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Trip Report to Oak Ridge National  
Laboratory (ANP) by John R. Heiks  
and Layton Wittenberg

The following is a rather detailed report of the information received from the Aircraft Nuclear Propulsion group at Oak Ridge National Laboratory during a two-day visit, November 12-13, 1953. This report is limited to a discussion of the phase work, preparation of materials, and analytical problems now in progress at ORNL. Although other fields of interest were briefly discussed they are not included here since they are being reported in detail by Dr. John Otto and Mr. Ralph Joyner who visited this same group November 16-17, 1953.

Phase Studies

A discussion with Dr. Barton of Oak Ridge National Laboratory and Dr. Insely of the National Bureau of Standards resulted in the following information concerning the phase studies now in progress at ORNL. The methods in use at ORNL include (1) thermal analysis, (2) differential thermal analysis, (3) quenching, (4) hot filtration, and (5) X-ray analysis. The choice as to method or combination of methods is dependent on the character and complexity of the system under investigation.

(1) Thermal Analysis: For regions of the ternary system where thermal analysis can be used it is preferred because of its simplicity and ease of operation.

ORNL for the most part uses graphite containers with graphite stirrers for this work. These containers are covered but not sealed. To minimize oxide formation and water contamination a dry helium atmosphere under a slight pressure is maintained above the material in the containers. Elevated temperatures are obtained by placing the graphite containers in commercial Hoskins "pot" furnaces. Cooling rates of approximately 5 degrees per minute are controlled manually. Temperatures are recorded automatically with conventional Brown or L and N temperature recorders using chromel-alumel thermocouples. Approximately 100 gram samples are used in these graphite containers.

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Some thermal analysis work has also been carried out in sealed nickel containers. These containers are constructed from 1" nickel pipe with a thermowell and filling tube welded in the top of the container. The advantage of this type container is that it can be loaded and sealed under dry box conditions after which it can be handled in the open without fear of contamination. These containers would have an added advantage when handling beryllium compounds where extra caution must be exercised because of their toxicity. Agitation for reaching thermal equilibrium is obtained by placing the entire furnace assembly on a rocking machine. The temperature measurements are made in the manner described above. A minimum of 20 grams of material are used in these containers.

(2) Differential Thermal Analysis: For the portion of this work being carried out by D.T.A. the material is contained in a 3/8" nickel tube with a 3/16" thermowell welded into one end. The material is loaded through the opposite end and sealed under dry box conditions.  $Al_2O_3$  in an identical nickel container is used as the reference material. The containers are set in a nickel block in order to obtain more uniform heating and cooling rates. No agitation is used in this work, however, the sample sizes are kept small, approximately 5 grams. Heating and cooling rates are controlled with Brown program controllers to about 1 deg./minute. Conventional Brown x, y recorders are used to record the temperature differential vs. temperature, chromel-alumel and in some cases AuPd - PtPd thermocouples are used for this work.

(3) Quenching: Quenching techniques are used in areas of these phase systems where thermal or D.T.A. methods can not be used for location of the liquidus or solidus lines because of glass formation. This technique is also used as a method of identifying new solid phases. This second use for the quenching technique is important in some cases for ascertaining the presence of compound formation.

A very small sample of material, about 2 to 3 milligrams, is placed in a 3/32" nickel tube which is sealed off at both ends under dry box conditions. After sealing the container is flattened in a vise or press to ensure good heat transfer between the container and sample. About ten such samples are then placed on a wire holder in a nickel block which is in turn placed in a "pot" furnace. The samples are held at the desired temperature for a minimum of 1/2 hour before they are dropped from the heating zone (nickel block) into an oil bath (Hy-vac oil) at room temperature. This is accomplished by a tripping arrangement which releases the wire holder and samples and allows them to fall into the oil bath directly under the furnace. Furnace temperatures are controlled by a Brown Pyr-O-Vane controller. A thermocouple junction



in the nickel block next to the samples is connected to a potentiometer for measuring the temperature of the samples before quenching. A second furnace (L. H. Marshall, Columbus, Ohio) is also being used for this work. With this arrangement one is able to drop the samples individually rather than all at once as described above. The advantage is that a temperature range can be investigated more efficiently. This is accomplished by dropping one or two samples at a given temperature then changing the temperature a couple of degrees followed by dropping the next one or two samples, etc.

After quenching the containers are cut open and the samples are given to a petrographer for analysis. Special precautions are not taken to minimize the elapse time between opening the samples and analyzing them or to keep the samples from picking up moisture. Dr. Insely maintains that phase changes after quenching are characteristic and can be identified by an experienced petrographer.

(4) Hot Filtration: This method is used primarily to determine the position of the solidus line in areas where solid solutions are expected. It is also used to ascertain whether complete solubility of the various components is obtained in certain questionable regions of the system even at the maximum temperatures encountered. The hot filtration is effected by a sintered nickel filter dip stick placed near the bottom of a nickel container. After temperature equilibrium is reached in a "pot" furnace on a rocking machine, a vacuum is applied to the dip stick drawing the liquid phase through the sintered nickel filter into the dip stick. After cooling to room temperature the composition of the two phases are determined analytically. No attempt is made to reuse the nickel filter or container.

(5) X-Ray: At the present time X-ray techniques are being used at ORNL to determine areas of solid solutions and new solid phases. ORNL has no high temperature X-ray equipment but feels that this will be an important additional tool for Mound.

In order to expedite the phase work at Mound ORNL will supply 1 kilogram each of  $UF_4$  and the binary compounds  $NaUF_5$  and  $Na_2UF_6$ .  $NaF$ ,  $LiF$ , and  $BeF_2$  are available commercially. Dr. Barton feels it would be advisable to begin our work on binary systems. In the ternary system  $NaF-BeF_2-UF_4$  the  $NaF-UF_4$  and the  $NaF-BeF_2$  binaries have been pretty well established, however, the  $BeF_2-UF_4$  system needs additional work. In the  $LiF-BeF_2-UF_4$  system the  $LiF-BeF_2$  system must be investigated further and some attention should be given to the  $LiF-UF_4$  binary.

### Beryllium Handling

Extreme precautions for handling beryllium compounds are exercised at ORNL. Wipes and air samples are taken on a routine basis by health physics in areas where beryllium compounds are handled. Chest X-rays are required approximately every three months for personnel working in these areas. A change-room system with showers required on leaving was used in the analytical laboratory where beryllium analyses were carried out.



## Purification of Raw Materials

The commercially available quantities of NaF, LiF, BeF<sub>2</sub>, and UF<sub>4</sub> always contain a few per cent of water. If these salts are dried in an oven, not much water is lost, but instead HF is evolved with the corresponding formation of some metal oxide. Traces of oxide in these salts are very undesirable for phase studies. The water can be expelled from these salts without the formation of any oxide if the salts are heated under an atmosphere of HF. Instead of purifying each original component, it is more desirable to weigh and grind together different proportions of commercial grade materials and subject these mixtures to the purification treatment, and then very carefully protect these different mixtures from moisture. Also, since the mixtures have lower melting points than the pure components, the equipment can be operated at a lower temperature to get a liquid phase when mixtures are used in place of pure materials.

At Oak Ridge there are various sizes of equipment for processing mixtures of several grams up to 250 pounds. For our purposes, it seems desirable to have one rig to handle several samples of about 20 grams each, and another rig to handle up to 5 pounds. All the component parts of this equipment to be described should be made of pure nickel metal.

The outer shell of both of these rigs is the same. It consists of a 4" pipe about 18" long, depending on the length of the tube furnace in which it sets. One end of the pipe is sealed with a solid metal plate made secure with a Heliarc weld. The opposite end of the pipe is fitted with a collar 7" in diameter. On the face of this collar is a grooved recess to hold a soft copper ring which acts as a sealing gasket. A circular plate cut to the size of the collar serves as a cover for the pipe. The cover plate has a protruding groove machined in it which fits directly over the copper sealing ring in the collar. The cover plate and the collar have been drilled so that they can be tightly bolted together.

For the rig to handle small samples the cover plate has three holes drilled through it. Through one of these holes is passed a Ni tube which extends to the bottom of the unit. Various gases are passed through this tube into the system. Another hole through the cover is the valve to vent the exit gases, while the third hole is a thermocouple well. A rack which can hold about 12 platinum or nickel crucibles - 30 mm. diameter - is made for inside of this rig. The crucibles are filled with the salt mixtures, the crucibles loaded onto the rack, the rack set inside of the rig, and the cover bolted on to the equipment. The rig is heated to 800° and HF passed through the system for 2 hours. The system is flushed with hydrogen to remove the HF and reduce any NiF<sub>2</sub> that was formed in the previous step. The exit gases are bubbled through water, and the fluoride content of the water periodically checked to determine the amount of HF per liter of the exit gas. The hydrogen is passed through the system until the HF per liter of hydrogen reaches a predetermined low value. Then the system is cooled under helium and opened only in the dry box.

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For a 5 pound sample the salt is placed directly into the Ni rig without a holding rack present. The top cover has another Ni tube through it which extends to the bottom of the rig and has a Ni filter across the bottom of this tube. After the purification treatment on the molten salts a gas pressure is applied to the rig which forces the molten salt through the filter, out the tubing, and into a receiver. The receiver is a Ni cylinder with a graphite liner and can be partially evacuated to help move the molten salt from the purification rig. The receiver is cooled under helium and opened only in the dry box. The filter helps to remove Ni metal, and other metal impurities from the molten salt.

Since HF is being used, the equipment must either be made of Cu or Ni. Nickel has to be used at very high temperature. "Hoke bellow valves" are used in the lines, and "Swage" type metal fittings to join the metal tubing. "Duragauge" bronze and nylon gauges can be used to measure the pressure. The helium and hydrogen gases are dried by passing them through traps cooled in "dry-ice" or liquid nitrogen. One soda-lime tube is used to remove the HF from the exit gases, and another is placed in the line before the vacuum pump to protect it from hydrogen fluoride.

Chemical Analyses of the Mixtures [NaF - BeF<sub>2</sub> - UF<sub>4</sub>] and [LiF - BeF<sub>2</sub> - UF<sub>4</sub>]

Chemical analysis is used to determine the purity of the raw materials as well as to determine the exact composition of any new compounds which might be formed. The complete elemental analysis of one of these salt mixtures is conducted in two steps. A sample of the salt mixture is taken for the first step to be analyzed for the cations while a second sample is used for the fluoride analysis.

The first step in the cation analysis is to get the salts into solution. These fluoride salts are readily soluble in hot 70 per cent perchloric acid. The addition of small amounts of boric acid aids solution by forming the highly volatile boron trifluoride. An excess of the boric acid is not critical since it is readily volatile itself. The solution should not be taken to dryness. Within 15-20 minutes the salts should be dissolved to give the cations Na<sup>+</sup> [or Li<sup>+</sup>], Be<sup>++</sup>, and UVI plus any traces of impurities such as Mn, Fe, Cr, and Ni. An alternate dissolution procedure using a fusion with sodium carbonate is also available.

The alkali metal ions are separated from Be and U by adding NH<sub>4</sub>OH which precipitates Be and U hydroxides. The hydroxides are washed free of the alkali metal, and the filtrate is taken for the alkali metal analysis which is usually done by the triple acetate method without going to dryness. The hydroxides are redissolved in HCl or HNO<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> slowly added to precipitate Be(OH)<sub>2</sub> while UVI forms a soluble carbonate

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complex. The U can then be determined in either of two ways: (1) Reduce UVI to UIV by using  $\text{Cr}^{++}$ , then do a potentiometric titration on the uranium using standard ferric nitrate, (2) pass the UVI solution through a Jones reductor and titrate with  $\text{Ce}^{\text{IV}}$  or  $\text{KMnO}_4$ . The amount of iron impurity must be low for this method.

The beryllium hydroxide is not fired to the oxide because the oxide is a very fine powder which can be easily scattered around the laboratory.  $\text{BeO}$  dust in the air is a health hazard; therefore a wet method is used for the beryllium analysis. This wet method depends upon the fact that beryllium and fluoride ions form the very stable complex,  $\text{BeF}_4^-$ ; therefore, the  $\text{Be}(\text{OH})_2$  ion can be dissolved in an excess of  $\text{KF}$ , and the hydroxide ions which are released can be titrated with standard  $\text{HCl}$ . A reprint of this procedure was obtained.

To determine the quantity of fluoride in a sample, the salt mixture is heated to  $1000^\circ$  inside of a Ni tube and steam is passed through this tube. The steam and  $\text{HF}$  that is formed are collected in a cold water-trap. When all of the fluoride has been distilled from the sample, the total fluoride in the water-trap is determined gravimetrically as  $\text{PbClF}$ . It was indicated that this method of removal of the fluoride from the salt mixtures was not always quantitative especially in the beryllium samples.

For the trace metals Fe, Ni, Cr, and Mn colorimetric methods have been developed. If it should become necessary to check for these trace metals, the details of these procedures are on hand.

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