

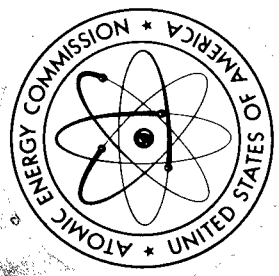
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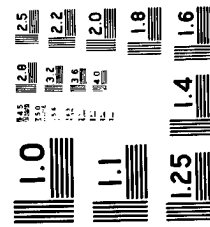
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Report No.  
ORO-2570-12

Report

on

( A METHOD FOR THE CONTROLLED ADDITION

OF OXYGEN TO COLUMBIUM )

APR 1968  
1968

FOREWORD

This report is based upon a thesis submitted by James Douglas Gerber to the Graduate Faculty of the University of Oklahoma in partial fulfillment of the requirements for the degree of Master of Engineering (Metallurgical Engineering). This investigation was part of the research program, "The Influence of Imperfections and Interstitial Contaminants on the Superconducting Behavior of Metals", supported by the United States Atomic Energy Commission under Contract AT-(40-1)2570.

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UNIVERSITY OF OKLAHOMA

Norman, Oklahoma

May, 1968

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ABSTRACT

A technique for making additions of small amounts of oxygen to columbium (niobium) is presented. The technique involves complete reduction of a carefully weighed metal-metal oxide mixture by the columbium in a sealed evacuated chamber at 900°C.

The oxygen pressure in equilibrium with the metal-metal oxide mixture was found to be quite critical. Large oxygen pressures resulted in severe surface oxidation while low oxygen pressures did not permit reduction in a reasonable amount of time. Using iron-wustite ( $Fe_xO$ ) mixtures, controlled additions of 15 to 300 ppm oxygen were made to columbium. The technique makes possible oxygen additions within 4 ppm of the desired composition.

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Superconducting behavior of columbium is also affected by the presence of interstitial impurities. Tedman et al. (4) showed that interstitial oxygen had a marked effect on critical current and field. Smith et al. (5) reported that interstitial hydrogen or the defects generated by its absorption affected superconducting behavior.

*Beck*  
*Smith* Experimental studies into the effects of interstitials on

mechanical properties and superconducting behavior of columbium have been hindered by the difficulties involved in controlling additions of these interstitials. A simple, reproducible technique for the addition of interstitial oxygen is especially needed. Methods previously used for oxygen additions include thermogravimetric methods, Sievert's method, low temperature oxidation in air, and the dissolution of an anodized layer. All of these methods cause the introduction of additional

impurities, involve complex apparatus, or are error prone. The work reported herein describes an improved method for accurate and reproducible additions of small amounts of oxygen to columbium.

## A METHOD FOR THE CONTROLLED ADDITION OF OXYGEN TO COLUMBIUM

### CHAPTER I

#### INTRODUCTION

The development of columbium alloys has received great attention in recent years because of their potential use in high temperature applications. They have also received considerable attention because of the superconducting properties of several columbium alloys.

Columbium has the desirable characteristic of retaining adequate strength and ductility at extremely high temperatures while possessing the ability to be worked and formed into useful shapes. Its disadvantages, common to all refractory metals, are extremely poor oxidation resistance at elevated temperatures and sensitivity of mechanical properties to interstitial impurities at lower temperatures.

Several investigators have studied the effects of interstitial impurities on mechanical properties of columbium. Ingram et al. (1) found a definite correlation between interstitial oxygen content and impact transition properties of columbium. Mincher and Sheely (2) correlated oxygen and strain aging response of columbium at 300°C. Wood and Daniels (3) reported hydrogen concentrations as low as 20 ppm to greatly influence the low temperature ductility of columbium.

## CHAPTER II

## THEORY

The method used to add controlled amounts of oxygen to columbium is based on the complete reduction by columbium of a carefully weighed amount of another metal oxide.

Because the equilibrium  $P_{O_2}$  associated with Cb-CbO mixtures is extremely low,  $10^{-25}$  atmospheres at  $1000^\circ\text{C}^*$ , and those over columbium-oxygen solutions lower, it might be concluded that columbium could effectively reduce almost any metal-metal oxide combination. However, this is an oversimplification. The proper choice of a metal-oxide system is complicated by the low rate of oxygen transport at these low pressures, and the difficulty in reducing any columbium suboxide formed during the reduction of the oxygen source material. Thermodynamically, oxide formation on columbium will be avoided as long as the oxygen partial pressure over the columbium is below the equilibrium pressure associated with the mixture Cb-CbO. The logical choice of a source for oxygen would be a mixture of Cb-CbO since oxide formation would be

precluded by nucleation difficulty. Calculations (shown in Appendix A),

\*Through the aid of a Richardson-Jeffes Chart, a portion of which is shown in Figure 1, the equilibrium  $P_{O_2}$ , associated with a given metal-metal oxide mixture, can be easily obtained.

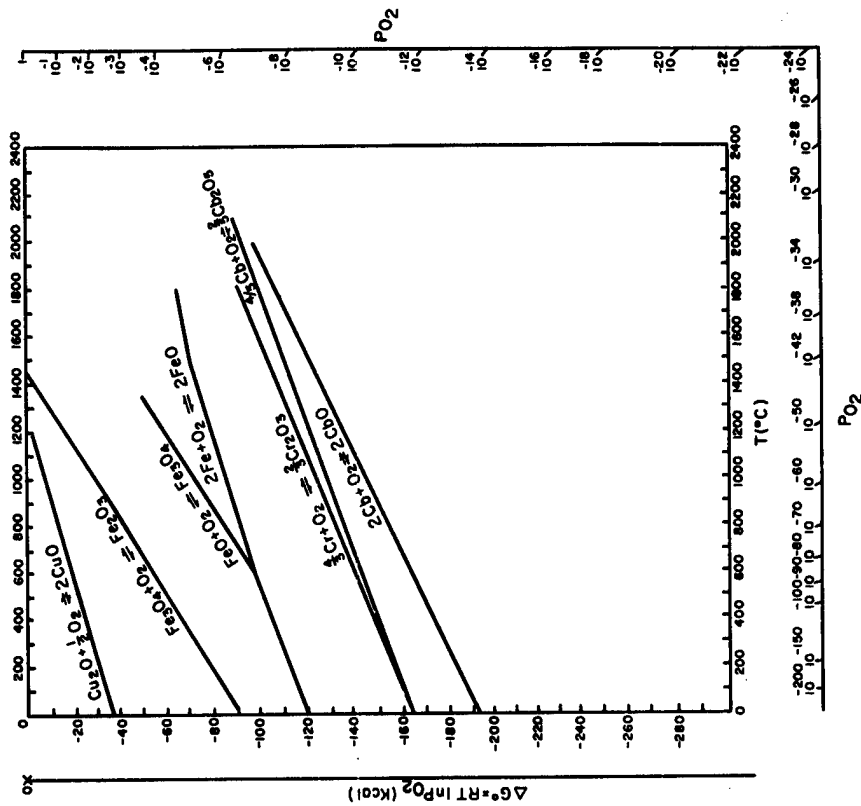


Figure 1. Standard Free Energy of Formation vs. Temperature.

using the kinetic theory of gases, indicate that the reaction at such extremely low oxygen pressures would proceed too slowly to be practical at 900°C. The rate of reaction can be increased by raising the temperature of reaction since, as can be seen in Figure 1, the oxygen partial pressures increase with temperature. Unfortunately, objectionable grain growth occurs in columbium at higher temperatures. However, the problem is not insoluble. Even if the dissociation pressure of  $\text{CbO}$  is exceeded, an oxide need not be formed (6). As long as the nucleation over-pressure on the surface of columbium is not exceeded, an oxide will not form. The surface oxygen pressure, in turn, is a function of the diffusion rate of oxygen into the bulk as it arrives at the surface.

Thus, the equilibrium partial pressure over a reducible oxide must be high enough to permit the reaction to occur in a reasonable time, but not high enough to nucleate an oxide on the columbium.

### CHAPTER III

#### EXPERIMENTAL PROCEDURE

The following procedure was established for making reproducible additions of oxygen to columbium using the reaction chamber shown schematically in Figure 2.

1. A weighed amount of oxide ( $\text{Fe}_3\text{O}_4$ ) was placed in a quartz boat with an excess of iron powder.
2. The boat and a weighed columbium sample in the form of a cylinder 8 mm diameter by 10 mm long were then placed in the combustion tube under a static vacuum of 5 microns or less.
3. After the iron-magnetite mixture was heated for one hour to form  $\text{Fe} + \text{Fe}_x\text{O}$ , the sample was transferred magnetically into the hot zone.
4. The columbium was then equilibrated with the  $\text{Fe-Fe}_x\text{O}$  mixture for the time required for complete reduction of the oxide.

Prereacting magnetite with iron powder was a precautionary measure to lower the oxygen pressure over the  $\text{Fe}_3\text{O}_4$  without changing the total oxygen content, thereby precluding surface oxide formation. Several experiments using  $\text{Fe}_3\text{O}_4$  rich in oxygen, resulted in the formation of

a small amount of a difficult-to-reduce oxide. The time selected for pre-reaction to produce a two phase Fe-Fe<sub>x</sub>O mixture was approximately one hour at 900°C.

A temperature of 900°C was found to be optimum for the reaction because of objectionable recrystallization and grain growth in the columbium at higher temperatures, and formation of columbium oxides at lower temperatures. The latter is determined by the variation of CbO dissociation pressure and oxygen diffusivity with temperature.

Table 1, shown below, gives the analysis of impurities in ppm by weight in the columbium used.

TABLE 1.  
CHEMICAL ANALYSIS OF COLUMBIUM  
Residual Elements in ppm by Weight Measured  
at Top and Bottom of Sample Rod

Element	Top	Bottom	Element	Top	Bottom
Al	<20	<20	Mo	< 20	< 20
B	< 1	< 1	N	50	40
C	<40	50	Ni	< 20	< 20
Cd	< 5	< 5	O	80	90
Co	<10	<10	Pb	< 20	< 20
Cr	<20	<20	Si	< 50	< 50
Cu	<40	<40	Sn	< 10	< 10
Fe	<50	<50	Ta	740	<500
H	3.1	3.3	Ti	< 40	< 40
Hf	<80	<80	V	< 20	< 20
Mg	<20	<20	W	195	85
Mn	<20	<20	Zr	400	<100

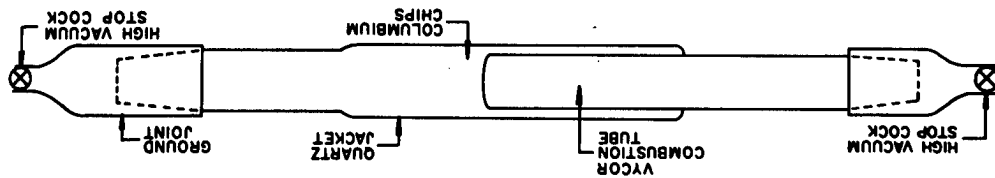


Figure 2. Schematic Illustration of Combustion Tube.

CHAPTER IV

DISCUSSION OF RESULTS

Table 2 shows the results of oxygen additions using nearly stoichiometric magnetite prereacted with high purity iron powder. When the oxide was given sufficient time to reduce, the amount of weight loss experienced by the oxide was equal, within experimental error, to that calculated. (Appendix C).

Table 3 shows the undesirable weight gain, as a function of volume or surface area, experienced by the sample when heated alone at 900°C using various combustion tube designs.

Calculations (Appendix B) indicate that the oxygen in the residual gas was negligible. Furthermore, diffusion of oxygen through quartz was certainly prevented by the evacuated outer jacket containing columbium chips. It is therefore presumed that the excess weight gain was due to gases adsorbed on the inside walls of the tube. Gas analysis indicates that there was no significant weight gain of gases other than oxygen. The presumption that undesirable weight gain was due to adsorbed gases was substantiated, by reduction in undesirable weight gain, after getting the reaction tube with .5 grams of columbium shavings. Unwanted weight gain increased again as the boat containing the Fe-Fe<sub>x</sub>O mixture was equilibrated with the sample, presumably due

OXYGEN ADDITIONS TO COLUMBIUM USING WUSTITE AS A SOURCE

TABLE 2

Sample	Weight Loss In Oxide (gms)	Weight Gain In Sample (gms)	Weight Gain In Sample (ppm)	Weight Gain In Sample Other Than From Oxide (ppm)
R12C	.001160	.001250	200	14
R13B	.000845	.000905	141	6
1A	.000370	.000407	50	5
2B	.001060	.001150	176	16
8R 2C	.000083	.000089	15	1
9R 2C	.000336	.000356	59	3
10R 2C	.000950	.000962	160	2
R 4A	.000185	.000253	40	10
1B	.001590	.001640	293	8

TABLE 3  
WEIGHT GAIN IN SAMPLE (COLUMBIUM ALONE AT 900°C)

Tube	No. of Samples	Average Pickup (gm)	Volume of Tube (mm <sup>3</sup> )	Area of Tube (mm <sup>2</sup> )	Approx. ppm
Epoxyed Quartz	5	.000235	9180	706.0	50
Graded Seal Rad = 15mm	3	.000166	5880	452.5	41
Apiezon Rad = 4mm	3	.000035	825	63.5	6
Graded Seal Rad = 9mm	8	.000050	1650	254.0	8
Graded Seal *	4	.000018	1650	254.0	3

\* Chamber gettered with columbium shavings prior to insertion of sample.

to adsorbed gas on the combustion boat. Finally, in all cases, the unwanted weight gain was not increased by increased reaction time. These factors clearly indicate the important role of adsorbed oxygen in explaining undesirable weight gain.

Table 4 shows the various metal-metal oxide mixtures used for oxygen additions.

TABLE 4  
OXIDES USED AS SOURCE FOR OXYGEN ADDITIONS

Oxide	Results	Equilibrium P <sub>O2</sub> at 900°C (Atms.)
Cb - CbO	No reduction in 48 hours	10 <sup>-28</sup>
Cb <sub>2</sub> O <sub>5</sub>	Thick black oxide after several hours	10 <sup>-24</sup> *
Fe <sub>2</sub> O <sub>3</sub>	Same as Cb <sub>2</sub> O <sub>5</sub>	10 <sup>-7</sup> *
Cu - CuO	Same as Cb <sub>2</sub> O <sub>5</sub> plus deposition of metallic Cu	10 <sup>-2</sup>
Fe <sub>x</sub> O-Fe <sub>3</sub> O <sub>4</sub>	a. Surface oxide, incomplete reduction b. Complete reduction, slight oxide	10 <sup>-15</sup> ..
Fe - FeO	Complete reduction	10 <sup>-17</sup>
Cr - Cr <sub>2</sub> O <sub>3</sub>	Same as CbO	10 <sup>-25</sup>

\* Listed is pressure in equilibrium with the oxide and next lower oxide. The oxygen pressure must have been higher than this in the single phase.

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columbium, encapsulated with relatively large amounts of magnetite in a quartz combustion tube, was heated to 1000°C for approximately 24 hours. The volatile oxide was observed as a very thin black deposit on the walls of the combustion tube\*. Volatile columbium oxides have not been reported below 1200°C. It should be pointed out that the surface temperature of the sample may have been much higher than the observed furnace temperature of 1000°C due to the very large free energy of formation of Nb<sub>2</sub>O<sub>5</sub>.

The second observation of interest was the indication of a protective oxide at temperatures between 900-1000°C. The protective oxide was noted after heating columbium in the presence of magnetite for several hours at 900°C. Once the sample became oxidized it appeared that little further reduction of magnetite took place, even after exposure times of five days at temperature. Roberson and Rapp (8) reported the formation of a compact, protective Nb<sub>2</sub>O<sub>5</sub> layer when columbium was oxidized at 1000°C and low P<sub>O<sub>2</sub></sub>. The protection afforded here could be due to a compact diffusion barrier or to voids formed by cationic diffusion. A dissociative mechanism, such as postulated for iron oxidation by Meussner and Fugii (9), could not be operative at these very low oxygen pressures. No attempt was made to identify the structure of the oxide formed during the present investigation.

An interesting observation was made when an oxygen addition was attempted in a cylindrical columbium sample in the cold worked condition rather than the annealed condition. The interior of the

---

\* This layer turned a pale yellow when heated in air indicating Nb<sub>2</sub>O<sub>5</sub>. The black deposit was undoubtedly oxygen deficient Nb<sub>2</sub>O<sub>5</sub> or NbO<sub>2</sub>, since columbium metal is less volatile at these temperatures.

## CHAPTER V

### GENERAL DISCUSSION

The Fe-Fe<sub>x</sub>O mixture having a P<sub>O<sub>2</sub></sub> of 10<sup>-17</sup> atmospheres at 900°C was found to be satisfactory for making oxygen additions. As discussed earlier, the P<sub>O<sub>2</sub></sub> is high enough to permit the reaction to proceed at a reasonable rate but not high enough to cause nucleation of an oxide on the columbium.

Similarly, the P<sub>O<sub>2</sub></sub> associated with an Fe<sub>x</sub>O-Fe<sub>3</sub>O<sub>4</sub> mixture (10<sup>-15</sup> atmospheres at 900°C) provided the desired results.

Cb-CbO and Cr-Cr<sub>2</sub>O<sub>3</sub> were unsuitable, apparently because reduction was hindered by the very low pressures involved. Using Fe<sub>2</sub>O<sub>3</sub> (P<sub>O<sub>2</sub></sub> > 10<sup>-7</sup> atmospheres at 900°C), or CuO (P<sub>O<sub>2</sub></sub> > 10<sup>-2</sup> atmospheres at 900°C), resulted in massive oxide formation on the columbium.

It is interesting to note that this is contrary to the results presented by Inouye (7) who successfully added oxygen to columbium at 1200°C with a Cu-CuO mixture at a lower temperature (P<sub>O<sub>2</sub></sub> of 3 x 10<sup>-8</sup> atmospheres). This may be due to the higher solution temperature used (1200°C) or to a much lower oxygen pressure than he reported, due to transfer through many bends and tubes in his complicated system.

Several additional observations were made during the course of experimental work. A volatile columbium oxide was observed when

sample recrystallized during the oxygen addition at 900°C as expected. The periphery however, (1mm) did not recrystallize. A similar sample without oxygen recrystallized throughout the entire cross-section. It appears that the recrystallization is hindered by interstitial oxygen. Presumably, the interior recrystallized before appreciable oxygen could diffuse into the core.

Finally it was observed that during the reduction of wustite to iron the oxide would reduce approximately 50 percent in the first eight to ten hours but very slowly thereafter. However, if the combustion tube was removed from the furnace several times during the reduction period and allowed to cool to room temperature, reduction would be completed in eight to ten hours. It is believed that early in the reduction a shell of iron is produced around each wustite particle through which oxygen must diffuse to continue the reaction. When the sample is cooled however, because of the difference in thermal expansion, the iron shell is broken, allowing further reduction of wustite to proceed to completion.

## CHAPTER VI

### CONCLUSIONS

Using iron-wustite mixtures as a source of oxygen, controlled additions of oxygen to columbium can be made at 900°C. For a 5 gram columbium sample, the additional weight gain from sources other than the oxide can be held to 2 ppm by using a small volume reaction tube and gettering adsorbed oxygen before the reaction.

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APPENDIX A

TIME TO TRANSFER ONE MILLIGRAM OF OXYGEN

TO COLUMBIUM AT 900°C

The number of molecules striking the surface of the columbium can be calculated by the kinetic theory of gases from the following equation (10):

$$N = \frac{\text{molecules}}{\text{cm}^2 \text{ sec}} = 0.230 n u$$

where n is the number of molecules per cubic centimeter which can be calculated as follows from the ideal gas law (assumed to be valid because of the very low pressures here):

$$n = \frac{n_o P V}{R T}$$

For an assumed oxygen pressure of  $10^{-23}$  atmospheres and a temperature of 900°C:

$$n = \frac{(6.023 \times 10^{23} \text{ molecules}) (10^{-23} \text{ atm}) (1 \text{ cm}^3)}{(82.06 \frac{\text{cm}^3 \text{ atm}}{\text{g mole OK}}) (1173^\circ\text{K})}$$

$$n = 6.2 \times 10^{-5} \frac{\text{molecules of oxygen}}{\text{cm}^3}$$

u is the root mean square velocity defined as follows:

$$u = \sqrt{3 RT/M}$$

$$u = \sqrt{\frac{3 (8.312 \times 10^7 \frac{\text{ergs}}{\text{deg mole}}) (1173 \text{ deg K})}{32 \frac{\text{g}}{\text{mole}}}}$$

$$u = 9.56 \times 10^5 \frac{\text{cm}}{\text{sec}}$$

The number of molecules/cm<sup>2</sup>sec is, therefore:

$$N = (0.230) (6.2 \times 10^{-5}) (9.56 \times 10^5) \\ = 13.62 \frac{\text{molecules}}{\text{cm}^2 \text{sec}}$$

The time required to transfer 1 milligram of oxygen to a sample having a surface area of 3 cm<sup>2</sup> (assuming a sticking probability of unity) is:

$$t = \frac{m_0 (\text{mg})}{M N A} \\ = \frac{(6.023 \times 10^{23}) (1 \times 10^{-3})}{(32) (13.62) (3)} \\ = 4.76 \times 10^{17} \text{ secs} \\ = 5.51 \times 10^{12} \text{ days}$$

## APPENDIX B

## AMOUNT OF RESIDUAL OXYGEN IN THE COMBUSTION TUBE

## AFTER PUMP DOWN

Using the ideal gas relationship and assuming the residual air to be 20% by weight oxygen, the residual oxygen in the air may be calculated.

$$PV = nRT$$

$$P = 5 \text{ microns}$$

$$V = .5 \text{ liters}$$

$$R = .08205 \text{ liter atmos/g mole}$$

$$T = 2980\text{K}$$

$$\frac{P}{5n} = \text{no. of moles } O_2$$

$$n = \frac{1}{5} \times \frac{10^{-3} \text{ mm Hg} \times \text{atmos} \times .5 \text{ liters}}{760 \text{ mm Hg} \times .08205 \text{ liter atmos} \times 2980\text{K}} \frac{\text{gm mole } O_2}{\text{gm mole}}$$

$$n = 2.682 \times 10^{-8} \frac{\text{gm moles} \times .32 \text{ gm}}{\text{gm mole}}$$

$$\text{wt of } O_2 = 8.6 \times 10^{-7} \text{ gms}$$

APPENDIX C

ANALYSIS OF ERRORS

Typical error (in ppm) due to sources other than the oxide:

$$\text{ppm} = \frac{1 \times 10^{-5} \text{ gm of excess oxygen}}{5 \text{ gm sample}}$$

= 2

Typical weighing error (in ppm, magnetite):

(Assume  $\pm 2 \times 10^{-6}$  gm of  $\text{Fe}_3\text{O}_4$ )

$$\text{ppm} = \frac{\frac{64 \text{ gm O}_2}{231.55 \text{ gm Fe}_3\text{O}_4} (2 \times 10^{-6} \text{ gm Fe}_3\text{O}_4)}{5 \text{ gm sample}}$$

= 0.1

Typical weighing error (in ppm, oxygen addition):

$$\text{ppm} = \frac{2 \times 10^{-6} \text{ gm O}_2}{5 \text{ gm sample}}$$

= 0.4



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