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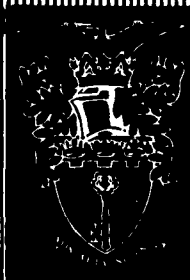
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**THE THERMAL EXPANSION OF
 β -SILICON CARBIDE AND SOME
TUNGSTEN-MOLYBDENUM ALLOYS**

by

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R O Y A L A I R C R A F T E S T A B L I S H M E N T

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SUMMARY

Thermal expansion coefficients of some tungsten-molybdenum alloys have been determined by X-ray diffraction methods over the temperature range $25^{\circ}\text{C} - 1200^{\circ}\text{C}$. Within experimental error the coefficients are independent of temperature over the range studied. β -silicon carbide has also been investigated. Values of the mean expansion coefficient $\bar{\alpha}_{1200}$ are as follows.

Composition wt % W	100	75	50	0	βSiC
at % Mo	100	85	66	0	
$\bar{\alpha}_{1200^{\circ}\text{C}} \times 10^6$	5.94	5.75	5.52	4.74	4.55

CONTENTS

	<u>Page</u>
1 INTRODUCTION	3
2 EXPERIMENTAL DETAILS	3
3 RESULTS	4
4 CONCLUSIONS	5
References	7
Illustrations	Figures 1-4
Detachable abstract cards	-

1 INTRODUCTION

The refractory metals, tungsten, molybdenum etc require a protective coating before they can be used at high temperatures in an oxidising atmosphere. It is considered that one of the requirements for a successful coating is that the mismatch between the thermal expansion of the coating and that of the base metal be small. R. Moreton¹ suggested that β -silicon carbide would function best as an oxidation-resistant coating when applied to a tungsten-molybdenum alloy with a thermal expansion matching that of the coating. The results quoted in the literature^{2,3} for the macroscopic thermal expansion coefficient of β -silicon carbide show considerable scatter but practically all lie between the values quoted for tungsten and molybdenum which form a continuous series of solid solutions. The present work was undertaken (a) to determine the form of the curve relating coefficient of thermal expansion and composition in the binary tungsten-molybdenum system (b) to redetermine the coefficient of thermal expansion of β -silicon carbide.

The lattice parameters of two tungsten-molybdenum alloys and β -silicon carbide were determined by X-ray diffraction methods at various temperatures between room temperature and 1200°C. The substances studied all have cubic symmetry and hence

$$\alpha_{X\text{-ray}} = \frac{1}{a} \cdot \frac{da}{dT}$$

where a is the side of the cubic unit cell. In general good agreement is obtained between α determined by X-ray methods and macroscopic measurements e.g. Wilson⁴. Discrepancies can arise in anisotropic materials if there are suitably oriented macroscopic imperfections in the bulk structure e.g. in the case of graphite⁵, but the question does not arise in the present instance since all the materials are isotropic. Small discrepancies may also arise at temperatures approaching the melting point T_M due to the thermal generation of vacancies, but again the question does not arise in the present study since the maximum temperature reached, 1200°C is only of the order $T_M/2$ for all materials investigated.

2 EXPERIMENTAL DETAILS

The alloys used were made by Murex Ltd using powder metallurgy techniques. Their homogeneity was checked and the nominal compositions confirmed by chemical analysis.

	50% Mo (nominal)	75% Mo (nominal)
Mo	49.9 wt %	74.8 wt %
W	50.4	24.9
C	0.03	0.03
S ₁	0.2	0.2

Conventional techniques were employed to determine lattice parameters as a function of temperature (see for example X-ray diffraction by polycrystalline materials - Institute of Physics 1955 - Chapter 9 - High temperature methods; Chapter 15 - Determination of accurate lattice parameters). A Unicam high temperature X-ray powder camera, Type S-150 was used. The molybdenum-tungsten specimens were in the form of flat discs approximately 5/16" across and 1/8" thick. One face was ground flat and mounted in the camera with this face perpendicular to the X-ray beam. The temperature of the specimen was measured by a Pt/Pt-Rh thermocouple in close proximity to the back of the specimen. The furnace chamber was continuously evacuated to a pressure $2 - 4 \times 10^{-4}$ torr. The film ring is mounted externally to the vacuum chamber so that the specimen and vacuum chamber were not disturbed until the study of that particular specimen was concluded. Measurements of the lattice parameter at room temperature were made at the beginning and end of each series of measurements as a check against movement of the specimen and contamination.

The lattice parameters of the tungsten-molybdenum alloys were calculated from the 222, 321, 400, reflections which occur in the range of Bragg angle $60-80^\circ$ in CuK radiation ($K\alpha_1$ 1.540 50A $K\alpha_2$ 1.544 34A $K\beta_1$ 1.392 17A). The results were corrected for errors in specimen mounting, penetration of X-ray beam into the specimen etc using the extrapolation function of Nelson and Riley⁶. In the case of the specimen of β -silicon carbide, a cylindrical powder specimen, 0.3 mm diameter, was used.

Lattice parameters were calculated from reflections 422, 333, 440 which occur in a similar angular range, $60^\circ - 80^\circ$, using Ni K radiation ($K\alpha_1$ 1.657 83A $K\alpha_2$ 1.661 68A $K\beta_1$ 1.500 08A).

3 RESULTS

The results for the tungsten-molybdenum alloys are shown graphically in Fig.1 in which lattice parameter is plotted against specimen temperature. Room temperature lattice parameters determined at the beginning and end of

each series of experiments are virtually identical from which it is deduced that no significant contamination of the specimens has occurred. Within the limits of experimental error, the lattice parameters are a linear function of temperature over the limited temperature range studied. The present results for the two elements are in good agreement with the results of previous investigations^{7,8} which are plotted on the same graph. From these curves the mean coefficients of thermal expansion between room temperature and 1200°C, $\bar{\alpha}_{1200}$ was calculated and these are shown in Fig.2 plotted against alloy composition (in atomic per cent). There is no evidence that $\bar{\alpha}_{1200}$ is other than a linear function of composition. It was unfortunate that an alloy of composition around 40-50 atomic % Mo was not available to establish this point with greater certainty. Fig.3 is a plot of room-temperature lattice parameter against composition. There is good agreement with the early results of Van Arkel⁹ and there is no evidence of any departure from Vegard's Law that lattice parameter is a linear function of atomic composition.

The results for β -silicon carbide are summarised in Fig.4 leading to a value $\bar{\alpha}_{1200} = 4.55 \times 10^{-6}$. Also shown are the results of a previous X-ray study by Taylor and Jones¹⁰ and a very recent macroscopic determination by Popper and Mchyuiddin¹¹ on a sample of pyrolytic silicon carbide. The agreement is satisfactory and there is no doubt that $\bar{\alpha}$ over this temperature range is lower than generally quoted in the literature.

The lattice parameters are accurate to about 1 part in 10000. The temperature of the furnace was manually controlled during an exposure within limits $\pm 10^\circ\text{C}$ at the highest temperatures. Measurements by other workers of temperature gradients in the furnace of this type of camera suggest that the temperature gradient in the specimen is considerably less than $\pm 5^\circ\text{C}$. It is therefore considered that the maximum source of error in specimen temperature is that imposed by manual control of the furnace temperature. An error of 20°C at the maximum temperatures reached corresponds to a spacing error of about 1 in 10000 which is the same as the uncertainty in the lattice parameter itself. The combined uncertainty in specimen temperature and lattice parameter lead to an estimated error in $\bar{\alpha}_{1200}$ of one or two per cent.

4. CONCLUSIONS

It has been shown that the mean coefficient of thermal expansion in the range room-temperature to 1200°C of alloys in the binary tungsten-molybdenum system, can be predicted with considerable accuracy by assuming a linear relation between $\bar{\alpha}_{1200}$ and atomic composition.

At the same time it has been shown that $\bar{\alpha}_{1200}$ for β -silicon carbide is 4.55×10^{-6} which is much lower than most values quoted in the literature although in good agreement with a very recent macroscopic determination and a previous X-ray value. This value, 4.55×10^{-6} lies outside the range of values encountered in the binary tungsten-molybdenum system.

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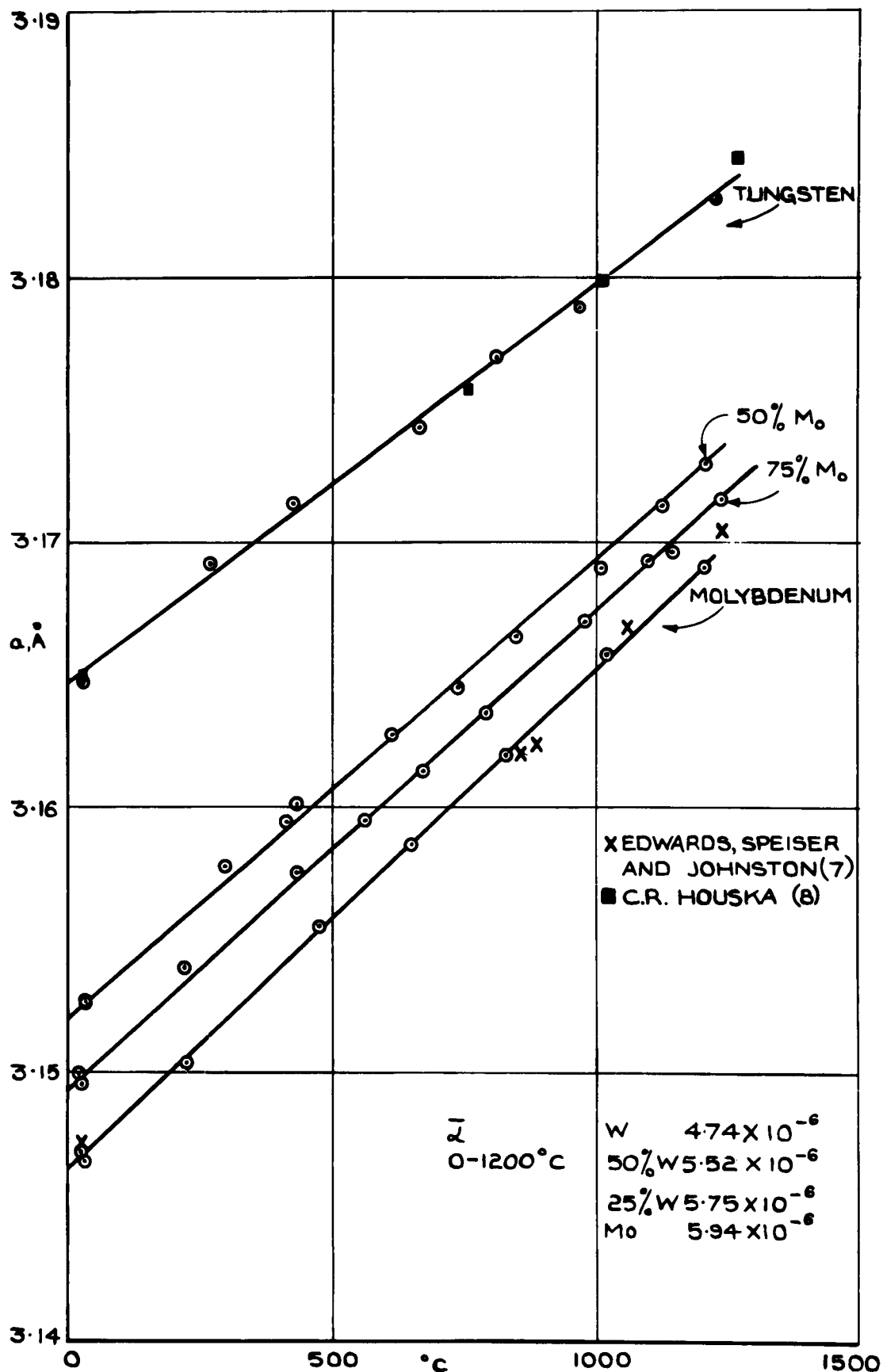


FIG. 1 MOLYBDENUM-TUNGSTEN ALLOYS
LATTICE PARAMETER v TEMPERATURE

Fig.2&3

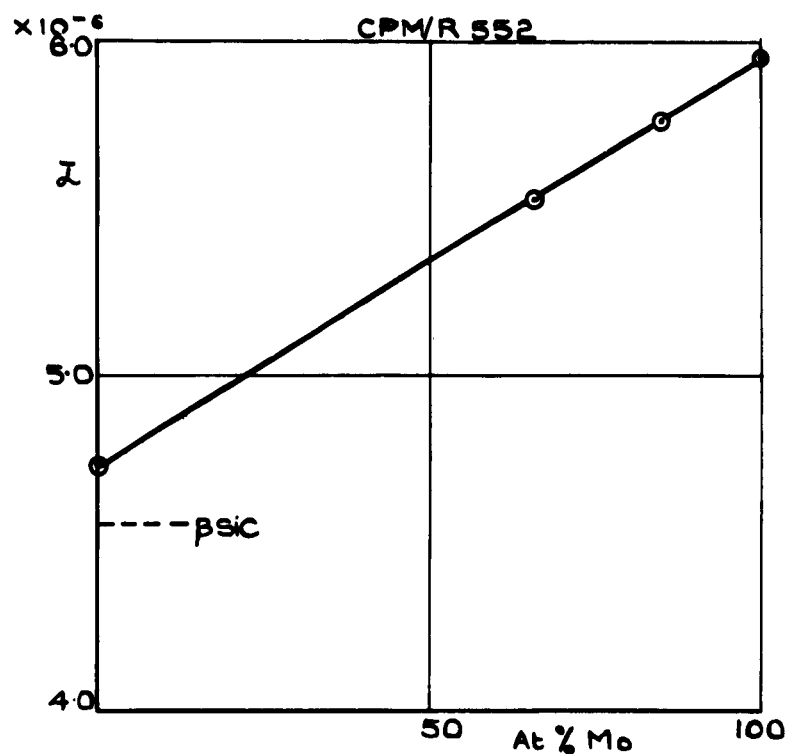


FIG. 2 THERMAL EXPANSION α ALLOY COMPOSITION

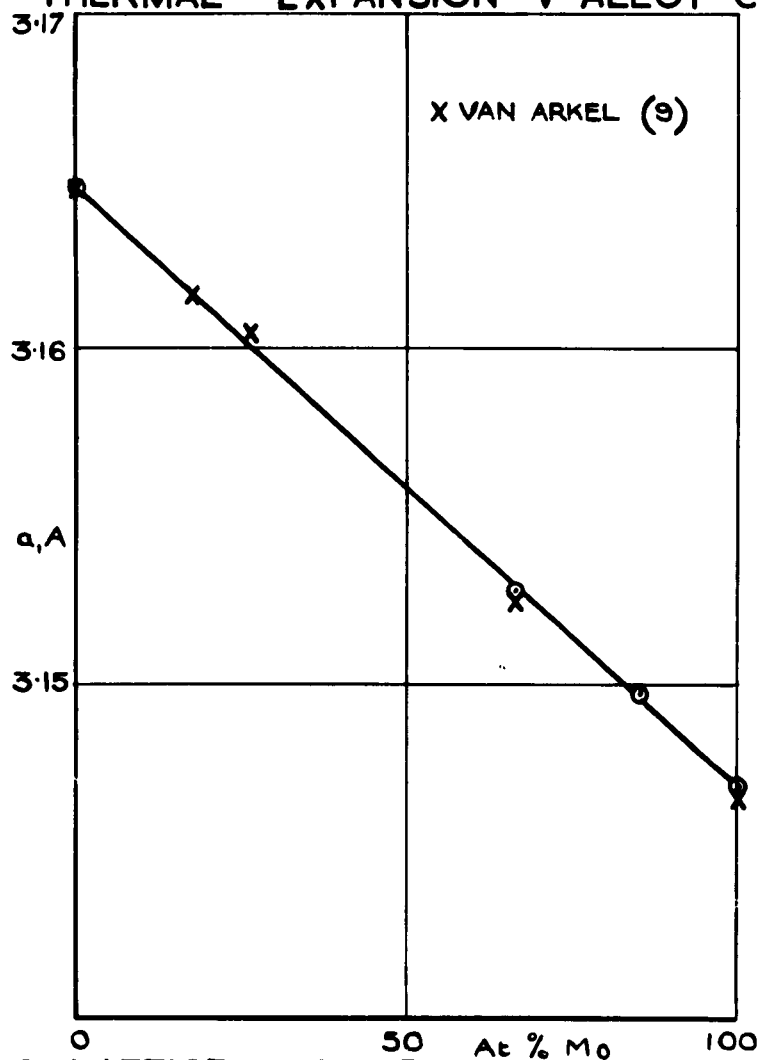


FIG. 3 LATTICE PARAMETER a ALLOY COMPOSITION

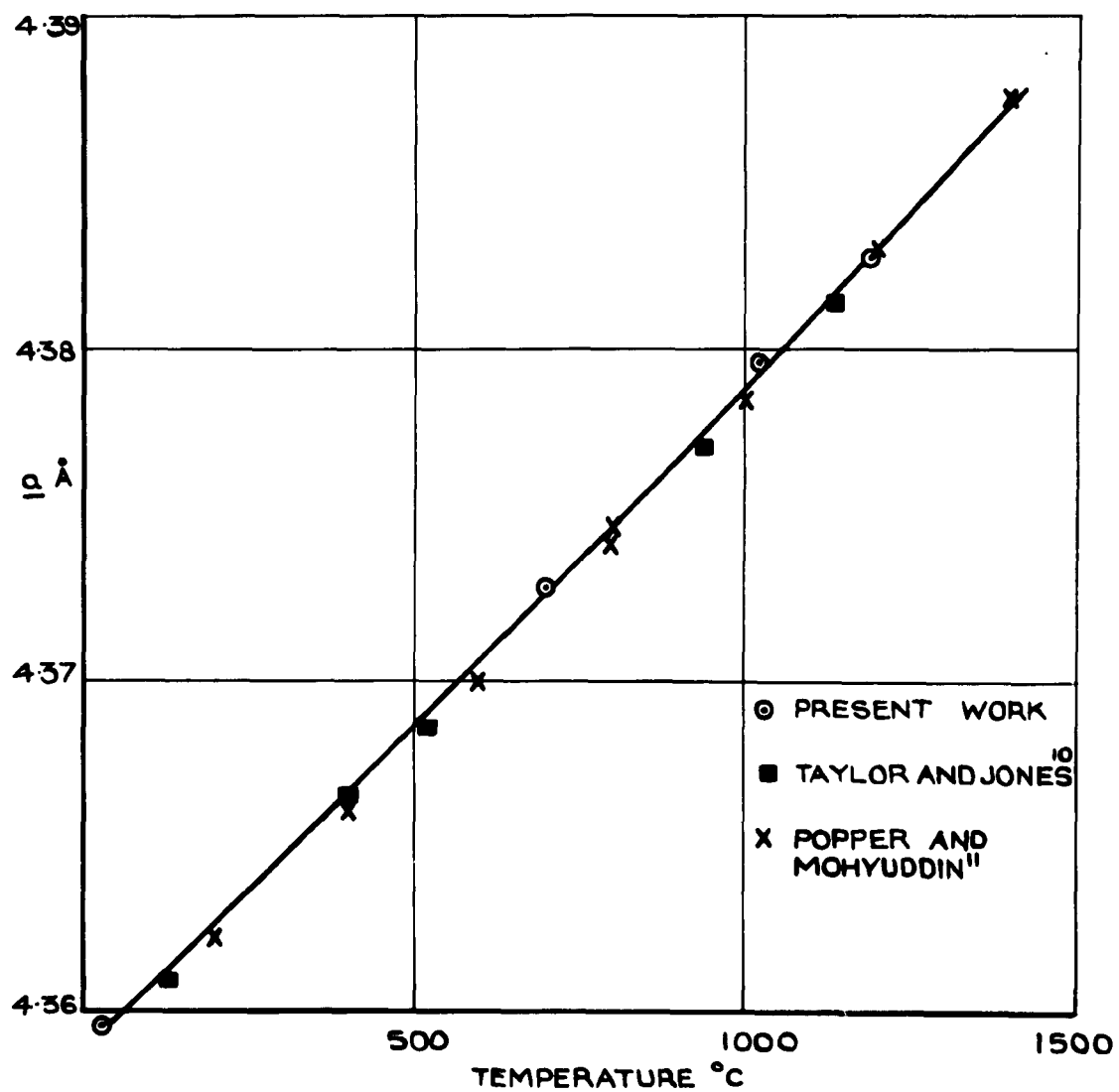


FIG. 4 β -SILICON CARBIDE LATTICE
PARAMETER ν TEMPERATURE

Clark, D Knight, D THE THERMAL EXPANSION OF β-SILICON CARBIDE AND SOME TUNGSTEN-MOLYBDENUM ALLOYS Royal Aircraft Establishment Technical Report 65049 March 1965 Thermal expansion coefficients of some tungsten-molybdenum alloys have been determined by X-ray diffraction methods over the temperature range 25°C - 1200°C. Within experimental error the coefficients are independent of temperature over the range studied. β-silicon carbide has also been investigated. Values of the mean expansion coefficient $\bar{\alpha}$ are as follows: 1200	536,413 : 666,764.5 : 669,275.28 Clark, D Knight, D THE THERMAL EXPANSION OF β-SILICON CARBIDE AND SOME TUNGSTEN-MOLYBDENUM ALLOYS Royal Aircraft Establishment Technical Report 65049 March 1965 Thermal expansion coefficients of some tungsten-molybdenum alloys have been determined by X-ray diffraction methods over the temperature range 25°C - 1200°C. Within experimental error the coefficients are independent of temperature over the range studied. β-silicon carbide has also been investigated. Values of the mean expansion coefficient $\bar{\alpha}$ are as follows: 1200
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(Over)

(Over)

Composition wt % Mo at % Mo $\times 10^6$ 1200°C	100	75	50	0	β atC
	100	85	66	0	
	5.94	5.75	5.52	4.74	4.55

Composition wt % Mo at % Mo $\times 10^6$ 1200°C	100	75	50	0	β atC
	100	85	66	0	
	5.94	5.75	5.52	4.74	4.55

Composition wt % Mo at % Mo $\times 10$ 1200°C	100	75	50	0	β atC
	100	85	66	0	
	5.94	5.75	5.52	4.74	4.55

Composition wt % Mo at % Mo $\times 10^6$ 1200°C	100	75	50	0	β atC
	100	85	66	0	
	5.94	5.75	5.52	4.74	4.55