

## FOREWORD

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The work reported forms the second part of a comprehensive investigation; Part I of which, on the W-C system, was published as a Technical Documentary Report, ASD-TDR-62-25, Pt. I, in March 1962.

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## ABSTRACT

This report deals with the solid solubility of boron and of beryllium in tungsten, together with the attendant problems concerning the tungsten rich borides and beryllides in equilibrium with W, and which are liable to precipitate. Brief supplementary data are given on the W-C system, following the previous investigation.

The study of the solubility of boron in tungsten shows this to be approximately 0.2 atomic %B at 2500°C, decreasing with temperature. The atomic nature of this solution presents a special, and it is believed, novel problem, in that it can be interstitial and substitutional. W-W<sub>2</sub> B forms a eutectic system, the eutectic temperature being about 2600°C. A high boron compound WB<sub>4</sub> has been observed.

In the tungsten - beryllium system which presented some special hazards which are described, the solubility of Be in W is found to be approximately 5 atomic % Be at the eutectic temperature ( $\approx$  2100°C). The solubility limit does not vary appreciably down to 1800°C and decreases to about 3 atomic % Be in the 1000/1300°C range. The solid solution is substitutional, and lattice spacing variations are described. The equilibrating phase is WBe<sub>2</sub> (hexagonal Laves structure). The diberyllide precipitates from the primary (W,Be) solution and is shown to have itself a significant homogeneity range.

This technical documentary report has been reviewed and is approved.



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CONTENTS

	PAGE
<u>SECTION 1: TUNGSTEN-BORON</u>	1
1. INTRODUCTION	1
2. PREVIOUS WORK	1
3. EXPERIMENTAL WORK	2
4. RESULTS	7
5. DISCUSSION AND SUMMARY	18
APPENDIX 1	24
APPENDIX 2	25
<u>SECTION 2: TUNGSTEN-BERYLLIUM</u>	37
1. INTRODUCTION	37
2. PREVIOUS INVESTIGATIONS	37
3. EXPERIMENTAL	39
4. RESULTS	44
5. DISCUSSION AND CONCLUSIONS	57
APPENDIX 3	61
<u>SECTION 3: TUNGSTEN-CARBON</u>	71
(BRIEF SUPPLEMENT)	
1. AGE-HARDENING EFFECTS	71
2. THE SOLID SOLUTION OF C IN Ta-W ALLOYS	72

## LIST OF ILLUSTRATIONS

Figures	Page
1. Boridised tungsten wire	27
2. Calibration curve for high-temperature camera as used in this work	27
3. Debye-Scherrer photographs of (a) Carburised and (b) Boridised Wire	28
4. Liquidus temperature in tungsten-boron system 0-33.1/3 atomic % boron	28
5. Lattice spacing/temperature curve for pure tungsten and boron-saturated tungsten	29
6. Etch pitting in pure tungsten. Murakami's reagent. x 800	29
7. W-2.00 atomic per cent boron, quenched from 2500°C. Electrolytically-mechanically polished. x 150	30
8. 1.19% B-W. Quenched from 2500°C. Murakami's reagent. x 1000	30
9. 0.78 atomic % B-W. Quenched from 2500°C. Electromechanically etched. x 800	31
10. 0.32 atomic % B-W. Quenched from 2500°C. Electromechanically etched. x 800	31
11. 0.14 atomic per cent B-W. Quenched from 2500°C. Electro-mechanically etched. x 800	32
12. 0.78 atomic per cent boron. Quenched from 1000°C. Electro-mechanically etched. x 800	32
13. 0.32 atomic per cent B-W. Quenched from 1000°C. Electro-mechanically etched. x 800	33
14. 0.14 atomic per cent B-W. Quenched from 1000°C. Electro-mechanically etched. x 800	33
15. 0.32 atomic per cent B-W. Quenched from 2500°C, heat treated for 3 hours at 1250°C. Electromechanically etched. x 800	34
16. 0.78 atomic per cent B-W. Quenched from 1000°C. Electro-mechanically etched. x 800	34

# Contrails

## LIST OF ILLUSTRATIONS (CONT'D)

Figures	Page
17. Schematic diagram of grain growth away from $W_2B$ precipitate after 2 minutes at 2500°C for sample in Fig. 16	35
18. $W_2B$ precipitate, formerly outlining the grain boundaries in Fig. 16 beginning to agglomerate after 3 minutes at 2500°C	35
19. Substructure in 0.32 atomic % B-W alloy	36
20. The proposed W- $W_2B$ equilibrium diagram	36
SECTION II	
1. (II) Pressure-vessel arrangement for W-Be alloy preparation and heat-treatment	67
2. (II) W- $WBe_2$ eutectic. (x 1200)	67
3. (II) 40% Be sintered compact after heating at 2500°C in pressure-vessel (W + eutectic). (x 500)	68
4. (II) 6.7% Be alloy, quenched from 2500°C. (x 2000)	68
5. (a) (II) Microprobe Analysis: Electron picture of eutectic alloy. (x 1000)	69
(b) (II) Microprobe Analysis: Typical specimen current scan in eutectic, as above	69
6. (II) Tentative W-Be Phase Diagram	70
SECTION III	
1. (III) Ageing Characteristics of Tungsten containing 0.075 at % Carbon aged at 1450°C (after quenching from 2450°C)	76
2. (III) Ageing Characteristics of Tungsten containing 0.075 at % Carbon aged at 1000°C (after quenching from 2450°C)	76
3. (III) Ageing Characteristic of Tungsten containing 0.075 at % Carbon aged at 1000°C & 1450°C after quenching from 2450°C	77
4. (III) W-C alloy (0.075 a/o C) solution treated and quenched. Etched in Murakami's reagent. (x 1000)	78
5. (III) W-C alloy (0.075 a/o C), solution treated and quenched; aged 1000°C, 92 hours. <u>Before</u> hardness peak. Electron micrograph. Carbon replica shadowed with Au/Pd. (x 20000)	78

## LIST OF ILLUSTRATIONS (CONT'D)

Figures	Page
6. (III) W-C alloy (0.075 a/o C), solution treated and quenched; aged 1000°C, 167 hours. <u>At</u> hardness peak. Electron micrograph, as Fig. 5. (x 20000)	79
7. (III) W-C alloy (0.075 a/o C), solution treated and quenched; aged 1450°C, 47 hours. Murakami's reagent. (x 2000)	79
8. (III) W-C alloy (0.075 a/o C), solution treated and quenched; aged 1000°C, 500 hours. Electron micrograph as before. (x 20000)	80

## LIST OF TABLES

Tables	Page
1. Lattice Parameters of Tungsten-Boron Solid Solutions (Wire Specimens)	9
2. W-B Alloys: Lattice Parameter Measurements (Arc-Melted Specimens)	11
3. The Temperature Variation of Tungsten Lattice Parameters in Boron Saturated Alloys	12
4. High Temperature X-ray Parameter Results	13
5. Metallographic Results	15
6. Interplanar Spacings Values for $WB_4$ (Co-radiation $K\alpha_1 = 1.78890 \text{ \AA}$ , $K\alpha_2 = 1.79279 \text{ \AA}$ )	18
7. Hägg's Ratio and the Radius of the Boron Atom in $Me_2B$ for Some Transition Metals	22
SECTION 2	
1. Maximum Solubility of Be in Transition Metals (atomic %)	38
2. Some Relevant Properties of W and Be	39
3. Typical Composition of Materials: Parts per million	40
4. As-weighed Compositions of W-Be Alloys	41
5. Homogeneity Data on W-Be Alloys, as-received	42
6. Chemical Analysis of W-Be Alloys	43
7. Constitution of W-Be Alloys, as received	45
8. Constitution and Lattice Spacing Results after various Heat-Treatments: (40% Be alloy throughout)	46
9. Lattice Parameter Results on Samples Extracted from the centre of Solid Pieces (40% Be Alloy)	48
10. X-ray Results on Samples Heated in the Pressure Vessel (40% Be Alloy)	48
11. Observations concerning Eutectic Temperature (40% Be Alloy)	49



LIST OF TABLES (CONT'D)

Tables	Page
12. Equilibrium Lattice-Spacings of the W $\leftrightarrow$ Be Solid-Solution	51
13. Lattice Dimensions of WBe <sub>2</sub> after Various Treatments	53
14. Interplanar Spacings for WBe <sub>2</sub> (A)	55
SECTION 3	
1. Lattice Spacing Change of Ta-W Solid Solution by C	73

# *Contrails*

## SECTION 1. TUNGSTEN-BORON SYSTEM

### 1. INTRODUCTION

The primary purpose of the work described was to determine the solid solubility of boron in tungsten. Within certain limitations caused mainly by the minuteness of the solubility, this end has been achieved, although necessarily the work requires extension, as will be indicated. A major question as to the atomic nature of the solubility arises however, and an attempt to resolve this problem will be described.

A limited study was carried out on ditungsten monoboride ( $W_2B$ ), the phase in equilibrium with the saturated solid solution. It is shown to exhibit no polymorphism (as might have been possible), retaining its tetragonal structure at all temperatures; the phase is also shown not to possess a significant homogeneity range. In addition to the phases already known in the W-B system, namely  $W_2B$ , WB, and  $W_2B_5$ , a new phase has been found which proves to be the same as that recently reported by Chrétien and Helgorsky<sup>(1)</sup>. Further work would be needed however on the exact chemical analysis of the compound.

### 2. PREVIOUS WORK

No satisfactory diagram for the W-B system can be found apart from knowledge on the borides themselves, e.g. Kiessling<sup>(2)</sup> although Hansen<sup>(3)</sup> suggests that it may be very similar to the Mo-B system which is known. No figure is given for the solubility of B in Mo however except that it is said to be "very low"<sup>(4)</sup>. More recent work by the Climax Molybdenum Co.<sup>(5)</sup> however suggested a slight decrease in molybdenum lattice spacing through boron solution, indicating that the boron dissolves substitutionally.

Little seems to be known about the solubility of boron in tungsten. Kiessling<sup>(4)</sup> merely reports the solubility to be very low, no spacing change being detectable. Samsonov<sup>(6)</sup> however found a considerable lattice parameter decrease from 3.1495 to 3.133 Å indicating a substitutional solution. In addition Samsonov reports that two phases could be seen metallographically in slowly cooled alloys containing more than 0.9 atomic % B suggesting that the solubility is of this order of magnitude.

A survey of available data about the solubility limits of boron in the Group V and VI transition metals neighbouring tungsten shows that very little indeed is known about any of these limits.

For tantalum, Kiessling reports that boron expands the lattice indicating an interstitial solution. A 10% B-Ta alloy quenched from 1270°C had a lattice parameter of 3.314 kX showing an increase of 0.018 kX over that for pure tantalum.

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The position concerning the tungsten borides is much clearer. Three borides are established:-

$W_2B$ , tetragonal CuAl <sub>2</sub> type	a = 5.553 kX, c = 4.730 kX	Melting point 2800°C (melts incongruently)
∫ WB, tetragonal MoB type	a = 3.109 kX, c = 16.896 kX	Melting point 2860°C, stable below 1850°C
β WB, orthorhombic CrB type	a = 3.18 kX, b = 8.4 kX, c = 3.06 kX	stable above 1850°C
∫ W <sub>2</sub> B <sub>5</sub> hexagonal D 8 <sub>h</sub> type	a = 2.976 kX, c = 13.84 kX	Melting point 2200°C

In addition to these a fourth boride WB<sub>4</sub> has been reported<sup>(1)</sup> though this has not been confirmed, until now.

### 3. EXPERIMENTAL

3.1 The experimental approaches used were:-

#### 3.11 X-Ray Examination

- (a) Lattice parameter measurements on quenched low-boron samples.
- (b) Thermal lattice expansion of pure tungsten and boron-saturated tungsten using the X-ray high temperature camera (as explained below).
- (c) Constitutional examination for the borides.

#### 3.12 Metallography

- (a) To detect the first traces of boride.
- (b) To observe the mode of precipitation, if any.

#### 3.13 Spark Treatment

To search for polymorphy in W<sub>2</sub>B.

3.14 Liquidus determination within the W-W<sub>2</sub>B range (which appeared previously unknown).

Note

Internal friction was tried in the case of W-C alloys<sup>(20)</sup> but proved unsuccessful. Its possible application to the W-B problem will be discussed later. It is thought however that this aspect has not been exhaustively explored and would prove a fruitful field for further work.

3.15 Chemical Analysis

(See Appendix 1)

3.2 Alloy Preparation

Two methods of preparing W-B alloys were used. These methods produce a boridised tungsten wire in the one case, and a small argon arc melted ingot in the other. They are in principle similar to those used in our previous work on W-C<sup>(20)</sup>.

3.3 Preparation of Wire Specimens

The tungsten wire of 0.025 cm. diameter was supplied by the General Electric Co. Ltd. (Osram) and had the following analysis (weight per cent):-

Mo	Fe	Cu	K	Na	Ca	C	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
0.04	0.01	0.005	0.01	0.001	0.01	0.001	0.01	0.005

Total purity > 99.9% W.

Small copper contact tubes were fitted to each end of a 15 cm. length of the wire which was arranged along the axis of a Pyrex tube with suitable electrical connectors. The wires could thus be heated by current to temperatures up to 3000°C in a stream of high purity argon. A disappearing filament pyrometer was used to measure the temperature. The latter was corrected for non-black body conditions and for the absorbing power of the glass envelope. Fast rates of quenching were obtained by cutting-off the current supply to the wires and increasing the flow of argon.

The boron-containing specimens were made by coating the tungsten wires with a slurry of finely divided  $W_2B$ . The amount of coating compound applied was varied by weighed amounts so as to give final wires of different compositions. The coated wires were held at  $1500^{\circ}C$  to promote adhesion and then at temperatures up to  $3000^{\circ}C$  to allow diffusion to proceed throughout the wire, yielding a consolidated alloy. A typical microstructure is shown in Fig. 1.

The chemically pure  $W_2B$  powder used, supplied by Borax Consolidated Ltd., had the following analysis, by weight:-

B 2.9  $\pm$  0.1% (theoretical 2.89)  
W 97.1  $\pm$  0.1% ( " 97.11) Cl residue  $<0.1\%$ .

The wires were heat-treated at various temperature levels and quenched in the Pyrex tube.

### 3.4 Preparation of Arc-Melted Ingots

The tungsten powder, supplied by Murex Ltd., had the following analysis (weight per cent):-

O <sub>2</sub>	Fe	Ni	Cr	Mo
$<0.20$	$<0.05$	$<0.02$	$<0.02$	$<0.03$

Total purity  $\gg 99.7\%$  W.

Weighed amounts of pure tungsten and ditungsten boride powders were initially mixed and compacted in a small press at 10 t.s.i. to give approximately ten gram pellets. These were pre-sintered on the water cooled copper hearth of a laboratory argon arc furnace with non-consumable tungsten electrode.

During the sintering stage and also initially during melting a vapour was given off (more noticeably for the case of the higher B alloy) which condensed to a pink colouration on the walls of the furnace and on the observation port. As an incidental this condensed phase was analysed by X-ray diffraction and proved to be a mixture of tungsten and boron oxide  $B_2O_3$ . The latter is consistent with the known scavenging effect of boron on oxygen in tungsten, noted by several authors, due to the very high heat of formation of  $B_2O_3$ .

It is thought that by this action the rather high initial amount of oxygen present in the pure tungsten powder was reduced to a negligible level in the final alloy. Each alloy was repeatedly melted and turned over in the arc furnace and finally given a prolonged heat treatment just below the solidus temperature.

Alloy powders were heat-treated in a tungsten boat at various temperature levels and quenched on the hearth of the arc furnace. The rate of quench thus achieved was however not as rapid as that for the wires. Chemical analysis was carried out throughout, as in the Appendix.

### 3.5 High Temperature X-ray Work

The reason for using this approach was that of a suspected interstitial/substitutional change-over of B atoms with temperature, which arose during the work; see later.

Preliminary experiments on the 19 cm. B.S.A. High Temperature X-ray Camera (built in this laboratory)<sup>(7)</sup> showed that some modifications were desirable in order to achieve the highest precision of lattice parameter measurement required. The principal factors contributing to good resolution in high temperature work are close control of the specimen temperature and good X-ray and specimen optical arrangement. In addition high vacuum is also essential for a reactive metal such as tungsten.

The steps taken were as follows:-

A fine collimating system was designed, after some experimentation, and this increased the resolution markedly, at the expense however of exposure time. In order to offset this latter disadvantage the aluminium foil diffraction windows used to retain the specimen in vacuum and allow the X-rays to expose the film were replaced by pre-formed  $18\frac{1}{2}$  cm. diameter beryllium windows. ("Araldite" thermo-setting resin proved useful in resolving the initial difficulty of obtaining a good high vacuum seal between the stainless steel collar of the camera perimeter and the beryllium windows.) A thin beryllium disc similarly replaced aluminium at the vacuum seal in the collimator entry. A beryllium window was also fitted to the Raymax 100\* X-ray set. In this way it proved possible to reduce the time of exposure by a factor of about 2.5. A  $1\frac{1}{2}$  hours exposure at 50 m.a. was found to give sufficiently strong and well resolved diffraction lines.

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Rotating anode, to permit highest X-ray intensity and a further reduction of exposure time.

The shorter exposure time also eased the problem of maintaining close temperature control of the specimen. Control was by a conventional method modified to take account of the low resistance (1 ohm) of the hemispherical Pt furnace halves. Current was fed into the furnace via one fixed and one variable step-down transformer and a variable resistance. The resistance was switched in and out of the circuit at the control point via a relay by an Ether Transistrol Temperature Instrument controlled by the Pt/13% Rh-Pt Thermocouple adjacent to the specimen in the camera. However even at this stage it was possible to control the specimen temperature to only  $\pm 5^{\circ}\text{C}$  at best at  $1000^{\circ}\text{C}$ . This variation, caused by random changes in furnace current during the exposure, was attributed to fluctuations in mains voltage and it was considerably reduced when a voltage stabilizer unit was fitted. Finally the specimen temperature could be held to  $\pm 1\frac{1}{2}^{\circ}\text{C}$  at  $1000^{\circ}\text{C}$ , and in some cases the temperature varied by as little as  $1^{\circ}\text{C}$  throughout the exposure. The vacuum was 0.025 microns, measured by ionisation gauge.

The result of these modifications was that parameter measurements at temperatures up to  $1200^{\circ}\text{C}$  could be made to an accuracy comparable with precision room temperature measurements.

### 3.6 Preparation of High Temperature X-ray Specimens and Calibration

A tungsten hair, made by dissolving down some of the pure tungsten wire, was used as the foundation for the two high temperature specimens; one basically a 1.92% B-W powder and the other pure tungsten. These were mixed with finely divided highest purity periclase ( $\text{MgO}$ ) to form a slurry, and coated on to the hair. The specimen was baked in vacuum at  $50^{\circ}\text{C}$  for two hours to drive off the water and consolidate it. Periclase was used as a binder because its lattice spacing/temperature graph is accurately known. This internal calibration removes the uncertainty caused by the position of the thermocouple relative to the specimen in the camera. In fact the difference between the indicated thermocouple temperature read by a potentiometer and the actual specimen temperature can be quite significant and is shown graphically in Fig. 2. The specimen temperature on this graph was obtained by using the  $\text{MgO}$  lattice parameters listed in Table 4 (see later) and converting these into temperature by means of the known parameter-temperature relationship.

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This  $\text{MgO}$  work formed the subject of a recent Interlaboratory Study on Thermal Expansion organised by the United States Bureau of Mines, in which we participated. The overall assessment appeared in a recent report<sup>(8)</sup>.



## 4. RESULTS

### 4.1 Preliminary Information

Preliminary parameter measurements on boridised wires gave spacings indistinguishable from those of pure tungsten. It was concluded that the solubility of boron in tungsten is indeed very low and that the highest precision methods of measuring the lattice parameters should be used.

An interesting early observation was that grain growth in the tungsten alloys was not inhibited by addition of boron as it was by carbon. This can be seen in the Debye-Scherrer photographs of boridised and carburised wires shown in Fig. 3 (a) and (b).

### 4.2 The Liquidus Temperature Determination

A series of fifteen alloys with boron contents in the range 0 to 33.1/3 atomic per cent were prepared and the liquidus temperatures determined in the argon arc furnace. In this technique the specimen was maintained in a half molten state and an optical pyrometer focussed just inside the solid-liquid boundary. Systematic errors arise due to the departure from black body conditions and the variation of emissivity with composition. The first of these was largely eliminated by calibration against similarly shaped standards - preferably in materials comparable to that being investigated. In this case pure tungsten, ditungsten boride, niobium and zirconium were used. The correction curve was a straight line. Reproducibility of the liquidus temperature measurements was to  $\pm 20^{\circ}\text{C}$  at  $3000^{\circ}\text{C}$ .

The result of these measurements is shown in Fig. 4. The W-W<sub>2</sub>B system is a eutectic one with the eutectic point located at a composition of about 23 atomic per cent boron. The eutectic temperature is at approximately  $2600^{\circ}\text{C}$ .

### 4.3 Lattice Parameter Measurements

The room temperature X-ray photographs of the quenched specimens both on the boridised wires and on the powder samples were taken with copper  $K\alpha$  radiation (wavelength  $K\alpha_1 = 1.54050 \text{ \AA}$ ,  $K\alpha_2 = 1.54434 \text{ \AA}$ ) using a 19 cm. Unicam camera. The camera assembly was allowed to stand in position for a length of time before the exposure, in order to equalise the temperature between the specimen and the environment; this was measured with a sensitive mercury-in-glass thermometer

reading to  $1/20^{\circ}\text{C}$ . The camera was modified in order to increase the precision of measurement by adapting the Van Arkel method of film mounting and improving the location of the film round the perimeter of the camera. A millimeter scale, calibrated against the similar scale on the Cambridge comparator was imprinted on the film before development to correct for shrinkage. Each film was measured twice with the travelling microscope capable of interpolation to 0.002 mm. After correction, the setting on a diffraction line could be repeated to within 0.01 mm. The  $K\alpha_1$  and  $\alpha_2$  reflections of the (222), (321) and (400) planes were measured and the parameter results for each were plotted against the Nelson-Riley function  $\frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$ .

The straight line resulting from this was extrapolated to  $\theta = 90^{\circ}$  in the usual way to correct for systematic errors. The results were as follows:-

#### 4.31 The Wire Specimens

Boridised tungsten wires were quenched from various temperatures as described previously and gave the lattice parameters set out in Table 1 below. These wires were saturated with boron as shown by the presence of free ditungsten boride detected under the microscope and thus should show the maximum parameter changes due to boron in solution at these temperatures.

TABLE 1

Lattice Parameters of Tungsten-Boron  
Solid Solutions (Wire Specimens)

Quenching Temperature (°C)	Lattice Parameter a (kX)	Reliability x 10 <sup>5</sup> (kX)	Δ a x 10 <sup>5</sup> (kX)
1700	3.158 48	± 2	3
1800	45	± 2	0
1900	48	± 2	3
2000	47	± 2	2
2000	48	± 2	3
2000	51	± 2	6
2100	49	± 2	4
2200	51	± 2	6
2300	51	± 2	6
2400	47	± 2	2
2400	50	± 2	5
2500	49	± 2	4
2600	51	± 2	6
2600	51	± 2	6
2700	55	± 3	10
2800	53	± 3	8

The change in lattice parameter at the eutectic temperature (2600°C) where the greatest solubility for boron would be expected to occur is barely significant 6 x 10<sup>-5</sup> kX. (The value of 10 x 10<sup>-5</sup> kX at 2700°C must be treated as unconfirmed since this was a single determination and at a temperature 100°C higher than the eutectic temperature.) It seems without doubt however that these results indicate a slight expansion of the lattice.

The lattice expansions are about one quarter to one third of those for the tungsten-carbon system and this, coupled with the knowledge that the boron atom is about 10% larger than that carbon atom, leads to the suggestion that the solubility of boron is considerably less than carbon and extremely small indeed.

This expansion suggests that the solution is an interstitial one, on balance. Moreover it seems difficult to draw a reliable parameter/temperature graph from these results thus rendering impossible its later transformation into a solid solubility phase boundary.

#### 4.32 The Arc-Melted Ingots

A series of finely divided alloys of composition 1.92% B, 10.42% B, 21% B and 26% B\*, that is alloys with free boride present, was given heat treatment at four temperatures 1450°C, 1800°C, 2100°C and 2500°C in a tungsten container in the argon-arc furnace. The tungsten container was designed so as to simulate black body conditions as far as possible and also to minimise the temperature gradient through the sample. The furnace atmosphere was thoroughly gettered prior to heat treatment by playing the arc in turn on three pure titanium buttons for a total time of 35 minutes. Previous experimentation has showed that this resulted in a negligible increase in hardness of the third button. The specimens were quenched in the tungsten container on the water cooled copper hearth. Temperatures were measured by means of a disappearing filament pyrometer sighted on to the specimen through an observation port. Corrections were made for departure from black body conditions in the same way as previously described for the boridised wires.

The results for the lattice parameter measurements including those for pure tungsten are given in Table 2 below.

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\* Atomic per cent throughout.

TABLE 2

W-B Alloys: Lattice Parameter Measurements (Arc-Melted Specimens)

Atomic per cent Boron, by Analysis	Heat Treatment	Tungsten Lattice Spacing (kX)	
Pure Tungsten	Slowly cooled from 2500°C	3.1590 <sub>4</sub> 3.1590 <sub>4</sub> 3.1591 <sub>9</sub> 3.1590 <sub>4</sub> 3.1590 <sub>9</sub> 3.1585 <sub>4</sub>	Mean value 3.1590 <sub>9</sub> $\pm 5 \times 10^{-5}$ kX
1.92	2 mins at 1950°C slow cooled to 1550°C, quenched	3.1585 <sub>4</sub>	
10.42	10 mins at 1850°C slow cooled to 30 mins at 1450°C, quenched	3.1585 <sub>9</sub>	
20.99	10 mins at 1850°C slow cooled to 30 mins at 1450°C, quenched	3.1585 <sub>9</sub>	
25.9	5 mins at 1800°C slow cooled to 25 mins at 1450°C, quenched	3.1583 <sub>4</sub>	
1.92	10 mins at 1800°C, quenched	3.1583 <sub>9</sub>	
10.42	10 mins at 1800°C, quenched	3.1585 <sub>9</sub>	
20.99	10 mins at 1800°C, quenched	3.1585 <sub>4</sub>	
25.9	1 min at 2200°C, 10 mins at 1800°C, quenched	3.1584 <sub>9</sub>	
1.92	10 mins at 2000-2100°C, quenched	3.1586 <sub>4</sub>	
10.42	5 mins at 2100°C, quenched	3.1586 <sub>4</sub>	
20.99	5 mins at 2100°C, quenched	3.1585 <sub>4</sub>	
25.9	2 mins at 2100°C, quenched	3.1582 <sub>9</sub>	
1.92	5 mins at 1800°C, 1 min at 2500°C, quenched	3.1590 <sub>4</sub>	
10.42	5 mins at 1800°C, 1 min at 2500°C, quenched	3.1587 <sub>8</sub>	
20.99	5 mins at 1800°C, 1 min at 2500°C, quenched	Incipient melting occurred, diffuse photo-graphs	
1.92	10 mins at 2500°C, quenched	3.1591 <sub>2</sub>	Mean value 3.1589 <sub>6</sub> at 2500°C
1.92	"	3.1590 <sub>2</sub>	
1.19	"	3.1587 <sub>4</sub>	
0.83	Analysed after the heat treatment	3.1590 <sub>7</sub>	
0.83	10 mins at 2500°C, quenched	3.1590 <sub>9</sub>	
.32	"	3.1587 <sub>8</sub>	

Those results which gave a Nelson-Riley extrapolation with maximum error limits of  $\pm 2 \times 10^{-5}$  kX (all but two values in Table 2) are averaged out for the various temperatures in Table 3 along with the mean pure tungsten value.

TABLE 3

The Temperature Variation of Tungsten  
Lattice Parameters in Boron Saturated Alloys

Temperature (°C)	Tungsten Parameter	Change from pure W $\times 10^{-5}$ (kX)
1450	3.1585 <sub>7</sub>	- 52
1800	3.1585 <sub>0</sub>	- 59
2100	3.1586 <sub>2</sub>	- 47
2500	3.1589 <sub>5</sub>	- 14

The smaller change in parameter at 1450°C compared with 1800°C is attributed to incomplete equilibrium at the former temperature.

These results show a considerable lattice contraction from the pure tungsten values, a result to be contrasted with the slight expansion found for the boridised wires. In addition this contraction increases with decreasing temperature. These seemingly conflicting results made it impossible to determine, from lattice-parameters alone, the primary solubility limit of B in tungsten by the usual scaling method.

The effect however is of particular basic interest and this forms part of the argument in the later discussion.

#### 4.4 High Temperature Camera, Results

X-ray photographs were taken on the high temperature camera as discussed using Co K $\alpha$  and K $\beta$  radiation (wavelength K $\alpha_1$  = 1.78890 Å, K $\alpha_2$  = 1.79279 Å, K $\beta_1$  = 1.62073 Å). Only comparative values for the tungsten and the boron-saturated tungsten specimens were

needed, and in this respect the technique is extremely sensitive..

A scale was exposed on each film before processing and the Nelson-Riley Extrapolation was again used to measure the tungsten and MgO parameters. The reflections measured for the tungsten film were (222), (310) and (220)  $K\alpha$  and (321) and (222)  $K\beta$ . The periclase reflections measured were (420), (400) and (222)  $K\alpha$ . The values obtained are shown in Table 4 and the results plotted in Fig. 5. It can be seen that there is no divergence between the two plots. The effect of the boron in solution is to cause the same contraction in parameters at all temperatures up to 1200°C.

As will be discussed, the particular interest was in the occurrence of any such divergence in rates on expansion, or of a discontinuity which could signify a change in boron atom positioning.

TABLE 4

High Temperature X-ray Parameter Results

Sample	Temperature °C (apparent)	W parameter (kX)	MgO parameter (where determined)	Temperature °C (true)
Pure W	8	3.1584	4.2100	15
	257	3.1627	4.2244	280
	519	3.1659	4.2389	530
	780	3.1704	4.2545	810
	903	3.1721	-	932
	1100	3.1752	4.2736	1130
	1200	3.1770	4.2808	1250
W-B Saturated Solution	8	3.1581	-	15
	354	3.1636	-	370
	551	3.1664	4.2437	570
	679	3.1684	-	702
	961	3.1727	-	995
	1163	3.1758	4.2777	1200

## 4.5 Metallographic Approach

A series of boron-containing alloys was melted and homogenised in the arc-furnace. Small lump specimens were taken from these ingots and heat treated in the tantalum tube furnace in an atmosphere of argon. When it became clear that the solubility was very low, a master alloy of nominally 1% B was made from which the low boron alloys were prepared.

A difficulty encountered with the low boron alloys was that etch patterns developed which would tend to mask any precipitation. An example of this is shown in Fig. 6. A new metallographic technique was tried and found to be very successful for these alloys; this is described in Appendix 2. In this way gross etch-pitting was avoided and it was possible to detect the smallest amount of precipitation.

The main results of the metallographic examination can be summarised in tabular form as follows (Table 5).



TABLE 5

Metallographic Results

Fig. No.	Alloy Composition by Analysis: atomic per cent boron	Heat Treatment	Constitution
7	2.00	Quenched from 2500°C	$\alpha W + W_2B$
8	1.19	" " "	"
9	0.78	" " "	"
10	0.32	" " "	"
11	0.14	" " "	$\alpha W$ } $\alpha W$ } $\alpha W$ } $\alpha W$ }
	0.14	" " "	} No $W_2B$
	0.08	" " "	
	0.04	" " "	
12	0.78	Slowly cooled from 2500°C and quenched from 1000°C	$\alpha W + W_2B$
13	0.32	"	$\alpha W + W_2B$
14	0.14	"	$\alpha W + W_2B$
	0.08	"	$\alpha W$ } $\alpha W$ }
	0.04	"	} No $W_2B$

The 1.92% B alloy shows the characteristic pink boride precipitate at the grain boundaries where it is almost continuous, and within the grains where it assumes a spherical shape. As the boron content is lowered, the boride precipitate within the grain is rapidly decreased and it can then be observed only at the grain boundaries. In the alloys quenched from 2500°C no boride can be seen in the 0.14% samples though this is not so for those with 0.32% B. The solubility limit would thus appear to lie between these two values at 2500°C. Judging from the amount of boride present in the higher boron content alloy it seems likely that the solubility is nearer to the lower of these values.

At the 1000°C temperature level boride can clearly be seen in the 0.14% B alloy but cannot be detected at lower levels of boron content.

The 0.32% B alloy was quenched from 2500°C and then held at 1250°C for 3 hours. There was a noticeable increase in the amount of boride present as spheroids within the grains, Fig. 15, in agreement with the decreased solubility at lower temperatures indicated above.

The 0.78% B alloy in the form of a small lump quenched from 1000°C, was metallographically examined, Fig. 16, and then heat treated at 2500°C for increasing lengths of time and quenched. After two minutes at 2500°C the grain boundaries were seen to have left the boride precipitate at many points on the previously polished surface (shown schematically in Fig. 17). After three minutes the boride previously surrounding the grain boundaries and present in "stringers" started to agglomerate, Fig. 18. Finally after 30 minutes at 2500°C the microstructure consisted of a randomly dispersed spherical boride precipitate within the grains surrounded by grain boundaries largely free from precipitate. This is strong evidence that solution and possibly some reprecipitation is occurring at this temperature.

An interesting observation made on some of the arc melted specimens was the presence of etch pit patterns which formed networks, Fig. 19. These were seen in only some of the low boron alloys and they did not occur throughout the specimen, only in one or at most two grains. Similar features were investigated by Wolff<sup>(9)</sup> and were found to be caused by low angle dislocation boundaries. In addition she found that only grains of certain orientations could be induced to reveal sub-boundaries by etch pitting. This is true also of our observations. For dislocations to be seen at all however it is usually necessary for them to be "decorated" by impurity atoms and it seems probable that boron is functioning in this way.

## 4.6 The Boride Phases

### 4.61 W<sub>2</sub>B

The boride phase which is in equilibrium with the W-boron solid solution is W<sub>2</sub>B. Its crystal structure, determined by Kiessling<sup>(4)</sup>, is tetragonal of the CuAl<sub>2</sub> type. This was confirmed in the present work. Examinations of the higher boron X-ray photographs listed in Table 2 showed the spacing of the W<sub>2</sub>B to be independent of temperature and to possess parameter values identical to those found by Kiessling. A 40 atomic % B-W alloy designed to be on the boron rich side of the W<sub>2</sub>B, and proved so by the presence of WB as well as W<sub>2</sub>B, also showed no significant change of lattice spacing. It can be concluded that the W<sub>2</sub>B has an extremely narrow range of homogeneity, if any.

It was thought that there might be a high temperature transformation of the  $W_2B$ , for instance to a hexagonal or cubic form, similarly to that found in  $W_2C$ . In order to test this possibility small powder samples rich in  $W_2B$  were quenched in the tantalum tube furnace from  $2500^\circ C$ . However only the normal tetragonal boride was found on X-ray analysis.

A more drastic quenching treatment was carried out on similar  $W_2B$  samples by sparking them with a vibrating  $W_2B$  electrode in the same way as for the  $W_2C$  (described more fully in the Final Report<sup>(20)</sup> on our W-C work). This method produces an extreme rate of quench from the melting point and was previously used successfully to retain the high temperature cubic form of  $W_2C$ . In this case however only the normal tetragonal  $W_2B$  was found. It must thus be concluded that the  $CuAl_2$  type of structure for  $W_2B$  is retained right up to the melting point.

#### 4.62 Higher Borides

In the course of making higher boron alloys it was possible incidentally to observe certain other borides reported in the literature, namely  $\beta$  and  $\delta$   $WB$  and  $\epsilon$  ( $W_2B_5$ ). It was, however, of great interest that in addition one alloy (80.6% B by analysis) showed an unknown diffraction pattern. This could be identified to be of tetragonal symmetry with lattice dimensions  $a_0 = 6.36$  kX,  $c_0 = 4.42$  kX<sup>\*</sup>. This phase is to be compared with the tetragonal  $WB_4$  phase reported by Chretien and Helgorsky<sup>(1)</sup> with the parameters  $a_0 = 6.33$  kX,  $c_0 = 4.49$  kX, and is seen to be a confirmation of it. The  $WB_4$  phase is likely to possess a homogeneity range so that the difference in parameter is not regarded as significant.

This phase has been indexed, and the interplanar spacings, indices and intensities are reported in Table 6.

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The method of Massalski and King<sup>(10)</sup> was used to determine the parameter and grateful acknowledgement is made for the use of their Tables, kindly donated by Dr. King.

TABLE 6

Interplanar Spacings Values for  $WB_4$   
 (Coirradiation  $K\alpha_1 = 1.78890 \text{ \AA}$ ,  
 $K\alpha_2 = 1.79279 \text{ \AA}$ )

Interplanar Spacing (d) $\text{\AA}$	I/I <sub>Z</sub> (visual)	h.k.l.
4.50	5	110
3.64	90 <sup>≠</sup>	101
3.17	30	200
2.58	80 <sup>≠</sup>	201
2.12	35	300
2.01	100 <sup>≠</sup>	310
1.91	20	301
1.64	35	321
1.54	20	410
1.35	40	421
1.30	15	213
1.22	20	501, 431
1.21	20	303
1.107	10 )	004
1.106	5 )	
1.090	25	104
1.075	15	114
1.018	20	611
1.005	15 )	442
1.003	8 )	
.986	10 )	304
.983	5 )	

5. DISCUSSION AND SUMMARY

As a general rule the measurement of lattice parameter is a very sensitive method of determining the type of solid solution formed between two elements. This is particularly true for interstitial solid solutions such as those formed by C and N in  $\alpha$  Fe, or C, N and O in Ta and Nb for example, where an appreciable lattice expansion occurs. This does not appear to be true for carbon and boron in tungsten, and boron in molybdenum however, and it seems possible that in these cases the solution is not of a simple type. A brief comparison with carbon is useful here in conjunction with boron.

The specific lattice expansion for carbon in tungsten ( $0.0007 \text{ kX/a/o}$ ) is considerably less than that for carbon in molybdenum ( $0.005 \text{ kX/a/o}$ ) and an order of magnitude less than that predicted by Vegard's law. Samsonov's work<sup>(11)</sup> on the reactive diffusion of carbon into tungsten gave an activation energy for carbon diffusion of 39.5 Kcals. This is a high value if simple interstitial diffusion is occurring. It may not be unconnected with the activation energy of 39.78 Kcals (1.7 ev) for the movement of vacancies in irradiated tungsten<sup>(12)</sup>. Association of vacancies and carbon atoms in some way may explain the strongly inhibiting effect of small amounts of carbon on the recrystallisation of tungsten. This possible association of vacancies may be reflected in the homogeneity range of  $W_2C$ , to be compared with  $W_2B$  which does not have a homogeneity range.

Boron does not inhibit recrystallisation in tungsten and has a much lower activation energy for diffusion according to Samsonov<sup>(11)</sup>. This state of affairs is the reverse of what one would expect if atomic size were the only criterion for determining the energy barriers for interstitial diffusion. Based on a consideration of atomic sizes only, the activation energies for diffusion should increase as the atomic radius of the diffusing atom increases as indeed it does for C, N and boron in  $\alpha$  Fe<sup>(13)</sup>. In fact in tungsten the reverse is true (although data for N diffusion is lacking) and it may be that this is connected with the increase in the first ionisation potentials, which parallels the increase in activation energy. It is probable that electronic factors play a larger part for Group VI transition metals, where the bonding between the metal and non-metal atoms is a subject of controversy.

$\Delta a$ , the difference in lattice parameter between a pure metal and its saturated solution is usually found to increase as the temperature increases, reflecting the greater solubility at higher temperatures. For boron in tungsten however  $\Delta a$  decreases as the temperature is raised. This cannot mean that boron is less soluble at higher temperatures since this is thermodynamically not favoured and is also contrary to the metallographic evidence; it is thought to be due to the special nature of the solution (to be discussed later).

The possibility of contamination must be considered even though the strictest precautions were taken to ensure that none should occur. The possible contaminants are O, N, C, copper (picked up from the hearth at the melting stage) and titanium, from the getter. The first two of these dissolve only in trace amounts in tungsten<sup>(14)\*</sup>. If either has any measurable effect on the parameter, which is unlikely, it would be to expand the lattice, and thus error from this source can be discounted. Carbon and titanium if present would also expand the lattice. Copper, if it goes into solution at all, would be expected to contaminate the same alloy equally at the different heat treatment temperatures, since these were all above the melting point of copper, and this is clearly not so.

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\* Also authors' recent assessment.

# Contrails

That boron does form a solid solution is established by the metallographic evidence. The direction of the spacing change, leaving aside its variation with temperature, is such as would be given by a smaller atom dissolving substitutionally amongst an array of larger atoms. This is contrary to expectation if the boron atom were assumed to have a radius of 0.86 Å. The size of the largest interstitial hole in the b.c.c. W lattice is 0.42 Å however, and it is clear that considerable distortion would be produced if the boron dissolved interstitially. There is much evidence e.g. from present knowledge of borides, to suggest that the boron atom is a very "variable" one in size, depending on the type of bonding and co-ordination involved.

From Kiessling's work on the transition metal boride phases, other than the  $Me_2B$  type where boron-boron bonds are established, the radius of the boron atom was found to be 0.86-0.88 Å. Pauling and Weinbaum's<sup>(15)</sup> studies on  $CaB_6$  report the radius of the boron atom to be 0.86 Å in a structure that consists of a three-dimensional framework of boron atoms with smaller metal atoms in the interstices. If 0.87 Å is taken as the mean value for the boron radius and 1.41 Å for tungsten then the radius ratio  $\frac{r_B}{r_W} = 0.62$ . According to Hägg's criteria for interstitial compound formation, if  $\frac{r_B}{r_W} > \frac{r_W}{r_W}$  about 0.59 then non-metal atoms cannot enter the metal lattice without severe distortion, and consequently with very little or no solid solubility, and simple structures do not occur. This is consistent with the tetragonal structure of  $W_2B$  and our finding of no apparent interstitial solubility, and is to be contrasted with the situation for carbon (radius ratio = 0.59) where a small interstitial solubility is observed, and  $W_2C$  is hexagonal at low temperatures and face-centred-cubic at high.

Consideration of the two metal-rich compounds  $W_2C$  and  $W_2B$  shows that in the former case the carbon atom is present with its normal atomic radius<sup>(16)</sup> 0.76 Å whereas in  $W_2B$  the apparent boron radius is 1.04 Å<sup>(2)</sup>. In view also of the fact that boron is present as isolated atoms in the  $W_2B$  structure, where the lattice is established by the metal atoms, it seems fair to suggest that the boron radius should be taken to be nearer 1.04 Å than 0.87 Å, in the two phases W and  $W_2B$ . If this is so, then boron becomes more like beryllium in size (1.11 Å) and would tend to dissolve in the tungsten lattice in a similar way, that is substitutionally (see Part 2 of this Report). This would be consistent with the decreased parameter observed.

In order to explain the form of this lattice parameter/temperature graph it is necessary to postulate that the boron atoms can sit in the lattice in an interstitial and substitutional manner at the same time. This substitution/interstitial balance is altered towards the latter at high temperatures and towards the former at lower temperatures. The introduction of a boron atom into the b.c.c. tungsten lattice will cause a region of

tetragonal distortion around it since such regions can be regarded as "nascent"  $W_2B$  lattices. Such regions of tetragonal distortion would respond anisotropically to stress and to increase in temperature. It is possible therefore that the change towards interstitial solution at higher temperatures may be reflected in anisotropic expansion coefficients or moduli for  $W_2B$  itself, or a tendency for the latter to change to a simpler crystal structure (e.g. cubic or hexagonal close-packed), where the B atoms can be interstitial with the minimum of distortion. The energetics of the solution may be such that the boron atoms are associated as an interstitial/substitutional pair. Boron is well-known to tend towards forming B-B bonds in the metallic lattice (but only ultimately for the higher B borides).

Any tendency for the solution to change its nature should be reflected in the high temperature parameter values. In fact the pure tungsten and boron-saturated tungsten curves parallel each other exactly up to  $1255^{\circ}C$ . Attaining equilibrium at these temperatures is likely to be a slow process however and very high temperatures, not possible in the present camera, would have to be used in order to explore this approach fully. It is probable that vacancies play a part in reaching the equilibrium interstitial/substitutional balance and these are not produced thermally in sufficient numbers until higher temperatures are reached.

The early results for the wire specimens are controversial. The only differences between these and the arc-melted specimens are in the source of tungsten used and the rate of quenching. It is difficult to see how the former could be the cause. (It would be fruitful however to repeat the experiments on electron-bombardment zone-refined material.) The quenching rate for the wires would be high enough to retain some excess vacancies in solution. With a large surface-volume ratio in the wires the number of vacancies quenched-in would be expected to be higher than for those in a block specimen. Vacancies however should contract the lattice though by a small amount(17) (18), probably by the order of 1 part in 20,000.

Stress, induced into the wires by the rapid quenching may have a critical effect on the substitutional/interstitial balance, displacing it in favour of interstitial solution. The latter coupled with the fact that rapid quenching is likely to approximate more nearly to equilibrium (which at high temperatures is towards an interstitial solution) are put forward to explain the wire results.

The hypothesis that stress could affect the balance could be tested by means of internal friction measurements, as for iron (see below).

Significant internal friction measurements have been made on tungsten(19), though so far this method has not been used successfully to reveal solute interactions.

The preceding arguments on the nature of the solid solution may also apply to the solubility of boron in other transition elements where the effective radius of the boron atom in the  $Me_2B$  compound is high. These elements are set out in Table 7 below.

TABLE 7

Hägg's Ratio and the Radius of the Boron Atom in  $Me_2B$  for some Transition Metals

Element	$\frac{rB}{rMe}$ (for $B = 87 \text{ \AA}$ )	$rB$ in $Me_2B$ Compound
Ta	0.60	1.10
W	0.62	1.04
Mo	0.63	1.03
Mn	0.69	1.01
Fe	0.69	0.97
Co	0.69	0.94
Ni	0.70	0.92

Kiessling found no solubility for boron in any of these except tantalum where an increased parameter was observed clearly indicating interstitial solubility. The radius ratio for tantalum is critically near Hägg's value and in interstitial solutions here seems not unlikely. On the other hand recent work on the Mo-B system gave a slight decrease in molybdenum parameter due to B in solution. The critically balanced position of tungsten is therefore understandable also from this viewpoint.

The position of iron is interesting and adds weight to the foregoing arguments. There is evidence to suggest that in this case boron is present both substitutionally(21) (22) (23) and interstitially at the same time, also in  $\alpha$  Fe. It has also been suggested that boron interacts strongly with dislocations in Fe, where discontinuous yielding has been observed.

The latter may also occur in the tungsten-boron solid-solution where dislocation networks have been observed possibly decorated by boron atoms, and this would merit further study.

Interstitial/substitutional balance has also been reported in a completely different system, the Cu-Ge(14) system.



The application of other techniques such as internal friction would be of considerable interest for the W-B system, as also would an extension of the high temperature X-ray work to very much higher temperatures, and a critical examination of the solubility of boron in these other transition metals, in co-ordination.

## 5.1 Summary

The solubility of boron in tungsten has been shown to be finite and of the order of 0.2 atomic % B at 2500°C decreasing to about 0.1 atomic % at 1000°C. The solid solubility boundary does not recede sharply as it does for carbon in tungsten. The solid solution is not of a simple type and it appears that boron dissolves in the lattice in a substitutional and interstitial manner at the same time. Further work has been suggested to confirm this and to elucidate the nature of the solid solution of boron in other transition metals.

Melting points have been determined in the range 0-33.1/3 atomic % boron. The eutectic temperature (2600°C) is the highest yet known for metal-boron systems.

The W-rich end of the W-B phase diagram proposed is shown in Fig. 20.

Ditungsten boride has been shown to be tetragonal at all temperatures and does not possess a significant homogeneity range.

A higher-boron compound,  $WB_4$ , has been found to be of tetragonal ( $ThB_4$  type) structure. This has been indexed and interplanar spacings are reported.

APPENDIX 1

DETERMINATION OF BORON IN ALLOYS OF THE W-B SYSTEM

The alloy in finely pulverised form was dissolved under reflux in a small volume of 100 volume hydrogen peroxide in a quartz or boron-free glass flask. The excess peroxide was decomposed by refluxing with caustic soda and the majority of the tungsten was precipitated by acidifying with sulphuric acid and digesting. After dilution to a suitable volume in a volumetric flask the liquid was centrifuged and an aliquot was taken from the supernatant liquid for the determination of boron absorptiometrically. Measurement was made at 620 m $\mu$  of the optical density of the boron - 1:1'-dianthrimide complex in strong sulphuric acid. The lower limit of detection of boron by this method was .04 atomic %.

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With acknowledgement to our colleague Mr. P. Stables.

## APPENDIX 2

### METALLOGRAPHY OF TUNGSTEN-BORON ALLOYS

This method was developed by G. Reinacher<sup>(25)</sup> for the noble metals, and was later developed for use with W, Re, and Mo by Dickinson<sup>(26)</sup>. Essentially the technique is a simultaneous application of electrolytic and mechanical polishing. An exceptionally smooth and strain-free surface can be quickly produced.

The specimen must be mounted in a conducting medium, for example, a mixture of iron powder and a thermo-setting resin. Some of the specimens examined in this investigation were extremely small ones in which it was important to be able to see the specimen in depth so that the correct section could be polished. A two-ply mounting technique was used where the bottom part, embracing most of the specimen, was made of a transparent mounting resin and the remainder made contact with part of the specimen and was the conducting resin. This composite was consolidated without pressure at 130°C.

Normal metallographic polishing was used down to a 600 grade silicon carbide finish. The specimen was held on a rotating Reinacher polishing cloth flooded with a slurry of gamma alumina powder and electrolyte which in this case was 3% H<sub>2</sub>O<sub>2</sub>. At the same time the specimen itself was made the electrode of an alternating current circuit with a period of 1.5 seconds and a current density of 0.04 amps/sq.cm. The other electrode used to complete the circuit was the metal base under the polishing cloth. Using fresh materials, a metallographic surface could be produced in this way in about ten minutes.

Preferential etching away or tearing out of small precipitate particles was avoided by utilising this method, as also was gross etch pitting found in conventional methods of preparation, particularly for the dilute tungsten alloys.

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\* "Diakon" supplied by I.C.I. Ltd. The electromechanical polishing apparatus is made by G. Struers, Denmark.

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Fig. 1. Boridised tungsten wire. x 500

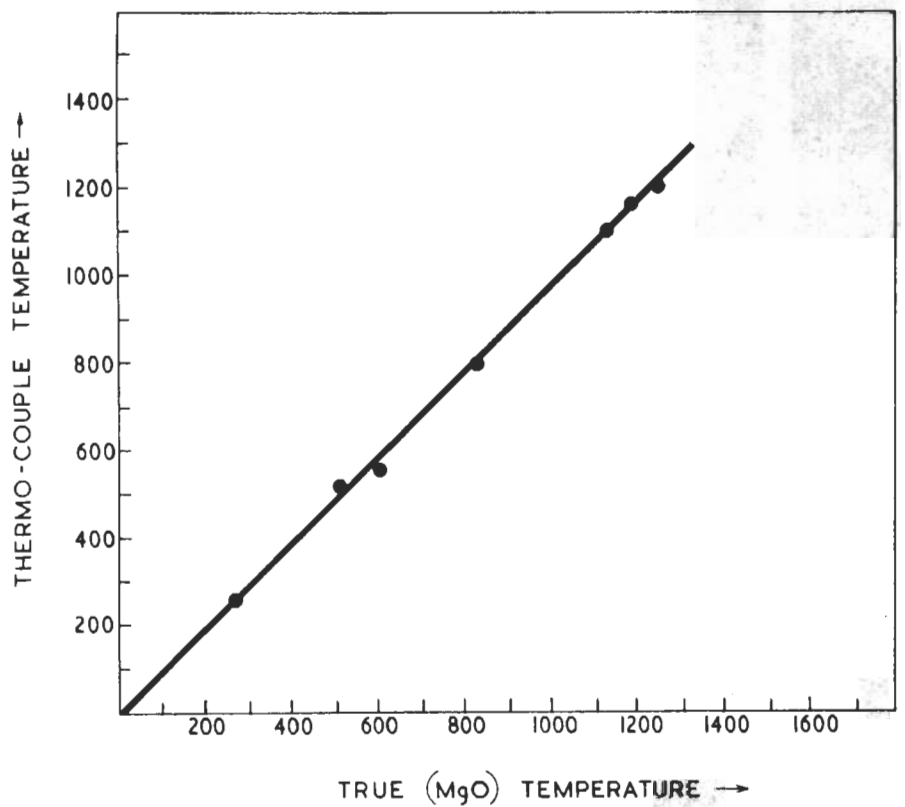
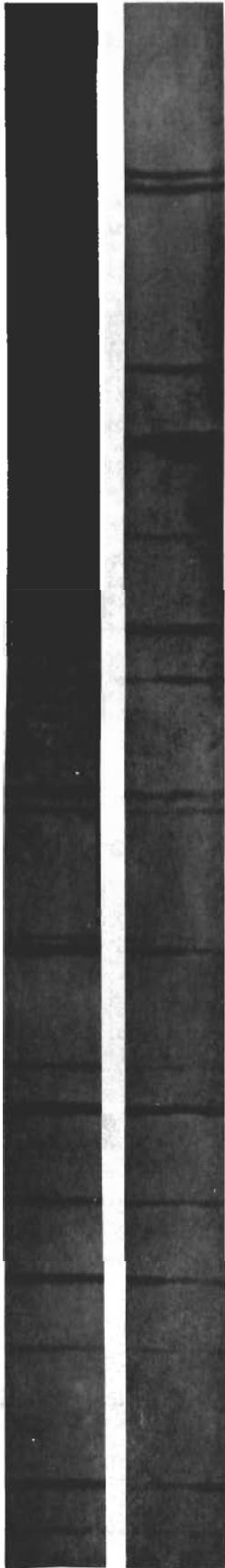


Fig. 2. Calibration curve for high-temperature camera as used in this work.



(a)

(b)

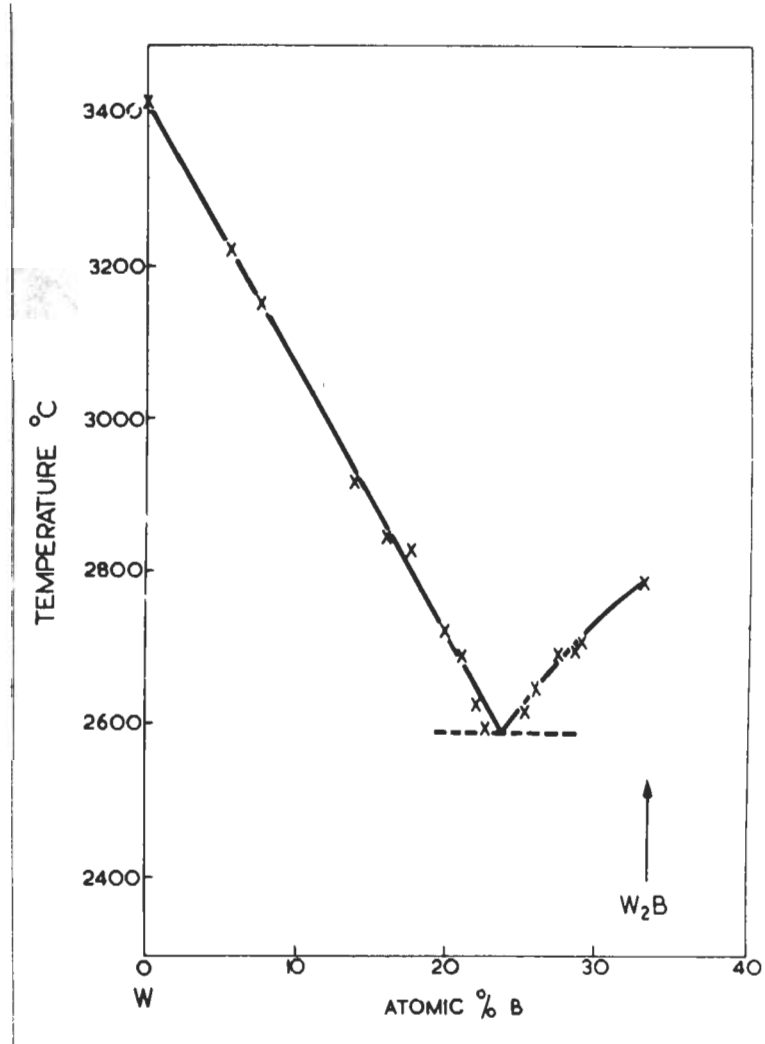


Fig. 4. Liquidus temperature in tungsten-boron system 0-33.1/3 atomic % boron.

Fig. 3. Debye-Scherrer photographs of (a) Carburised and (b) Boridised Wire.

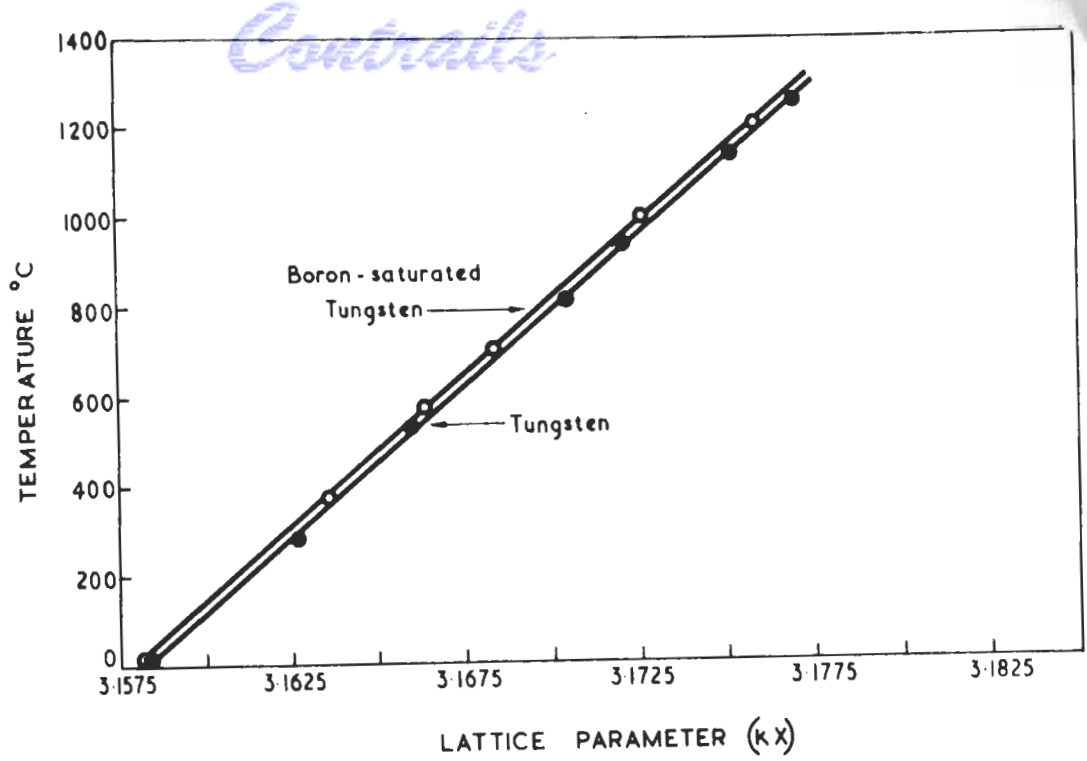


Fig. 5. Lattice spacing/temperature curve for pure tungsten and boron-saturated tungsten.

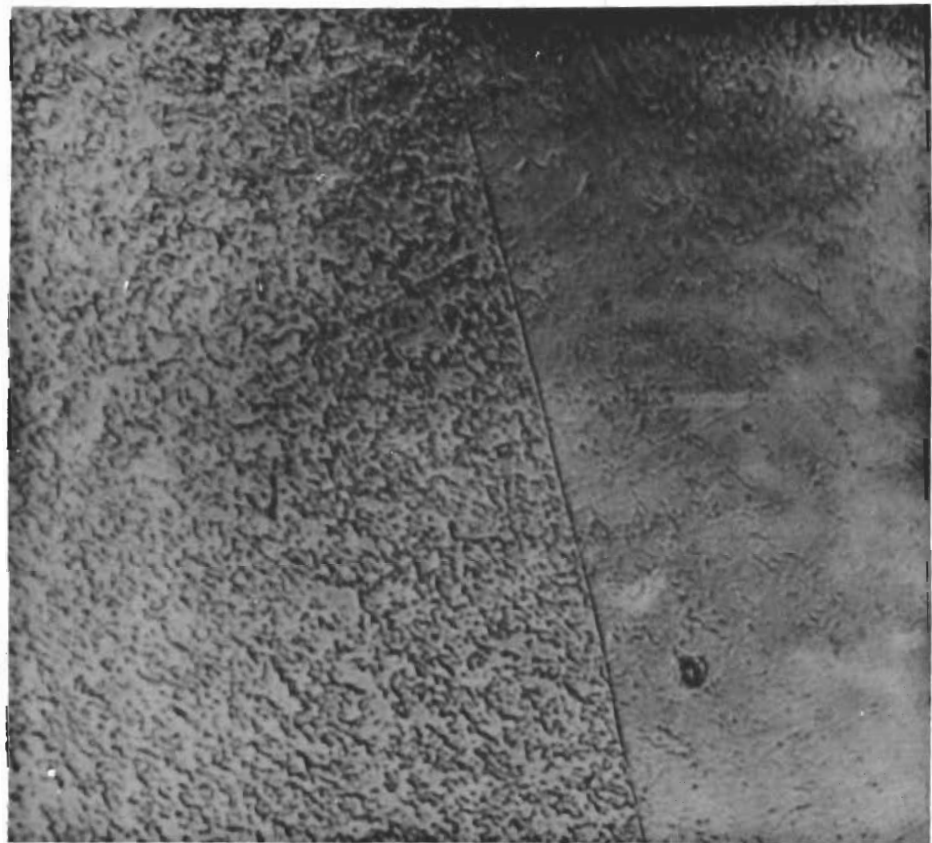


Fig. 6. Etch pitting in pure tungsten. Murakami's reagent. x 800

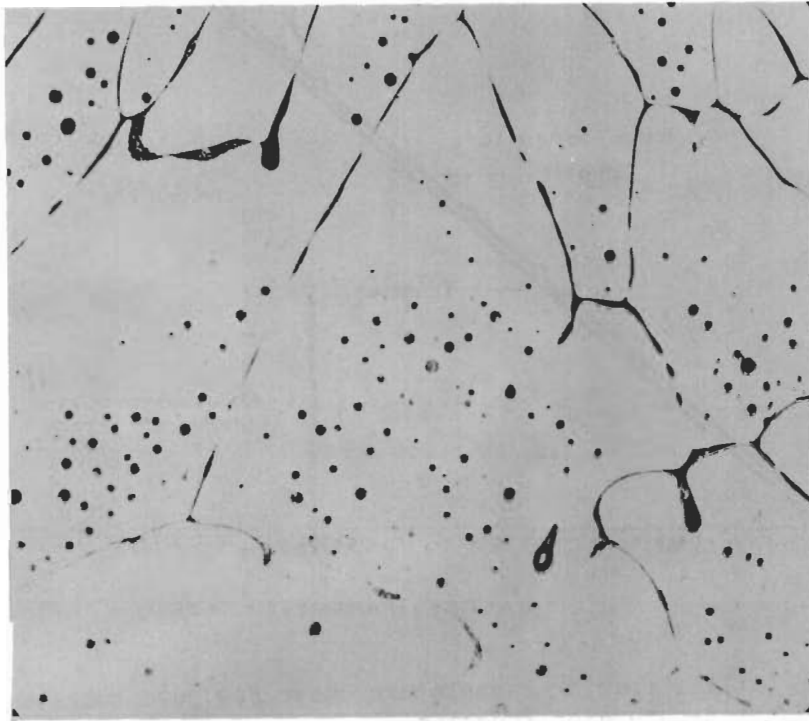


Fig. 7. W-2.00 atomic per cent boron,  
quenched from 2500°C. Electrolytically-  
mechanically polished. x 150

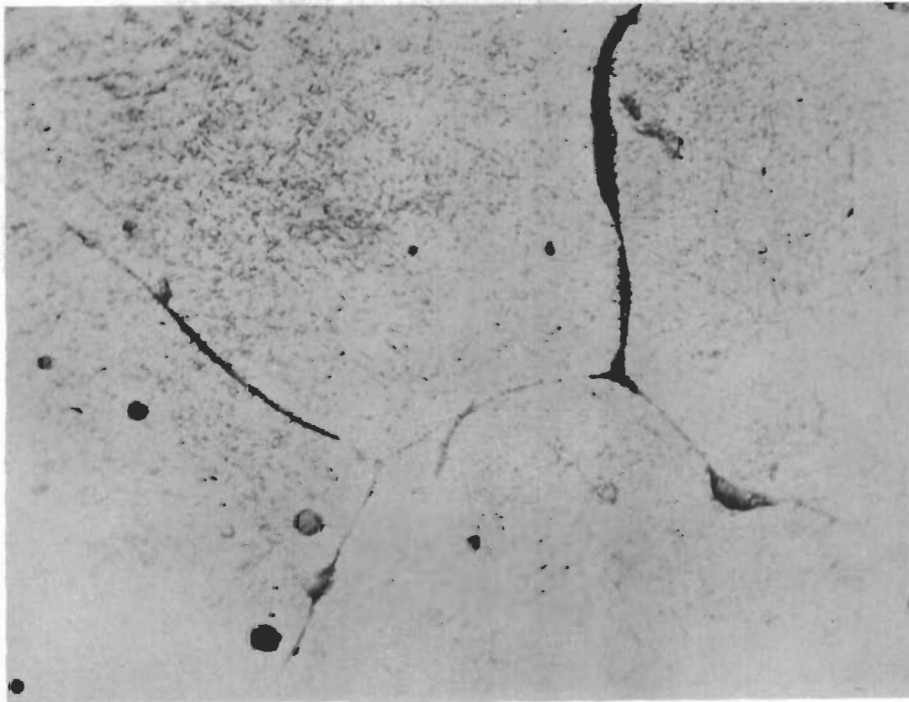


Fig. 8. 1.19% B-W. Quenched from 2500°C.  
Murakami's reagent. x 1000



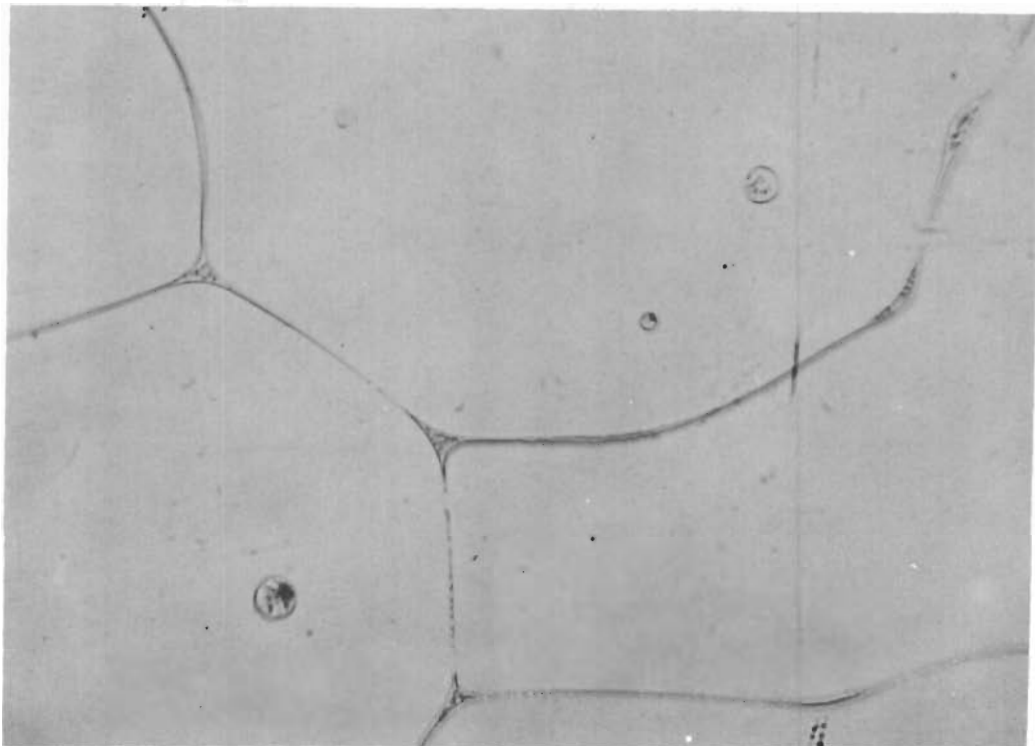


Fig. 9. 0.78 atomic % B-W. Quenched from 2500°C.  
Electromechanically etched.

x 800

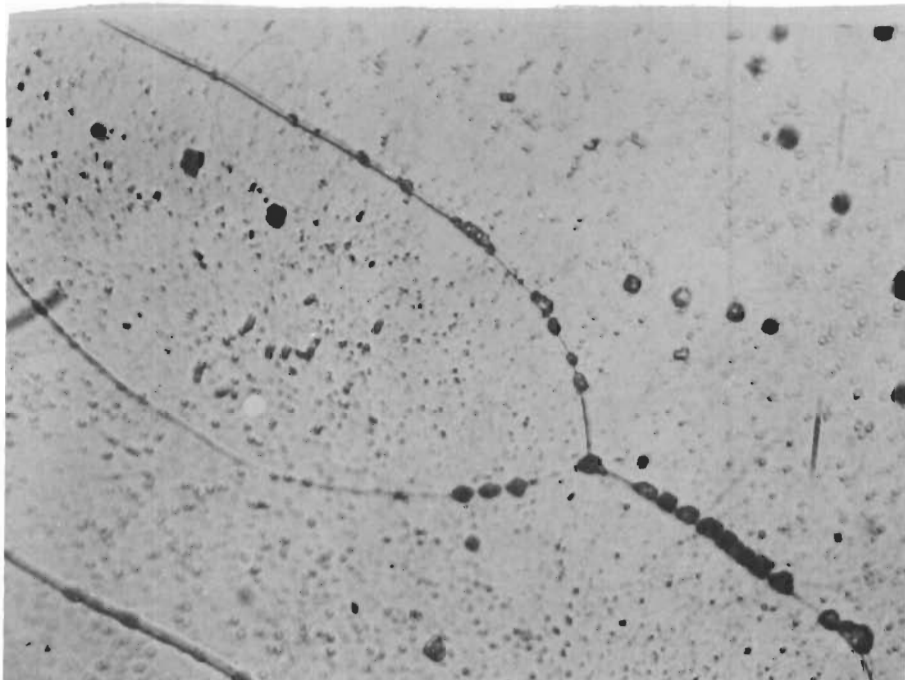


Fig. 10. 0.32 atomic % B-W. Quenched from 2500°C.  
Electromechanically etched.

x 800

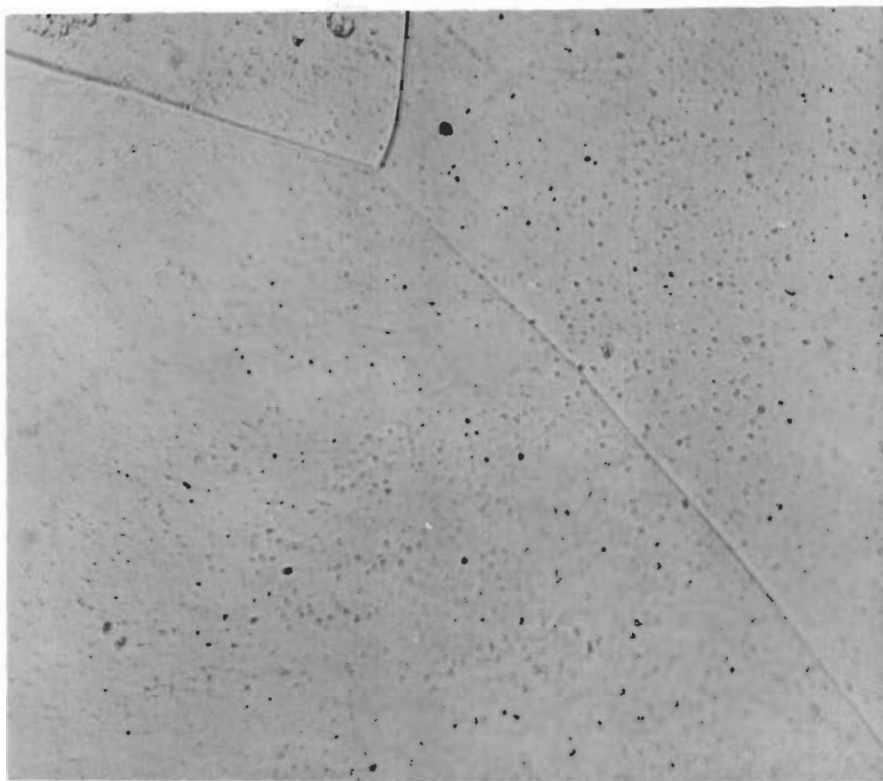


Fig. 11. 0.14 atomic per cent B-W. Quenched from 2500°C. Electromechanically etched. x 800



Fig. 12. 0.78 atomic per cent boron. Quenched from 1000°C. Electromechanically etched. x 800

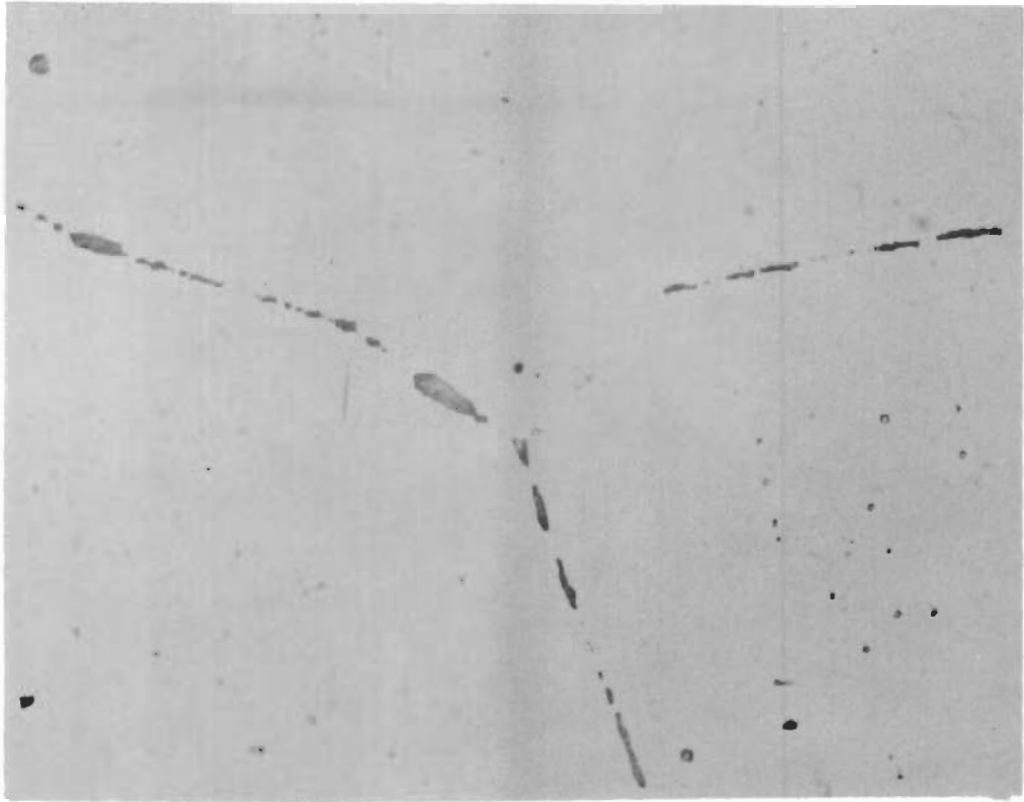


Fig. 13. 0.32 atomic per cent B-W. Quenched from 1000°C. Electromechanically etched. x 800

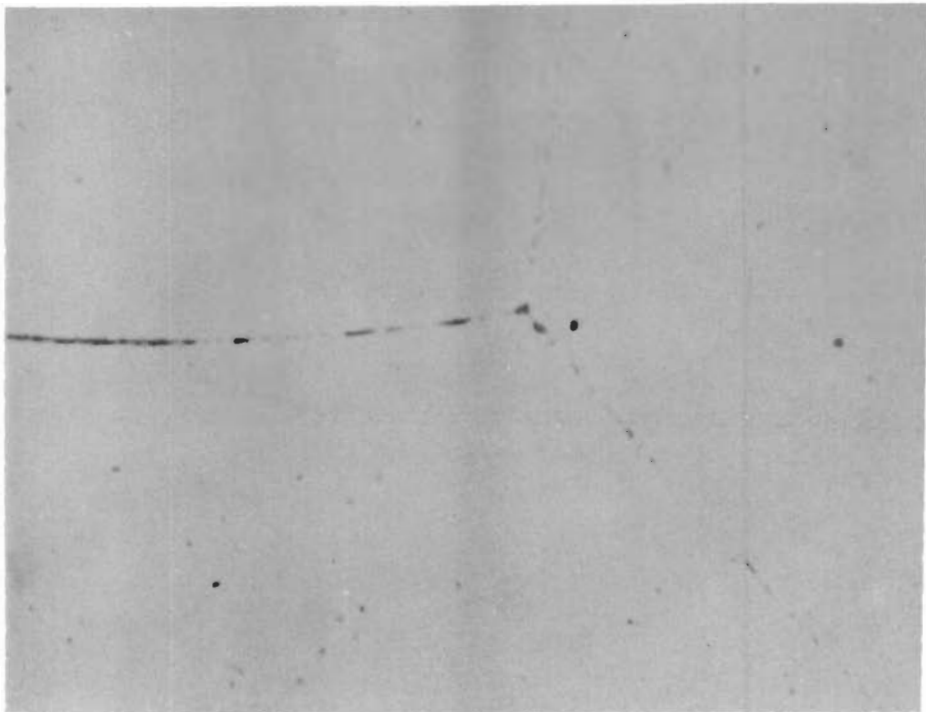


Fig. 14. 0.14 atomic per cent B-W. Quenched from 1000°C. Electromechanically etched. x 800

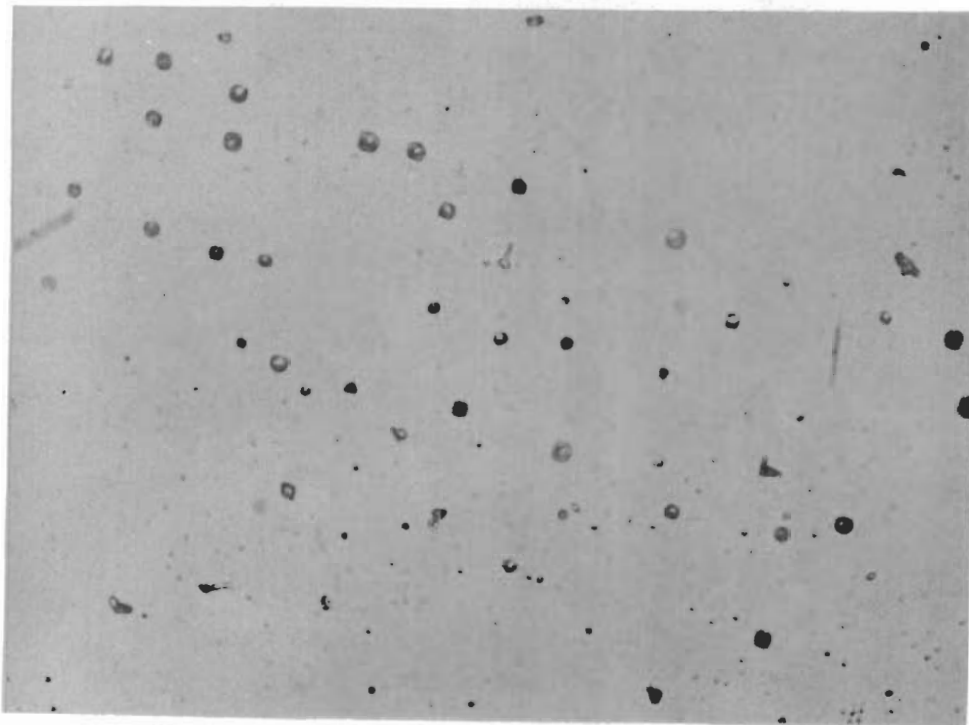


Fig. 15. 0.32 atomic per cent B-W. Quenched from 2500°C, heat treated for 3 hours at 1250°C. Electromechanically etched. x 800

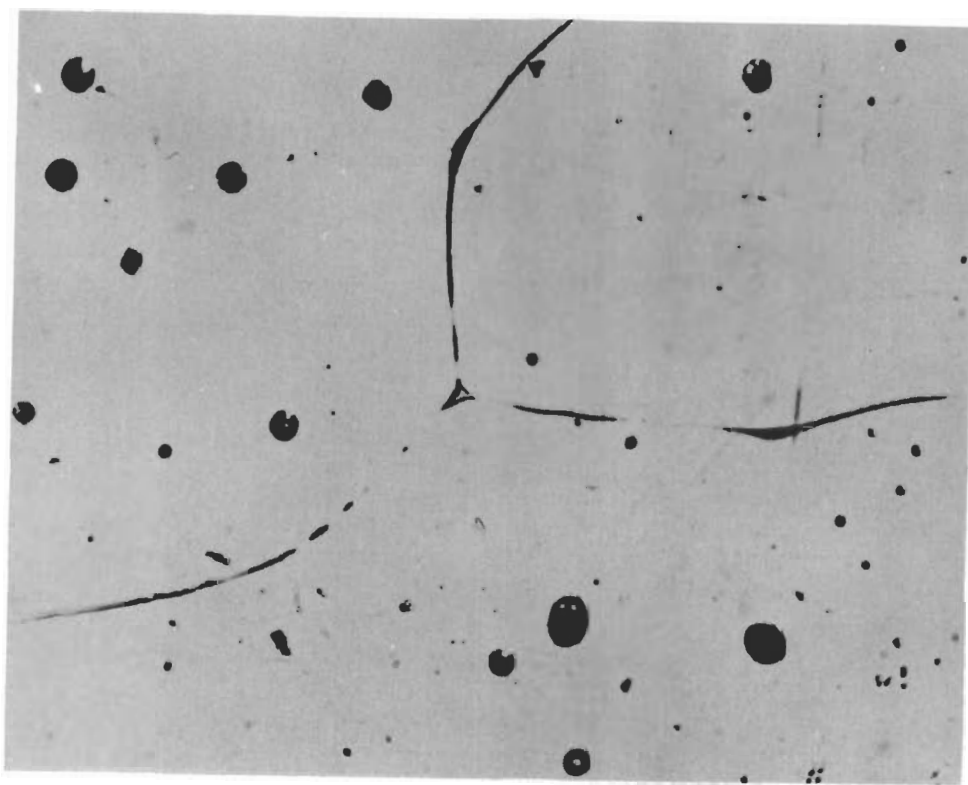


Fig. 16. 0.78 atomic per cent B-W. Quenched from 1000°C. Electromechanically etched. x 800

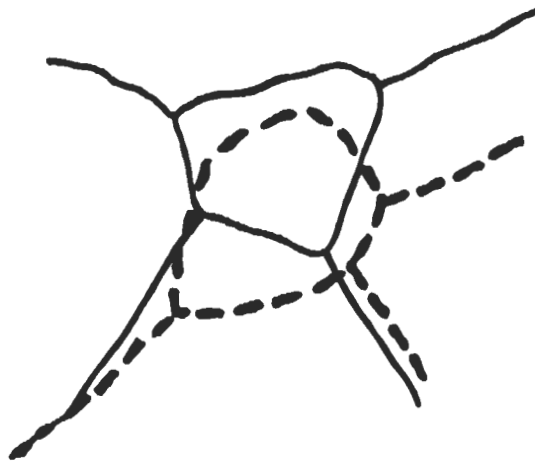


Fig. 17. Schematic diagram of grain growth away from  $W_2B$  precipitate after 2 minutes at  $2500^{\circ}C$  for sample <sup>2</sup> in Fig. 16.

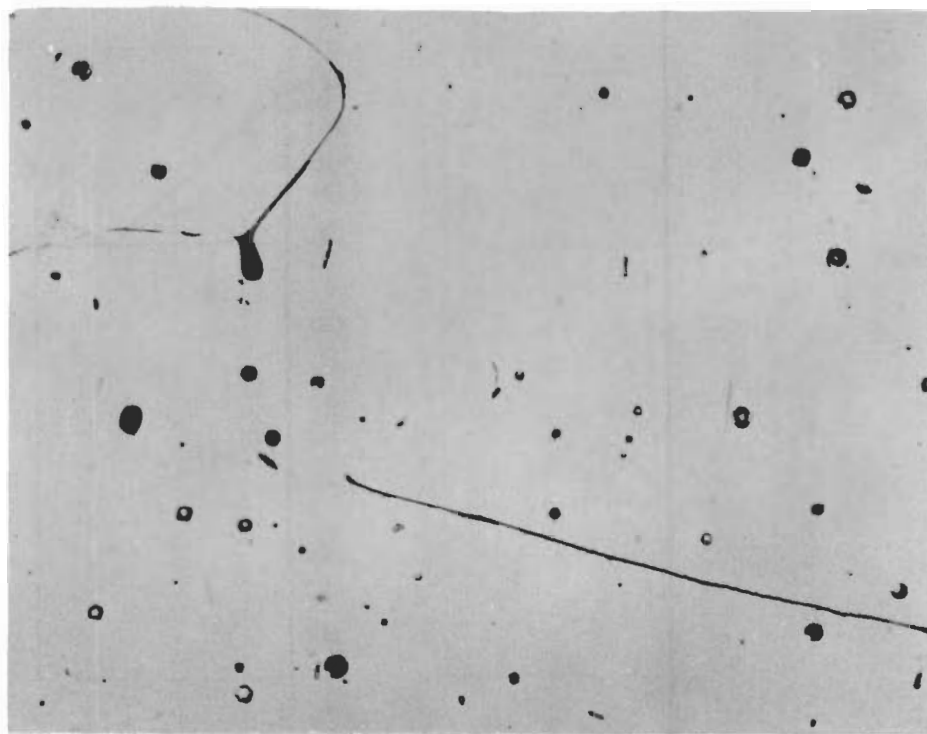


Fig. 18.  $W_2B$  precipitate, formerly outlining the grain boundaries in Fig. 16 beginning to agglomerate after 3 minutes at  $2500^{\circ}C$ .



Fig. 19. Substructure in 0.32 atomic % B-W alloy. x 400

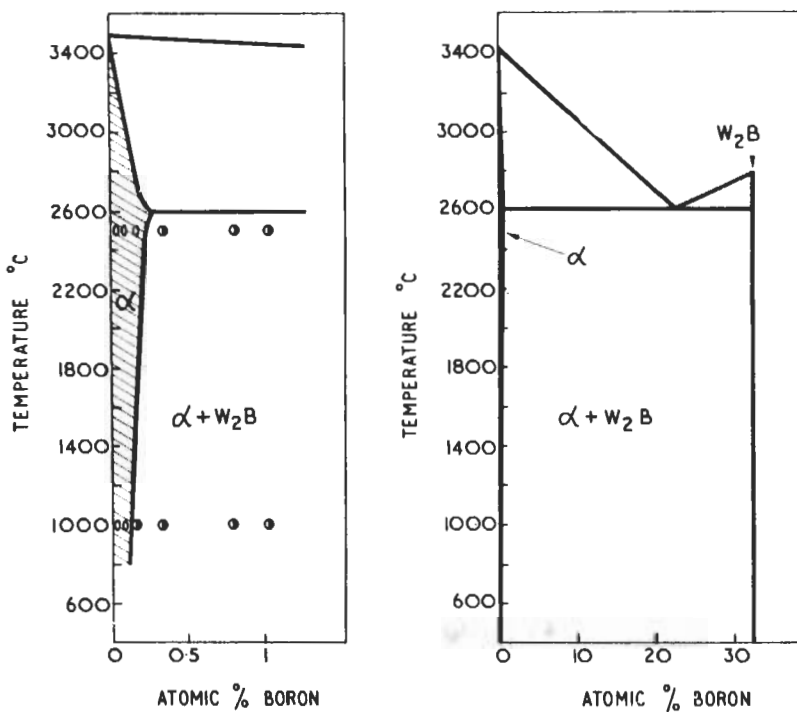


Fig. 20. The proposed W-W<sub>2</sub>B equilibrium diagram.

## SECTION 2. TUNGSTEN-BERYLLIUM SYSTEM

### 1. INTRODUCTION

The tungsten-rich portion of the W-Be phase diagram had so far been entirely unexplored, and the present work had the object of determining the solid-solubility of beryllium in primary tungsten. An attendant problem was that of studying the W-richest compound formed between the two metals. The work also involved a limited consideration of the Be-richer portion of the diagram.

Work on this system is made inherently difficult by the liability to the rapid loss of beryllium at the high temperatures necessary to equilibrate with tungsten, as well as by the health hazard involved.

The principle technique of examination used was that of X-ray analysis for the determination of lattice parameters, and of the constitution of specific alloys; with, however, a limited amount of microscopic and microprobe-analysis work. The high beryllium vaporisation losses experienced initially necessitated the development of a pressure-vessel heat-treatment technique which greatly helped in overcoming these, and in deriving the equilibria.

### 2. PREVIOUS INVESTIGATIONS

No previous work has been done on the solid-solubility of beryllium in tungsten, and any available information concerning this system is confined to the beryllides, with stress on the Be-rich rather than W-rich alloys. A paper by Misch<sup>(1)</sup> describes the beryllides  $WBe_2$  and  $WBe_{13}$ , the former being a hexagonal Laves phase of the  $MgZn_2$  type of structure with  $a^{13} = 4.446 \text{ \AA}$  and  $c = 7.289 \text{ \AA}$ . The  $WBe_{13}$  phase is shown to have a tetragonal lattice of the dimensions  $a = 10.14 \text{ \AA}$ ,  $c = 4.23 \text{ \AA}$ . Paine and Carrabine<sup>(2)</sup> have recently reported the existence of a compound " $WBe_{20}$ " which is cubic ( $a = 11.64 \text{ \AA}$ ) and isomorphous with  $MoBe_{20}$  and  $ReBe_{20}$ .

Passing reference should be made to the recent more general interest in high-Be beryllides as potential compounds for high temperature applications<sup>(3)</sup>, (particularly for attractive oxidation resistance) which included some consideration of tungsten beryllides<sup>(4)</sup>. A compound " $WBe_{22}$ " was here reported, which however may be the same as  $WBe_{20}$ .

It is of interest briefly to consider the broader information available on the solubility of Be in transition metals, although very sparse. A summary of known data, arranged according to the Periodic Table, is given in Table 1. A comparison can be made with tungsten.

TABLE 1

Maximum Solubility of Be in Transition Metals (atomic %)

Group Long Period	IV	V	VI	VII	VIII		
1st	<u>Ti</u> $\beta$ 6 to 13   $\alpha$ <6	<u>V</u> <4.4 at 900°C	<u>Cr</u> 9.2	<u>Mn</u> -	<u>Fe</u> $\alpha$ 33   $\gamma$ -	<u>Co</u> 12	<u>Ni</u> 15.3
2nd	<u>Zr</u> $\beta$ ~2   $\alpha$ -	<u>Nb</u> -	<u>Mo</u> 0.5%	<u>Tc</u> -	<u>Ru</u> -	<u>Rh</u> -	<u>Pd</u> ~0.7
3rd	<u>Hf</u> $\beta$ -   $\alpha$ -	<u>Ta</u> -	<u>W</u> -	<u>Re</u> -	<u>Os</u> -	<u>Ir</u> -	<u>Pt</u> 1.28

The table shows that in the first long period appreciable solubility exists for Be in both the BCC and FCC metals, while in the second period a major decrease occurs. In the third long period there are practically no data.

The Mo-Be system should show some similarity to the W-Be system. This phase diagram has been investigated by Climax Molybdenum Co. (3) and from hardness measurements the solubility of Be in solid Mo (containing up to 0.05 wt.-% carbon) has a maximum of 0.53 a/o at the eutectic temperature. Only a small amount of X-ray work had been carried out, but it was shown that Be contracted the Mo lattice indicating that substitutional solid-solution occurred.

A comparison of some physical properties of W and Be relevant to this investigation is given in Table 2.



TABLE 2

Some Relevant Properties of W and Be

	Beryllium	Tungsten
Crystal structure	Close packed hexagonal a = 2.2810 kX c = 3.5760 kX	Body centred cubic a = 3.1588 kX
Atomic radius	1.13 Å	1.41 Å
Density	1.85 gr/cm <sup>3</sup>	19.3 gr/cm <sup>3</sup>
Melting point	1283°C	3410°C
Boiling point	2400-2970°C *	6700°C
Vapour pressure	<u>°C</u> <u>atmos.</u>	<u>°C</u> <u>atmos.</u>
	1800                      0.01	3940                      0.001
	2100                      0.1	4440                      0.01
	2500                      1.0	5080                      0.1
		5930                      1.0

Variously reported.

The atomic size difference is about 20%, indicating the possibility of a substitutional solid-solution: the incongruity of vapour pressures is clear.

### 3. EXPERIMENTAL

#### 3.1 Alloy Preparation

After careful consideration of the health risks involved, it was decided to have the basic W-Be alloys prepared by another laboratory (The Fulmer Research Institute Ltd.) which was specially equipped to handle beryllium powder. The health hazard necessitated the use of a glove box and other special precautions for most operations, particularly since powder metallurgical techniques were used in alloy preparation. The procedure generally followed that used by Misch<sup>(1)</sup> but with modifications.

The Be powder was obtained from the Consolidated Zinc Corporation, and was of particle size -200 mesh B.S.I. Beryllium oxide was the chief impurity.



TABLE 4

As-weighed Compositions of W-Be Alloys

No.	Be (remainder W)	
	Atomic %	Weight %
1	0.5	0.025
2	1	0.05
3	2	0.10
4	5	0.26
5	10	0.54
6	40	3.2
7	66.7	9.0 (Compound WBe <sub>2</sub> )
8	70	10.2
9	93	39.4 (Compound WBe <sub>13</sub> )

3.2 Homogeneity Tests and Heat-Treatment

The alloys as obtained from Fulmer were examined by X-ray analysis to determine the constitution and to test for the existence of any heterogeneity within them.

Preliminary investigations on the 2 and 5 a/o Be alloys after solution-treatment at 2600°C indicated no change in lattice parameter from pure W and thus the absence of any Be in solid solution. These alloys were later re-heated and melted in the argon arc-furnace, on the assumption that solution in W could thus be enhanced. However, X-ray test again indicated no Be to be present, either in solid-solution or as WBe<sub>2</sub>. It was concluded that Be had been lost by vaporisation and suspected that this may have been already largely the case for the low Be alloys as received.

Homogeneity tests were carried out on the as-received 5, 10, and 40 a/o Be alloys, including spacing measurements and constitutional determinations for various portions of the same alloy. The results are shown in Table 5.

TABLE 5

Homogeneity Data on W-Be Alloys, as-received

Sample (atomic %)	Spacing of primary W (kX)*	Constitution
5% Be, centre of pellet	3.1582	W. No WBe <sub>2</sub> visible.
5% Be, edge of pellet	3.1587	W. No WBe <sub>2</sub> visible.
10% Be, centre of pellet (1)	3.1568	W + WBe <sub>2</sub> , small amount.
10% Be, edge of pellet (1)	3.1581	W. No WBe <sub>2</sub> visible.
10% Be, centre of pellet (2)	3.1570	W + WBe <sub>2</sub> , small amount.
10% Be, edge of pellet (2)	3.1575	W. No WBe <sub>2</sub> visible.
40% Be, pellet (1), area (a)	3.1561	W + WBe <sub>2</sub> , medium amount
40% Be, pellet (1), area (b)	3.1559	" (fairly constant)
40% Be, pellet (2), area (a)	3.1558	"
40% Be, pellet (2), area (b)	3.1563	"

\* Accuracy  $\pm 0.00005$  kX

These results indicated that for the 5 and 10% Be alloys heterogeneity existed between different compacts of the same alloy and also within the pellets themselves. The 40% Be alloy could be considered to be reasonably homogeneous.

In order to try and detect the possible presence of small amounts of WBe<sub>2</sub> in the as-received alloys of low Be content, a series of photographs was taken using a Guinier-Hagg focussing camera. After a 48 hour exposure (at 15 M.A.) the 2 and 5% Be alloys revealed no trace of WBe<sub>2</sub>, but the 10% Be alloy a small amount of this compound.

To verify the X-ray evidence of heterogeneity in the high tungsten alloys and the failure to detect Be in solution in the 2 and 5% Be alloys, it was decided to arrange for chemical analyses. The first

analyses were carried out by Dr. R. C. Chirnside at the Hirst Research Centre of G.E.C. Ltd. Subsequent analyses were carried out in our own laboratories by Mr. P. Stables using the same techniques. The method of analysis is given as an Appendix at the end of the report. The results are shown in Table 6.

TABLE 6

Chemical Analysis of W-Be Alloys

Sample Nominal (atomic %)	Beryllium (weight %)	Nominal (weight %)
1% Be	(a) <0.005 (b) <0.005 (c) 0.006	0.05
5% Be	(a) 0.23 (b) 0.18	0.26
10% Be (a)	(a) 0.35 (b) 0.29	0.54
10% Be (b)	(a) 0.46 (b) 0.23 (c) 0.25	0.54
WBe <sub>2</sub> (66.7% Be)	(a) 6.7 (b) 7.0	9.0

It will be noted that the Be content was significantly lower than the nominal in every case, and in the "1 atomic % Be" alloy was hardly detectable. The difference in Be content between samples of the same alloy indicated considerable heterogeneity. These results confirmed the X-ray indication of non-uniformity.

It was thus decided to concentrate a large part of the work on the 40% Be alloy for lattice spacing studies which, apart from relative homogeneity, had the advantage of fairly high WBe<sub>2</sub> content enabling the spacings of both the tungsten solid-solution and the compound WBe<sub>2</sub> to be determined accurately. It also allowed some tolerance to Be loss during heat-treatment, whilst still in the two-phase regions.

The first technique used was to anneal the alloy in powder form inside a tungsten block containing a cavity for holding the sample and

for temperature measurement with an optical pyrometer under approximately black-body conditions. In this series of experiments the alloy was heated in the argon arc-furnace by applying the arc to the exterior of the tungsten block to various temperatures, from which they were quenched. The objective was to obtain a lattice-spacing/temperature graph by annealing the alloy at a series of temperatures. Even with this alloy, however, difficulties were encountered with Be loss at temperatures above 1800°C.

For higher temperatures a pressure-vessel system was devised and is shown in section in Fig. 1. The sample is placed in a small tubular-drilled tungsten-container with a tight-fitting carrying-rod which acts as a stopper. The whole arrangement is heated in a tantalum-tube furnace where temperatures up to 2500°C could be attained. By this technique Be loss was eliminated or at least greatly reduced and even molten Be-bearing alloys could be produced.

A technique was developed for producing dilute beryllium alloys by first preparing standard mixtures of the 40% Be alloy and pure tungsten. The respective powders were passed through a 380 mesh sieve and intimately blended in a rotating mixer. The powder mixtures were then packed into a tungsten pressure-vessel and heated in the tube furnace to varying high temperatures (1800-2500°C). In the process, diffusion and sintering to a solid mass occurred and homogeneous equilibrated alloys were produced. The alloys could be said to be homogeneous since X-ray analysis of different portions revealed lattice spacings and constitution to be constant. By this method it was possible to obtain significant results in delineating the solubility limit of Be in W. Dilute alloys were produced in sufficient quantity for chemical and X-ray analysis and for microscopic examination.

A limited investigation was carried out on W-Be alloys using an electron probe microanalyser, with the idea of possible direct determination of the solubility limit. This will be detailed later.

## 4. RESULTS

### 4.1 Preliminary Experiments

A general X-ray constitutional survey was made of the alloys as prepared by Fulmer and results are given in Table 7.

TABLE 7

Constitution of W-Be Alloys, as received

Alloy (atomic %, nominal)	Constitution (observed)
0.5% Be	W pure - no compound.
1.0% Be	W pure - no compound.
2% Be	W pure - no compound.
5% Be	W-Be solid solution - no compound.
10% Be	W-Be solid solution + $WBe_2$ (small amount).
40% Be	W-Be solid solution + $WBe_2$ (medium amount).
66.7% Be (= $WBe_2$ , nominal)	$WBe_2$ + W small amount.
70% Be	$WBe_2$ of spacing larger than in the 66.7% alloy. Possibly trace of W and a further phase.
93%	$WBe_{13}$ . Small amount of further phase ( $WBe_{20}$ ).

At this stage, lattice-spacing changes through Be solid-solution in primary tungsten were observed, namely contractions. The decrease throughout showed the solution to be substitutional. Another interesting feature was that appreciable lattice parameter variations occurred within the beryllide  $WBe_2$  indicating that a limited W  $\longleftrightarrow$  Be homogeneity range for the compound existed.

The above results indicated that a reasonable approach to equilibrium had been achieved with the higher beryllium alloys, the two compounds  $WBe_2$  and  $WBe_{13}$  being formed at the approximately correct Be levels. In the 70 and 93% a/o Be alloys there is evidence of additional phases and in the 93% alloy the additional interplanar spacing values correspond to those of  $WBe_{20}$ <sup>(2)</sup>.

A large proportion of the work carried out on this system has been devoted to various heat-treatments of W-Be alloys followed by determinations of the resulting lattice-spacings of the primary tungsten and  $WBe_2$  phases. Several methods of heat-treatment were investigated and a series of lattice-spacings for a range of temperatures was obtained. The spacing results obtained using a hollow tungsten block heated in the arc furnace are given in Table 8.

TABLE 8

Constitution and Lattice Spacing Results after various Heat-Treatments:  
(40% Be alloy throughout)

Heat Treatment	Spacing of Primary W (kX)	Constitution and Remarks
Pure W	3.1588	W
Alloy "as received"	3.1560	W + $WBe_2$
1400°C, 60 mins	3.1565	W + $WBe_2$ } .
1550°C, 40 mins	3.1561	W + $WBe_2$ } .
1650°C, 30 mins	3.1567	W + $WBe_2$ } .
1750°C, 20 mins	3.1560	W + $WBe_2$
2000°C, 6 mins	3.1563	W + $WBe_2$ . Only trace of $WBe_2$ present.
2000°C, 12 mins	3.1573	W only: shows that Be loss increased with time.
2160°C, 1 min	3.1560	W + $WBe_2$
2320°C, 2 mins	3.1573	W only: high loss by vaporisation, no $WBe_2$ .
2600°C, ½ min	3.1558	W + $WBe_2$

Using the above method of heat-treatment the spacing results show a small variation up to 2000°C. On exposing at 2000°C and above for any length of time, vaporisation of Be became severe, making it impossible to attain an equilibrium condition. The annealing times of ½ minute at 2600°C and 1 minute at 2000°C did not



# Contrails

appear to have been long enough to change the state of the samples from that of the "as received" condition.

In an attempt to reduce beryllium loss, a further series of anneals was carried out using solid pieces of alloy, the centre portion of which was extracted after heat-treatment for X-ray analysis, on the assumption that the outer layers would act as a protective shell to the core. Results are given in Table 9.

The results indicated that beryllium was still being lost using this method, and even at 1800°C there was a considerable loss of Be, the vaporisation increasing with increasing annealing time.

For high temperature equilibria, therefore, it was essential to use a sealed system, if possible with beryllium overpressure and the tungsten pressure vessel had to be used. Results obtained by this technique on the 40% Be alloy are shown in Table 10.

In this case the X-ray constitution showed that Be loss had been greatly reduced. The primary tungsten spacing was constant between 1800°C and 2150°C, the value being 3.1560 kX which is identical to the "as received" value.

To supplement the lattice spacing/temperature data for low temperature equilibrium, the 40% alloy was given anneals at various temperatures down to 1000°C. The 1000°C anneal was carried out after the alloy (as received) had been sealed in an evacuated silica tube. The remaining treatments were carried out in the tantalum tube furnace. The results are given in Table 10.

TABLE 9

Lattice Parameter Results on Samples Extracted from the centre of Solid Pieces (40% Be Alloy)

Sample	Lattice Spacings (kX)		
	Primary W a	WBe <sub>2</sub>	
		a	c
Pure W	3.1588	-	-
40% alloy, as received	3.1560	4.478	7.354
1800°C, 25 mins	3.1558	4.465	7.346
1800°C, 60 mins	3.1569	Trace compound present	
1900°C, 20 mins	3.1569	4.462	7.338
2000°C, 14 mins	3.1566	Trace compound present	

TABLE 10

X-ray Results on Samples Heated in the Pressure Vessel (40% Be Alloy)

Treatment	Spacing	Constitution
1800°C, 60 mins	3.1561	W + WBe <sub>2</sub>
2000°C, 3 mins	3.1561	"
2050°C, 20 mins	3.1562	"
2150°C (molten)	3.1561	"
2150°C (molten)	3.1560	"

Lattice Parameter Results on 40% Be Alloy, Pressure Vessel  
Treated at Lower Temperatures

Treatment	Lattice spacing of primary W (kX)
1000°C, 1 week	3.1573
1000°C, 1 month	3.1573
1300°C, 6 hours	3.1572
1400°C, 1 hour	3.1565
1400°C, 2 hours	3.1567
1400°C, 3 hours 10 mins	3.1568

An experiment to gain an indication of the eutectic temperature in the system W-WBe<sub>2</sub> was carried out by observation of sintering and melting of the 40% beryllium alloy-powder after annealing in the tantalum-tube furnace in a pressure-vessel, and quenching from a series of increasing temperatures. Results obtained are given in Table 11.

TABLE 11

Observations concerning Eutectic Temperature (40% Be Alloy)

Temperature (°C)	Observation
1575	No sintering occurred.
1720	"
1800	Slight sintering.
1920	"
2010	Further sintering but powder still friable.
2050	Similar to above.
2150	Alloy molten.

The eutectic temperature was thus located as lying between 2050°C and 2150°C, and in view of the sudden transition from loose sintering to a molten aggregate it is estimated that the 40% Be alloy is close to the eutectic composition.

The WBe<sub>2</sub> alloy (66.7% Be) was heated to 2250°C in a pressure-enclosure and found to be molten, indicating that the melting point of WBe<sub>2</sub> lies between the eutectic temperature (≈ 2100°C) and 2250°C.

## 4.2 Principal Experiments

### 4.21 Solubility-Limit Studies

Using the technique of diluting the 40% Be alloy with tungsten to produce high-tungsten alloys (as described previously) followed by homogenising at high temperature, further significant results were obtained. A mixture reacted at 2500°C was found by chemical analysis to contain 6.7% Be; both microscopy and X-ray analysis here indicated the presence of a small amount of WBe<sub>2</sub>. The lattice parameter of the primary tungsten was 3.1566 kX, in line with substitutional solid-solution of Be approaching its maximum: the latter corresponding to a lattice-parameter of approximately 3.1560 kX. Another mixture reacted at 2500°C and analysed as 2.97% Be was found to be single phase by X-ray examination and microscopy. The lattice-parameter of the primary tungsten in this case was 3.1572 kX, also indicating (as it did constitutionally) that this alloy was within the solubility-limit of Be in W. The solubility-limit can therefore be bracketed between 3 and 6.7% Be.

A considerable amount of work was carried out on these W/40% Be alloy mixtures in the pressure-vessel arrangement with the view to locating the solid-solution boundary more closely. However, this did not succeed (without the supplementary evidence below) since all the low Be mixtures on reaction in the pressure-vessel yielded lattice-parameters of 3.1572 kX or greater. The equilibrium lattice-parameters for different temperature levels, using the pressure-vessel technique, are summarised in Table 12.

It was of some additional interest to see whether any phase transformation might possibly occur in WBe<sub>2</sub> at relatively low temperatures. The alloy was therefore annealed at 1000°C inside a small W pressure-container, which was itself sealed into an evacuated silica tube. The sample was heat-treated for periods of firstly, a week, secondly a month. After these treatments certain additional diffraction lines appeared, suggesting the

possibility of the existence of a low temperature phase. Some additional lines were observed also after other low-temperature heat-treatments, but not in all cases. The indication thus is of the possible occurrence of a new low-temperature form, but this would require confirmation.

TABLE 12

Equilibrium Lattice-Spacings of the W-Be  
Solid-Solution

Temperature (°C)	Lattice Parameter (kX)
1000	3.1573
1300	3.1572
1400	3.1568
1650	3.1560
1800	3.1561
2000	3.1561
2050	3.1562
2150	3.1561
2500	3.1566

The spacing is seen to be constant to  $\pm 0.0001$  kX between 1650 and 2150°C (eutectic temperature) indicating that the solubility of Be is constant over this temperature range. As reported above, a lattice-spacing of 3.1572 kX corresponds to a Be solubility of 3% and therefore the solubility at 1000 and 1300°C can be said to be about this value. Assuming a linear lattice-spacing change with Be content (i.e. that Vegard's law holds for the system) the minimum lattice-spacing (3.1560 kX) would correspond to a solubility of about 5 atomic % Be, and in view of the 3% Be solubility at 1000°C, and the fact that the 6.7% alloy already contains significant amounts of compound, it is possible to conclude that the maximum solubility-limit lies between 4 and 6% Be.

An attempt was made to determine the solubility-limit using the 40% Be "as-received" alloy and comparing this with standard mechanical mixtures of the two constituents; the technique however, was found to be too insensitive to obtain significant results. Another attempt was made to bracket the solubility by controlled vaporisation of  $WBe_2$  from a 40% Be alloy. The idea was to produce an alloy with Be in solid-solution, but with successive reduction in  $WBe_2$  through vaporisation loss to vanishing point. This condition however was found extremely difficult to achieve and there was a complication in that Be was lost from the solid-solution at the same time.

#### 4.22 $WBe_2$ Studies

The hexagonal lattice dimensions of the compound  $WBe_2$  (Laves phase) were also measured after the various heat-treatments of the 40% Be alloy. In an attempt to compare the lattice dimensions on either side of the homogeneity range, the 70% Be alloy was also heat-treated and the lattice constants determined. The dimensions obtained for both alloys are shown in Table 13. The mean volumes-per-atom in the hexagonal unit cell have also been evaluated as shown. The values obtained by Misch<sup>(1)</sup> are shown for comparison.

TABLE 13

Lattice Dimensions of WBe<sub>2</sub> after Various Treatments

Alloy and Heat-Treatment	Lattice parameters (kX units)			
	a	c	c/a	Mean atomic volume kX
Values obtained by Misch	4.437	7.274	1.639	
70% Be as-received (1650°C)	4.569	7.414	1.644	9.79
70% Be 1700°C (40 mins)	4.505	7.403	1.643	9.76
70% Be 1800°C (20 mins)	4.457	7.328	1.644	9.45
70% Be 2000°C (5 mins)	4.474	7.355	1.644	9.56
40% Be as-received	4.478	7.354	1.642	9.58
40% Be 1800°C (25 mins)	4.465	7.346	1.645	9.51
40% Be 1800°C (40 mins)	4.458	7.324	1.643	9.45
40% Be 1900°C (20 mins)	4.462	7.338	1.645	9.49
40% Be 2050°C (20 mins)	4.450	7.318	1.645	9.41

The figures obtained on the 40% Be composition which gave lattice-spacing/temperature values for the W side of the WBe<sub>2</sub> homogeneity range, are seen to decrease with increasing temperature, indicating a change in Be content with temperature.

It was expected that from the 70% Be alloy a similar set of values would be obtained for the Be-side of the homogeneity range. However, a complication arises in that this alloy contains a small amount of free tungsten in the "as-received" condition and after heat-treatment. The spacing values obtained therefore would not necessarily correspond to equilibrium for the Be-side of the WBe<sub>2</sub> homogeneity range. The spacing values obtained for

# Contrails

the 1800°C treatment are almost identical to those for the 40% alloy. This is explained by Be loss during the experiments as revealed by X-ray analysis showing an increase in free tungsten. In general, however, the spacing values obtained using the 70% alloy are larger than the corresponding 40% values and decrease with increase in temperature. The overall maximum dimensions for the WBe<sub>2</sub> phase are those "as-received" for the 70% Be alloy: the minimum<sup>2</sup> those for the 40% alloy at 2050°C. The calculated interplanar spacings for the maximum and minimum lattice constants are given in Table 14. In the two "as-received" alloys, the 70% lattice constants are the larger, implying that an increase of Be in the WBe<sub>2</sub> lattice has the effect of expanding it: an effect opposite to that in the primary W solution. Straight W ↔ Be substitution in WBe<sub>2</sub> ought to have caused a contraction; a possible explanation could be the presence of vacancies in the WBe<sub>2</sub> lattice at the W-end of the homogeneity range which are progressively filled with Be atoms on traversing it towards the Be-rich end. The lattice dimensions of WBe<sub>2</sub> decrease with increasing temperature implying that the number of vacancies increase with temperature and that the W-rich WBe<sub>2</sub> phase boundary advances towards the W-end.



TABLE 14

Interplanar Spacings for  $WBe_2$  (Å)

For minimum lattice constants d	For maximum lattice constants d	Intensity	hkl
3.86	3.97	W	100
3.67	3.72	W	002
3.42	3.50	W	101
2.66	2.72	W	102
2.229	2.290	VS	110
2.065	2.099	VS	103
1.931	1.982	VW	200
1.905	1.949	S	112
1.834	1.857	VW	004
1.709	1.749	VW	202
1.516	1.547	S	203
1.459	1.499	W	210
1.432	1.469	W	211
1.356	1.390	S	212
1.330	1.356	W	204
1.288	1.322	S	300
1.254	1.282	VS	213
1.214	1.246	W	302
1.145	1.160	S	205
1.115	1.144	M	220
1.071	1.099	W	310
1.035	1.055	S	215
0.981	1.005	W	313

VS = very strong      M = medium      VW = very weak  
 S = strong            W = weak

## 4.23 Microscopic Examination

The microscope has had limited use in this investigation since most of the work has been done on sintered alloys which were porous and non-consolidated. The three photomicrographs shown refer to alloys produced by the pressure-vessel technique. The structure in Fig. 2 was obtained by annealing the 40% Be alloy at 2200°C. The sample consisted of a fillet of pure W-WBe<sub>2</sub> eutectic which had permeated between the tungsten-container and the central carrying rod. Fig. 3 shows another part of the melted 40% Be alloy, consisting of spherical islands of primary W-Be solid solution in a background of WBe<sub>2</sub> eutectic. (This structure was investigated under the microprobe analyser, but due to the presence of porosity in the sample it was not possible to obtain any significant estimate of Be-contents by this means.) Figs. 2 and 3 give direct evidence that W and WBe<sub>2</sub> form a eutectic (at 2100°C, as determined above).

Fig. 4 shows the 6.7% Be alloy produced by sintering at 2500°C. The background is W-Be solid-solution and the precipitate WBe<sub>2</sub> in grain-boundary regions. The dark area is typical of the porous nature of the alloys.

## 4.24 Microprobe Analysis

It was thought attractive to try to determine the solubility limit of Be in W and the composition of the compound by microprobe analysis. Beryllium of course is too light an element to be detected at the present, but it was hoped that the local tungsten concentrations could be revealed by difference and by comparison with standard pure tungsten. This was undertaken with the kind help of Mr. T. Mulvey of the A.E.I. Research Laboratories, Aldermaston (who is a pioneer in this field and was in fact responsible for the original development of the A.E.I. microprobe analyser). Initial attempts were vitiated by micro-porosity and asperities of the surface which were unavoidable in the partly melted samples. However, more success was achieved by a W-Be sample which had completely melted. It was the same as that shown by micrograph in Fig. 3, namely the fillet of [(W, Be) + WBe<sub>2</sub>] eutectic between two tungsten faces. Fig. 5 (a) shows an electron scanning picture of this. The contrast is here reversed compared with the optical micrograph, otherwise the details are similar. Also shown in Fig. 5 (b) is a specimen current scan record taken across the eutectic. Here the peaks correspond to the composition WBe<sub>2</sub>, as determined accurately by Mr. Mulvey by point analysis using the tungsten L<sub>α</sub> line. The troughs correspond

to the W solid-solution. The trough composition is very close to that for pure tungsten: so close in fact that a reliable quantitative estimate of Be in solution was not possible. The A.E.I. estimate is here only the descriptive one of "a few atomic per cent" Be in W solid solution, and indeed entirely consistent with our own results. The scan does however confirm  $WBe_2$  as the compound, and the micro-scan difference between pure W and the Be-saturated W is visually well apparent on the instrument. (Note: This microprobe analysis, being on a friendly basis, had here necessarily to be curtailed; however, the first indications are encouraging and, if there is an opportunity, would make a further, more quantitative microprobe study well worthwhile.) One incidental fact arising from the scan (Fig. 5 (b)) is that of dimensions: the size of W and  $WBe_2$  particles being of the order of 1 to 2 microns.

## 5. DISCUSSION AND CONCLUSIONS

The results obtained may be summarised as follows:

- 5.1 The solid solubility of Be in W is considerable. It is in the order of 5 atomic % Be, at the eutectic temperature, although the value can at this stage be bracketed to no closer than between 4 and 6% Be.
- The solubility-limit does not vary appreciably with temperature between 2100 and 1800°C; it decreases to approximately 3% Be in the range 1000 to 1300°C.
- 5.2 The solid-solution is substitutional with a maximum contraction of the tungsten lattice from 3.1588 to 3.1560 kX, i.e. by 0.09% (linear).
- 5.3 The tungsten-richest compound formed was shown to be the diberyllide, and the system between the (W, Be) solution and  $WBe_2$  is a eutectic one.
- 5.4 The eutectic temperature was located as between 2050 and 2150°C, and the eutectic composition at around 40 atomic % Be.
- 5.5 The compound  $WBe_2$  is confirmed to be a Laves phase (hexagonal  $MgZn_2$  type structure)<sup>2</sup>, and found to possess a significant homogeneity range  $(WBe_2 \pm x)$  with the following range in lattice dimensions:  
Minimum  $(W\text{-rich end})$   $a = 4.550, c = 7.318$  kX;  $c/a = 1.645$ .  
Maximum  $(Be\text{-rich end})$   $a = 4.569, c = 7.414$  kX;  $c/a = 1.644$ .

This compares with values given by Misch of  $a = 4.437$ ,  $c = 7.274$  kX,  $c/a = 1.639$ . A recession with temperature of the W-rich  $WBe_2$  phase-boundary is indicated by spacing variations.

It would appear therefore that the solid solution within the  $WBe_2$  lattice (in contrast to that in W) is not one of substitution of W atoms by Be, but that probably vacant Be sites in the Laves phase lattice are successively occupied; however structural verification of this effect would be of interest.

The melting point of  $WBe_2$  was found to be not far above the eutectic temperature, and certainly below  $2250^\circ\text{C}$ .

5.6 The results have been summarised in the form of a tentative phase-diagram shown in Fig. 6.

The principal difficulty throughout this investigation was that introduced through the incongruity in vapour-pressure between W and Be, and by the interfering effect of beryllium loss and its control. This shows itself in many facets, particularly the unpredictability of Be content after any one heat-treatment and the possible appearance of heterogeneity even in any one sample. However, this could be largely overcome by the pressure-enclosure technique, although it still makes the data less complete or precise than had been hoped. The vapour-pressure of Be increases from  $10^{-2}$  to 1 atm. between 1800 and  $2500^\circ\text{C}$ , which is the main range of present interest. Also the compound  $WBe_2$  suffers from the fact that its stability is pressure-sensitive. Thus, for example, on heating to high temperatures under atmospheric (argon) pressure the phase dissociated into its component elements instead of melting, and only by heating in the pressure-vessel could it be melted.

Structurally the occurrence of the finite homogeneity range of  $WBe_2$  seems of special interest in this connection. One might well interpret the above vacation of Be lattice-sites within the Laves phase (spacing increases with Be content) as already a sign of the relatively weak bonding of Be atoms within this structure, and as a "lattice evaporation" preceding the full decomposition of the structure: assisted by the already intense thermal vibrations of the Be-atoms. A corresponding interpretation can of course be given to the effects observed in the primary W-Be solution, with its extremely easy loss from the BCC lattice. Only here the lattice-spacing change occurs in the opposite sense, because, owing to its size, the Be atoms are held substitutionally, however loosely so.

Considered overall, therefore, we might say that the first addition of Be to W caused their substitutional entry into the body-centred cubic lattice, but that even here the vibrational energy of the Be atoms is so great that bonding is only a very loose one and their escape readily facilitated by

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The term "distillation" of Be from the lattice sites might not be amiss.

external factors (temperature, reduced pressure etc.). The excess beryllium would (a) (at high temperatures) appear in immediate gaseous form, co-existing with the solid W-solution, and (b) (at lower temperatures) tend to transform those BCC parent lattice regions where it is already segregated in higher concentrations\* into configurations of Laves phase ( $WBe_2$ ) type. This can probably already occur on a micro-scale for compositions lower than those corresponding to equilibrium saturation, owing to local Be fluctuations. Then upon reaching saturation the  $(W, Be) \rightarrow WBe_2$  transformation will of course become massive.

The Laves-phase structure is known in numerous transition-metal base systems as precipitating from the primary BCC solutions, and implies an atomic rearrangement to achieve maximum close-packing of the two atom-species (discussed in some detail in ref. 6). In the present case the Laves-phase beryllide would, at the W-end, initially have deficient Be atom-sites, which may be readily filled or vacated within the limited non-stoichiometric range  $WBe_{2-x}$ . A practical consequence of such lattice holes is that they invite occupation by certain third (impurity) atoms.

Another, favourable, implication of this loose bonding of Be atoms in the tungsten beryllide is that, under oxidising conditions at high temperatures, some of the Be would diffuse to the surface to form a thin adherent BeO film; this probably would in part account for attractive oxidation resistance which this and other transition metal beryllides are known to have.

Comparing the W-Be and the W-B systems, although the vapour-pressures of Be and B are similar, the B atom is much more firmly bonded. Also the compound formed ( $W_2B$ ) is very stable and melts congruently at  $2800^\circ C$ , in contrast to  $WBe_2$  where the W-Be bond is weak enough for it to dissociate (unless under pressure at temperature).

In the present work, the Be loss was minimised by using the high-pressure technique. However, even then, low Be alloys with W lattice saturation could not be obtained. In view of the above characteristics, this is not really surprising. Also in the pressure-vessel experiments the container walls had to be tungsten itself, so that some Be abstraction by diffusion was inevitable.

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Such segregation being particularly easy in this system, again because of preceding local losses or transient local enrichment during Be diffusion to the surface.

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APPENDIX 3

NOTES ON CHEMICAL ANALYSIS METHODS USED ON W-Be ALLOYS

(With acknowledgement to Dr. R. C. Chirnside,  
The General Electric Co. Ltd., Hirst Research  
Centre, Wembley)

1. THE SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM  
IN TUNGSTEN-BERYLLIUM ALLOYS

1.1 Principle

The alloy is dissolved in a mixture of nitric and hydrofluoric acids and the solution fumed with sulphuric acid.

A colour is then developed with the beryllium and p-nitro benzene-azo-orcinol in a 0.4 N sodium hydroxide solution buffered with borate and citrate.

Interfering ions are held in solution by the addition of E.D.T.A.

The optical density of the coloured solution is measured at 515 m $\mu$  and the beryllium content found by reference to a calibration curve.

1.2 Reagents

1.21 p-Nitro benzene-azo-orcinol 0.03%

To 0.03 g of the dye add 100 ml of 0.1 N NaOH solution. Stir mechanically for 5 hours, then set the solution aside in the dark overnight. Decant the clear solution into an amber coloured bottle. If necessary, filter the solution through a No. 540 Whatman filter paper to obtain a clear solution. Renew at fortnightly intervals.

1.22 Standard beryllium solution - strong

Dissolve 0.4915 g of beryllium sulphate ( $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  AnalaR grade) in water. Add 2 ml of 5 N  $\text{H}_2\text{SO}_4$  and dilute to 250 ml so that 1 ml  $\equiv$  100  $\mu\text{g}$  Be.

1.23 Standard beryllium solution - weak

Dilute 25 ml of the strong solution to 250 ml so that 1 ml  $\equiv$  10  $\mu\text{g}$  Be. Prepare this solution as required.

## 1.24 Buffer solution

Dissolve 89 g of tri-sodium citrate dihydrate, 56 g of sodium tetraborate (borax) and 72 g of sodium hydroxide in 400 ml of water and make up to 500 ml. Store in a polythene bottle.

## 1.25 E.D.T.A. solution

Dissolve 10 g of the disodium salt in 200 ml of water.

## 1.3 Preparation of Calibration Curve (0-200 $\mu\text{g}$ Be)

To six 100 ml beakers add 0 (blank), 2, 5, 10, 15 and 20 ml of the standard weak beryllium solution (1 ml  $\equiv$  10  $\mu\text{g}$  Be).

Add water to each beaker to bring to a volume of 35 ml, and follow by the addition of 10 ml of E.D.T.A. solution. Allow to stand for 5 minutes. Add 10 ml of buffer solution and again allow to stand for 5 minutes.

Transfer the contents of the beakers to 100 ml volumetric flasks and dilute to c. 90 ml. Measure very carefully 5 ml of the dye solution, using a pipette, into the flasks, dilute to 100 ml with water and shake thoroughly, then set the flasks aside for 10 minutes.

Measure the optical densities at 515 m $\mu$  on a spectrophotometer using a 4 cm cell with the blank solution in the reference cell.

Plot the optical densities obtained against  $\mu\text{g}$  of beryllium. In the range 0-200  $\mu\text{g}$  Be the calibration graph is almost linear.

A new calibration curve must be prepared each time the p-nitro benzene-azo-orcinol solution is renewed.

## 1.4 Procedure

Weigh off a portion of the sample to contain not more than 200  $\mu\text{g}$  of beryllium and transfer to a platinum dish. Add 2 ml of hydrofluoric acid and a few drops of nitric acid and cover with a platinum lid. When solution is complete rinse in the cover add 1 ml of sulphuric acid (1 + 6) and evaporate just to dryness to eliminate fluorides; avoid prolonged heating.

Add 35 ml of water to the dish and allow to digest on a steam bath for 15 minutes. Stir occasionally to aid solution of beryllium sulphate.



# Contrails

Allow to cool, then add 10 ml of E.D.T.A. solution and set aside for 5 minutes.

Pour the liquid into a 100 ml beaker containing 10 ml of buffer solution and stir to dissolve tungsten compounds. Pour back some of the solution into the platinum dish to dissolve any adhering tungstic oxide and rinse into the beaker.

After allowing to stand for 5 minutes transfer the solution to a 100 ml standard flask and dilute to c 90 ml. Add by means of a pipette exactly 5 ml of the dye solution and dilute to 100 ml.

After 10 minutes measure the optical density at 515 mu using a 4 cm cell with a reagent blank in the reference cell.

Determine the beryllium content of the sample by reference to the calibration graph and express the result as a percentage by weight.

## 1.5 Notes

The relationship between the optical absorption of the coloured beryllium lake and beryllium content is particularly dependent on the concentration of the p-nitro benzene-azo-orcinol solution. It follows, therefore, that old solutions of the reagent which may have deteriorated on storage must not be used, also that a new calibration graph must be prepared each time a fresh solution of the dye is dispensed.

The reagent solution alone has a fairly high optical density at the wavelength used for the tests so that great care must be exercised in pipetting out the 5 ml portions to be used in the analysis.

It is a wise precaution to run a standard, prepared by adding a known volume of the standard beryllium solution (1 ml  $\equiv$  10 ug Be) to some beryllium-free tungsten metal, at the same time as the tests.

## 1.6 References

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2. THE GRAVIMETRIC DETERMINATION OF BERYLLIUM  
IN TUNGSTEN-BERYLLIUM ALLOYS

2.1 Principle

The alloy is dissolved in a mixture of nitric and hydrofluoric acids and the solution fumed with sulphuric acid.

The residue is extracted with water, a small excess of ammonia is added to dissolve the tungstic oxide and to precipitate beryllium hydroxide.

The precipitate is filtered off, washed, redissolved and reprecipitated. The beryllium hydroxide is then ignited to the oxide and weighed.

2.2 Reagents

2.21 Ammonium nitrate solution 2%

Dissolve 2 g of the crystals in 100 ml of water and make just ammoniacal to litmus.

2.22 Ammonia solution (1 + 1)

Dilute 0.880 ammonia with an equal volume of water.

2.23 Sulphuric acid (1 + 1)

Add sulphuric acid (S.G. 1.84) to an equal volume of water.

2.24 Sulphuric acid (1 + 6)

Add 20 ml of sulphuric acid (S.G. 1.84) to 120 ml of water.

2.3 Procedure

Weigh off a portion of sample to contain between 10 and 100 mg of beryllium and transfer to a platinum dish of c. 75 ml capacity. Add 5 ml of hydrofluoric acid and about 1 ml of nitric acid and cover the dish with a platinum lid. When solution is complete rinse in the lid, add 1 ml of sulphuric acid (1 + 1) and evaporate to fuming to eliminate fluorides; fume strongly for 2-3 minutes.

Allow the dish to cool, then add 30-40 ml of water and heat on a steam bath for about 15 minutes; stir occasionally with a glass rod to aid solution of the beryllium sulphate.

# Contrails

To the hot solution add a few drops of litmus solution, then add cautiously ammonia solution (1 + 1) to the change point of the indicator, then add a slight excess to dissolve tungsten compounds.

Heat the solution to boiling, boil for 1 minute, then stir in a small quantity of ashless floc and filter the precipitate on a 9 cm Whatman No. 41 filter paper. Wash the paper 3-4 times with warm 2% ammonia nitrate solution. Retain the filtrate.

Transfer the filter paper back to the dish, add 10 ml of sulphuric acid (1 + 6) and heat the dish on a water bath for a few minutes. Stir occasionally to macerate the filter paper and to dissolve the beryllium hydroxide.

Add 40 ml of hot water, stir, then add a few drops of litmus solution and make just ammoniacal, then add a few drops excess to ensure solution of any residual tungsten. Boil for 1 minute. Filter and wash the precipitate as before.

Combine the filtrates from the two precipitations, acidify with sulphuric acid (1 + 6) and evaporate to about 40 ml. Make slightly ammoniacal and boil the solution for 1 minute to precipitate any trace of beryllium which may have escaped precipitation earlier in the procedure. Filter and wash any precipitate, as already described.

Transfer the two filter papers and precipitates to a weighed platinum crucible, ignite gently at first, finally at 1000°C in a muffle furnace, cool and reweigh the crucible to obtain the weight of beryllium oxide. Calculate the weight of beryllium metal ( $\text{Be} = 0.3605 \times \text{BeO}$ ) and express the result as a percentage by weight.

## 2.4 Notes

The method is applicable only to alloys which are free from other metals giving insoluble hydroxides by ammonia precipitation.

Beryllium hydroxide is slightly soluble in solutions containing appreciable amounts of free ammonia and hence it is desirable to restrict the amount of excess ammonia used in the precipitation of the beryllium. Under these conditions a clean separation of beryllium from the large amount of tungsten present is not obtained in a single precipitation and re-precipitation is essential. If a sample weight greater than 0.5 g has been used, a second re-precipitation may be required to ensure complete removal of the tungsten. It is in any case advisable to check the purity of the weighed beryllium oxide by X-ray or spectrographic examination.

# *Contrails*

Because of the slight solubility of beryllium hydroxide in ammoniacal solutions, it is necessary to examine the filtrates from the main ammonia precipitations for any small amount of beryllium that has escaped precipitation. The amount of precipitate so obtained should be very small, if any, and a single precipitation suffices.

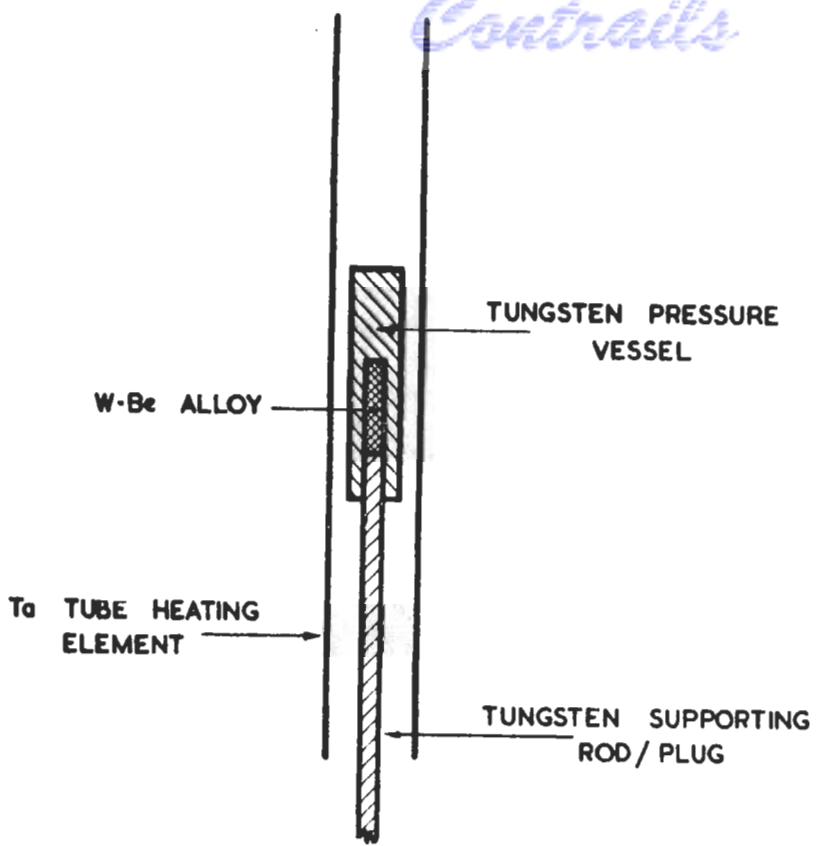


Fig. 1 (II) Pressure-vessel arrangement for W-Be alloy preparation and heat-treatment.



Fig. 2 (II) W-WBe<sub>2</sub> eutectic. (x 1200)

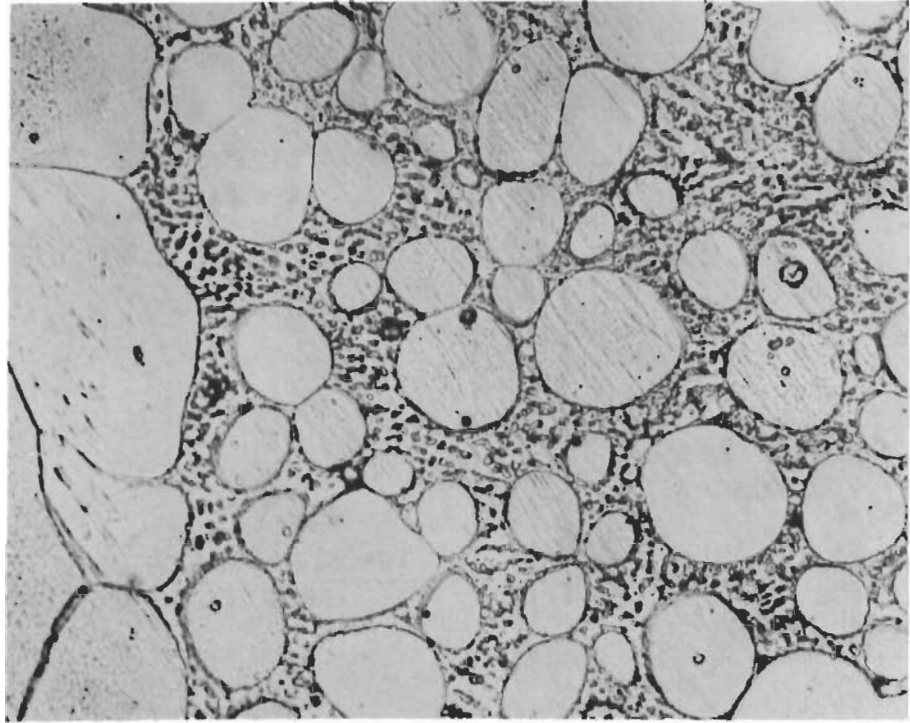


Fig. 3 (II) 40% Be sintered compact after heating at 2500°C in pressure-vessel (W + eutectic). (x 500)

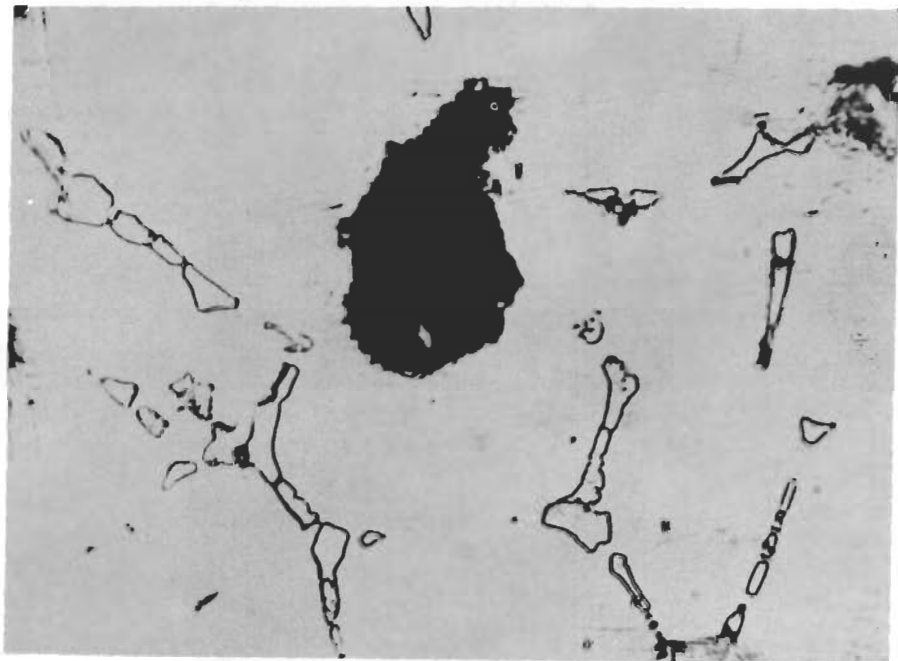


Fig. 4 (II) 6.7% Be alloy, quenched from 2500°C. (x 2000)

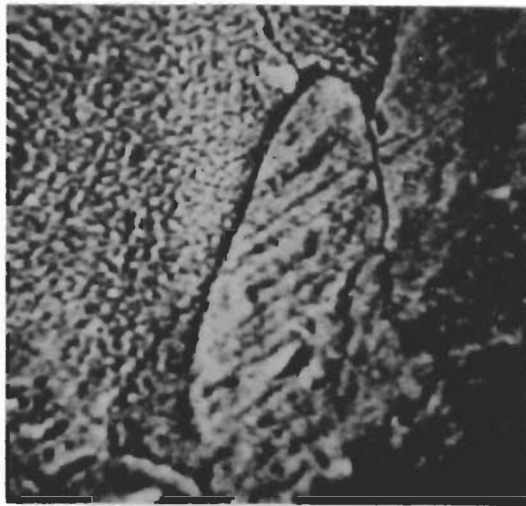


Fig. 5 (a) (II) Microprobe  
Analysis: Electron  
picture of eutectic  
alloy. (x 1000)

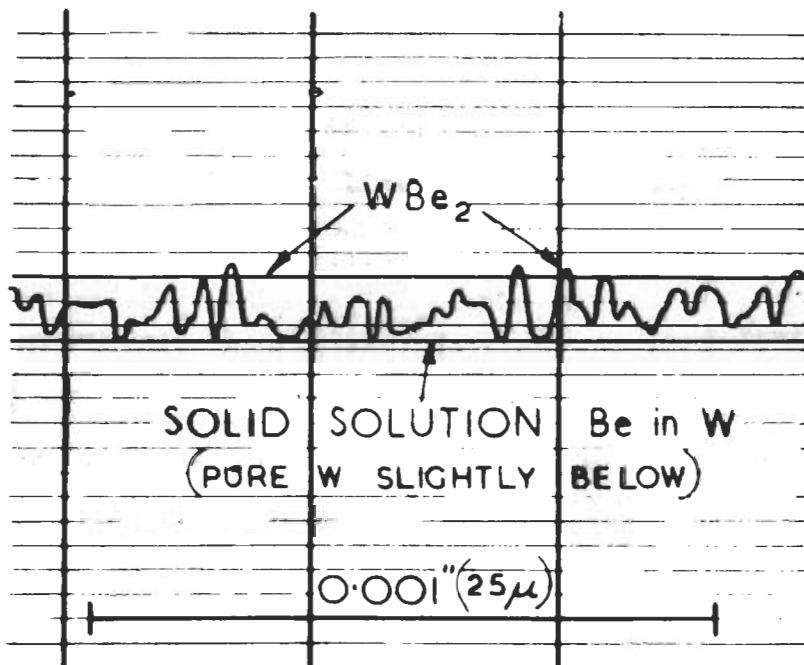


Fig. 5 (b) (II) Microprobe Analysis: Typical  
specimen current scan in eutectic,  
as above.

TENTATIVE W-Be PHASE DIAGRAM

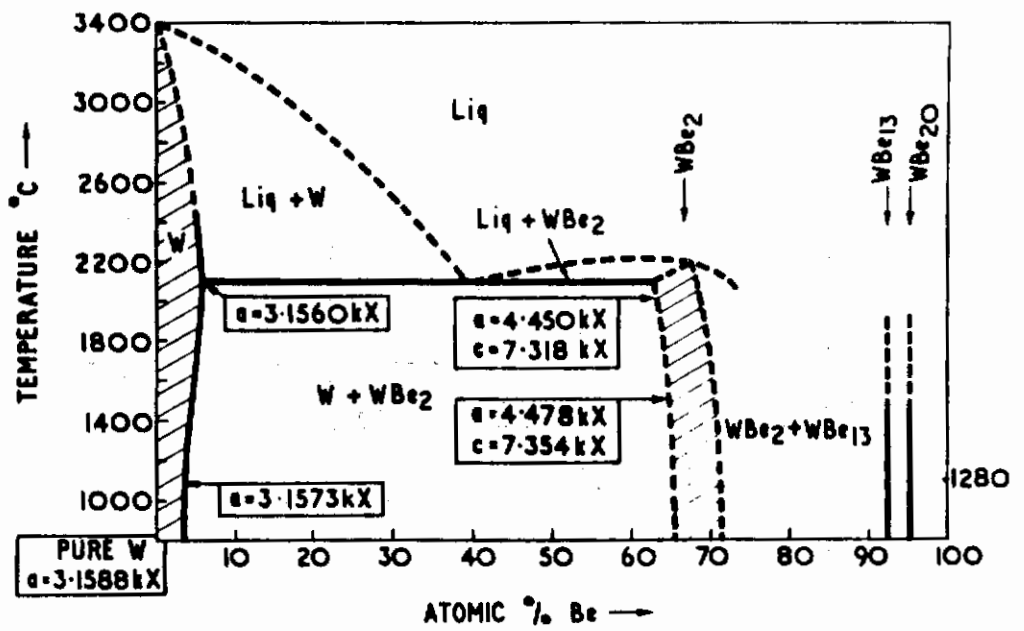


Fig. 6 (II)



SECTION 3. TUNGSTEN-CARBON SYSTEM: BRIEF SUPPLEMENT

The determination of the solid solubility of carbon in tungsten had already been fully reported in our Report of 25th August, 1961 (which appeared as ASD Document No. ASD-TDR-62-25 PTI March 1962). However, two subsidiary aspects were dealt with in a limited amount of subsequent work. These were:

- (1) the age-hardening of W by  $W_2C$ .
- (2) the Ta-W-C system, solubility aspect.

It is here proposed briefly to report this additional work.

1. AGE-HARDENING EFFECTS

A principal result of the preceding work was the existence of a small solid solubility of C in W, receding from about 0.3 atomic % C at the eutectic temperature ( $2400^{\circ}C$ ) to an insignificant value below  $2000^{\circ}C$ . The possibility of precipitation and of dispersion-hardening is therefore, given; and it was attractive to study this. Unfortunately the amount of work that could be done under the circumstances was only very limited, and the following results should be regarded as only exploratory. The desirability of further study is clear. A particular attraction lies in the fact that  $W_2C$  should be able to remain in a stable fine-particle dispersion up to very high temperatures, yet by quenching from temperatures within the solubility region (between say  $2000$  and  $2700^{\circ}C$ ) and subsequent controlled annealing at different lower temperatures it may be possible to produce varying degrees of hardenability and of strengthening. Varying rates of cooling from within the solubility field provide a further factor of interest, as well as of course C-content.

Experiments were carried out on the 0.075 atomic % C alloy which is well within the solubility-limit at the eutectic temperature.

Samples of large crystal-size were solution-treated for ten minutes at  $2450^{\circ}C$  in the argon-arc furnace and quenched. Ageing was carried out in vacuo, one half of the specimens being treated at  $1450^{\circ}C$ , and the other half at  $1000^{\circ}C$ . The specimens were aged for a series of times ranging from a few minutes to 600 hours, and then quenched. The results are given in graphical form in Fig. 1. They show that a small, but distinct hardness

increase takes place at both temperatures, the hardness peak occurring after 30 hours at 1450°C and after 160 hours at 1000°C. For comparison both these data are plotted jointly on a logarithmic scale in Fig. 3.

The aged specimens were studied using the optical and electron microscope. In the solution-treated condition, Fig. 4 and (electron-micrograph) Fig. 15\*, the structure is featureless apart from a general pattern of etch-pits in the former, characteristic of tungsten and varying from grain to grain. At the hardening peak no change is yet observed, as to be expected since the appearance of a precipitate will be associated with softening. The electron-microscope, however, shows the appearance of small craters (Fig. 6), and it is possible that these are the regions of stress and nascent precipitation revealed by the etchant. In the overaged condition, a distinctive precipitate of pale pink colour appears both in the grain boundary region (Fig. 7) and occasionally within a grain. The majority of the precipitate, however, is likely to be very finely dispersed, and the electron micrograph (Fig. 8) would appear to confirm this view, showing fewer and deeper craters where apparently the carbides had been located.

As mentioned these ageing experiments can be considered as only indicative and the desirability of much more detailed work is suggested, particularly the study of the dispersion-hardening effects. The hardening of tungsten by  $W_2C$  has certainly been demonstrated in principle and although the degree of hardening is fairly small under the conditions chosen, it can almost certainly be increased and modulated by further experiment.

## 2. THE SOLID SOLUTION OF C IN Ta-W ALLOYS

In the earlier course of the work on the solubility of carbon in pure tungsten (when this was still thought on the borderline of detectability by lattice-spacing changes), the following idea was put forward: To utilise the known facts of (a) a much higher solubility of carbon in tantalum, and (b) the continuous solid-solution formation in the Ta-W system, in order to extrapolate the primary solution boundary W-C from the series (Ta—W)-C. Carbon saturated Ta-W alloys were to be used. The lattice-spacing change of C in pure Ta is more appreciable than that in W (although controversial, see below), and in the Ta-W system Vegard's law is nearly obeyed.

A series of eight pure W-Ta alloys were prepared in the first place by melting small ingots in an argon arc-furnace and subsequently carburising each by remelting with small amounts of graphite. Melting continued until all free carbon had reacted, the prime object having been to ensure the presence of some excess free carbide  $(Ta,W)_2C$  in equilibrium with a saturated (Ta,W) matrix solution.

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Electron microscopy with the kind help of Dr. B. B. Argent, University of Sheffield.

A complication arose however. For pure Ta, carbon addition expanded the lattice, as it did, to a lesser extent, for pure W. However, an apparent and consistent contraction of the BCC lattice occurred through carbon for alloys containing both Ta and W. The results are shown in Table 1.

TABLE 1

Lattice Spacing Change of Ta-W Solid Solution by C

Composition, atomic % Ta (remainder W)	Lattice Spacing <sup>a</sup> (kX)	Difference $\Delta$ a, through C-solution (kX)
Pure Ta, <u>without</u> C	3.2958	-
Pure Ta, C-saturated	3.3028	+ 0.007
79.0           "	3.2204	- 0.04
49.1           "	3.2018	- 0.013
16.8           "	3.1654	- 0.005
9.0            "	3.1567	- 0.010
Pure W, without C	3.1586 <sub>3</sub>	-
Pure W, C-saturated	3.1584 <sub>3</sub>	+ 0.0001 <sub>8</sub>

This anomaly is attributed to the fact that for any given W:Ta ratio in the base alloy, carbon addition alters this proportion in the matrix in favour of higher W, owing to the stronger C-affinity to Ta. Thus the observed matrix spacing appears lower, owing to the enriched tungsten content, the associated carbide being richer in Ta.

This result, while of interest in itself, rather militates against the original intention of trying to "extrapolate" the W-C terminal solubility from the (Ta-W)-C series. In view of the fact that the solubility limit of C in W has now been determined without the use of a third element, this particular approach had rather lost interest and was not continued any further.

Its pursuance would need a much more comprehensive research to be initiated. This could still be a worthwhile project though any such evaluation of the Ta-W-C system would have to be on an independent basis.

# Contrails

One interesting aspect which arises is that spacing changes within the BCC solution and the carbide series would provide a useful quantitative means of deriving partitioning of the elements between these phases. Microprobe analysis could here prove of added value.

A result of incidental interest is the lattice-expansion by C in Ta solution, namely by 0.0070 kX. This contradicts previous published work claiming a lattice contraction of Ta by interstitial C (Smirnova and Ormond<sup>(1)</sup>, see also Pearson<sup>(2)</sup>: results which seemed unlikely). Ours agrees in principle with Vaughan, Stewart and Schwartz's<sup>(3)</sup> result of a small expansion of Ta by C. In our work the expansion is in fact appreciably larger, as it corresponded to a quench from 2500°C, as against a 1000 and 1500°C anneal in the Battelle work, which would again appear consistent.

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Part III

1. Smirnova, V. I. and B. F. Ormond: Doklady Akad. Nauk. SS SR 96, 1954, p. 557.
2. Pearson, W. B.: Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, 1958, p. 957.
3. Vaughan, D. A., O. M. Stewart and C. M. Schwartz: B.M.I. Report 1472, 1960.

# Contrails

## AGEING CHARACTERISTICS OF TUNGSTEN CONTAINING

0.075 at. % CARBON AGED AT 1450 °C

(AFTER QUENCHING FROM 2450°C)

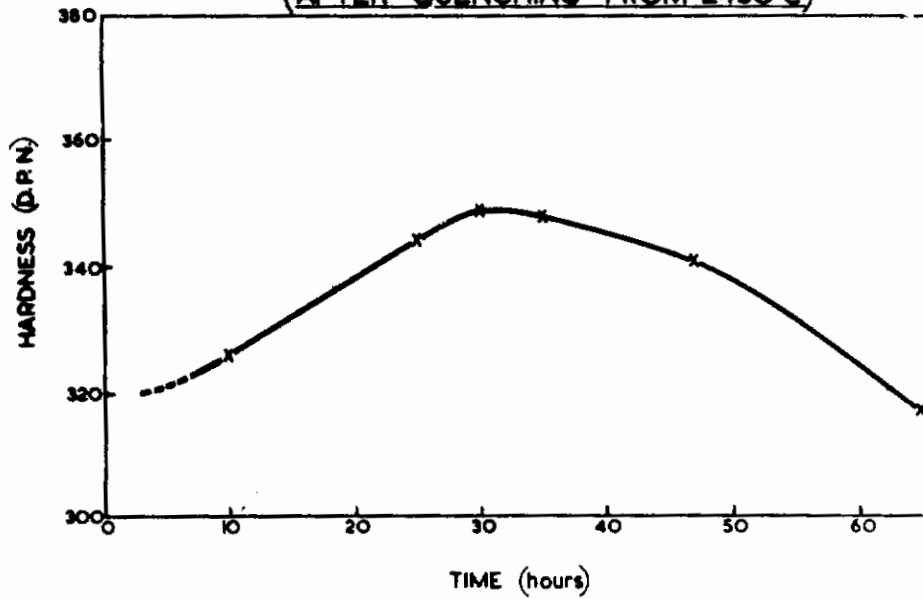


Fig. 1 (III)

## AGEING CHARACTERISTICS OF TUNGSTEN CONTAINING

0.075 at. % CARBON AGED AT 1000 °C

AFTER QUENCHING FROM 2450°C)

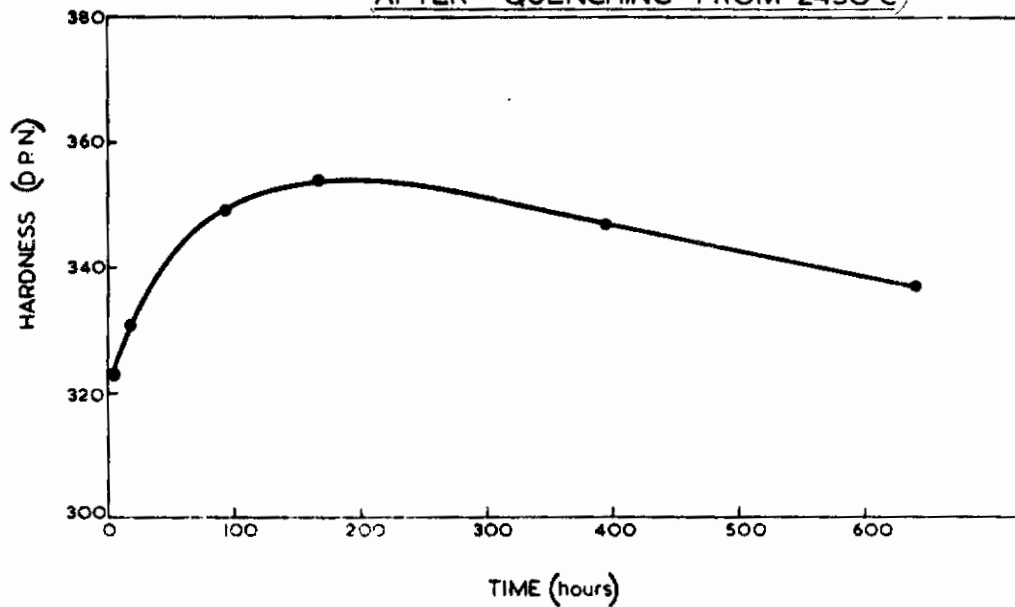


Fig. 2 (III)

AGEING CHARACTERISTIC OF TUNGSTEN CONTAINING

0.075 at. % CARBON AGED AT 1000°C & 1450°C

AFTER QUENCHING FROM 2450 °C

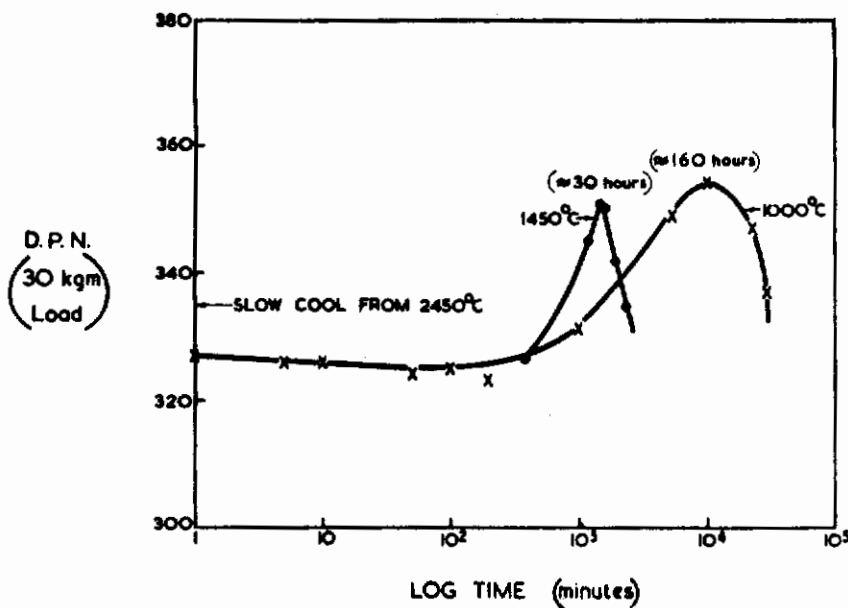


Fig. 3 (III)

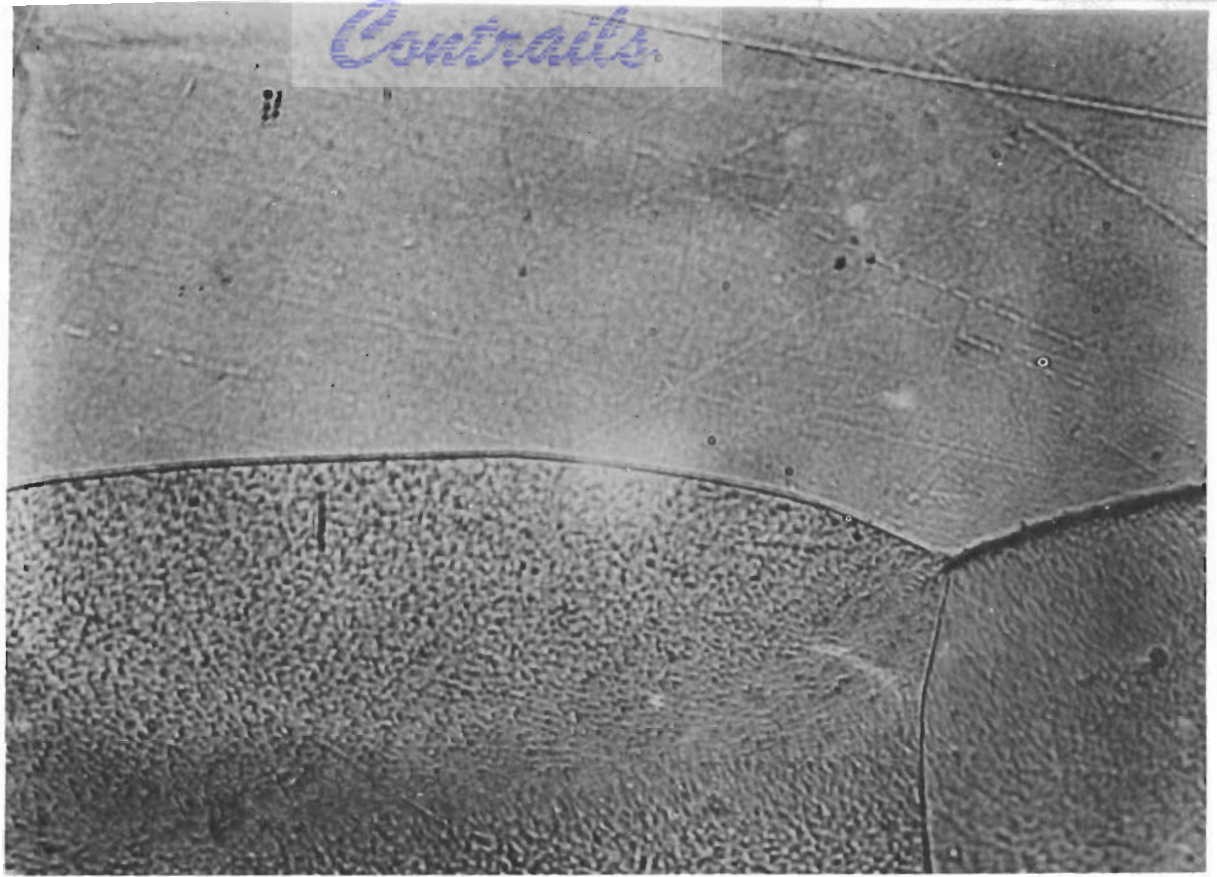


Fig. 4 (III) W-C alloy (0.075 a/o C) solution treated and quenched.  
Etched in Murakami's reagent. (x 1000)

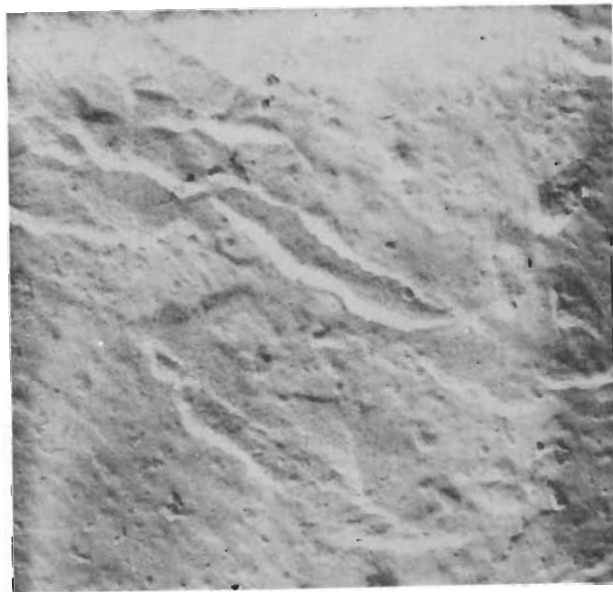


Fig. 5 (III) W-C alloy (0.075 a/o C), solution treated  
and quenched; aged 1000°C, 92 hours.  
Before hardness peak.  
Electron micrograph. Carbon replica shadowed  
with Au/Pd. (x 20000)



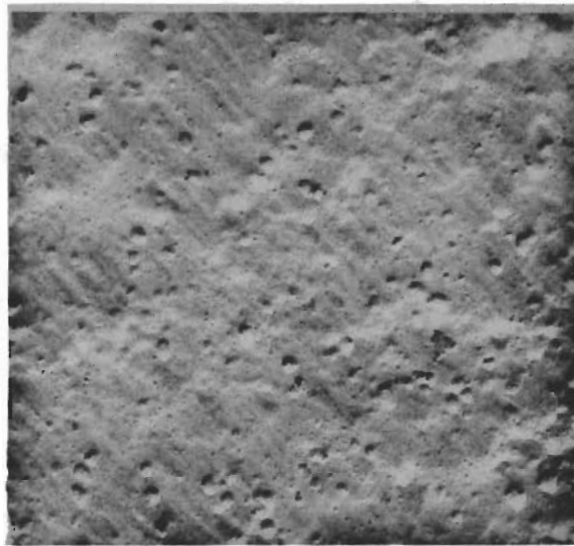


Fig. 6 (III) W-C alloy (0.075 a/o C), solution treated and quenched; aged 1000°C, 167 hours.  
At hardness peak.  
Electron micrograph, as Fig. 5. (x 20000)

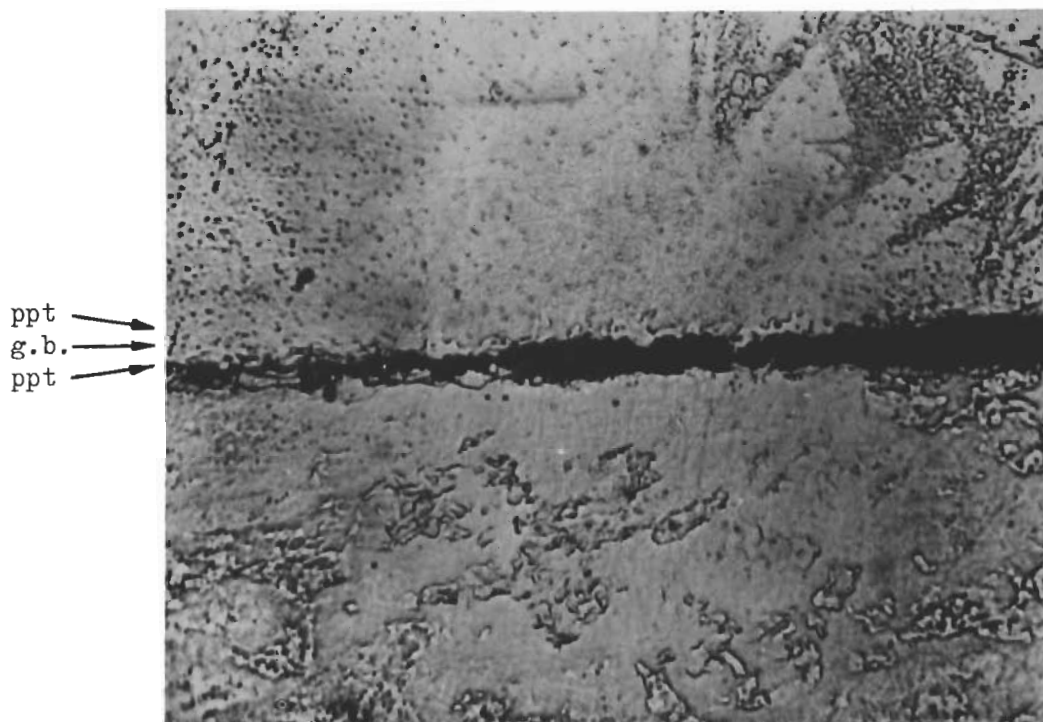


Fig. 7 (III) W-C alloy (0.075 a/o C), solution treated and quenched; aged 1450°C, 47 hours.  
Murakami's reagent. (x 2000)

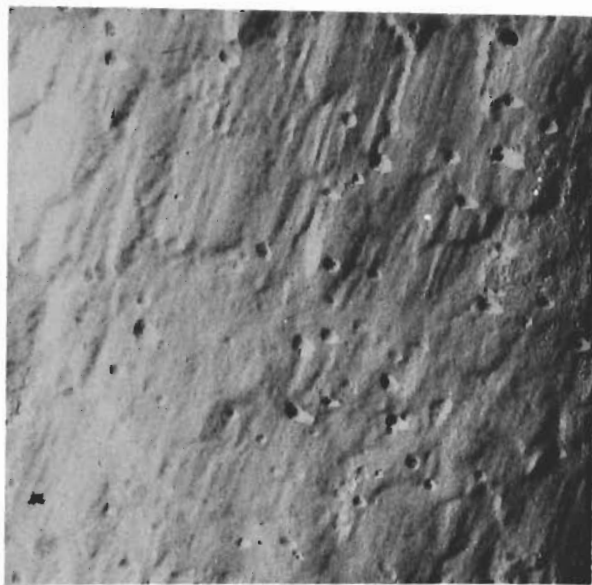


Fig. 8 (III) W-C alloy (0.075 a/o C),  
solution treated and quenched;  
aged 1000<sup>o</sup>C, 500 hours.  
Electron micrograph as before.  
(x 20000)