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SINTERING AND PROPERTIES OF URANIUM AND THORIUM MONOSULFIDES

MASTER

by

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I. INTRODUCTION

Uranium and thorium monosulfides have been under investigation because of their potential as reactor fuel materials. In addition, information gathered is a useful guide to the corresponding plutonium technology. Initial work on fabrication and evaluation was presented in an earlier paper; this paper is intended to clarify and supplement those results.

II. PREPARATION PROCEDURES

Monosulfide powders were synthesized as shown in Figure 1 on a 250 gram scale. Uranium turnings were broken down to a very reactive powder by means of three hydriding-dehydriding cycles. This powder was then reacted with a stoichiometric amount of H_2S at 400°C to give a mixture of U and US_2 which, in turn, was homogenized to the monosulfide phase at 1700°-1800°C. When homogenization was done in vacuum, a product containing about 99.5 w/o US phase was obtained. Argon processing gave a less pure material of about 98% purity. Production of thorium monosulfide by the same method was somewhat complicated by the existence of two stable thorium hydrides and the product generally contained around 97 w/o monosulfide phase.

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Specimens used in this work were, for the most part, isostatically pressed at 55,000 psi from -200M powders containing 1 w/o wax binder. Firing was done in an induction furnace using a tungsten crucible as a susceptor. Before homogenization the sulfide mixtures had to be handled in an inert atmosphere to prevent oxidation of the free metal. The homogenized powders, however, were quite inert at room temperature and operations which generated little heat, including pressing, could be performed safely in air.

III. STRUCTURAL CHARACTERISTICS OF MONOSULFIDE BODIES

(A). Sintering Studies

When US compacts were fired in vacuum, solid-phase sintering occurred at a relatively slow rate. This is illustrated in Figure 2 which shows that, although densification increased with homogenization temperature, a maximum of only 86% theoretical was achieved in one hour at temperatures up to 2000°C. Extending the soak period to 14 hours at 1800°C did increase the density to 89% theoretical but a total weight loss of 18.5% occurred during this time. The secondary phase in this material occurred as discrete particles of UO_2 which showed no reaction with US up to 2100°C.

Figure 3 shows that improved densities were obtained in argon where sintering took place in the presence of a liquid phase and weight loss was minimized. The secondary phase in this material was predominately UOS which could be observed on the grain boundaries. It formed a liquid eutectic with US at about 1740°C. Densification showed an inverse relationship to particle size, maximum density being achieved at 1740°C by the -325M body but not until 1900°C by the -100M body. Only closed porosity remained at the maximum densities of 91-92% theoretical. Higher temperatures served merely to increase the grain size with some consolidation of pores but no increase in density. Grain growth is shown to have been quite extensive in these bodies. In comparison, the average grain size of the solid-phase sintered bodies ranged from 30 to 81 microns.

X-ray and chemical analysis established that UOS was present in vacuum-processed material at lower temperatures but became unstable at 1700°-1800°C, breaking down probably in the following manner: $2UOS \dashrightarrow UO_2 + US + S\uparrow$. There is strong evidence that this decomposition was related to a drop in the S/U ratio of the US phase from >1 to < 1. It should be noted that final S/U ratios of the US discussed thus far varied from 0.96 to 1.00.

Thorium monosulfide differed from US in that the oxysulfide was the stable oxide phase in vacuum as well as argon. A liquid eutectic was formed between ThOS and ThS at about 1950°C leading to extremely rapid liquid-phase sintering to densities as high as 98% theoretical.

Solid solutions were formed between US and ThS in two ways. The first involved firing mixtures of the homogenized powders. Figure 4 shows that complete solid solubility was not achieved until 2050°C where the lattice parameters very closely approximated the straight line relationship of Vegard's law. The second method utilized homogenization of blends of the low temperature mixtures and produced complete solid solution at 1700°-1800°C. The relative stability of ThOS was demonstrated by the fact all oxygen contamination occurred as ThOS, with no UOS or UO_2 detected.

Figure 5 is a composite summary of all these structures. In (a) is shown solid-phase sintered US with the black areas representing porosity, the discrete gray particles, UO_2; (b) shows liquid-phase sintered US, the gray intergranular phase being UOS; (d) shows dense ThS in which the ThOS can be found as a needlelike precipitate on certain crystal planes within the grains as well as on the grain boundaries and (c) shows a 50:50 solid solution to be a sort of compromise structure with ThOS found on the grain boundaries and as faint precipitate trails within the grains.

(B). Lattice Parameter Variations

The lattice parameter of US, which has the NaCl structure, was found to vary from 5.487 to 5.491Å for material processed in vacuum having S/U ratios ranging from 0.96 to 1.03. The only consistent behavior was shown by the preparations having ratios very close to stoichiometric 1.0. Without exception, these materials had parameters close to the maximum cited and a value of $a_o = 5.4905 \pm .0005$Å has been chosen as the best value for pure stoichiometric US. This corresponds to a theoretical density of 10.84 g/cc and is in good agreement with Cater[1] who worked with exceptionally pure sulfide. The variations in parameter for the non-stoichiometric preparations have been attributed to a combination of a defect structure and slight oxygen solubility.

Argon processing caused the lattice parameter to drop to as low as 5.481Å whereas the minimum in vacuum was 5.487Å. This suggested that nitrogen, the main contaminant of tank argon, might be going into some of the anion positions of the US lattice. A contraction would be expected since the ionic radius of N^{-2} (1.569Å) is some 17.5% smaller than that of S^{-2} (1.903Å)[2]. Accordingly, mixtures of US with up to 10 m/o UN were fired in vacuum. Figure 6 shows that 10 m/o UN lowered the lattice parameter significantly at 1650°C. More extensive solid solution is indicated at 1825°C where the lattice parameter progressively decreased with increasing UN with, however, a strong positive deviation from Vegard's law. The UN was also observed to progressively inhibit grain growth. An X-ray of the 10 m/o body fired at 1825°C showed only a single phase. This, plus the shape of the lattice parameter curve, indicates that UN is soluble in US to an even greater degree.

(C). GROOVE ETCHING

When polished sections of US bodies were etched with a 10:1 H_2O_2-H_2SO_4 solution an unusual Widmanstatten-like structure was generated within the grains which had originally appeared single phase. This is shown in Figure 7. At high magnification this structure was found to consist of grooves of varying thickness and depth. Initially, this phenomenom was attributed to selective etching of the high energy planes of stacking faults[3]. Recent work, however, indicates that it is more likely the etching-out of UC which has so nearly the same color as US in unetched sections as to be invisible. When a US polished section was observed in slowly heated water the same Widmanstatten structure first became apparent at 80°C and was quite clearly defined at 100°C. This ease of attack would point to a uranium carbide. The monocarbide is favored because on several X-ray patterns four or five very faint low angle lines corresponding to its FCC cell were found. Chemical analyses established that carbon was present as 100-300 ppm and undoubtedly it was furnished by the gases employed during processing.

IV. PROPERTY DETERMINATIONS

(A). Melting Point

A modification of the Mendenhall wedge technique in hydrogen was used to determine the melting point of monosulfides which had been vacuum-sintered at 2000°C. As shown in Figure 8, the melting point dropped from 2450°C for US to a minimum of about 2300°C for the 75 m/o ThS solid solution, then increased to 2335°C for ThS. There was no significant difference in the values obtained for solid solutions made by the two different methods. Values obtained for argon-processed US showed no lowering of the melting point due to the presence of UOS. Bodies of such material have, however, shown greater tendency to deform at elevated temperatures.

(B). Electrical Resistivity

Room temperature electrical resistivities for the same 2000°C solid solution series are shown in Figure 9. The general pattern of a resistivity increase at 25 m/o ThS followed by a steady drop to ThS was found to be typical of all such series once complete solid solution had been achieved. A general trend for both US and ThS was to higher resistivities with higher firing temperatures, perhaps due to increased grain growth or change in stoichiometry. The resistivity of a US specimen showed a small but definite increase in resistivity with temperature, from 179 $\mu\Omega$-cm at 25°C to 181 $\mu\Omega$-cm at 50°C. In this respect, therefore, US behaves as a metal.

(C). Thermal Conductivity

Using the Powell ball technique, Dr. McElroy at ORNL determined the thermal conductivity of US at 75°C to be 0.0264 cal/cm-sec-°C, about 35% higher than that determined for stoichiometric UO_2 in the same apparatus. Not enough work has yet been done to establish the temperature dependency. The value for US is much lower than one might expect for a material with so many metallic characteristics. However, if, as for many metals, the conductivity of US remains fairly constant with temperature, it would still represent a considerable improvement over oxide systems. The fact that US is a ferromagnetic material with a Curie temperature below room temperature[4] would additionally point toward such behavior.

(D). Oxidation

The oxidation behavior of the monosulfides was studied in some detail using a DTA apparatus in which a dynamic flow of oxygen was maintained through the sample powders. Figure 10 shows some typical thermograms. The sharp exothermic peaks indicate ignition. Sintered bodies were found to ignite at approximately 100°C higher than the powders.

Uranium monosulfide powders showed ignition at 360-370°C in air at one atmosphere with three strong exothermic peaks occurring in rapid succession. The only other reactions noted up to 1250°C were a comparatively weak exothermic peak at 540°C and a similarly weak endothermic peak at 765°C. X-ray analyses and other sources suggest the following took place:

365°C: $US \dashrightarrow UOS \dashrightarrow UO_2 \dashrightarrow U_3O_7$

540°C: $U_3O_7 \dashrightarrow U_3O_8\ (UO_3)$

765°C: $UO_3 \dashrightarrow U_3O_8 + O$

Thorium monosulfide ignited in the range 460°-510°C with the occurrence of only two strong exothermic peaks corresponding to: $ThS \dashrightarrow ThOS \dashrightarrow ThO_2$. A weak endothermic peak at 725°C can not be readily explained as it would appear to be analogous to the 765°C peak for US. Solid solution bodies had less than a linear increase in oxidation resistance from US to ThS. X-ray patterns revealed that they oxidized directly to UO_2-ThO_2 solid solutions. In addition, weak lines were found for U_2O_5 which increased in intensity towards oxidized US.

The oxidation of US was also studied at reduced oxygen pressures. With a dynamic flow of oxygen through the sample, the main effects of reducing the pressure from 760 to 14 mm were: (1) the lowering of the strong peak intensities by a factor of 20, and (2) the raising of the upper temperature of the oxidation range from 377 to 532°C. Static conditions produced similar effects. At 0.5 mm static oxygen pressure the first peak essentially disappeared, leaving only one pronounced oxidation peak at 570°C.

(E). Compatibility with Metals

Uranium monosulfide showed good compatibility with many metals which might be used as cladding, matrix, bonding or thermocouple materials. Two types of tests were run. The first was preliminary to irradiation tests which are now getting started in the MTR reactor at Idaho Falls. It consisted of clamping various metals between US disks and immersing the assembly in NaK at 800°C for two weeks. The second type of test consisted of firing US pellets containing 25 v/o of metal filings at various temperatures in vacuum or argon. A combination of X-ray and metallographic analysis was used to confirm reaction or lack of it. The results are given in Table I.

NaK showed no reaction with US under the given conditions. Ta did not react with US up to the maximum temperatures of 1980°C in vacuum or 1930°C in argon. It did scavenge some nitrogen from the argon to form some TaN but did not react with the small areas of UOS present. Mo showed no reactions at all in vacuum or argon up to the maximum temperatures used. Nb showed no reaction in the extended NaK test or in vacuum up to 1980°C. V showed no reaction in NaK and even as a liquid above its melting point of 1730°C did not react with US. As might be expected, Zr did react. The small reaction gone in the 800°C test was probably a Zr-rich solid solution. At 1650°C a small decrease in lattice parameter plus the two-phase appearance of the polished section indicated partial solid solution of Zr in the US, and at 1825°C all indications were that solid solution was complete. A structure similar to that of liquid-phase sintered US was observed. W-26% Re thermocouple wire showed no reaction in vacuum up to 1980°C. Finally, US did not react with the W crucible used in vacuum by Cater[1] or with the W wedges used in hydrogen during melting point determinations.

BIBLIOGRAPHY

1. E. D. Cater, P. W. Gilles and R. J. Thorn, "Uranium Monosulfide. I. Vaporization, Thermodynamics, and Phase Behavior", J. Chem. Phys., 72 (2) 608-618 (1961).

2. Armour Research Foundation, "Development of Methods for Low-Temperature Sintering of Ceramic Materials", Project No. 129-926G, Report No. 6.

3. J. P. Hugo and P. D. Shalek, "Groove Etching in Uranium Monosulfide", J. Inst. of Metals, 90, 215-16 (1962).

4. M. A. Kanter, C. W. Kazmierowicz, "Ferromagnetic Transition in Uranium Monosulfide", to be published.

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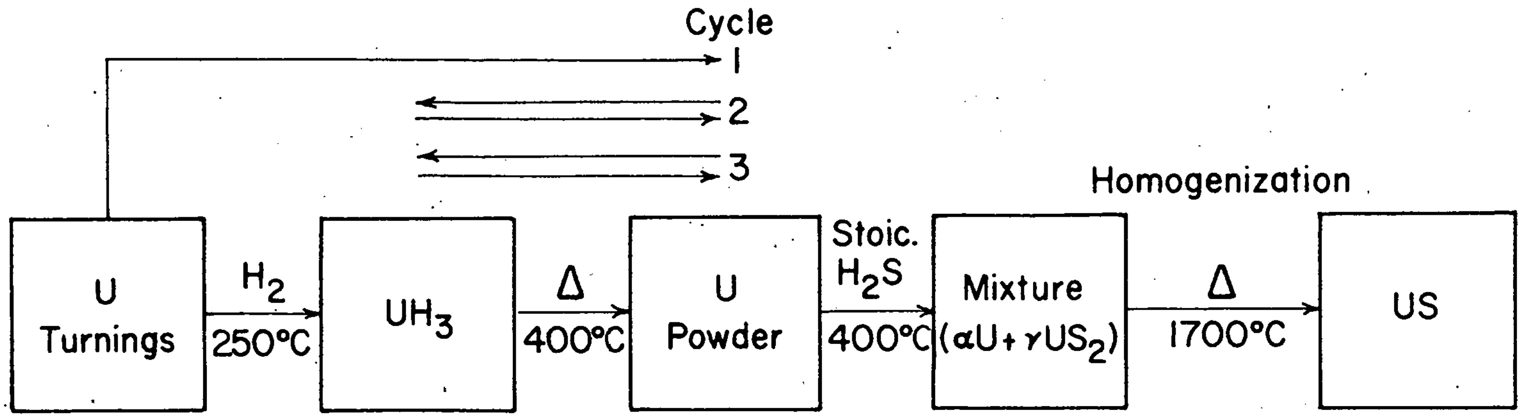

Fig. 1. Synthesis of uranium monosulfide.

Figure 2.

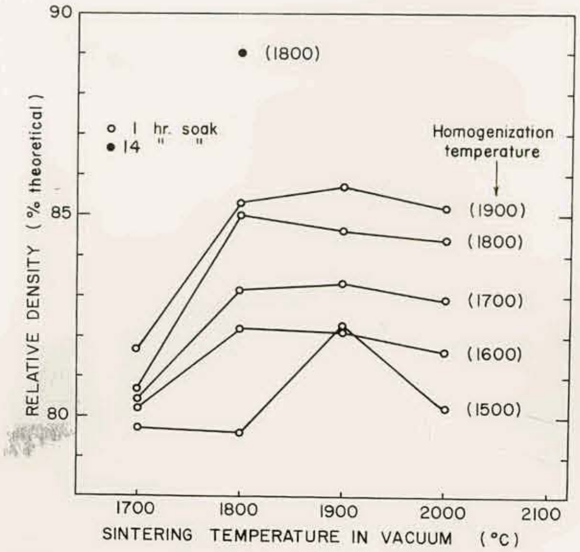

Fig. 3. Solid-phase sintering study for material of 98-99 wt % US phase.

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Figure 3.

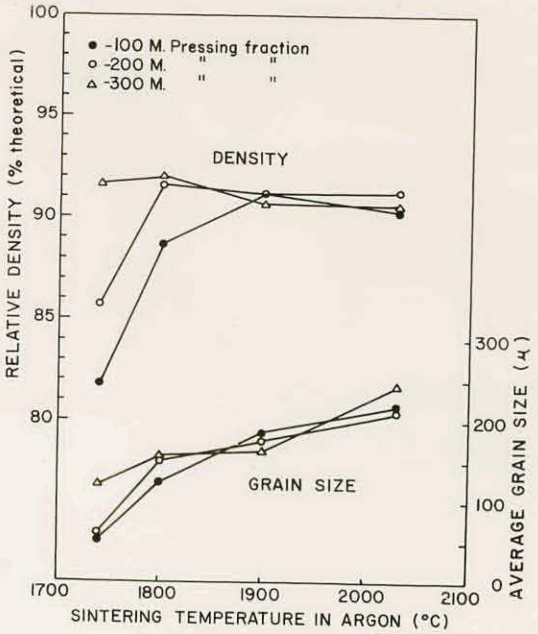

Fig. 4. Liquid-phase sintering study for material of 98-99 wt % US phase. (Soak time - 4.5 hours.)

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Figure 4.

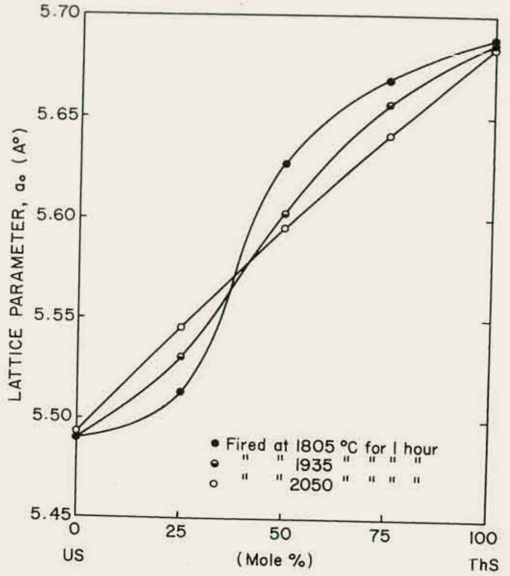

Fig. 5. Predominant cell size of US-ThS mixtures vs. composition.

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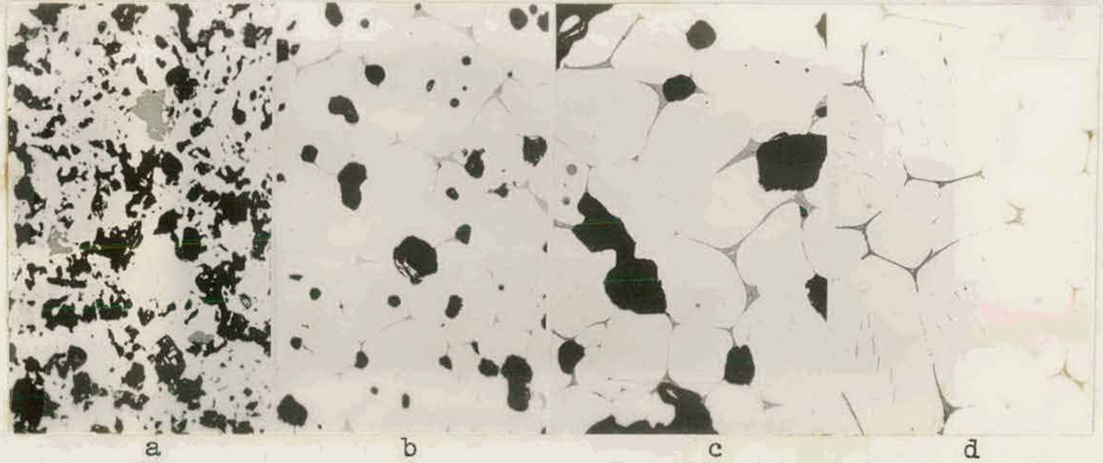
Figure 5. Representative Monosulfide Structures. (Unetched X125)



(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.

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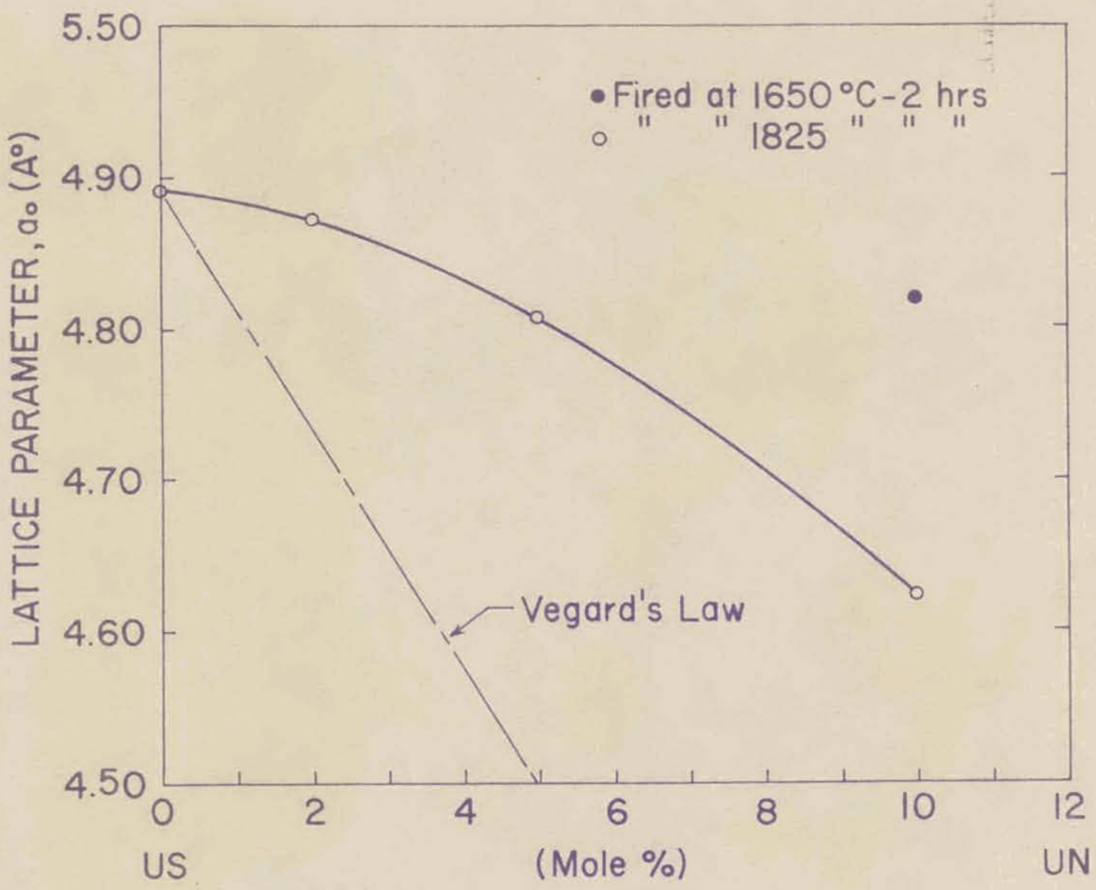
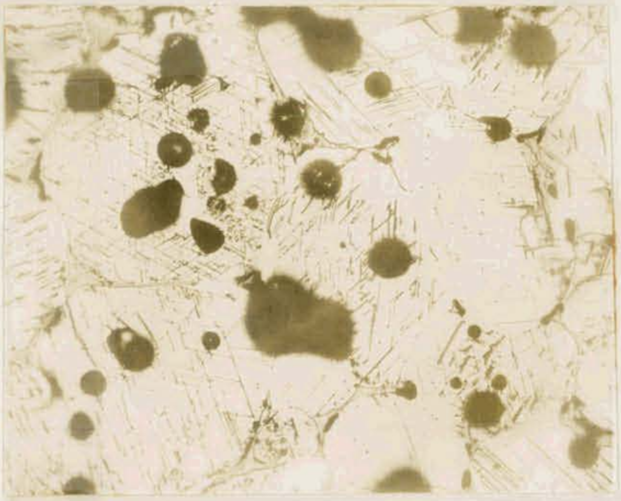


Fig. 6 [redacted] Lattice parameters of US-UN solid solutions.

Figure 7. US, sintered in argon at 1800°C to 92% T.D., showing groove etching from 10:1 H_2O_2/H_2SO_4 mixture (X250).



Micro 34360

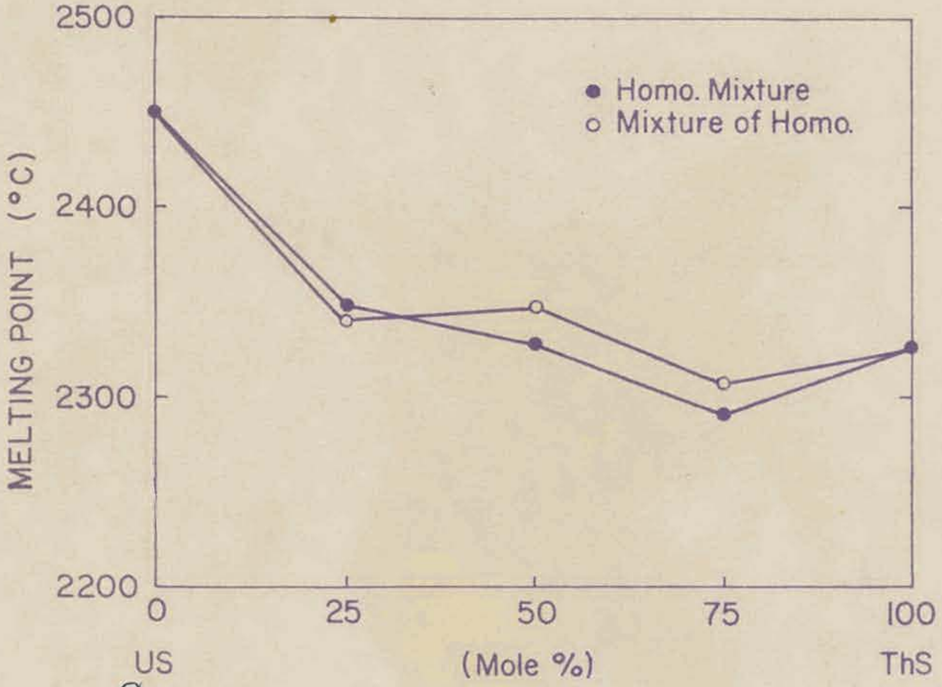


Fig. 8 Melting points of US-ThS solid solutions.

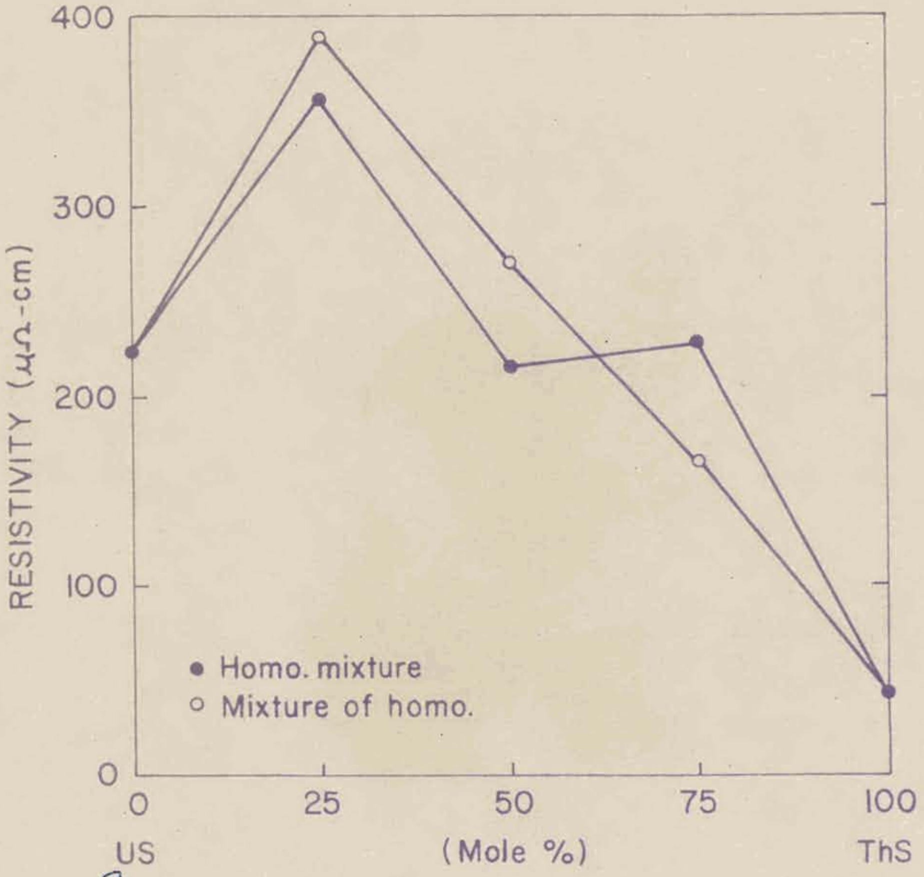


Fig. 9 Electrical resistivity of US-ThS solid solutions.

Figure 10.

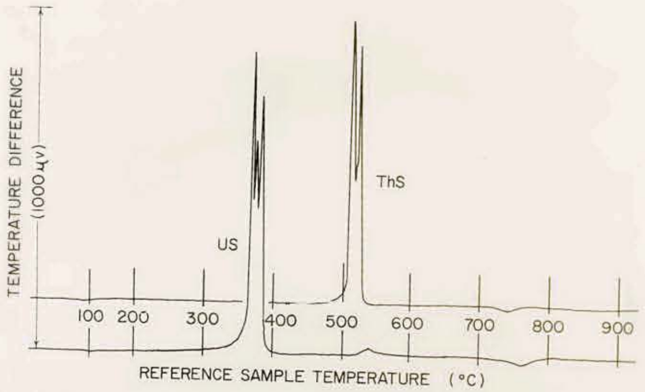


Fig. 7. Representative D. T. A. thermograms for US and ThS in dynamic air at one atmosphere. (Samples diluted to 25 vol % in Al_2O_3 ; heating rate - 5 °C per minute.)

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Metal Contacting US	Heat Treatment			
	800°C-340 hr NaK	1650°C-2 hr Vacuum	1825°C-2 hr Vacuum	1980°C-1 hr-Vacuum or 1930°C-2 hr-Argon
Ta		N.R.*	N.R.	N.R.-vac.; N.R. with US or UOS in argon-some TaN.
Mo		N.R.	N.R.	N.R.-vac.; N.R. with US or UOS in argon.
Nb	N.R.	N.R.	N.R.	N.R.-vac.
V	N.R.	N.R.	N.R. (V as liquid) →	→ vac.
Zr	0.7 mil reaction zone-possibly SS.	Partial SS of Zr in US.	Complete SS of Zr in US. →	→ vac.
W-26 Re		N.R.	N.R.	N.R.-vac.
W	N.R. to melting point of US (2460°C) in vacuum or H_2.			
Type 304 Stainless	N.R.			

* No Reaction

Table I. Compatability of US with various metals.