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FORMATION AND CHARACTERIZATION OF THE A15-TYPE
STRUCTURE IN CHEMICAL VAPOR DEPOSITED
TUNGSTEN-RHENIUM ALLOYS

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Submitted as a thesis to the Graduate Council of the University of Tennessee in partial fulfillment of the requirements for the degree of Master of Science.

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AUGUST 1967

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TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
II. LITERATURE SURVEY	4
Chemical Vapor Deposition of Alloys	4
The Al ₅ -Type Structure	7
III. EXPERIMENTAL PROCEDURE	11
Deposition of Alloys	11
Annealing Treatments	15
Metallography and Hardness Measurements	15
Phase Identification and Crystal Structure	
Determination	16
Chemical Analysis	17
IV. RESULTS	19
Composition and Temperature Range of Formation	
of the Al ₅ Phase	19
Stability of the Al ₅ Phase	22
Microstructures, Phase Analysis, and Hardness	25
Lattice Parameter and Crystal Structure Type	31
V. DISCUSSION	41
VI. CONCLUSIONS	44
REFERENCES	46

LIST OF TABLES

TABLE	PAGE
I. Chemical Analysis Techniques for Tungsten-Rhenium	
Alloys	18
II. Phases in As-Deposited Tungsten-Rhenium Alloys	20
III. Impurity Content of Tungsten-Rhenium Deposits	23
IV. Phases in As-Deposited and Annealed Tungsten-	
Rhenium Alloys	24
V. Ratio of Diffractometer Peak Heights	26
VI. Hardness of As-Deposited and Annealed Alloys	32
VII. Calculated and Experimental X-Ray Diffraction	
Intensities for the Al ₅ -Type Phase in a	
Tungsten-Base Alloy	35
VIII. Calculated and Experimental Neutron Diffraction	
Intensities for the Al ₅ Phase in a Tungsten-	
Base Alloy	39

LIST OF FIGURES

FIGURE	PAGE
1. Tungsten-Rhenium Vapor Deposition Apparatus	12
2. Calibration of Optical Pyrometer	14
3. Vapor-Deposited Phases Shown in Relation to the Tungsten-Rhenium Phase Diagram	21
4. Microstructures of As-Deposited Tungsten-Rhenium Alloys: (a) Single-Phase Beta Alloy Containing 20 Per Cent Rhenium Deposited at 1100°C., 200X; (b) Beta (Principal Phase) Plus Al5 Alloy Containing 26 Per Cent Rhenium Deposited at 1200°C., 150X; and (c) Al5 (Principal Phase) Plus Beta Alloy Containing 28 Per Cent Rhenium Deposited at 1100°C., 250X.	27
5. Microstructures of Tungsten-Rhenium Alloy Deposits Annealed at 1500°C. for 1000 hours: (a) Single-Phase Beta Alloy Containing 20 Per Cent Rhenium, 300X; (b) Beta Plus Sigma Alloy Containing 29 Per Cent Rhenium, 500X.	29
6. Location of Electron Microprobe Measurements in the Beta and Al5 Phases. 200X	30
7. Lattice Parameter of the Al5 Phase as a Function of the Rhenium Content of the Alloy	33

ABSTRACT

An Al₅-type phase was identified in vapor-deposited tungsten-rhenium alloys by x-ray and neutron diffraction, metallography, and hardness measurements. The crystal structure was established as an Al₅ type by comparing experimental x-ray and neutron diffraction integrated intensities with calculated intensities based on the usual atomic arrangement for Al₅-type phases. The composition range for the existence of this phase varied with temperature, but was near to W₃Re; in the temperature range investigated, 1000 to 1500°C., the phase occurred alone or coexisted with the tungsten-rich terminal solid solution (beta phase) or with sigma phase. The phase was about four times harder than the beta phase, possibly limiting the usefulness of alloys containing the Al₅ phase as a major constituent. Transformation to beta or to beta plus sigma phases during long-time anneals at deposition temperatures showed that the phase was metastable. Electron microprobe analyses revealed no substantial difference in composition between coexisting beta and Al₅ phases. In addition, the lattice parameter of the Al₅ phase, whether occurring alone or coexisting with beta or sigma, varied linearly with alloy composition. The metastable nature, compositional similarity with beta, and continuous variation in lattice parameter show that the formation of the Al₅ phase is characteristic of the vapor-deposition process. Based on a proposed reason for formation during deposition, the Al₅ phase would not be expected to form in beta- or beta-plus-sigma phase alloys subjected to service at elevated temperatures.

CHAPTER I

INTRODUCTION

Chemical vapor deposition, as used in the recent literature (1),* refers specifically to the chemical reaction of gaseous species at a heated surface to produce a solid deposit, thus distinguishing the process from other vapor deposition processes such as vacuum metallizing. In the present research, chemical vapor deposition refers to the particular process whereby tungsten and rhenium hexafluorides (WF_6 and ReF_6) were reduced by hydrogen at a heated surface to produce a solid tungsten-rhenium alloy deposit and hydrogen-fluoride gas.

In 1962 an investigation of chemical vapor deposition was begun at the Oak Ridge National Laboratory to assess the potential use of the process as a fabrication technique for refractory metals. Tungsten deposition studies indicated that the advantages of the process as compared with other fabrication processes included relatively simple and inexpensive equipment, lower temperatures, higher purity, and the ability to deposit coatings, flat stock, tubing, and various other shapes (2). Concurrently the vapor deposition of UO_2 raised the possibility of directly fabricating integral fuel elements for nuclear reactors (3).

Wrought tungsten, although strong, is also brittle near room temperature. Wrought tungsten-25 weight per cent rhenium alloys, however,

*Denotes reference. See page 46.

are ductile at temperatures as low as -75°C . Low-temperature ductility is advantageous during handling, assembly, and machining operations. Thus, the incentive for vapor depositing tungsten-rhenium alloys was to obtain the advantages of chemical vapor deposition along with strength and ductility.

Codeposition studies in 1964 revealed a previously unreported cubic phase in certain tungsten-rich alloys deposited in the temperature range 450 to 700°C . (refs. 4,5). The new phase occurred alone or coexisted with the tungsten-rich terminal solid solution depending upon alloy composition and deposition temperature. The phase was tentatively identified as an Al5-type phase, that is, having the same type crystal structure as W_3O , by comparison with the x-ray diffraction pattern of another Al5-type phase.

Tungsten-rhenium alloys containing primarily the Al5 phase were substantially more brittle than the solid solution at room temperature as was evidenced by the relative ease of crushing the two types of deposits to powder for x-ray diffraction studies. Mechanical properties might also be affected at higher temperatures. For these reasons optimum use of vapor-deposited alloys required characterization of the Al5 phase. In addition, this problem presented a possible opportunity to supplement the tungsten-rhenium phase diagram (6,7) using vapor deposition to prepare the alloys, possibly the first such application to metallurgical research. Thus, this research had overlapping practical and academic aspects.

The purpose of this study was to characterize the new phase found in vapor-deposited tungsten-rhenium alloys. Characterization included the following specific areas of study:

1. Metallographic examination to determine the appearance and distribution of the phase in the microstructure.
2. Hardness measurements to account for the brittleness of alloys containing the phase.
3. Temperature and composition limits for formation during deposition.
4. Stability and transformation products of the phase during anneals at elevated temperatures.
5. Lattice parameter measurements as a function of the composition of the phase.
6. Confirmation of the crystal structure type and ordering arrangement, hence confirmation of the identity of the new phase as an Al₅ type.

Achieving the above goals involved the deposition of alloys containing up to 50 per cent rhenium at 100°C. intervals between 1000 and 1500°C. and annealing of as-deposited alloys in the temperature range 1300 to 2000°C. Phases present in the alloys were determined from x-ray diffraction patterns of powder samples, and standard procedures were used also for chemical analyses, electron microprobe analyses, metallography, and hardness measurements. The crystal structure was established by correlating intensity peaks on x-ray and neutron diffractometer traces with calculated intensities based upon a proposed atom arrangement.

CHAPTER II

LITERATURE SURVEY

Chemical Vapor Deposition of Alloys

Vapor deposition processes are not of recent origin. Tungsten, for example, was deposited by thermal decomposition of WF_6 vapor in 1909 (ref. 8), by hydrogen reduction of WCl_5 vapor in 1923 (ref. 9), and by the de Boer type process in 1934 (ref. 10). Rhenium was deposited by thermal decomposition of rhenium halides in 1930 (ref. 11). These few references to early work were selected from the book entitled Vapor Deposition by Powell, Oxley, and Blocher (1), which is a valuable reference due to the comprehensive survey of vapor deposition theory, methods, and applications. Numerous references to metals, alloys, and nonmetals prepared by vapor deposition processes are included therein.

The feasibility of preparing alloys by vapor deposition has been demonstrated in many systems, mainly in the preparation of alloy coatings on base metals to improve a particular property, such as oxidation resistance. In many such cases the alloy constituents were supplied to the base by a displacement (or interchange) reaction wherein the base metal participates in the reaction. For example, in the aluminizing (12) and chromizing (13) of iron the following reactions occur:

In other cases the alloy constituent was deposited on the base metal by a surface catalyzed reduction reaction, such as the chromizing of iron (13) by the reaction:

Whether deposition occurred by the displacement or reduction reaction, alloying occurred by interdiffusion between the deposited metal and the base metal. Thus, the manner of obtaining alloys in most prior work (deposition followed by diffusion) differed from that of the present research, which involved the simultaneous deposition of both alloying metals (tungsten and rhenium) on a chemically inert substrate. Only a few references to similar codeposition processes were found in the literature, and these are reviewed below. In no case was a previously unknown phase found in the vapor-deposited alloys.

Molybdenum-tungsten alloy coatings were obtained by thermal decomposition of a mixture of the metal carbonyls at about 500°C. (ref. 14); the coatings should have contained 18 or 19 atomic per cent tungsten on the basis of the carbonyl vapor pressures, although an analysis was not performed. X-ray diffraction patterns revealed a body-centered cubic structure practically identical to that of molybdenum. The deposits were hard and brittle, possibly due to carbon contamination (unstated and undetermined) from the carbonyl coating gas.

Nickel-iron alloys of the Permalloy type (approximately 45 to 80 per cent nickel) were deposited as films about 2500 angstroms thick on glass substrates by thermal decomposition of mixtures of iron and

nickel carbonyls (15,16). Carbon contamination of the films was indicated by the magnetic properties, which also were the main evidence for alloy formation.

Niobium-tantalum alloys were deposited by hydrogen reduction of a mixture of the metal pentachlorides at about 1000°C.; however, neither the compositions obtained nor x-ray or metallographic evidence for alloy formation was stated (17).

The superconducting compound Nb_3Sn was deposited by hydrogen reduction of the mixed chloride vapors NbCl_5 and SnCl_2 or NbCl_5 and SnCl_4 at temperatures ranging from 730 to 1200°C. (refs. 18,19). The composition range obtained was 73.3 to 81.4 atomic per cent niobium, and the deposits were single phase having the A15-type structure. This compound also crystallizes in the A15-type structure when prepared by other methods, such as arc melting. An interesting aspect of this work was that Nb_3Sn coatings of uniform thickness having an oriented columnar grain structure occurred when the substrate, either platinum or gold, reacted with the first niobium deposited to form the A15-type structures Nb_3Pt or Nb_3Au . When tantalum and tungsten substrates were used, epitaxial deposition of niobium occurred before nucleation of the Nb_3Sn compound; and the deposit eventually assumed an uneven, nodular form.

Niobium-zirconium alloy coatings were deposited by the simultaneous hydrogen reduction of the metal chlorides at about 1000°C. in order to provide a protective coating on stainless steel for liquid-metal service (20). A large excess of zirconium in the gas phase was required in order to obtain the desired niobium-1 per cent zirconium alloy.

Chromium-titanium alloy coatings on refractory metals for oxidation resistance were obtained by simultaneous hydrogen reduction of the metal chlorides (21). The intended composition, 50 per cent chromium-50 per cent titanium, was not ascertained by chemical analysis, but metallographic evidence for nonuniformity of composition was obtained.

Tungsten-rhenium alloys were deposited by the simultaneous thermal decomposition of the metal chlorides at about 1300°C. (ref. 22). X-ray diffraction showed that alloys containing 16.3 and 24.5 per cent rhenium consisted of two phases: the body-centered cubic solid solution and sigma phase. No evidence of the Al5-type structure was found in these alloys. Tungsten-rich alloys prepared by the simultaneous hydrogen reduction of the hexafluorides at lower temperatures may have contained the Al5-type structure, as evidenced by hardness and brittleness in the as-deposited condition.

In summary, the literature reveals that the vapor-deposited alloys were not usually extensively characterized; vapor deposition has not been used in the determination of phase boundaries; and, with the possible exception of the tungsten-rhenium deposition studies (22), vapor deposition has not produced a previously unknown phase in any alloy system investigated.

The Al5-Type Structure

The material having the Al5 structure and erroneously described as beta-tungsten was apparently first prepared by electrolysis of a fused mixture of WO_3 and alkali metal phosphates (23) and by

electrolysis of alkali metal tungstates (24) at temperatures below 700°C. However, the contention that "beta-tungsten" was an allotropic modification of pure tungsten was eventually contradicted by density determinations and decomposition behavior during heat treating (25). A "beta-tungsten" sample containing a small amount of normal body-centered cubic tungsten had a density of 15.0 grams per cubic centimeter compared with 18.5 grams per cubic centimeter for 99.9 per cent pure body-centered cubic tungsten, and the sample decomposed into tungsten and tungsten dioxide after heating 3 hours in vacuum at 750°C. Consideration of spacing in the Al5 structure led to the conclusion that "beta-tungsten" was actually W_3O . X-ray diffraction revealed the Al5-type structure with the atoms randomly distributed on the atomic sites.

Literature references to phases having the same crystal structure as W_3O use the terms beta-tungsten structure, Al5-type structure, and Cr_3O -type structure. The latter term is apparently used in some cases because Cr_3O was found to be ordered and many Al5-type structures conform to the same ordering arrangement (26,27). The structure occurs frequently in binary systems involving transition elements. At least thirty-nine such phases were known in 1958 (ref. 27).

The nominal composition for Al5-type structures is A_3B . In the binary systems rhodium(vanadium, niobium, and chromium) and platinum(vanadium, niobium, and chromium), the phases appeared to have a narrow composition range around the stoichiometric composition (28). In all these cases the phases were ordered with eight atoms in the unit cell occupying the following positions:

A atoms: $1/4, 0, 1/2$; $1/2, 1/4, 0$; $0, 1/2, 1/4$; $3/4, 0, 1/2$; $1/2, 3/4, 0$;
 $0, 1/2, 3/4$;

B atoms: $0, 0, 0$; $1/2, 1/2, 1/2$.

Rhenium-tungsten alloys were included in the same investigation (28). Arc-melted alloys containing about 60 per cent tungsten, annealed at 1200°C . for 72 to 120 hours and quenched in cold water, contained sigma and another phase, the latter being neither identified nor discussed.

Other investigations of tungsten-rhenium alloys have not revealed the presence of the Al₅-type structure (29,30,6). In the most recent and most thorough phase diagram investigation, the basis for the presently accepted phase diagram, arc-melted alloys containing 30 per cent rhenium and higher were vacuum annealed at 1600°C . for several hundred hours until equilibrium was achieved (6). X-ray diffraction showed that tungsten-rich alloys consisted of the body-centered cubic and sigma phases or sigma only, depending upon composition.

Theoretical aspects of the Al₅-type structure have been treated in some detail. The lattice parameters of A₃B compounds having the structure were correlated with the Goldschmidt radius of the A atoms, which are arranged in chains (coordination number 2) in the three mutually perpendicular directions of the cubic axes (28). In another study the apparent radii of the A and B atoms in the structure were compared with the Goldschmidt radii (26). Effective coordination number 12 radii were deduced for elements in compounds crystallizing in the A-15 type structure, and from these the lattice constants could be reproduced

to within 0.03 angstrom (ref. 31). In a study of atomic size effects in thirty-nine phases (the total number known at the time) the occurrence and lattice parameters were also related to the Goldschmidt coordination number 12 radii (27). According to this study a necessary, but not sufficient, condition for occurrence of the structure is that the Goldschmidt coordination number 12 radii of the component elements do not differ by more than about 15 per cent. Also, the lattice parameter of Al₅-type phases with a given A-element depends linearly on the Goldschmidt coordination number 12 radius of the B-element. When the B-element remains the same, the dependence of lattice parameter on the Goldschmidt coordination number 12 radius of the A-element appears to be substantially linear.

Thus, the literature indicates that the Al₅-type structure occurs frequently in binary systems involving transition elements, the structures usually conform to a certain ordering scheme, and both the occurrence and lattice constants can often be correlated with the atomic size of the elements involved.

CHAPTER III

EXPERIMENTAL PROCEDURE

Deposition of Alloys

Tungsten-rhenium alloys were deposited in the apparatus shown schematically in Figure 1. Hydrogen was metered by a Brooks Instrument Company, Inc., flowmeter having a glass tube, number 2-15-A, and an 1/8-inch-diameter stainless steel ball float calibrated at 70°F. (21°C.) and one atmosphere. The WF_6 and ReF_6 were metered separately by Hastings-Raydist, Inc., mass flowmeters calibrated also at 70°F. and one atmosphere. In the deposition chamber the alumina mandrel, 0.325 inch in outside diameter and 3 inches long, was heated by contact with a resistance heated 1/8-inch-diameter carbon rod supported in water-cooled holders. The metered and premixed gases reacted on the heated mandrel to produce a solid alloy deposit and gaseous hydrogen fluoride by the reactions:

At the end of the deposition period, the hexafluoride flows were stopped; and the deposit slowly cooled to room temperature in a hydrogen atmosphere. No reaction occurred between the deposit and the alumina mandrel, and the deposit could be mechanically removed without difficulty.

Figure 1. Tungsten-rhenium vapor deposition apparatus.

Practically all unreacted fluorides that passed through the deposition chamber were reduced in the scavenger furnace, thus minimizing contamination of the vacuum pump with metal fluorides. The cold trap ($-70^{\circ}\text{C}.$) minimized backstreaming of pump oil vapor that causes carbon contamination of the deposits. The desired system pressure was maintained by throttling the vacuum pump, and was monitored by a mercury manometer which could be read to about ± 1 torr. Excess hydrogen was burned and the hydrogen fluoride was diluted with water in the scrubber for disposal.

Temperature was measured by a Pyro optical pyrometer sighted directly on the deposit. The pyrometer was calibrated by sighting on a deposit in which a stainless steel sheathed Chromel-P-Alumel thermocouple was embedded. The Chromel-P-Alumel thermocouple had previously been compared to a platinum-platinum 10 per cent rhodium thermocouple while inserted together in a $3/8$ -inch-diameter alumina tube with the beads about $1/16$ inch apart. The thermocouples agreed within $\pm 5^{\circ}\text{C}.$ over the range 600 to $1200^{\circ}\text{C}.$ The temperatures indicated by the pyrometer and thermocouple plotted as a straight line over the range 825 to $1250^{\circ}\text{C}.$ as shown in Figure 2. Higher temperature calibration of the pyrometer was obtained by extrapolation of the data. This calibration included the correction for emissivity of the deposit and absorption in a clean silica glass window. Although the deposit coated the entire 3-inch-long mandrel, only the center one-inch-long section for which the temperature was observed during deposition was used for evaluation.

Figure 2. Calibration of optical pyrometer.

Alloys were deposited at temperatures of 1000 to 1500°C. and a pressure of 5 torrs. The volumetric hydrogen-to-(WF₆ + ReF₆) ratio was 15; the volumetric WF₆-to-ReF₆ ratio was varied from 0.7 to 10 in order to obtain different alloys, and the deposition time for each alloy was 2 hours.

Annealing Treatments

The alloys were vacuum annealed at temperatures from 1300 to 2000°C. in a furnace having a tantalum heating element, tantalum heat shields, and a water-cooled stainless steel outer wall. The samples were located inside a tantalum crucible, 3/4 inch in diameter and 4 inches long, during annealing. Temperatures were measured under essentially blackbody conditions by sighting a pyrometer on the tantalum crucible through slits in the heat shields. Pressures of 10⁻⁹ to 10⁻⁷ torr were maintained during heating and for the duration of the anneal by an oil diffusion pump. A liquid nitrogen cold trap minimized carbon contamination of samples by oil vapor.

Metallography and Hardness Measurements

Conventional metallographic techniques were used to prepare samples for examination of sections perpendicular to the substrate. All samples were etched in a solution composed of one part of a 58 weight per cent NH₄OH solution and one part of a 30 weight per cent H₂O₂ solution.

Hardness measurements were made on metallographic samples with a Kentron hardness machine using a 136-degree diamond pyramid indenter and

a 500-gram load. Several evenly spaced indentations were made across the thickness of the samples in order to obtain an average hardness value.

Phase Identification and Crystal Structure Determination

A 0.1- to 0.2-gram sample of each deposit was crushed to powder using a hardened steel mortar and pestle. A small portion of the powder was stuck to a silica glass fiber coated with Vaseline, and mounted in a Norelco Debye-Scherrer camera. The radiation used was copper K alpha produced at 35 kilovolts and 20 milliamperes. Exposure times of 16 to 20 hours ensured that weak lines and minor phases were detected. An estimate of the proportions of phases present was made on the basis of apparent line densities, and the line positions were measured to the nearest 0.001 centimeter on a Norelco film reader.

X-ray diffractometer traces were made with a Norelco diffractometer equipped with a NaI (Tl) scintillation counter. The 2 theta scan rate was 1/4 degree per minute.

Neutron diffractometer scans were made in the Oak Ridge Research Reactor. For this purpose approximately 30 grams of alloy powder in a cylindrical cell were irradiated with neutrons of wavelength 1.093 angstroms. Values of 2 theta ranged from 2 to 66 degrees. A plot of diffraction peak intensity versus 2 theta was obtained by point counting at intervals of 0.1 degree 2 theta. Experimental integrated intensities were obtained from the plot by determining the area under each peak with a planimeter.

Chemical Analysis

The powder used for phase identification by x-ray diffraction was used also for rhenium analysis. The rhenium content of phases was determined by an electron probe. Carbon, hydrogen, oxygen, nitrogen, fluorine and trace metals were determined in samples adjacent to the location from which x-ray samples were taken. The types of analyses employed and the precision values applicable to the analysis of tungsten-rhenium alloys are presented in Table I.

TABLE I

CHEMICAL ANALYSIS TECHNIQUES FOR TUNGSTEN-RHENIUM ALLOYS

Element	Analytical Technique	Precision (95% Confidence Level)
Rhenium	Gravimetric, electron probe	$\pm 1\%$ and $\pm 5\%$, respectively
Carbon	Spectrophotometric	± 25 to $\pm 40\%$ for 20 and 5 p.p.m.; respectively
Hydrogen	Vacuum fusion-chromatograph	$\pm 10\%$ up to 50 p.p.m.
Oxygen	Vacuum fusion-chromatograph	$\pm 10\%$ up to 50 p.p.m.
Nitrogen	Vacuum fusion-chromatograph	$\pm 10\%$ up to 50 p.p.m.
Fluorine	Spectrophotometric	± 10 to $\pm 50\%$ for 20 and 1 p.p.m., respectively
Trace metals	Spectroscopic	Depends on element

CHAPTER IV

RESULTS

Composition and Temperature Range of Formation of the Al₅ Phase

The phases found in as-deposited alloys are listed in Table II. These data show that the deposits usually consisted of either the tungsten-rich terminal solid solution beta, the Al₅ phase, or a mixture of the two phases. Sigma phase occurred in some deposits of high rhenium content, and occurred along with the Al₅ and beta phases in two deposits at 1500°C. Three solid phases can coexist in a binary system only at a eutectoid or peritectoid temperature or under conditions of nonequilibrium.

Phases present in various as-deposited alloys are also shown in relation to a portion of the tungsten-rhenium phase diagram in Figure 3. Phase boundaries involving the as-deposited phases are shown as broken lines in the 1000 to 1500°C. region, while previously established equilibrium phase boundaries are shown as solid lines. Figure 3 shows that the homogeneity range of the Al₅ phase is relatively wide and is not centered about the nominal composition A₃B. Vapor-deposited alloys containing 26 per cent rhenium, the approximate optimum composition for ductility in wrought alloys, contain amounts of the Al₅ phase dependent upon deposition temperature. The phase was previously found to be dominant in alloys containing 15 and 26 per cent rhenium and was the only phase in an alloy containing 37 per cent rhenium, all deposited at 600°C. (refs. 1,2).

Table II

PHASES IN AS-DEPOSITED TUNGSTEN-RHENIUM ALLOYS

Deposition Temperature (°C.)	Rhenium (wt. %)	Phases Present ^a		
		β	Al5	Other
1000	19.1	S	b	b
	21.9	W	S	b
	23.0	W	S	b
	25.6	W	S	b
	31.6	b	S	b
	34.0	b	S	b
	59.0	b	b	(x)S
1100	13.5	S	b	b
	14.8	S	b	b
	19.6	S	b	b
	23.7	S	W	b
	24.7	M	S	b
	26.1	S	W	b
	28.5	b	S	b
1200	42.4	b	S	b
	11.1	S	b	b
	13.5	S	b	b
	16.6	S	b	b
	18.4	S	b	b
	25.8	S	W	b
	37.4	b	S	b
1300	44.7	b	S	(σ)W
	50.8	b	S	(σ)W
	21.8	S	b	b
	22.2	S	b	b
	23.9	S	b	b
1400	31.1	S	W	b
	37.7	b	S	b
	43.5	b	S	b
1500	52.0	b	b	(σ)S
	57.0	b	b	(σ)S
	8.3	S	b	b
	26.2	S	b	b
	28.6	S	b	(σ)W
	34.0	M	M	(σ)W
	37.3	M	M	(σ)W
	57.2	b	b	(σ)M
	59.3	b	b	(σ)M

^aSymbols refer to amounts of phases estimated from x-ray line intensities: S is strong; M is medium; W is weak.

^bSought but not found.

Figure 3. Vapor-deposited phases shown in relation to the tungsten-rhenium phase diagram.

The impurity content of deposits selected at random are shown in Table III. The major impurity was oxygen, some of which may have been derived from the alumina mandrel. The deposits also contained traces of calcium and magnesium (0.0001 to 0.001 weight per cent) and silicon (0.001 to 0.01 weight per cent). The amounts of other metallic impurities were below the limits of detection of the spectroscopic analysis.

The Al₅ phase has not been found in alloys prepared by the usual powder metallurgy and arc-casting techniques and is not shown on the presently accepted phase diagram (6). The first reason proposed to explain the absence of the phase in these alloys was that low diffusion rates below 1500°C. caused the transformation to equilibrium products to be slow. Thus, if the Al₅ phase were an equilibrium phase, the usual alloy preparation techniques ordinarily would not allow sufficient time for formation. An alternate explanation is that the Al₅ phase is a nonequilibrium phase that can be formed only by vapor deposition or similar technique. Annealing treatments, which will now be described, showed conclusively that the Al₅ phase is a nonequilibrium phase.

Stability of the Al₅ Phase

The temperature stability of the as-deposited structures was determined by annealing alloys containing from 14.8 to 57.2 per cent rhenium at temperatures from 1300 to 2000°C. and determining the phases present by x-ray diffraction powder patterns. The results of these anneals are shown in Table IV. At all temperatures investigated above 1300°C. the Al₅ phase transformed to beta or beta plus sigma. In alloys annealed at 1300°C. for 700 hours the amount of Al₅ phase was always

Table III

IMPURITY CONTENT OF TUNGSTEN-RHENIUM DEPOSITS

Deposition Temperature (°C.)	Rhenium (wt. %)	Impurity (p.p.m)				
		Carbon	Fluorine	Hydrogen	Nitrogen	Oxygen
1000	31.6	20	27	2	< 1	89
1100	13.5	40	< 6	11	< 1	56
1100	26.1	30	< 6	4	3	50
1200	16.6	20	< 5	< 1	< 1	60
1200	25.8	< 20	< 5	2	1	70
1200	37.4	20	< 5	1	< 1	120
1300	22.2	20	< 5	2	< 1	190
1400	43.5	< 20	< 5	1	< 1	51
1500	34.0	20	< 5	1	< 1	44

TABLE IV

PHASES^a IN AS-DEPOSITED AND ANNEALED TUNGSTEN-RHENIUM ALLOYS

Deposition Temperature (°C.)	Rhenium (wt. %)	Annealing History													
		As-Deposited			2000°C.		1800°C.		1500°C.		1450°C.		1300°C.		
					20 hr.		100 hr.		1000 hr.		1000 hr.		700 hr.		
		β	Al5	σ	β	σ	β	σ	β	σ	β	σ	β	Al5	σ
1000	21.9	W	S	b									S	W	b
	23.0	W	S	b									S	W	b
	25.6	W	S	b									W	S	b
	34.0	b	S	b									M	W	M
1100	14.8	S	b	b	S	b	S	b			S	b			
	19.6	S	b	b	S	b	S	b	S	b					
	23.7	S	W	b					S	b			S	W	b
	24.7	M	S	b	S	b	S	W	S	W					
	28.5	b	S	b	S	W	S	W	S	W	S	W	S	W	W
	42.4	b	S	b			b	S	M	S	M	S	M	b	S
1200	18.4	S	b	b							S	W			
	25.8	S	W	b							S	W	S	b	b
	37.4	b	S	b							S	M			
	50.8	b	S	W	b	S					b	S			
1300	31.1	S	W	b									S	b	W
1500	26.2	S	b	b									S	b	b
	28.6	S	b	W							S	M			
	34.0	M	M	W							S	W			
	37.3	M	M	W							S	M			
	57.2	b	b	M							b	S			

^aSymbols refer to amounts of phases estimated from x-ray line intensities: S is strong; M is medium; W is weak.

^bSought but not found.

less than in the as-deposited condition. This is shown by the change in intensity ratios of the (211) Al₅ reflection to the (200) beta reflection presented in Table V. In addition, lines corresponding to sigma phase appeared in the x-ray patterns of some of the alloys following the annealing treatment at 1300°C. (Table IV). The results of these annealing studies show that the Al₅ phase is metastable and decomposes into products consistent with an extrapolation of the presently accepted equilibrium phase boundaries to 1300°C.

Microstructures, Phase Analysis, and Hardness

The microstructure of alloy deposits varied with kind and amount of phases present. The single-phase beta deposit shown in Figure 4a has a fine-grained structure in the first deposited region and coarse columnar grains similar to those of unalloyed tungsten deposits (2). The two phases, beta and Al₅, are clearly distinguished in Figure 4b. The matrix or continuous phase in this structure is the beta phase as shown by the larger hardness indentation. The hardness of the Al₅ phase is much greater than that of other phases encountered in both as-deposited and annealed alloys. Although not clearly shown in Figure 4b because the beta phase is underetched, the overall grain structure of the deposits containing both the beta and Al₅ phases was similar to the all-beta phase deposits. Because of this similarity and the nature of the interaction of the two phases with the etchant, differentiation between the beta and Al₅ phases was difficult when the samples were heavily etched.

TABLE V

RATIO OF DIFFRACTOMETER PEAK HEIGHTS

Deposition Temperature (°C.)	Rhenium (wt. %)	Intensity Ratio ^a	
		As-Deposited	Annealed at 1300°C. for 700 hr.
1000	23.0	25	0.1
1000	34.0	∞	2.1
1100	23.7	3.9	0.1
1100	28.5	∞	21
1300	31.1	1.3	0
1500	26.2	0.2 ^b	0

^a(211) Al5 to (200) beta.

^bWeak Al5 phase reflection shown by diffractometer but not by Debye-Scherrer powder pattern.

Figure 4. Microstructures of as-deposited tungsten-rhenium alloys: (a) single-phase beta alloy containing 20 per cent rhenium deposited at 1100°C., 200X; (b) beta (principal phase) plus Al5 alloy containing 26 per cent rhenium deposited at 1200°C., 150X; and (c) Al5 (principal phase) plus beta alloy containing 28 per cent rhenium deposited at 1100°C., 250X.

Figure 4c shows the microstructure of a deposit consisting primarily of the Al5 phase. The minor constituent, beta phase, was confined to the small slightly darker areas and a thin layer on the last deposited surface (top) of the deposit.

In addition to the transformation previously discussed, recrystallization and/or grain growth occurred during annealing. Figure 5 shows typical microstructures of alloys annealed at 1500°C. for 1000 hours. The grains of the single-phase beta alloy shown in Figure 5a are still elongated in the growth direction but are much larger than in the as-deposited condition (Figure 4a). The microstructure of Figure 5b shows the transformation products of the Al5 phase, namely sigma in a beta matrix.

If the phase relationships for vapor-deposited alloys shown in Figure 3, page 21, are interpreted as if equilibrium existed, the coexisting beta and Al5 phases would differ in composition by approximately 5 to 8 per cent rhenium in the temperature range 1000 to 1400°C. This apparent difference in composition does not actually exist, however, as was shown by electron microprobe analysis of the two phases. Measurements were made randomly in an Al5 phase particle and the beta matrix as shown by the approximately 1-micron-diameter spots in Figure 6. The rhenium content by weight per cent determined at these points was:

<u>Beta Matrix</u>	<u>Al5 Phase</u>
30.3	27.9
25.5	24.6
29.5	26.9
28.5	28.3
27.9	29.0
28.6	28.1
28.0	Average 27.5
Average 28.3

Figure 5. Microstructures of tungsten-rhenium alloy deposits annealed at 1500°C. for 1000 hours: (a) single-phase beta alloy containing 20 per cent rhenium, 300X; (b) beta plus sigma alloy containing 29 per cent rhenium, 500X.

Figure 6. Location of electron microprobe measurements in the beta and Al5 phases. 200x.

These data reveal no substantial difference in composition between the two phases, and support the conclusion, based on annealing studies, that the Al₅ phase occurring in as-deposited alloys is metastable.

The diamond pyramid hardnesses of alloys deposited at 1100°C. and annealed at 1500°C. are compared in Table VI. These data show that the hardness of the beta phase increases gradually with increasing rhenium content, and the hardness of the alloy increases abruptly when the Al₅ phase becomes the major constituent. Annealing at 1500°C. resulted in a large decrease in hardness, even in alloys having sigma as the major phase.

Lattice Parameter and Crystal Structure Type

Debye-Scherrer patterns for the new phase found in this investigation could be indexed assuming a cubic unit cell. Lattice parameters were calculated by use of a computer program including a Nelson-Riley extrapolation (32). Values of the lattice parameter of the phase, later confirmed as an Al₅ type, ranged between 4.9817 ± 0.0005 angstroms and 5.0196 ± 0.0003 angstroms and varied linearly with the rhenium content of the alloy as shown in Figure 7. The linear relationship holds for the Al₅ phase in both single- and two-phase regions; this fact agrees with the electron microprobe analyses presented previously.

The structure was identified as a Al₅ type by comparison of calculated and experimental x-ray and neutron diffraction intensities. The typical cubic Al₅-type structure has the space group Pm $\bar{3}$ n with eight atoms in the unit cell: A atoms in 6(c) positions, $1/4, 0, 1/2$; $1/2, 1/4, 0$; $0, 1/2, 1/4$; $3/4, 0, 1/2$; $1/2, 3/4, 0$; $0, 1/2, 3/4$ (alpha sites); and B atoms

TABLE VI

HARDNESS OF AS-DEPOSITED AND ANNEALED ALLOYS

Rhenium (wt. %)	As-Deposited ^a		Annealed ^b	
	Phases	Hardness (D.P.H.)	Phases	Hardness (D.P.H.)
13.5	β	420		
14.8	β	450		
19.6	β	440	β	450
23.7	β^c Al5	500 ^c	β	630
24.7	β Al5 ^c	1740 ^c	β^c σ	450
28.5	Al5	1630	β σ^c	800
42.4	Al5	1830	β σ^c	1030

^aDeposition temperature 1100°C.^b1500°C, 1000 hr.^cMajor phase.

Figure 7. Lattice parameter of the Al₅ phase as a function of the rhenium content of the alloy.

in 2(a) positions, 0,0,0 and 1/2,1/2,1/2 (beta sites), (ref. 27). The structure factors and x-ray intensities calculated for a completely ordered unit cell in a stoichiometric alloy (W_3Re) are shown in Table VII, wherein f_W and f_{Re} are the x-ray atomic scattering factors for tungsten and rhenium, respectively. The structure factors could have been calculated for the completely disordered or any partially ordered state since x-ray diffraction cannot distinguish order in the unit cell. This is true because f_W and f_{Re} are nearly identical and, therefore, the structure factors and x-ray intensities computed for the ordered and random arrangements are essentially the same. For the same reasons, nearly the same x-ray intensities would occur for stoichiometric and nonstoichiometric compositions. However, x-ray diffraction can be used to establish if the atomic coordinates are those given above for Al5 phases.

X-ray intensities were calculated from the expression (33)

$$I = cp \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} F_{hkl}^2$$

where

I = integrated intensity of an hkl reflection,

c = proportionality constant,

p = multiplicity,

$\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$ = Lorentz-polarization factor,

F_{hkl}^2 = structure factor for the hkl reflection.

TABLE VII

CALCULATED AND EXPERIMENTAL X-RAY DIFFRACTION
INTENSITIES FOR THE Al₅-TYPE PHASE IN
A TUNGSTEN-BASE ALLOY^a

hkl	F_{hkl}	Relative Intensity, I/I_{210}	
		Calculated	Experimental
100	0	0	0
110	$-2f_W + 2f_{Re}$	0	0
111	0	0	0
200	$2f_W + 2f_{Re}$	36	27
210	$-4f_W$	100	100
211	$2f_W + 2f_{Re}$	80	66
220	$-2f_W + 2f_{Re}$	0	0
221,300	0	0	0
310	$-2f_W + 2f_{Re}$	0	0
311	0	0	0
222	$-6f_W + 2f_{Re}$	8	9
320	$-4f_W$	23	27
321	$2f_W + 2f_{Re}$	41	43
400	$6f_W + 2f_{Re}$	16	17
322,410	0	0	0
330,411	$-2f_W + 2f_{Re}$	0	0
331	0	0	0
420	$2f_W + 2f_{Re}$	12	11
421	$-4f_W$	22	26
332	$2f_W + 2f_{Re}$	11	11
422	$-2f_W + 2f_{Re}$	0	0
430,500	0	0	0
431,510	$-2f_W + 2f_{Re}$	0	0
333,511	0	0	0
432,520	$-4f_W$		
521	$2f_W + 2f_{Re}$	70 ^b	61 ^b
440	$6f_W + 2f_{Re}$		
441,522	0	0	0
433,530	$-2f_W + 2f_{Re}$	0	0
531	0	0	0
442,600	$2f_W + 2f_{Re}$	17	11
610	$-4f_W$	14	17
532,611	$2f_W + 2f_{Re}$	50	44

^aW-34% Re.

^bOverlapping peaks grouped and counted together.

Experimental integrated intensities were determined for an alloy containing 34 per cent rhenium by standard techniques using a Norelco diffractometer and a NaI (Tl) scintillation counter. Observed intensities are compared with calculated values (both normalized to the strongest, 210, reflection) in Table VII. Although the calculated values were not corrected for thermal vibrations, the close agreement between calculated and experimental intensities confirms that the atomic coordinates in the unit cell are actually those for the Al5-type structure.

Neutron diffraction was used in the same manner to investigate order in the unit cell. This was possible because the neutron scattering factor of rhenium is about double that of tungsten. An alloy containing both beta and Al5 phases was first irradiated, but interpretation of the diffraction pattern was complicated by overlapping beta and Al5 peaks. Then, a single-phase-Al5 alloy containing 38.9 per cent rhenium was irradiated. Since the alloy contained rhenium in excess of the stoichiometric composition, W_3Re , the unit cell could not be completely ordered; therefore, intensities were calculated using structure factors which allowed for the nonstoichiometric composition and imperfect order.

Let occupation probabilities be defined as follows:

r_α = fraction of alpha sites occupied by tungsten,

w_α = fraction of alpha sites occupied by rhenium,

r_β = fraction of beta sites occupied by rhenium,

w_β = fraction of beta sites occupied by tungsten.

Then

$$r_{\alpha} + w_{\alpha} = 1,$$

and

$$r_{\beta} + w_{\beta} = 1.$$

Since the structure has three times as many alpha sites as beta sites, a material balance for tungsten yields

$$\frac{3}{4} r_{\alpha} + \frac{1}{4} w_{\beta} = M_w,$$

where M_w is the atom fraction of tungsten.

Solving for w_{β} and r_{β} gives

$$w_{\beta} = 4 M_w - 3 r_{\alpha},$$

$$r_{\beta} = 1 - 4 M_w + 3 r_{\alpha}.$$

The structure factors in Table VII, page 34, were modified by including the occupation probabilities in the following manner;

$$F_{hkl} = A(r_{\alpha} f_W + w_{\alpha} f_{Re}) + B(r_{\beta} f_{Re} + w_{\beta} f_W),$$

where A and B are the constants for each hkl reflection and f_W and f_{Re} are now the neutron atomic scattering factors for tungsten and rhenium, respectively. Arbitrary values were assigned to r_{α} , thereby fixing the corresponding values of w_{α} , r_{β} , and w_{β} , and structure factors were

calculated for each reflection. The intensities were calculated from the expression

$$I = c \frac{p F_{hkl}^2}{\sin \theta \sin 2\theta},$$

which is applicable to a cylindrical powder sample fully bathed in the neutron beam (34). The terms in this expression are analagous to those in the expression for x-ray intensity. In these calculations the Debye-Waller temperature factor was treated as invariant and equal to unity. The calculated intensities are compared with experimental intensities, both normalized to the 400 reflection, in Table VIII. For comparative purposes the experimental intensities were scaled on the basis that $I_{400}^{\text{exp}} = I_{400}^{\text{calc}}$ because the 400 reflection is independent of the degree of order, that is, terms involving r_α , w_α , r_β , and w_β cancel from the expression for F_{400} .

The value of r_α which minimizes the function (35)

$$R = \frac{\sum_{hkl} \left| |F_{hkl}^{\text{exp}}| - |F_{hkl}^{\text{calc}}| \right|}{\sum_{hkl} |F_{hkl}^{\text{exp}}|}$$

assures closest agreement between calculated and experimental data consistent with the constraints imposed (neglect of temperature and absorption factors and possible errors in the neutron scattering factors). Values of R computed for four values of r_α are shown below; the minimum in R occurred near $r_\alpha = 0.73$.

TABLE VIII

CALCULATED AND EXPERIMENTAL NEUTRON DIFFRACTION INTENSITIES FOR
THE A15 PHASE IN A TUNGSTEN-BASE ALLOY^a

hkl	Intensity, $I/I_{400} \times 33$					Experimental
	Calculated					
	$r_\alpha = 0.65$	$r_\alpha = 0.70$	$r_\alpha = 0.73$	$r_\alpha = 0.75$	$r_\alpha = 0.80$	
100	0	0	0	0	0	0
110	0.7	2	4	5	9	6
111	0	0	0	0	0	0
200	31	35	36	37	39	38
210	90	88	81	79	75	90
211	85	94	98	100	106	99
220	0.2	0.6	1	1	2	0.9
221, 300	0	0	0	0	0	0
310	0.3	0.9	2	2	3	3
311	0	0	0	0	0	0
222	11	9	7	7	5	7
320	36	35	33	32	31	26
321	77	86	89	91	96	84
400	33	33	33	33	33	33
322, 410	0	0	0	0	0	0
330	< 0.1	0.3	0.5	0.7	1	0.9
411	0.2	0.9	1	1	2	
331	0	0	0	0	0	0
420	28	31	32	33	35	94
421	48	46	43	42	39	
332	26	29	30	31	33	

^aW-38.9% Re.

r_{α}	0.65	0.70	0.73	0.75	0.80
R	0.111	0.067	0.050	0.052	0.079

These results imply that the unit cell of the Al5 phase containing 38.9 per cent rhenium is partially ordered as follows:

$r_{\alpha} = 0.73$ or 4.4 tungsten atoms on alpha sites,

$w_{\alpha} = 0.27$ or 1.6 rhenium atoms on alpha sites,

$r_{\beta} = 0.79$ or 1.6 rhenium atoms on beta sites,

$w_{\beta} = 0.21$ or 0.4 tungsten atoms on beta sites.

A slightly closer agreement between calculated and experimental intensities might have been obtained by using values of r_{α} slightly above 0.73; however, the agreement obtained was satisfactory for the accuracy of the experimental data. Although not demonstrated in this study, the Al5 phase would be expected to become increasingly ordered as the composition approached the stoichiometric value, namely W_3Re .

CHAPTER V

DISCUSSION

Nevitt (27) examined atomic size effects in about thirty Al₅-type structures and found that a necessary, but not sufficient, condition for occurrence of the structure is that the Goldschmidt coordination number 12 radii of the component elements do not differ by more than about 15 per cent. The Goldschmidt radii for tungsten and rhenium differ by only about 3 per cent (36). Nevitt also found a linear relationship between lattice parameters of Al₅-type structures and Goldschmidt coordination number 12 radii for the A atoms (assuming a nominal composition A₃B). Using 1.41 angstroms as the Goldschmidt radius for tungsten, the lattice parameter of the tungsten-rhenium Al₅ phase determined from Nevitt's correlation is about 5.03 angstroms. Experimentally determined lattice parameters for the tungsten-rhenium Al₅ phase range between 4.9817 and 5.0196 angstroms. Thus, a necessary condition for occurrence of the Al₅ phase is fulfilled in the tungsten-rhenium system and the lattice parameter of the phase is consistent with values determined for a large number of Al₅-type phases.

An interesting question arising from this investigation is why the metastable Al₅ phase, instead of the equilibrium phases, forms during deposition. Although a completely satisfactory explanation cannot be given now, some basic considerations help to understand this phenomenon. When two phases are in equilibrium at a constant temperature and

pressure, the compositions are constant and independent of the overall composition of the alloy. This requires a segregation of the alloying elements. For example, assuming that sigma and beta are the equilibrium phases at 1300°C. for an alloy of overall composition corresponding to 30 per cent rhenium, the equilibrium composition of sigma would be about 43 per cent rhenium and that of beta about 25 per cent rhenium. Such large composition differences would be unlikely to occur between adjacent regions of a vapor-deposited alloy without considerable migration of the deposited atoms by surface and volume diffusion. At temperatures below about 1400°C. in the tungsten-rhenium system, the time required for such migration and segregation is probably too long for completion during the deposition process itself, as evidenced by the fact that equilibrium was not achieved at 1300°C. in 700 hours. One might expect that sigma and beta phases with nonequilibrium compositions (more nearly equal to one another) might form. However, the Al₅ phase is apparently more stable than sigma phase compositions below about 43 per cent rhenium (Figure 3, page 21).

The suggestion that large composition differences do not occur between physically adjacent phases deposited at temperatures below about 1400°C. is substantiated by the electron microprobe analyses and the variation in the lattice parameters of the Al₅ phase with overall composition shown in Figure 7, page 33. This figure illustrates that the lattice parameter of the as-deposited Al₅ phase, whether occurring alone or coexisting with beta or sigma, decreases approximately linearly with increasing rhenium content for all represented deposition temperatures.

Although the slope of the line in Figure 7, page 33, is only -0.0014 angstrom per per cent rhenium, the consistency of the data indicates that the composition of the Al₅ phase varies continually, even when two phases are present. These observations suggest that the composition of the phases is largely determined by the composition and sticking factors of the reacting gases and less by surface diffusion.

In wrought tungsten-rhenium alloys rhenium has a ductilizing effect that is retained at low temperatures. The tungsten-25 weight per cent rhenium alloy, in particular, is ductile at -75°C . In the as-deposited condition, this alloy contains different amounts of the Al₅ phase, depending upon deposition temperature; and the embrittling effect of this phase may limit the usefulness of as-deposited alloys having the phase as the major constituent. However, the Al₅ phase transforms on heating, and a single-phase beta alloy can be obtained at no higher temperature than is required for wrought alloys. The Al₅ phase was never observed to form from beta or sigma during annealing, and the amount of the Al₅ phase always decreased in alloys containing the phase in the as-deposited condition. These observations together with the metastable nature of the Al₅ phase and the proposed reason for formation during deposition lead to the conclusion that the Al₅ phase is unlikely to form in alloys subjected to service in the temperature range where the phase forms by deposition.

CHAPTER VI

CONCLUSIONS

1. An Al₅-type phase occurs in tungsten-rhenium alloys prepared by hydrogen reduction of tungsten hexafluoride and rhenium hexafluoride in the temperature range 1000 to 1500°C. The phase occurs alone or coexists with beta or sigma depending upon alloy composition and deposition temperature.

2. The Al₅ phase is about four times harder than beta and much more brittle.

3. The Al₅ phase is metastable as evidenced by transformation to beta or to beta plus sigma phases during anneals at deposition temperatures, and the beta-sigma phase boundaries on the equilibrium phase diagram can apparently be extrapolated at least to 1300°C. Single-phase beta alloys can be obtained by annealing vapor-deposited alloys at no higher temperatures than are required for wrought alloys.

4. In an alloy containing 38.9 per cent rhenium the Al₅ phase is partially ordered, with rhenium atoms occupying about 27 per cent of the 6(c) positions and tungsten occupying about 21 per cent of the 2(a) positions.

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