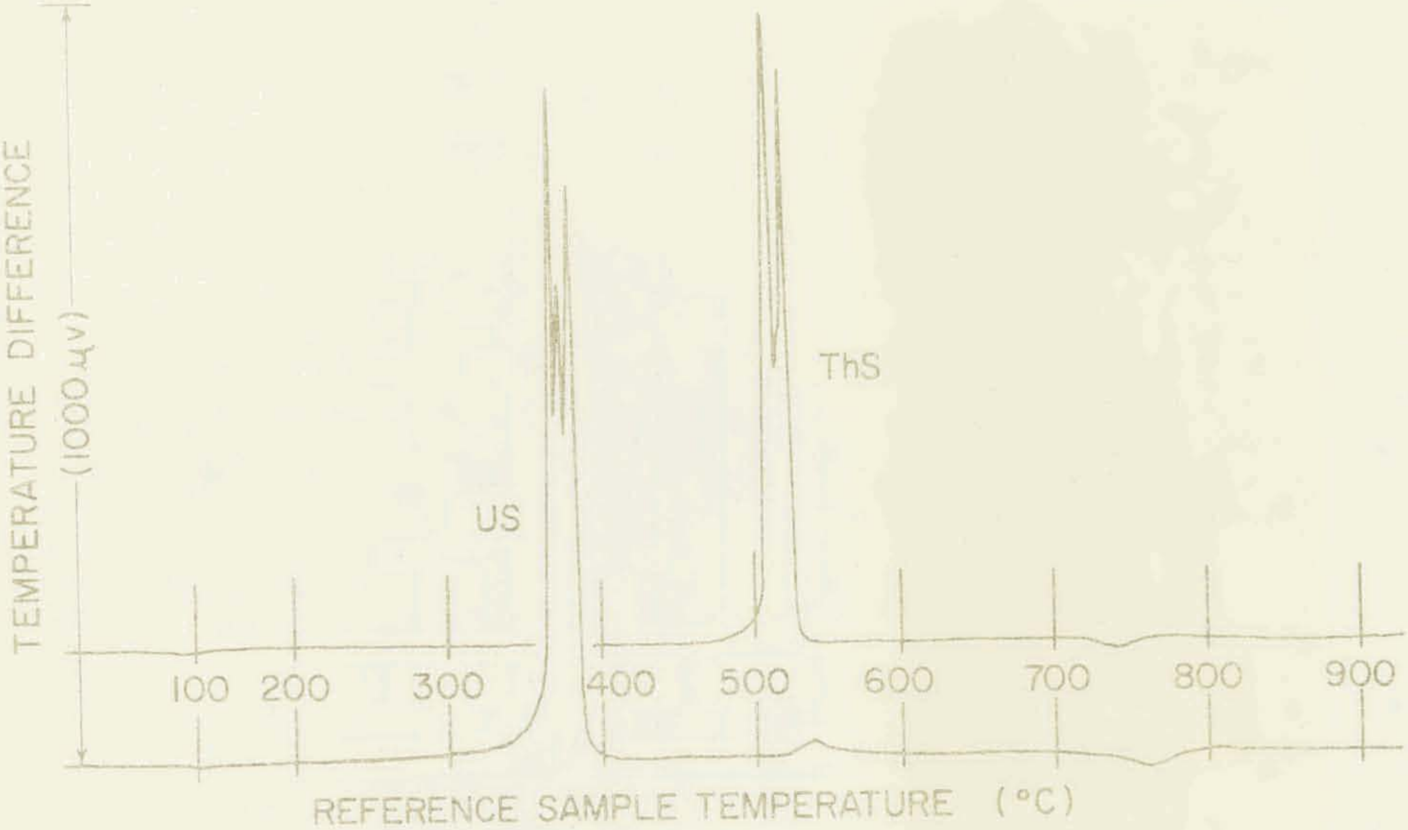

Fig. 6. Representative D. T. A. thermograms for US and ThS in dynamic air at one atmosphere. (Samples diluted to 25 vol % in Al_2O_3 ; heating rate - 5 °C per minute.)

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