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THE PREPARATION AND PROPERTIES OF DISTILLED YTTRIUM*

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Abstract

Distillation procedures used for purifying yttrium metal, producing metal containing less than 150 ppm oxygen and lower concentrations of most of the other common impurities, are discussed. Some of the physical and mechanical properties of the distilled yttrium indicate: (1) a melting point of 1510°C, (2) a solid state transformation at 1459°C obtained from high temperature resistivity data, (3) a Rockwell H hardness of 60 and (4) improved rolling and swagging characteristics.

INTRODUCTION

In recent years, as yttrium compounds have become increasingly available in high purity, a great deal of attention has been directed toward the study of the physical and chemical properties of this element and the evaluation of its commercial utility. The properties of the metal have made it of interest in several nuclear applications, and in addition, yttrium metal forms alloys that have interesting high temperature applications. One major objective in the preparation of the metal has been to obtain high quality metal which could be easily fabricated. Since oxygen, one of the primary interstitial impurities, was known to have harmful effects on the mechanical properties of other hexagonal metals, major emphasis has

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been placed on decreasing its concentration in yttrium metal. Many methods of producing pure yttrium metal have been used in the past with varying degrees of success. The preparation of pure yttrium metal by distillation was studied in this investigation, because this method had been found to be suitable for purifying some of the more volatile rare-earth metals.

KROLL¹ has found that a vapor pressure of 1.8 mm of Hg is sufficient to enable a metal to be distilled on a commercial basis. At a temperature of 2000°C, the vapor pressure of yttrium² is 0.50 mm of Hg. The vapor pressures of several impurities commonly found in yttrium metal indicate their concentrations in yttrium can be lowered quite easily by this method. However, titanium, iron and nickel have vapor pressures near that of yttrium and probably would not be removed. Since the oxygen impurity present at this temperature is the non-volatile Y_2O_3 , it would not be appreciably vaporized, except possibly as a sub-oxide. This will be discussed in more detail later in the paper.

EXPERIMENTAL

The vacuum furnace used in the distillation process is shown in Fig. 1. It contains a simple tantalum cylinder as the heater, surrounded by granular graphite insulation 420 microns in size, all enclosed in a fused silica tube, and heated by induction. The distillation column, which is 1 1/2 - 2 inches in diameter x 7 inches high, was fabricated from tantalum or tungsten sheet inside an inert gas arc welder from a procedure described by DAANE³. Tantalum crucibles were preferred from the standpoint of fabrication, but have a lifetime of only one-fourth that of a tungsten

1. QUARTZ SIGHT GLASS
2. "O" RING
3. WATER COOLING COILS
4. BRASS LID
5. DISTILLATE

6. BAFFLES
7. DISTILLATION COLUMN
8. YTTRIUM
9. INDUCTION COIL
10. GRAPHITE INSULATION

11. BRASS VAC HEAD
12. RUBBER GASKET INSIDE BRASS COUPLING
13. TANTALUM SHIELD
14. TANTALUM HEATER
15. SILICA TUBE

Figure 1

crucible.

The yttrium metal used in the distillations was prepared either by the direct reduction of yttrium fluoride with calcium, or by the intermediate alloy process⁴. The yttrium metal and the vacuum furnace were vacuum outgassed to a high temperature, 1700 and 2400°C respectively, previous to each run. Distillation was then accomplished by heating the column to 2000-2200°C at a pressure of not more than 5×10^{-4} mm of Hg. Temperature measurements were made with a Leeds & Northrup disappearing type optical pyrometer sighting through a small hole in the condenser. By using a 1 1/2-inch diameter distillation column with a 5/8-inch hole in the baffle, 50-100 g of metal could be condensed per hour, and using a 2-inch column with a 3/4-inch hole in the baffle, approximately 100-200 g could be condensed in one hour. The purpose of the baffle was two-fold. (1) It served to collimate the vapor and (2) it acted as a radiation shield for the condenser.

The temperature of the condenser was controlled by the position of the outside shields and the baffles inside the column. This temperature was usually maintained at 1200-1400°C. The yttrium distillate was normally removed from the condenser by means of a lathe. However, another suitable method utilizes a 50-50 volume per cent mixture of nitric acid and hydrofluoric acid, which dissolves tantalum quite readily. This rather potent mixture has practically no effect on the yttrium metal, because a thin coating of fluoride formed on the yttrium metal acts as a protective film to further attack.

Analysis

A typical analysis of the distilled yttrium is given in Table I.

TABLE I

Analysis of distilled yttrium metal (ppm)			
Carbon	40	Nickel	9 b
Nitrogen	25	Copper	50 b
Oxygen	120 b	Hydrogen	4
Silicon	10 b	Titanium	150
Aluminum	60 b	Zirconium	60
Iron	100	Magnesium	5 b
Tantalum	60 b	Fluorine	50
Calcium	10 b	Chromium	50 b

b - Indicates spectroscopic determination.

Strangely enough, the oxygen content of the distillate decreased as the carbon or oxygen content of the starting material increased. The condenser temperature also appears to have a slight effect on the purity of the condensate since the oxygen content increased slightly with an increase in temperature over the temperature range of 1000-1400°C.

Physical Properties

Literature values for the melting point of yttrium metal have ranged from 1475 to 1550°C, indicating that the melting point is greatly affected by the presence of relatively small amounts of impurities. The melting point of distilled yttrium was determined using the method of PIRANI AND ALTHERTHUM⁵ by observing, with an optical pyrometer, the temperature at which a small hole in the sample filled with molten metal. The optical pyrometer used in the determinations was standardized "in situ" against pure nickel and platinum metals. From an average of more than 10 measurements on yttrium, a value of 1510°C was determined for the melting point of this metal.

HANAK⁶ measured the lattice constants of distilled yttrium obtained from this investigation and reported $a=3.648 \text{ \AA}$ and $c=5.735 \text{ \AA}$.

The electrical resistivity of distilled yttrium was investigated as a function of temperature from 20°C to the melting point. The direct current potentiometric method described by HERMANN⁷ was employed for determining the electrical resistance values at various temperatures. The samples were heated in an atmosphere of argon to prevent evaporation at higher temperatures, and the temperature of the sample was measured by a Pt-Pt/13% Rh thermocouple placed at the center of the sample. All connections to the yttrium metal were made with tantalum to minimize contamination of the sample. The resistivity (ρ) was calculated from the relation $\rho = \frac{\pi r^2 R}{L}$ using the dimensions of the sample and values of the resistance calculated from emf measurements and Ohm's law. The data obtained can be represented by a smooth curve from room temperature to approximately 1450°C; at this point the metal exhibits an abrupt increase in resistivity over a temperature range from 1450-1470°C due to the hexagonal close packed-body centered cubic transformation of the metal. Above this temperature, the curve was again smooth. The midpoint of the transformation was found at 1459°C. The room temperature value for the resistivity of 61 micro ohm centimeters compares favorably with that determined by COLVIN⁸ of this laboratory, who measured the resistivity of yttrium from near 0°K to room temperature. The resistivity of yttrium at 1500°C was 230 micro ohm centimeters. These results are shown in Fig. 2.

Mechanical Properties

The average hardness of arc melted buttons of distilled yttrium was found to be 45 on the diamond pyramid hardness scale and 60 on the Rockwell

Resistivity of Distilled Yttrium

Figure 2

H scale. Microhardness measurements on some of the first metal distilled have shown a wide variation in the hardness of individual grains; the variation ranging from 45 to 110 on the diamond pyramid hardness scale in some cases. It was found that distilled yttrium could be cold rolled easily into thin sheets, as shown by reducing a sample from 0.275 inch to 0.018 inch without intermediate annealing. This represents a total reduction of more than 90%.

DISCUSSION

It has been shown that yttrium metal can be significantly separated from its impurities by distillation at high temperatures, especially with respect to oxygen. Iron, titanium and nickel are exceptions, since their vapor pressures are quite close to that of yttrium. However, recent experiments have shown that iron and titanium can be removed from yttrium by filtration through a porous tungsten filter or by the addition of tungsten powder to the distillation column. Since this work will be the substance of another report, it will not be discussed in detail here.

The mechanism for transferring oxygen from the boiler section to the distillate is not exactly known. Assuming the oxygen is completely present as Y_2O_3 , several paths are possible; (1) dissociation of Y_2O_3 to the gaseous elements, (2) dissociation of Y_2O_3 into a gaseous lower oxide and oxygen, (3) vaporization as Y_2O_3 , (4) reaction with the container to form a gaseous lower oxide of the container material, (5) reaction with the container to form gaseous oxides with both the sample and crucible material, (6) or by reaction with the yttrium metal to form a gaseous lower oxide. Thermodynamically, it can be shown that dissociation

to the gaseous elements yields a very low partial pressure of oxygen for this system. Mechanism (3) can be eliminated since mass spectrometric studies by WALSH AND WHITE⁹ on Y_2O_3 show none of this species present in the vapor phase. They have determined the partial pressures of YO and O over Y_2O_3 from vaporization studies in tungsten effusion cells. Calculations based on this information show that about 50 ppm of oxygen could be transferred by process (2). When the same investigators used tantalum effusion cells in place of the tungsten, they observed a higher rate of vaporization of oxygen containing species, which they attributed to a reaction with the tantalum forming TaO and YO. It is also quite possible that appreciable amounts of oxygen can be obtained from path (6), since yttrium itself is a reducing agent.

From these considerations, it is apparent that the means by which oxygen is transported to the distillate may be quite complex; small amounts being added from path (2) and somewhat larger amounts from the last three mechanisms. However, it is interesting to note that the oxygen content of the distilled metal was essentially the same in this investigation regardless of whether tantalum or tungsten crucibles were used. A more detailed examination of the volatile products coming from the distillation column by means of a mass spectrometer would be quite interesting in this respect.

Evidence of a high temperature crystal modification in yttrium has been found by several investigators. The value of 1459°C found in this investigation is believed to be more reliable than previous data due to the purity of the metal used. It is interesting to note that EASH¹⁰ found a decrease in the resistivity with an increase in temperature at the

transformation point. The variance may be due to the different technique used for measuring resistivities in the two investigations.

As a result of the high temperatures used in these distillations, a large amount of tantalum was dissolved by the yttrium refluxing down the sides of the column. This resulted in a saturated solution of tantalum in yttrium, from which tantalum dendrites precipitated. Since the rare-earth metals are known to be very good scavengers, the tantalum precipitated out in pure form as shown by analysis. The superconducting transition temperature for tantalum¹¹ which is extremely sensitive to impurities, was found to be very nearly the same for these dendrites as for the purest tantalum available from other sources.

REFERENCES

- ¹ W. J. KROLL, Trans. Am. Electrochem. Soc., 87 (1945) 571.
- ² R. J. ACKERMAN AND E. G. RAUH, J. Chem. Phys., 36 (No. 2) (1962) 448.
- ³ A. H. DAANE, Rev. Sci. Instr., 23 (No. 5) (May 1952) 245.
- ⁴ O. N. CARLSON, J. A. HAEFLING, F. A. SCHMIDT AND F. H. SPEDDING, Preparation and Refining of Yttrium Metal by Y-Mg Intermediate Alloy Process, U. S. Atomic Energy Commission Report IS-49, Iowa State University of Science and Technology, September 1959.
- ⁵ M. PIRANI AND H. ALTERTHUM, Z. Elektrochem., 29 (1923) 5.
- ⁶ J. J. HANAK, High Temperature Allotropy of the Rare-Earth Elements, unpublished Ph. D. thesis, Iowa State University of Science and Technology Library, Ames, Iowa, 1959.
- ⁷ K. W. HERRMANN, F. H. SPEDDING AND A. H. DAANE, J. Metals (July 1957).
- ⁸ R. COLVIN, Iowa State University, private communication (1959).
- ⁹ P. N. WALSH AND D. WHITE, J. Am. Cer. Soc., 43 (5) 1960) 229-233.
- ¹⁰ D. T. EASH AND O. N. CARLSON, Trans. Am. Soc. Metals, 52 (1960).
- ¹¹ C. A. SWENSON, Iowa State University, private communication (1959).

FIGURE CAPTIONS

- Fig. 1.**
(1) Quartz sight glass;	(9) Induction coil;
(2) "O" ring;	(10) Graphite insulation;
(3) Water cooling coils;	(11) Brass vac head;
(4) Brass lid;	(12) Rubber gasket inside
brass coupling;
(5) Distillate;	(13) Tantalum shield;
(6) Baffles;	(14) Tantalum heater;
(7) Distillation Column;	(15) Silica tube.
(8) Yttrium;	

Fig. 2. Resistivity of distilled yttrium.

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