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THE DETERMINATION OF HYDROGEN AND OXYGEN IN NIOBIUM BY THE VACUUM FUSION AND SUB-FUSION METHODS

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PHYSICAL METALLURGY DIVISION

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SUMMARY OF RESULTS

The results of an investigation carried out to ascertain the most satisfactory vacuum analytical technique for the determination of hydrogen and oxygen in niobium are reported.

It is shown that sub-fusion analytical procedures for hydrogen tend to yield low results if temperatures higher than 1600°C are used, and sub-fusion extraction in the temperature range 1200° to 1400°C is recommended.

The preferred method for oxygen determination is vacuum fusion in a platinum bath at a temperature of 1900° - 1950°C, with the addition of fresh platinum between analyses.

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INTRODUCTION

The extensive use of the refractory metals in newer applications has necessitated continued development and improvement of analytical technique to obtain more accurate gas analysis.

To this end, the Gas Analysis Laboratory of the Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys has, since 1960, participated in round-robin analytical exercises sponsored by the Advisory Group for Aeronautical Research and Development in which a number of NATO countries are represented.

In the period 1960 and 1962, analyses were carried out on niobium, molybdenum, tantalum and tungsten, and the hydrogen, oxygen and nitrogen values as determined by different techniques using two vacuum fusion units were reported in Mines Branch Investigation Report IR-62-23.

Since then, the Gas Analysis Laboratory has participated in three further series of round-robin AGARD exercises, as well as carrying out analyses on niobium received from other sources.

The first series of AGARD samples (No. 28, No. 29 and No. 30) for which oxygen as well as hydrogen determination was required, was analysed by a platinum bath method (Internal Report PM-T-63-5).

The second series of samples (No. 56, No. 86, No. 106, No. 156 and No. 206) was also analysed for hydrogen and oxygen by platinum bath (Internal Report PM-T-64-2).

The last series of samples (D13, D31, D49, E23, and E41) for which analyses was reported (Internal Report PM-T-64-6) was for hydrogen determination only, and for this reason a sub-fusion extraction method was employed.

During the course of this work, additional niobium especially selected as laboratory reference standards was also analysed to provide a means of cross-checking and correlating the values obtained with technique details. In this way, results were compared and evaluated and it was found that hydrogen analyses lacked agreement.

The information initiated an additional series of tests, the results of which indicate that the hydrogen analyses previously reported were low due to the use of too high a crucible temperature during analysis.

For the sake of brevity, details concerning operation of equipment and basic analytical procedure are omitted from this report.

APPARATUS

Two vacuum fusion units were employed in the analysis of niobium. The units are described in Mines Branch Investigation Report IR 62-23 and are of different design throughout. For identification the units are designated the A and the C unit.

The vacuum fusion A unit employs the usual copper oxide oxidant and differential freeze-out method for gas analysis, whereas the C unit uses a palladium diffusion tube and a manganese dioxide (Hopcalite) oxidant, and freeze-out. In both units, gas determination is by measurement of internal pressure in a calibrated volume, by means of McLeod gauges.

To ensure that results were not affected by analytical equipment rather than technique, the A unit was partially dismantled and cleaned twice during the tests. During the first take down, fresh copper oxide was introduced and during the second, the original furnace evacuation pump was replaced with another having a much higher pumping speed.

SAMPLING AND SAMPLE PREPARATION

The importance of sampling and sample preparation are well realized and although most samples and sample material used in this work was pre-selected, it is desirable that the sample preparation technique used should be described.

With exception of samples for which specific instructions were received, all other niobium was prepared for analysis in the simple, yet highly effective manner described below.

Niobium, while held in a vise was cut to rough sample size (0.7 to 1.2g) by hacksaw, slowly and carefully so that it did not become more than slightly warm. The samples were then filed on all surfaces, first with a coarse file, then with a fine file, weighed, rinsed in high purity benzene, dried and placed in the apparatus. Samples were not touched by hand after filing and all tools were degreased before use.

ANALYSIS OF NIOBIUM

The accurate gas analysis of niobium requires strict control over extraction conditions.

In early work, attempts to analyse niobium using conventional vacuum fusion procedures were seldom satisfactory because of the relatively small amounts of gas involved and difficulties in maintaining suitable reaction conditions within the crucible.

To evaluate various analytical techniques, laboratory reference standard samples were selected and analysed, together with niobium received from AGARD and other sources.

The reference samples selected for testing were UK Nb2 and US MSG, which were received from AGARD in the first round-robin tests. Analysis results, for sample UK Nb2 by platinum bath and sub-fusion extraction are shown in Table 1.

Hydrogen

Examination of the results listed in Table 1 show that sub-fusion analysis at temperatures of 1000-1400°C gives higher hydrogen values than those obtained by higher temperature extraction or vacuum fusion.

The data obtained indicated that a maximum as well as a minimum temperature limit should be imposed in application of the method for hydrogen determination.

Analysis of niobium of low hydrogen content, such as US MSG as shown in Table 2, tended to be in close agreement regardless of technique, but at higher levels, such as shown in Table 3, the disagreement in results obtained by high as opposed to low temperature extraction was greater.

Although an optimum extraction temperature was not clearly established due to insufficient sample material, it is expected that no serious disagreement would result using an extraction temperature in the range 1300°C $\pm$ 100°as indicated by the hydrogen recovery versus extraction temperature curve in Figure 1.

It should be noted that the data plotted in Figure 1 were obtained entirely from results of a series of samples from a single rod and, therefore, it is desirable that the evidence be confirmed by further work on other sample material.

TABLE 1

The Effect of Analysis Technique on Hydrogen and Oxygen Determination

Analytical Methods	Hydrogen wt %	Oxygen wt %	Remarks
Fusion in platinum bath 1900-1950°C	0.000396	0.00179	Average of 21 hydrogen and 20 oxygen determinations in A and C units.
Sub-Fusion 2250°C	0.000164	0.00142	Average of 4 determinations A unit.
Sub-Fusion 2000°C	0.000159	0.00177	Average of 6 determinations A unit.
Sub-Fusion 1900°C	0.000228	0.00138	Average of 10 determinations A unit.
Sub-Fusion 1800°C	0.000255		2 determinations A unit.
Sub-Fusion 1600°C	0.000372		Single determination A unit.
Sub-Fusion 1400°C	0.000460		Average of 5 determinations A unit.
Sub-Fusion 1200°C	0.000483		2 determinations C unit.
Sub-Fusion 1000°C	0.000418		2 determinations A unit.
Sub-Fusion 1150-950°C (followed by fusion in a platinum bath at 1925°C for oxygen determination)	0.000350	0.00109	Analysis in A unit, temperature decreasing (furnace cooling) during first 5 minutes of extraction.
Sub-Fusion 1350-1030°C	0.000423		Analysis in A unit, temperature decreasing (furnace cooling) during first 5 minutes of extraction.

TABLE 2

Hydrogen Analysis for Niobium Sample US MSG

Method		Hydrogen, wt %
Platinum bath	1900°C	0.000280
"		0.000258
"		0.000250
"		0.000197
"		0.000135
"		0.000097
Sub-fusion	1620°C	0.000230
		0.000199
	1600°C	0.000184
		0.000183
	1400°C	0.000152
		0.000133
		0.000080
	1200°C	0.000144
	1070°C	0.000184
	1000°C	0.000170

TABLE 3

Hydrogen Analysis by Different Laboratories

Laboratory	Hydrogen, ppm					Method
A	10.6	10.8	10.3	10.2	10.3	Sub-fusion 1400°C CuD/mg Cl
B	10.4	9.8	9.9	10.0	10.1	Sub-fusion 1400°C Pd Osmosis tube
C	8.1	9.2	9.2	12.0	10.7	Sub-fusion 1800°C Gas Chromatograph
D	10.5	11.4	10.7	11.0	11.0	-
Canada, Mines Branch	8.5					Sub-fusion 1170°C followed by fusion at 1925°C
"	8.9					Sub-fusion 1030°C
"	8.3					Sub-fusion 1170°C
	10.3					Sub-fusion increasing temperature 1030-1350°C over ten minute period.

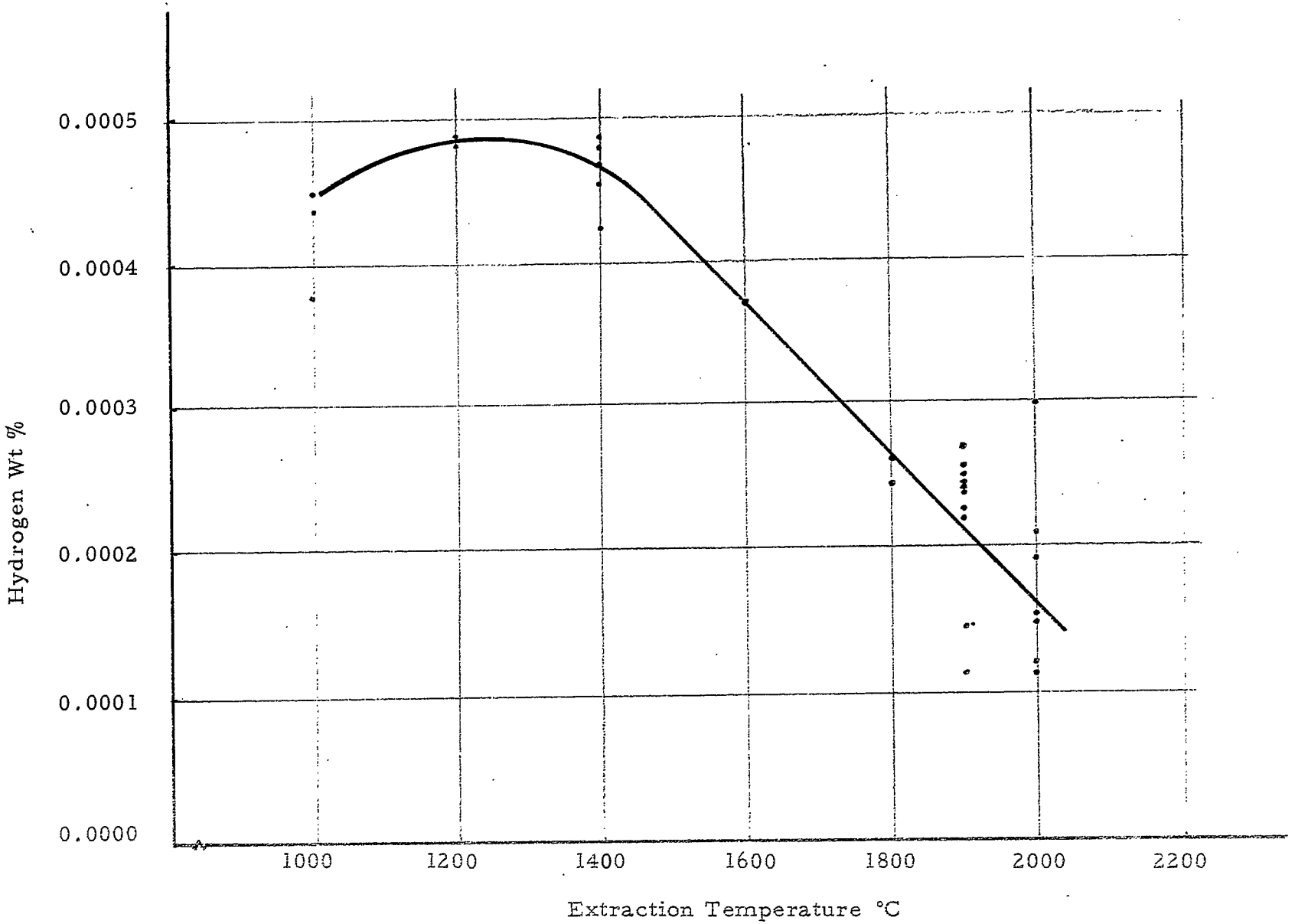

Figure 1. Effect of Extraction Temperature on Hydrogen Determination.

Oxygen

Of the gas extraction techniques investigated the highest oxygen results were obtained using a platinum bath.

From earlier experience it was found that poor bath conditions were the main cause of variability in gas recovery and it is clear that for satisfactory vacuum fusion that the bath should remain fluid and have a clean surface so that sample solution, reaction and gas evolution can proceed with least possible hinderance. For these reasons, in all tests since early 1963, using the platinum bath method, an additional small amount of high purity platinum has been added to the bath before the introduction of the sample to be analysed. The platinum is normally in the form of 1/8 in. diameter wire, weighing 0.1 to 1 g and is added about 3 min before sample addition, this being about the minimum time required to ensure complete degassing and allow preparations for adding the sample before a reappearance of surface film.

While sub-fusion extraction analysis of massive niobium at temperatures of 1900-2250°C yielded consistent and reproducible results, only at 2000°C was the same value achieved as those obtained by vacuum fusion in a platinum bath, and at both higher and lower temperatures the results were lower.

The sub-fusion extraction method is ideally suited for oxygen analysis of samples having small cross section such as small pellets, loosely sintered powders or compacted material.

Analysis of niobium pellets (sample P4G niobium about 1/16 in. diameter) by vacuum fusion, sub-fusion and radioactivation as shown in Table 4 points out the effectiveness of the sub-fusion method. For vacuum analysis the sample was enclosed in a tin cup; however, a platinum cup may be used if desired.

TABLE 4

Comparison of Oxygen Analysis of Niobium Having Small Cross Section

Method	Oxygen Analysis, wt %		
Vacuum fusion by platinum bath	0.010	0.009	
Sub-fusion 2000°C	0.014	0.013	0.012
Radioactivation*	0.012		

* Radiotracer Laboratory, Mineral Sciences Division, Mines Branch.

Low analysis results were obtained in tests employing high temperature fusion at 2250-2350°C in a dry crucible (no platinum or iron bath).

Hydrogen and Oxygen

There are indications that both hydrogen and oxygen (and possibly nitrogen) may be determined with accuracy from the same sample provided that suitable extraction conditions are maintained.

The method proposed and under current investigation, has as its objective both sub-fusion for hydrogen and vacuum fusion in a platinum bath for oxygen using a single sample.

The procedure is as follows:

The vacuum fusion apparatus is prepared and outgassed in the normal manner, platinum is added to the crucible then degassed at a temperature of 1900-1950°C until suitable blank conditions are achieved. The temperature is then lowered to 1350°C and the sample is dropped onto the solidified bath surface and hydrogen is extracted for 5 min. The temperature is then rapidly raised to 1925°C at which temperature the sample dissolves in the bath and the remaining gases are released. Gas analysis is done in the normal way. To prepare for the next sample, a small amount of platinum is added to the bath (to insure a high platinum to sample ratio at the surface). With most vacuum fusion equipment this procedure will not require additional time since the platinum may be added and degassed in the furnace section while gas analysis is carried out in the main body of the unit.

A sub-fusion procedure is proposed for hydrogen and oxygen analysis in niobium based upon the data obtained in this investigation, which entails extraction at 1300°C for hydrogen, then raising the temperature to 2000°C for oxygen. By this method very little nitrogen is released in comparison with the fusion technique.

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