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CONTRACT NO. N.62558-3591

USE OF REACTIVE ATMOSPHERES FOR THE TREATMENT OF B.C.C. METALS

Quarterly Engineering Progress Reports Nos.
1. and 2.

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USE OF REACTIVE ATMOSPHERES FOR THE TREATMENT OF B.C.C. METALS

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Period 1st October 1962 to 31st March 1963.

For Metallurgy Department

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Project Supervisor

Principal Investigator

SYNOPSIS.

This report covers the first six months' work on the Project, and so serves as Progress Reports Nos. 1 and 2, combined.

From the broad field of the "Use of Reactive Atmospheres for the Treatment of B.C.C. Metals", the problem of improving the sinterability of tungsten has been selected, the immediate objective being to lower the sintering temperature by use of reactive atmospheres.

The first three months were devoted to an extensive literature survey. The most relevant papers, covering several aspects of activated sintering, and the reactivity of tungsten to halogen-containing atmospheres, have been summarised. Information concerning present commercial practice for the sintering of tungsten powder was obtained from Murex Ltd.

During the second three month period, apparatus for sintering tungsten compacts in reactive atmospheres has been designed, set up, and tested. Initially, atmospheres containing iodine and hydrogen, with argon as diluent, have been used. Pressure is usually reduced.

A supply of tungsten has been obtained, after discussion on suitability, from Murex Ltd. Some simple sintering tests have been made, and although results were poor, the information obtained has guided the design of apparatus, and the planning of the programme. Work has reached the stage when a series of tests under controlled conditions can be made. Preliminary tests (to be reported in next Progress Report) have given encouraging results.

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ILLUSTRATIONS

1. INTRODUCTION

The activated sintering of tungsten has been selected as the first topic for investigation, under the above heading, since improvements in sintering technique would have immediate commercial importance.

Powder Metallurgy is the accepted method of fabricating tungsten products. Standard commercial practice involves three major steps, namely pressing, presintering and sintering. Presintering is done for about an hour at a temperature around 1100°C, to give the "as pressed" product enough strength to be handled when fitting it into the sintering furnace. Sintering is accomplished by raising the temperature to about 3100°C by passing a high current through the presintered bar.

One of the main drawbacks of this sintering method is that a very high temperature is required to obtain an acceptable density. A coarse grain structure results, and the "as sintered" bar is very brittle at room temperature. The brittleness is also partly associated with the interstitial impurity content.

Although there is still no full understanding of the cause of low temperature brittleness in b.c.c. metals, it is well known that a reduction of the interstitial content of these metals lowers the ductile/brittle transformation temperature.

Reduction of sintering temperature and improvement of mechanical properties of "as sintered" tungsten (including reduction of interstitial content) can probably be best achieved by activated sintering, using atmospheres containing halogens, or other reactive elements.

So far, work under the present Contract has been devoted to a literature survey (including collection of thermodynamic and kinetic data on tungsten/halogen reactions), to the carrying out of a few preliminary tests, and to the building, calibration and testing of a suitable apparatus.

After consultation with Murex Ltd., Rainham, Essex, a supply of tungsten powder and "presintered" bar has been obtained.

2. LITERATURE SURVEY

2.1. Activated Sintering (Reactive Atmosphere).

2.1.1. Iron-Chromium Alloys (Ref. 1.). Homogeneous iron/chromium alloys (25% Cr) were prepared by pressing mixed iron and ferrochromium powders impregnated with ammonium iodide, and sintering at 1150°C. The mechanism combined internal chromising and activated sintering. The work was extended to cover chromium rich alloys, and commercially pure chromium.

2.1.2. Iron (Ref. 2, 3.). The activated sintering of iron powders, using halide formation and reduction cycles, has been described by M. Eudier. The iron powder compacts were sintered in boxes at about 1100°C, the activating atmosphere being provided by ammonium fluoride and ammonium chloride (singly or together). Dissociation of the ammonium salt produced hydrogen halides which reacted reversibly with the iron:

$$Fe + 2\,HX \rightleftharpoons Fe\,X_2 + H_2 \qquad (X = F \text{ or } Cl).$$

A mixture of ammonium chloride and fluoride seemed to be more effective than either salt alone, and the control of temperature for good activation was less critical.

The reaction led to a marked increase in surface diffusion and to the transfer of atoms via the gas or liquid phase (depending on temperature, pressure and halide used).

Eudier also claimed a marked increase in ductility of the activated sintered product, as compared with normal sintering. The improvement in mechanical properties was still more enhanced when certain mixed powders (e.g. Fe-Si) were used.

2.2. <u>Tungsten-halogen Reactions</u>.

It is intended to use tungsten-halogen reactions in order to activate the sintering process for tungsten and its alloys. A good idea of suitable temperature ranges for reversible reaction, and of partial pressures of reactants can be obtained from the diagrams reproduced in Fig. 1. (Ref. 4.). These diagrams refer to reactions of the type $W + 2HX \rightleftharpoons WX_2 + H_2$ .... (1).

With the less stable halides (e.g. iodides), activation may be obtained by the reversible reaction $W + 2I \rightleftharpoons WI_2$ .... (2), there being no need for a reducing agent (H_2) to be present.

According to Moore and Jolly (Ref. 5.), gaseous WI_2 forms from 250°C, and remains stable up to 1200°C. Above this temperature, there is an increasing tendency for reaction (2) to proceed to the left, and above

1600°C there is no reaction between tungsten and iodine.

Fortunately reactions (1) and (2) for iodine are reversible in the same temperature range, and after studying them separately, it might be of interest to see the effect of both reactions taking place simultaneously.

The possibility of using inter-halogen compounds (e.g. IBr, IF_5, ICl) for activation is being kept in mind.

2.3. Effect of small additions of other metals on sinterability of tungsten.

The sinterability of tungsten powder in a hydrogen atmosphere depends on purity and particle size. Small quantities of other metals can be beneficial. Nickel, added as a powder (0.5 to 2%) or as a coating on the tungsten particles decreases the sintering temperature of tungsten to approximately 1100°C (Ref. 6.). This is an example of metal activation.

According to Braun and Sedlotschek (Ref. 7.), the mechanical properties of tungsten can be improved by small amounts of alloying elements. The best results (increased recrystallisation temperature; deoxidation) were obtained with small additions of Zr, Hf, Th and Ti. The possibility of using these metals or their halides in conjunction with an activating atmosphere is being kept in mind.

2.4. Other methods of activation.

Experiments have shown that ultrasonic vibrations and the use of high frequency induction heating increase the rate and change the nature of diffusion and phase transformations in certain metals and alloys (Ref. 8, 9, 10, 11, 12).

The direct effects on sintering rates and properties of sintered products do not appear to have been studied yet.

3. EXPERIMENTAL WORK

3.1. Preliminary Experiments. A number of tests were made in simple apparatus while the main apparatus was being designed and built. These methods were used, as described briefly below.

(A) A tungsten powder compact was suspended in the centre of a vertical transparent silica tube, with a tungsten boat containing iodine suspended a little below the compact. Argon was passed slowly upwards through the tube. The compact was heated by means of an induction coil outside the tube, the iodine being volatilised by radiated heat.

A surface reaction did occur, but there was little penetration into the tungsten specimen. Needle-like crystals (of tungsten iodide, presumably) grew on the tungsten surface when the quantity of iodine was increased.

It was difficult to assess the temperature of the tungsten, since iodine condensed on the silica tube, obscuring the test-piece.

(B) The tungsten compact with a little iodine (10 to 500 mg.) were placed in a refractory boat, in a tube furnace. Argon was passed through, over the iodine before the tungsten. After purging in the cold, the argon flow was reduced to a minimum to avoid too rapid sweeping away of iodine vapour, and the furnace heated. Temperature ranged from 900 to 1250°C, treatment times (at temperature) from 2 to 8 hours.

There was no noticeable difference between the specimens treated in iodine and those treated in argon alone. Little or no sintering occurred. It is believed that the iodine all evaporated and was carried out of the reaction zone before the temperature was high enough for any reaction between iodine and tungsten to occur.

(C) It was thought that there would be more chance of reaction if the tungsten compact was impregnated with iodine. With a reasonably quick rate of heating, the iodine would drive other gases from the pores, remain at one atmosphere pressure within the pores, and then only slowly be replaced by argon.

Before pressing, the tungsten powder was immersed in a solution of iodine in carbon tetrachloride. After drying, at room temperature, the powder was pressed, and heated as in method (A).

Again, iodine (and tungsten di-iodide) condensed on the cold silica tube, making observation of the tungsten temperature difficult.

The results were definitely improved, but the specimens were still not strong enough for normal metallographic preparation. The effective treatment time, during which conditions were favourable for the reaction $W + 2I \rightleftharpoons WI_2$, was of necessity short.

3.2. <u>Tungsten Powder</u>. After consultation with Murex Ltd. (Dr. G.L. Miller, Dr. F. Cox) a supply of tungsten powder considered sufficient for all the experimental work, has been obtained. In addition Murex Ltd. have prepared an "as pressed" bar and a presintered bar, from the same batch of powder. Test-pieces can be cut from the bars, or made from tungsten powder, as required.

3.3. Design of Apparatus. The apparatus is illustrated by Fig. 2. It mainly consists of the following: -

1) Furnace "2" is a rectangular chamber lined with heating tape and its temperature (20-200°C) is controlled by a thermostat. To obtain uniform temperature within this "halogen source" chamber it is equipped with a motor-driven fan.

The temperature of this furnace will control the vapour pressure of the halogen, or in other words, the partial pressure of the halogen in the carrier gas (argon) entering the reaction tube.

2) Furnace "1" is a silicon carbide tube furnace containing the "reaction" or "reaction sintering" tube, which in turn contains the "as pressed" tungsten specimen. The furnace tube is made of transparent silica; however, there is provision to change it to mullite when it becomes necessary due to the higher operating temperatures.

3) Furnace "3" is similar to Furnace "2" in design; however, instead of controlling the partial pressure of the halogens entering the reaction tube, it is set at such a temperature as to ensure that the halogens leaving the reaction tube will not condense before the pressure is measured. The pressure here is measured by a glass spiral Bourdon Gauge, which works in conjunction with a mercury manometer and galvanometer light source and scale.

4) The halogens leaving Furnace "3" made to condense in a liquid air trap.

5) The two very fine needle valves, one between the liquid air trap

and the vacuum pumps and the other within the argon purifier and Furnace "2", will control the argon (carrier gas) flow rate (being calibrated with a flowmeter) as well as the total pressure of the system.

6) The last main parts are the vacuum rotary and diffusion pumps.

This apparatus should allow us to study the effects produced by variables on the sintering behaviour of "as pressed" tungsten specimen, such as partial pressure of the halogen, sintering temperature, sintering time, and total pressure of this dynamic system.

The apparatus is also versatile enough to be adapted for metal halide activation.

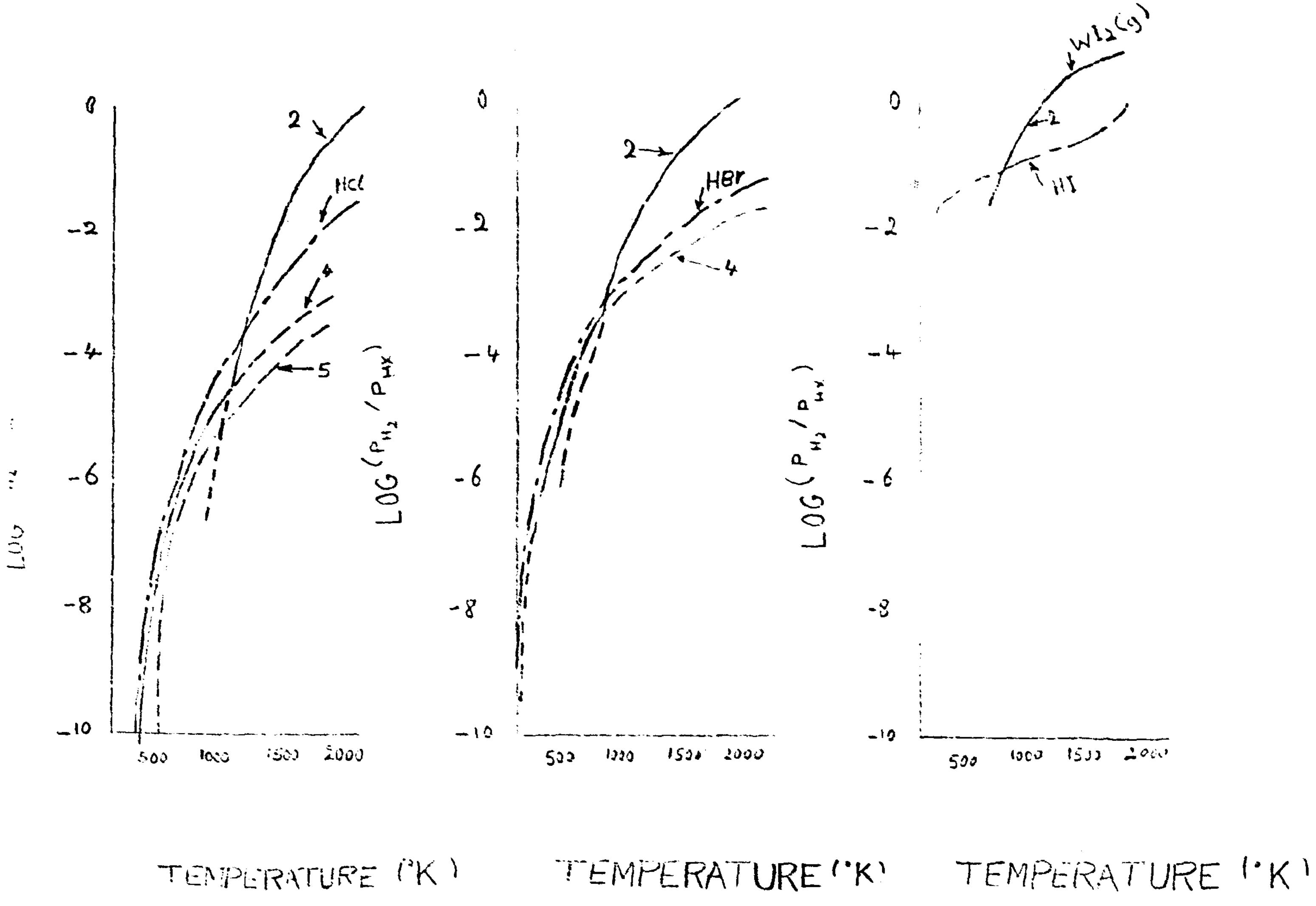
3.4. Calibration of Apparatus. Using cylinder argon, controlled at 2 - 3 p.s.i. pressure, it has been found possible to obtain varied and controlled low pressures inside the apparatus. The two needle-valves are adjusted to obtain the required pressure between them combined with a suitable rate of flow. The fitting of a flow meter permanently between the argon purifier and the first needle-valve, is being considered.

3.5. First Experiments. A few trial runs have been made, iodine being introduced into the gas stream and kept flowing overnight. However, there have been "teething troubles", and further details will be held over to the next Progress Report.

4. CONCLUSIONS

Work on the project has reached the stage when a series of tests can be made under controlled conditions, so that the factors governing the activated sintering of tungsten can be studied. Temperature of sintering will not exceed 1100°C in the first series, since a silica reaction tube is being used. Silica, being transparent, has the advantage that iodine vapour can be observed, giving a fair indication that the vaporising system is functioning, and deposits on the tube walls can be clearly seen.

The preliminary tests were not very informative, because there was insufficient control of conditions. In the tests now being prepared, variables will be pressure and composition of the reactive gas, total pressure of the system, time and temperature. Argon is the carrier gas, iodine and hydrogen the reactive constituents.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-6
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500
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2000
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HBr
4
TEMPERATURE (°K)
LOG (P_{H_2}/P_{HX})
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$WI_2(g)$
2
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TEMPERATURE (°K)

(a) (b) (c)

Fig. 1

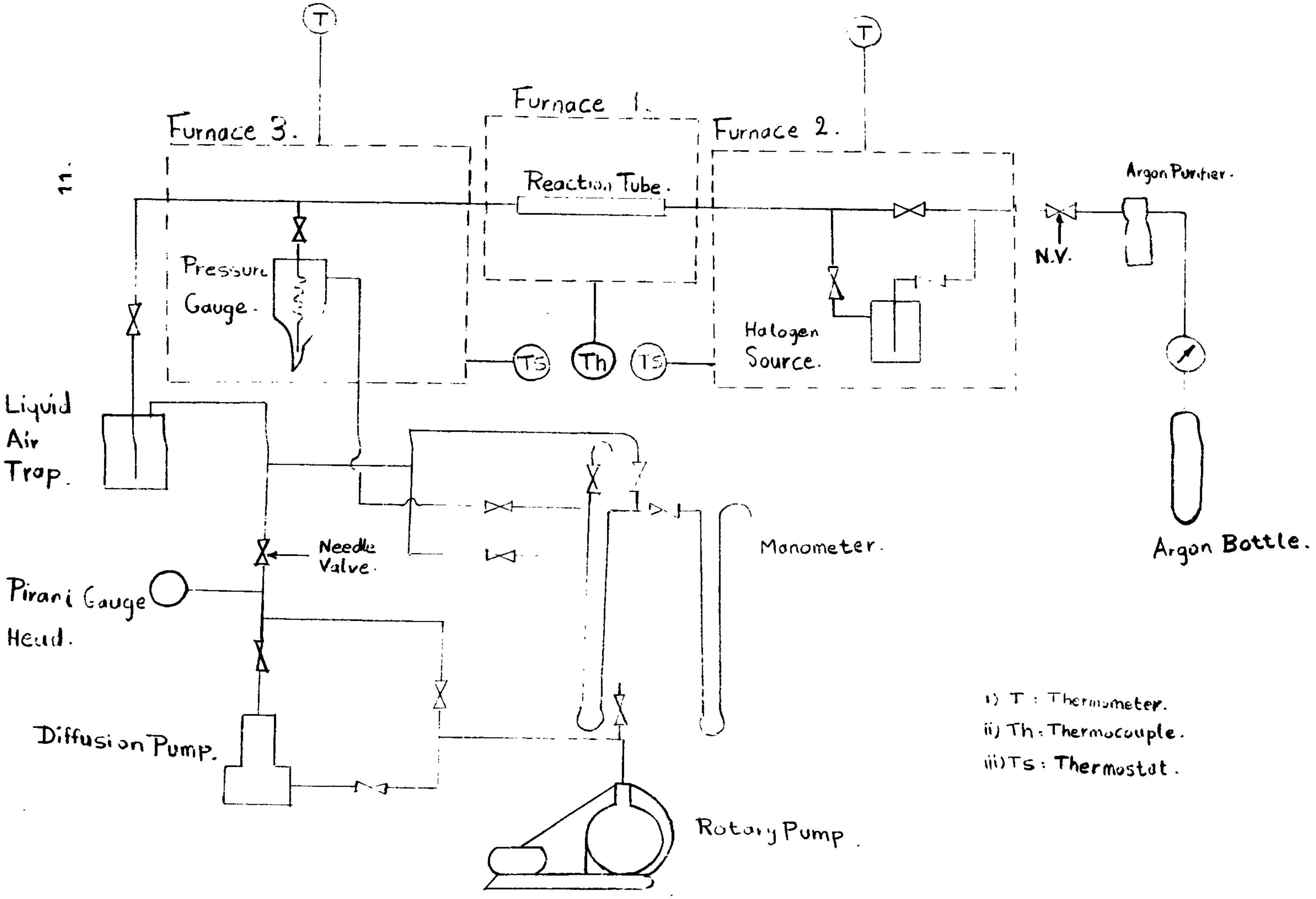
T
T
Furnace 3.
Furnace 1.
Furnace 2.
Reaction Tube.
Pressure Gauge.
Halogen Source.
Argon Purifier.
N.V.
TS
Th
TS
Liquid Air Trap.
Needle Valve.
Pirani Gauge Head.
Manometer.
Argon Bottle.
Diffusion Pump.
Rotary Pump.
i) T : Thermometer.
ii) Th : Thermocouple.
iii) Ts : Thermostat.

Fig. 2.

5. REFERENCES

(1) Ministry of Supply Contract No. 6/Gen/1242/CF/14.b. (Item III). (R.L. Samuel, N.A. Lockington, Diffusion Alloys Ltd.). Progress Report No.4., March 1951, and later reports. (Continued as Contract No.6/Exptl/2418/CB.38.b.).

(2) M. Eudier, Symposium on Powder Metallurgy, Inst. of Metals 1954,p.59.

(3) M. Eudier, Proc. Metal Powder Assoc. 1957, (1), 5-9.

(4) L.L. Quill, Editor, Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics McGraw - Hill Book Co., New York(1950) p.288.

(5) J.A. Moore and C.M. Jolly. G.E.C. Journal, Vcl. 29, No.2., 1962.

(6) Agte, Curt. Vyzkummy ustav pro praskovon met., Prague, Hutnicke Listy, vol.8. 1953, p.227-234.

(7) A.G. Quarrell, Editor, "Nb, Ta, Mo and W" - H. Braun and K. Sedlotschek, p.361.

(8) R.I. Garber, L.M. Polyakov, G.N. Matik, Fiz. metal. metalloved, 10 No. 4 (1960) 570-6.

(9) N.A. Lockington, Metal Treatment and Drop Forging 1957, <u>24</u>, 29-33.

(10) R.L. Samuel and J.D. Samuel. ASTIA Document. AD - 214791.

(11) A.N. Minkevich and G.N. Ulybin. Metallovedenie i Term. Obrabotka Metallov. April 1959. 4. 48-51.

(12) Yu.V. Grdina and L.T. Cordeeva. Izu. Uuz. chern. Metallurgya. July 1959, 7, 97-100.