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THE REACTIONS OF THE SODIUM-, POTASSIUM-, AND THE LITHIUM TUNGSTEN BRONZES IN THE SOLID STATE

by

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A

THESIS

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Approved by M. E. Straumanis
Research Professor of Metallurgy

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INTRODUCTION

The first part of this dissertation has the intention of determining whether MoO_3 forms solid solutions with Na-W bronze corresponding to the formula $NaWO_{3(1-x)}(MoO_3)_x$ and whether the so-called "sodium-molybdenum bronze" exists.

The next part is concerned with the solubility of K-W bronze in Li-W bronze at high temperatures, in a vacuum, and the last part of this work has the intention of studying the solubility of K-W bronze in Na-W bronze at different temperatures.

The interest in this work is of a purely scientific nature rather than of academic interest.

PART I

REVIEW OF THE LITERATURE

As early as 1895, Stavenhagen and Engels[1] obtained, by electrolytic decomposition of fused sodium molybdate, $3Na_2O\cdot7MoO_3$, a compound $Na_2Mo_5O_{15}$ which they called "Molybdenum Bronze" because of its similarity in physical and chemical properties to the alkali-tungsten bronzes.

Later on, Canneri[2] carried out systematically a series of experiments on the partial reduction of the compounds of the molybdates. The results of the reduction were as follows:

> 1) Reduction of hydrogen: A slow current of pure, dry hydrogen was passed over the polymolybdate at 450°C. in a Heraeus furnace, until partial reduction was complete (several hours). The hydrogen was stopped; the temperature was raised to 800-900°C., maintained for some time at this temperature, cooled and digested in hot water to remove all unaltered molybdate. In all cases, the residue had all the physical and chemical properties of MoO_2. The reduction was as follows:

$R_2Mo_2O_7 + H_2 \dashrightarrow R_2MoO_4 + MoO_2 + H_2O$, where

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[1] A. Stavenhagen and E. Engels, "Über Molybdänbronzen". Ber. Deutsch. Chem. Ges. 28: 2281-2282. (1895)

[2] G. Canneri. Gaz. Chim. Ital. 60: 113-125. (1930)

R is an alkali metal.

2) Reduction with Sn: A mixture of MoO_3 and alkali carbonate (in proportions corresponding to the different molybdic acids) was fused to a clear liquid, and Sn was added slowly to the latter; when the reaction was completed, the mixture was cooled, digested in hot water, and filtered. The filtrate was an intensely blue, colloidal solution containing "molybdenum blue", which always indicates the presence of penta- or sexivalent molybdenum.

3) Reduction by electrolysis: Forty grams of mixtures of varying proportions were electrolyzed with 3-4 amps., at 2-3 volts, for one hour in an electric furnace. The product was digested in hot water, made alkaline with Na_2CO_3, the residue treated alternately with alkali and dilute HCl, then with water, and dried. The results with Na, K and Li polymolybdates showed that, in general, electrolysis leads to MoO_2, which is disseminated as copper-colored crystals in the fused mass. With certain proportion of MoO_3 and base, additional compounds of MoO_3 and the reduction compounds were formed. Electrolysis of Na_2MoO_4 led to metallic molybdenum. In the system $MoO_3 \cdot Na_2O$, two definite compounds were formed, the compound $Na_2O \cdot 4MoO_3 \cdot MoO_2$ from a mixture of the proportions $3Na_2O \cdot 7MoO_3$, and the compound $Na_2O \cdot 5MoO_3 \cdot MoO_2$ from mixtures of the proportions $Na_2O \cdot 5MoO_3$ and $Na_2O \cdot 6MoO_3$. The second compound had a metallic lustre, was purple-red in liquids and violet when dry. The yields of both compounds were low, i.e., only a few decigrams from 40 grams of both. With intermediate proportions of MoO_3 and Na_2O, only MoO_2 was obtained. In the system $MoO_3 \cdot K_2O$, the results were similar. Up to $4MoO_3$ per K_2O, only MoO_2 was formed, but above this proportion of MoO_3, a blue compound, $K_2O \cdot 5MoO_3 \cdot MoO_2$, was also formed (1 gram from 40 grams of mixture in the proportions of $4MoO_3/K_2O$). This time it had a blue color. In the system MoO_3-Li_2O, only MoO_2 was formed from mixtures up to $4MoO_3$ per Li_2O. At higher concentrations of MoO_3, a small yield of a violet-colored compound, $Li_2O \cdot 4MoO_3 \cdot MoO_2$ was obtained. These products of electrolytic reduction resembled the so-called tungsten bronzes both in chemical and physical properties, i.e., in metallic aspect, density, and in solubility in water and hydrochloric acid.

The "compounds", $Na_2O\cdot 4MoO_3\cdot MoO_2$, $Na_2O\cdot 5MoO_3\cdot MoO_2$, $K_2O\cdot 5MoO_3\cdot MoO_2$, and $Li_2O\cdot 4MoO_3\cdot MoO_2$ were isolated by Canneri, and a study of their properties, in particular their behavior against hydrogen chloride at temperatures near 600°, was made. Structoral formulas of the following type were proposed:

$$O: \ Mo\ O\cdot MoO_2\cdot O\cdot MoO_2\cdot OR'_2 \ (R' = Na, Li)$$

and $$O: \ Mo(OR')\ O\cdot(MoO_2\cdot O)_5R' \ (R' = Na, K)$$

In the next year, Burgess and van Liempt[3] showed that, by electrolytic reduction of fused, acid, sodium molybdates of varying composition with molybdenum electrodes, MoO_2 and "molybdenum blue" were produced, but no products resembling the tungsten bronzes. Table I (p. 5) shows the results of Canneri, interpreted by Burgess and van Liempt. The results of Burgers and van Liempt were obtained on the basis of analysis. According to Magneli[4], Hagg obtained only molybdenum oxides in similar experiments.

The purpose of the present work was, therefore, to try to find out whether the so-called "molybdenum bronze" can be prepared by other methods and whether mixed

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[3] W. G. Burgers and J. A. M. van Liempt, "Zur Kenntnis der Molybdänbronzen". *Z. Anorgan. Chemie* 202: 325-328. (1931)

[4] A. Magneli, "Crystal Structure Studies of Molybdenum and Tungsten Oxides and Related Compounds". *Nova Acta Reg. Sc. Upsaliensis*, Series 4, vol. 14, 15-16, No. 8. (1949)

TABLE I

Sodium Molybdenum Bronzes, Obtained by Canneri and Explained by Burgers and van Liempt.

Starting Substances	According to Canneri	According to Burgers and van Liempt
$Na_2O \cdot 2MoO_3$	MoO_2 (brownish) red	MoO_2 (reddish violet)
$3Na_2O \cdot 7MoO_3$	$Na_2O \cdot 4MoO_3 \cdot MoO_2$ (blue)	MoO_2 (reddish violet)
$Na_2O \cdot 3MoO_3$	MoO_2 (brownish red)	MoO_2 (reddish violet)
$Na_2O \cdot 4MoO_3$	Mixture of MoO_2 with $Na_2O_5 \cdot MoO_3 \cdot MoO_2$	MoO_2 (reddish violet)
$Na_2O \cdot 5MoO_3$	$Na_2O \cdot 5MoO_3 \cdot MoO_2$ (Violet)	Molybdenum (dark) blue
$Na_2O \cdot 6MoO_3$	$Na_2O \cdot 5MoO_3 \cdot MoO_2$ (Violet)	Molybdenum (dark) blue
$Na_2O \cdot 8MoO_3$		Molybdenum (dark) blue
$Na_2O \cdot 20MoO_3$		Molybdenum (dark) blue

bronzes or solid solutions of the formula $NaWO_3(WO_3MoO_3)_x$ exist. The following qualitative experiment was made. Na-W bronze was mixed with molybdenum trioxide and heated. A deeply blue-colored substance was obtained. The question that arose was whether this blue compound was a solid solution of $Na(WO_3)(MoO_3)_x$ or whether other processes occurred. In order to decide this, a systematic investigation was made. At the same time, the possibility of the existence of molybdenum bronzes was examined.

Preparation of Sodium-Tungsten Bronze

A series of experiments was performed to prepare the pure Na-W bronze. The principal aim was to prepare pure Na-W bronze, i.e., a bronze containing little or no WO_3 in solid solution.

The starting materials were: sodium tungstate, tungstic oxide, and metallic tungsten. The Na_2WO_4 was prepared by heating $Na_2WO_4 \cdot 2H_2O$ in a porcelain crucible and then transferring it, while still warm, to a bottle with a glass stopper.

The tungstic oxide was prepared by heating tungstic acid in air, to 900°C., and keeping it at that temperature for an hour. The metallic tungsten was a finely divided, chemically pure powder.

Utmost care was taken to see that the powders were kept in air-tight bottles, so that they might not pick up moisture or be contaminated by impurities. The starting materials were weighed out in proper amounts, intimately mixed and finely ground with a pestle in a mortar. The contents were then transferred to a porcelain crucible which was closed with a copper lid. The crucible was then firmly placed in a holder made of chrome-nickel wire and lowered carefully into the porcelain tube of the vacuum furnace (Fig. 1, p. 8) until the wire touched the bottom of the tube. The resistance-tube furnace had chromel wire windings; the highest temperature in the center of the furnace was measured by a chromel-alumel thermocouple and read directly from a Brown potentiometer. The temperature recorded on the Brown potentiometer was tested by means of the melting-point method and also by a Hoskin's meter.

The experimental arrangement of the first method consisted of a crucible containing chemically pure antimony, in which a thermocouple, protected by a thin glass tubing, was centrally heated.

The temperature of antimony remained constant when its freezing point of 630°C. was reached, and the Brown potentiometer was so adjusted that the pointer of the potentiometer scale showed the correct temperature.

On the Hoskin's meter, the temperature was directly read on its dial, and it also confirmed the accuracy of the adjusted potentiometer.

The glass cover, which tapered off into the glass mercury manometer, was fitted to the porcelain tube (Fig. 1). The joint was greased with vacuum grease to make the tube airtight. The furnace was connected by means of a rubber tube to the vacuum pump (Fig. 2, p. 9). The vacuum assembly included a mercury diffusion pump, as well as the tubing valves and a driving motor. Ordinarily, only the mechanical pump was used; a pressure as low as a thousandth of a millimeter Hg could be obtained. The mechanical pump was started. The degree of evacuation of the furnace was indicated by the difference between the two levels of the mercury manometer. This generally took two to five minutes, if there were no

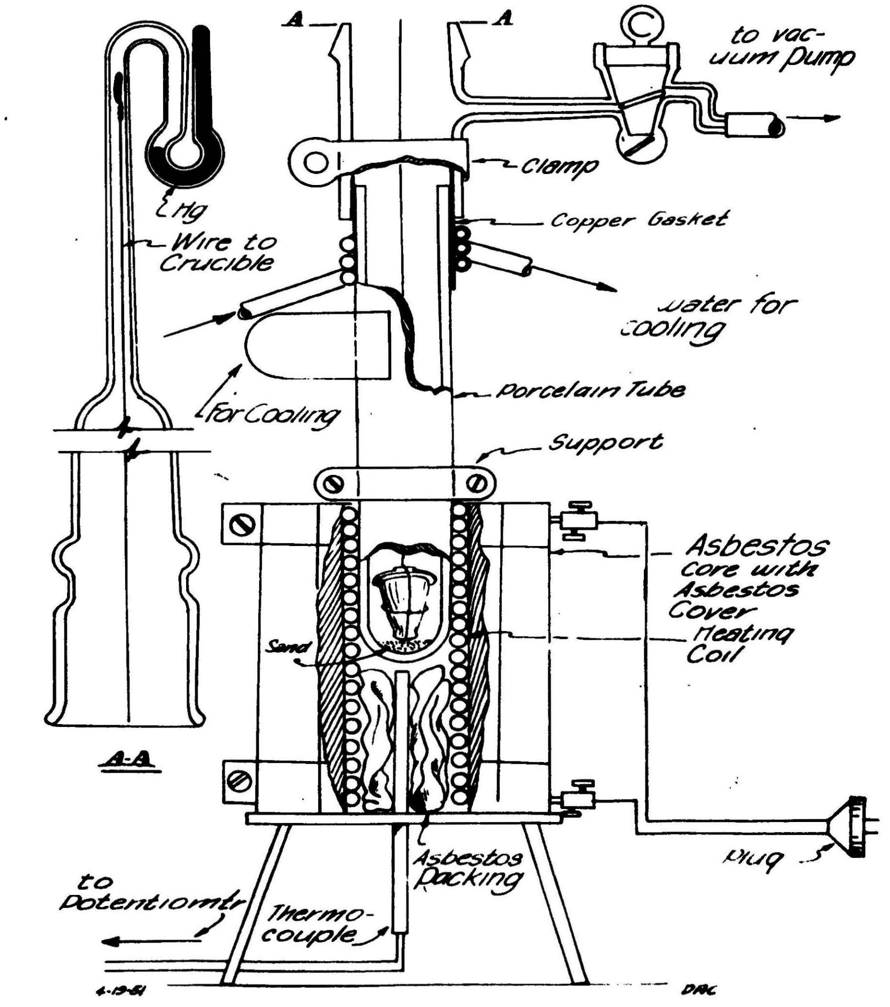

Fig. 1: The Schematic Diagram of the Vacuum Furnace

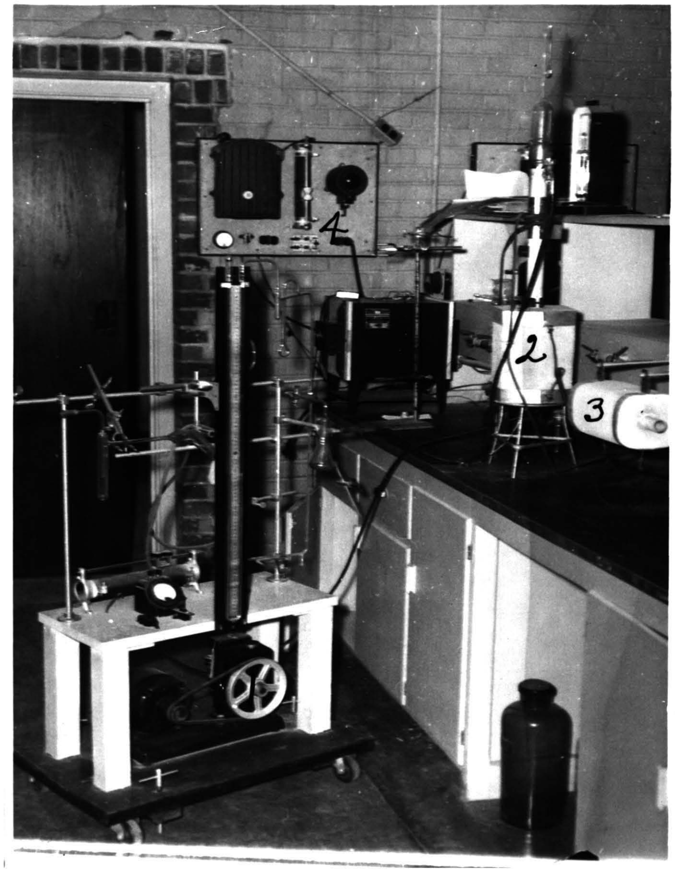

Fig. 2: The Complete Arrangement of the Heating and Vacuum System, showing 1) Vacuum pump; 2) Vacuum furnace; 3) Horizontal resistance furnace; 4) Controls for Brown's Potentiometer.

leaks in the apparatus. Then the valvas were closed, and the pump was shut off.

The mixture was heated to the necessary temperature and held "on" for a given time; then the furnace was cooled down to room temperature, the valves were opened to admit air, the grease removed from the joints by means of a paper towel, the glass cover lifted, and the crucible raised up, by means of the wire holder, out of the porcelain tube.

The product, Na-W bronze, was digested with distilled water containing sodium hydroxide to get rid of the excess, free tungstic oxide, if any; then a drop or two of concentrated hydrochloric acid was added for neutralization of the base, the bronze again washed with distilled water and dried very slowly on a hot plate. The x-ray examination of the bronzes was made for the identification of the products obtained and for the measurement of the lattice constants.

The preparation of $NaWo_3$ was made according to the equation:

$$\begin{array}{lll} 3\,Na_2WO_4 + & 2WO_3 + W & = 6NaWO_3 \\ 587.5 & 463.8 \quad 183.9 & \\ 5.88 & 4.64 \quad 1.84 & \end{array}$$

<u>Experiment 1</u>

The charge, consisting of

W	1.40 grams
WO_3	3.00 grams
Na_2WO_4	6.50 grams
Total	10.90 grams

(Sample No. 8) shows an excess of Na_2WO_4 and was chosen because it has been shown that the best results are obtained when the reaction takes place under a cover of excess sodium tungstate[5]. The charge was heated in a vacuum to 870°C., kept at that temperature for two hours, and then cooled slowly. The product consisted of bright yellow crystals. It was washed in the way already described; an x-ray photograph of the powder was made, and the lattice constant was measured. a = 3.8430 kX (Film No. 489) was obtained. This lattice constant corresponded to a sodium bronze containing 11% WO_3.

Experiment 2

To diminish the WO_3 content of the previous sample, the tungsten content of the charge was made higher than that theoretically required, and the Na_2WO_4content was nearly doubled. The composition of this charge was as follows:

W - - - - 2.90 grams
WO_3 - - - 6.00 grams
Na_2WO_4 - 14.00 grams

The heating temperature was 870°C., and the time of heating was increased to four hours. The product so obtained (Sample No. 9) was very dark yellowish. Some tungsten remained undissolved. The reason for this excess of undissolved tungsten might have been due to the prevailing high temperature which decomposed the bronze.

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[5] M. E. Straumanis, "The Sodium Tungsten Bronzes I Chemical Properties and Structure". J. Am. Chem. Soc. 71: 679. (1949)

The sample was, in this case, washed with distilled water containing sodium hydroxide, sodium peroxide, and, finally, with hydrofluoric acid in order to try to dissolve the tungsten. Despite this treatment, very small amounts of tungsten particles still persisted in the bronze (a = 3.8406 kX of Film No. 490). The WO_3 content corresponded to 14%.

Experiment 3

In the last experiment, the tungsten content of the charge was higher than that theoretically required, and the temperature was very high. Here the tungsten amount was kept low. The temperature and the time were decreased also. The purpose of this charge was to prepare a bronze with no tungsten left undissolved. The composition of the charge was as follows:

W - - - - 0.62 grams
WO_3 - - - 1.52 grams
Na_2WO_4 - 5.88 grams

The heating temperature was 820°C., and the time of heating three hours. The product obtained (Sample No. 11) was brighter yellow in color than Sample No. 9. No undissolved tungsten was observed. The a = 3.8431 kX (Film No. 493) corresponded to 10.9% of WO_3.

Experiment 4

The attempt in experiment 3 to prepare a better-looking bronze, free from tungsten, succeeded, but the free WO_3 of the bronze in solid solution was still high. This time the amount of tungsten was increased slightly and the temperature was lower. The composition of the charge was as follows:

W - - - - - 0.65 grams
WO_3 - - - 1.52 grams
Na_2WO_4 - 5.58 grams

The heating temperature was 770°C., and the time of heating three hours. Very dark, dirty-looking, yellowish crystals were obtained. An x-ray picture was made, but no attempt was made to calculate the lattice constant (Film 494).

Experiment 5

In Experiment 4, the color of the bronze appeared to be somewhat darker than usual golden-yellow bronze. Here, more of tungsten was added than in the previous experiment, and the temperature was increased with the belief that the excess tungsten and higher temperature might improve the product. The composition of this charge was as follows:

W - - - - - 0.70 grams
WO_3 - - - 1.52 grams
Na_2WO_4 - 5.58 grams

The heating temperature was 820°C., and the time of heating three hours. The product looked well formed and brighter in color. There was no residual tungsten. The lattice constant $a = 3.8432$ kX (Film No. 493) corresponded to 10.8% of WO_3.

Experiment 6

The charge of Sample 14 was three times as much as that of Experiment 5, but the experimental conditions were identical. The composition of this charge was as follows:

W - - - - 2.10 grams
WO_3 - - - 4.56 grams
Na_2WO_4 -16.74 grams

The lattice constant a = 3.8436 kX (Film 497) corresponded to 10.2% of WO_3. Hence, Sample No. 16 was used for the investigation of the so-called "molybdenum bronze" because there seemed to be no possibility of preparing a sodium bronze with a lower WO_3 content.

X-ray Examinations of the Samples

In order to determine the lattice constants of the Na-W bronzes prepared and the solubility limits of the various bronzes, the following apparatus and technique have been used.

The x-ray machine used was made by the Picker X-ray Corporation of America. The x-ray powder camera (Fig. 3, p. 15) was designed by Dr. M. E. Straumanis and was made in Rolla by Professor Kilpatrick of the Department of Mechanical Engineering. It is precision machined throughout, a modified Debye-Scherrer type of camera, with a cylindrical diameter of 64 millimeters. Some of the main features of the experimental procedure were as follows:

1) So tiny a specimen was used that any corrections, due to absorption by the specimen, are reduced to a vanishing amount. A thin layer of Fisher's Cello-Seal was used for glue. The powder was stuck to the outside of a piece of practically non-absorbent beryllium-lithium-boron (Lindemann) glass rod having a diameter as small as 0.05 to 0.08 mm. The finished powder mount had a diameter in the neighborhood of 0.15 mm.

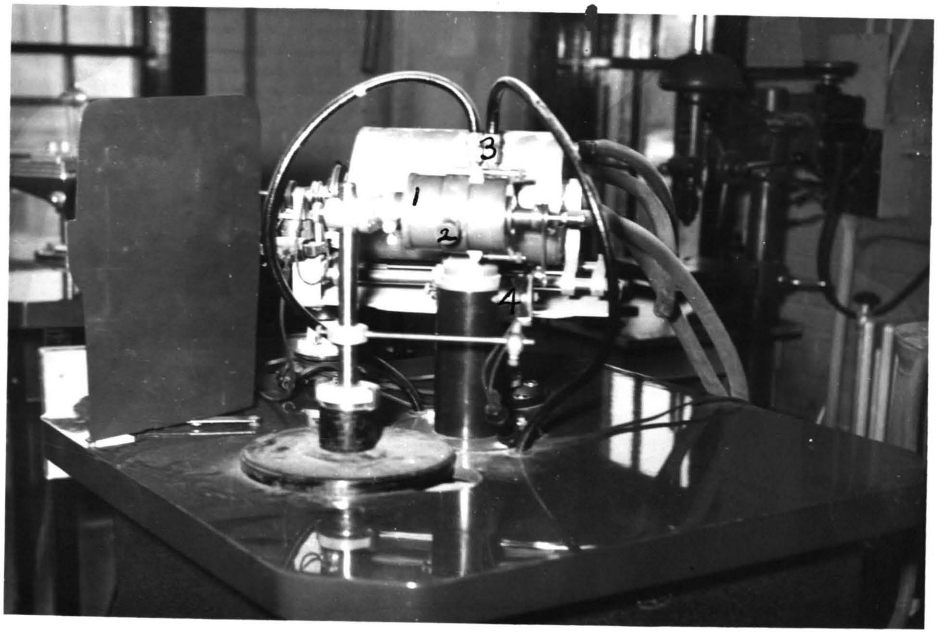

Fig. 3: The Arrangement of the X-ray Camera on the Diffraction Unit, showing 1) X-ray camera; 2) X-ray exit port; 3) Water tube for cooling x-ray tube; 4) Motor.

2) The specimen was accurately centered under a microscope (see Fig. 4, p. 17). Such centering reduces the volume swept out by the specimen in rotating and consequently diminishes the width of a powder-photograph line.

3) The specimen was accurately centered to the film cylinder axis, thus eliminating errors due to lack of centering[6].

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[6] M. E. Straumanis. Journal of Applied Physics 20: 726-734. (August, 1949)

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4) The angle measurement became independent of camera diameter, and thus the errors due to film shrinkage, after the process of developing and drying, were eliminated.

The comparator used to measure the films had a travelling carriage and a fixed microscope (see Fig. 5, p. 18). The film, between two glass plates on the carriage, could be adjusted by means of screws. The micrometer screw had a pitch of one millimeter; the micrometer drum had 1,000 divisions, so that the least count was 0.001 mm.

Determination of the Lattice Constant by Using Back Reflection Technique

The equation for the measurement of the lattice constant of the cubic sodium-tungsten bronze is derived in the following manner: Bragg's equation shows that

$$\lambda = 2d \sin \vartheta \qquad (j)$$

where

ϑ is the Bragg reflecting angle,

d is the interplanar spacing, and

λ is the wavelength of the radiation under consideration (in this case, Co-radiation).

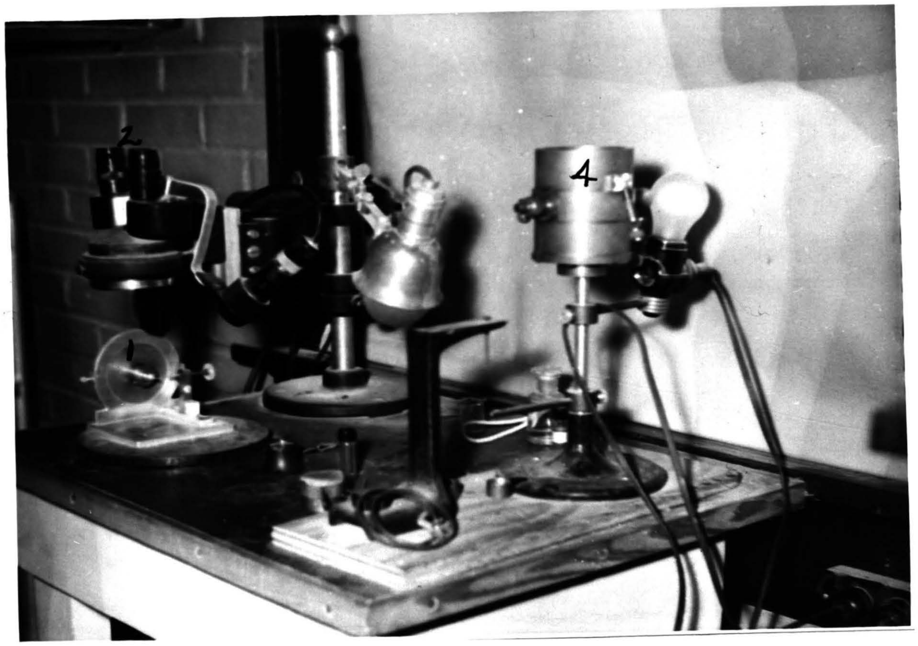

Fig. 4: Set-up for Mounting, Centering, Coating of Glass Rod and the Arrangement for Observation of the Position and for Centering of Powder Specimens, showing 1) Camera cover held by frame; 2) Microscope; 3) Illuminator; 4) Camera.

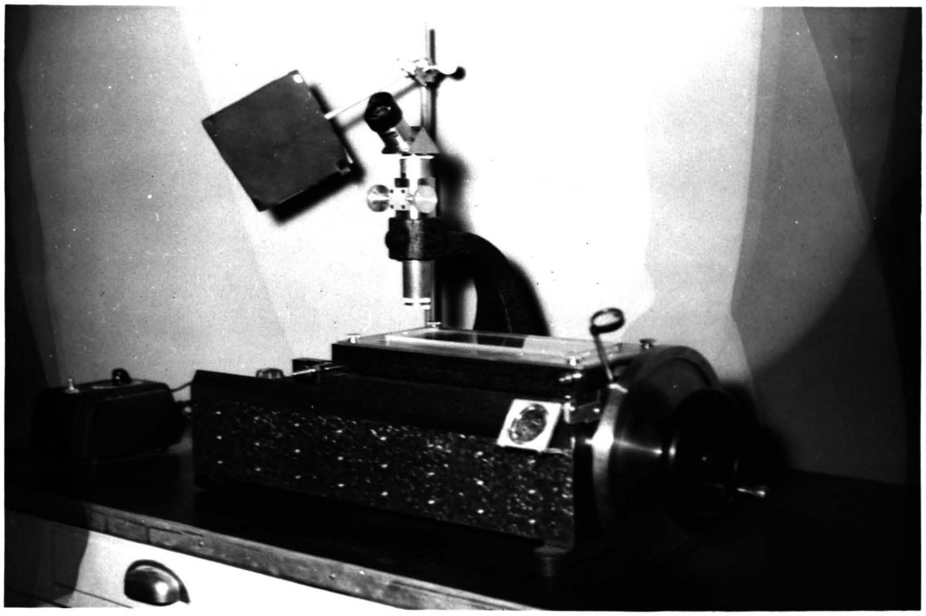

Fig. 5: The Comparator for Film Measurements.

We obtain

$$d = \frac{\lambda/2}{\sin\vartheta} \tag{k}$$

The Bragg angle ϑ can be expressed as a function of the lattice constant a and of the Miller indices instead of the spacing d. For a cubic crystal, the lattice constant a can be written as

$$a = \frac{d}{\sqrt{h^2+k^2+l^2}} \tag{l}$$

where

h, k, l are the Miller indices of any set of atomic planes in a crystal.

Now, substituting the value of d (from (k)) in (l), we obtain

$$a = \frac{\lambda/2}{\sin\vartheta\sqrt{h^2+k^2+l^2}} \tag{m}$$

or

$$a = \frac{\lambda/2}{\cos\varphi\sqrt{h^2+k^2+l^2}}$$

where

$\varphi = 90^\circ - \vartheta$

φ = Back reflection angle.

The Bragg angle ϑ of any plane hkl can be found from the film measurement record. When ϑ is very large, that is, nearly 90°, a small error of measuring gives only a very small deviation of the $\sin\vartheta$ value; it will not affect the precision of the lattice constant determination too much. These large Bragg angles are in the back reflection region.

Another reason for using back reflection technique appears on differentiating Bragg's equation (k), while d is regarded as constant and λ as a variable.

$$d\lambda = 2d \cos\vartheta \, d\vartheta$$

$$\frac{d\vartheta}{d\lambda} = \frac{1}{2}d \frac{1}{\cos\vartheta}, \text{ or } (\sec\vartheta)/(2d) \qquad \text{(o)}$$

Equation (o) shows that a doublet, such as Co $K\alpha_1$-$K\alpha_2$ (λ equal to 1.7853 and 1.7892 kX, respectively, $d\lambda$ = 0.041 kX) will be resolved much more in the region of large values of ϑ than of small ones, because the angular separation for any given wave length separation $d\lambda$ and interplanar spacing d varies as $\sec\vartheta$. Such doublets can be seen in Fig. 8 and Fig. 13. Also at large ϑ, the error due to absorption is much reduced.

Indexing of the Film

Films of the cubic Na-W bronze with Co-radiation were indexed by a graphic method using reciprocal lattice[7]. The procedure for indexing the film was as follows:

1) The radius of the reflecting circle was calculated by the following equations, assuming that the radius r_1 of Cu-radiation is unity.

$$a = \lambda_1\sqrt{\frac{r_1}{2p}} \qquad \text{(a)}$$

$$a = \lambda_2\sqrt{\frac{r_2}{2p}} \qquad \text{(b)}$$

where

a is the lattice constant

λ_1 is the wavelength of Cu-$K\alpha_1$ = 1.5374kX.

r_1 is the radius of Cu-$K\alpha_1$ reflecting circle which is usually

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[7] M. E. Straumanis. Zeit. Krist. (A) 104: 167-177. (1942)

taken as 10 cm.

r_2 is the radius of reflecting circle for Co-K radiation

p is the equidivision on the diameter of the reflecting circle

λ_2 is the wave length of the Co-radiation = 1.7853 kX.

From the Equations (a) and (b),

$$r_2 = r_1 \frac{\lambda_1^2}{\lambda_2^2} \qquad (c)$$

Substituting the values of r_1, λ_1, and λ_2 in Equation (c), we get

$$r_2 = 10 \frac{(1.5374)^2}{(1.7853)^2} = 7.416 \text{ cm.}$$

2) By using the radius found in (1), the reflecting circle was drawn.

3) From the center of the diameter of the reflecting circle, all of the double Bragg angles of the diffraction lines were drawn by starting from the left of the reflecting circle, toward the right (Fig. 6, p. 22). A number of intersecting points between the angles and the circumference of the reflecting circle were obtained. From these intersecting points, projections were made to the diameter of the circle.

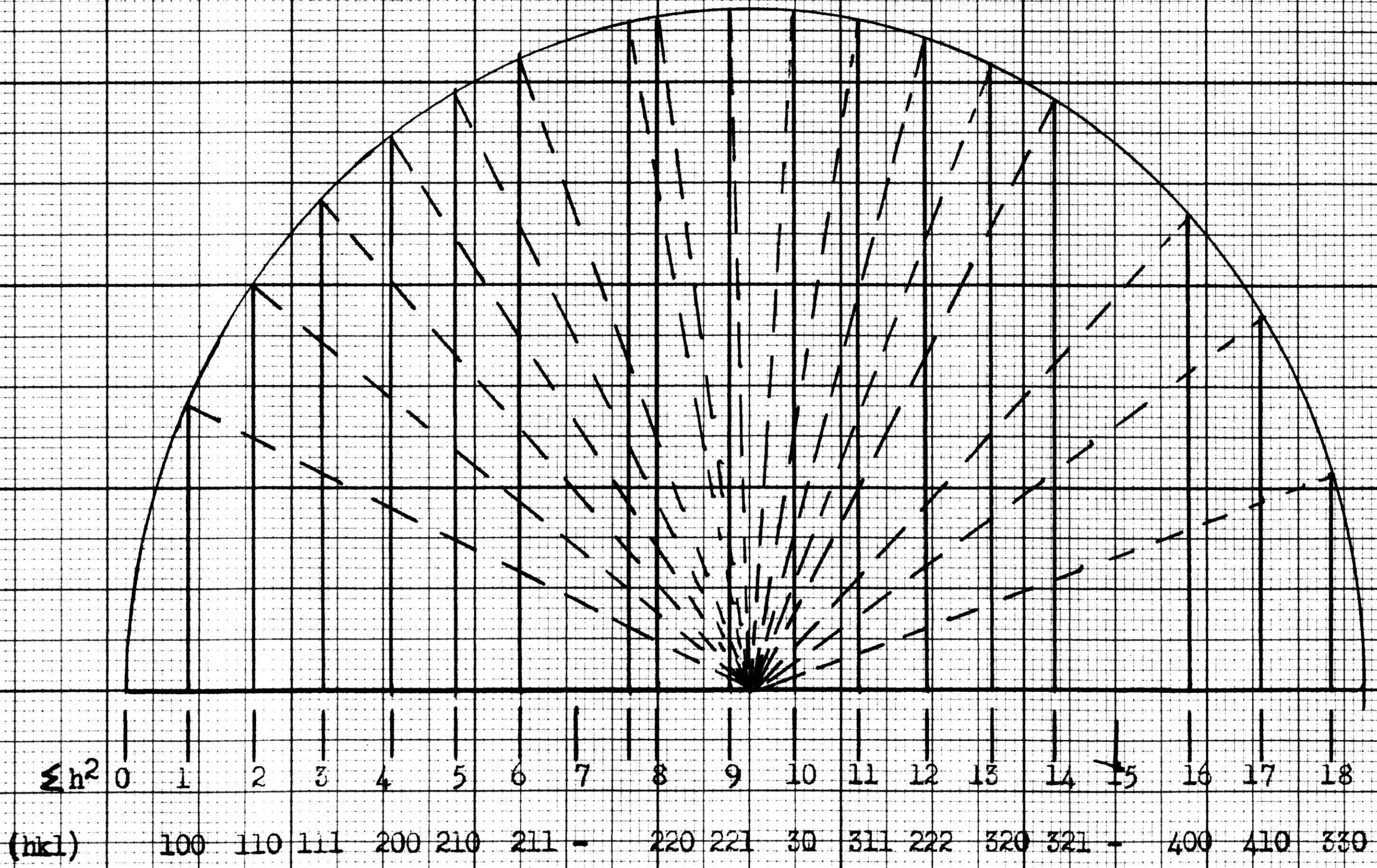
4) The equidivisions between the projections were then found.

5) The current number was assigned to each point on the basis of starting from the left end zero, then 1, 2, 3, etc., till the last projection on the right end was numbered (Fig. 6).

6) The number of each projection on the diameter indicated the sum of $(h^2-k^2-l^2)$ the corresponding diffraction line on the film. The sum of $\leqq h^2$ for each line was split into three integers as indices of the line, e.g., for $\leqq h^2 = 17$, h = 2, k = 2, and l = 3; or h = 4, k = 1, and l = 0.

After the film was indexed, the exact measurement of the film and the determination of the lattice constant could be made. An example of film measurement

Fig. 6: Indexing graph for Na-W bronze.



is shown in Table 2.

TABLE 2

Example of Film Measurement and Calculation

Film No. 497, Na-W Bronze - yellow color

Sample No. 16 - Exposure one hour

Co-radiation - 40kv, 10MA

Front-Reflection Lines

Intensity	s.	v.s.
Complete Reading, in mm., right	65.288	71.704
Complete Reading, in mm., left	35.235	28.847
Total, right and left	100.523	100.551

100.535 = Average total, left and right

Back-Reflection Lines

Intensity	s.	w.	v.s.	m.
hkl	410 α_1	410 α_2	330 α_1	330 α_2
Comp. Rdg., mm., rgt.	168.793	168.392	161.072	160.320
Comp. Rdg., mm., left	131.627	132.012	139.359	140.125
Total, R and L	300.420	300.404	300.431	300.445

300.425 = Average total, left and right

Right minus left = 4φ mm	37.166	36.380	21.713	20.195

Circumference = 300.425-100.535 = 199.890 mm.

f = factor to convert the length in mm. to angle in °s

$$f = \frac{360}{4 \times 199.890} = 0.45025$$

$(R-L) \times \underline{f} = \varphi$ in °s	16.734	16.380	9.776	9.093
$\varphi = 90 - \vartheta$ and $\vartheta = 90 - \varphi$	73.266	73.62	80.224	80.907

Sin ϑ = Cos φ	0.957652	0.959412	0.985479	0.987433
$\lambda/2 \cdot \sqrt{h^2+k^2+l^2}$	3.68047	3.68851	3.787172	3.795445
a in kX= $\frac{\lambda\sqrt{h^2+k^2+l^2}}{2\,Cos\,\varphi}$	3.8432	3.8446	3.8430	3.8437

a_0 = 3.8436 kX (Average)

The Determination of WO_3 Content in Sodium-Tungsten Bronze

$NaWO_3$ absorbs WO_3, forming a solid solution. This absorption is accompanied by the shrinkage of its lattice. The shrinkage was used to determine the composition of the resulting bronzes. The lattice constants were found by the powder method, as shown in Table 2. The relationship between the WO_3 dissolved in Na-W bronze and the lattice change of the latter had been worked out by previous investigators. The graph has been reproduced here, as shown in Fig. 7 (p. 25). The ordinate of this graph shows the lattice constant of Na-W bronze, plotted against the percentage of WO_3 dissolved in the bronze (100%, all together).

If we know the lattice constant of a Na-W bronze, the percentage of WO_3 in this bronze can be read directly from the graph.

Example: Number 16, Experiment 6, Film No. 497 (see Fig. 8, p. 26).

Lattice constant 3.8436 kX

WO_3 dissolved in the bronze, 102% by weight

The precision claimed was sufficient to determine the tungstic oxide content of the bronzes with an accuracy

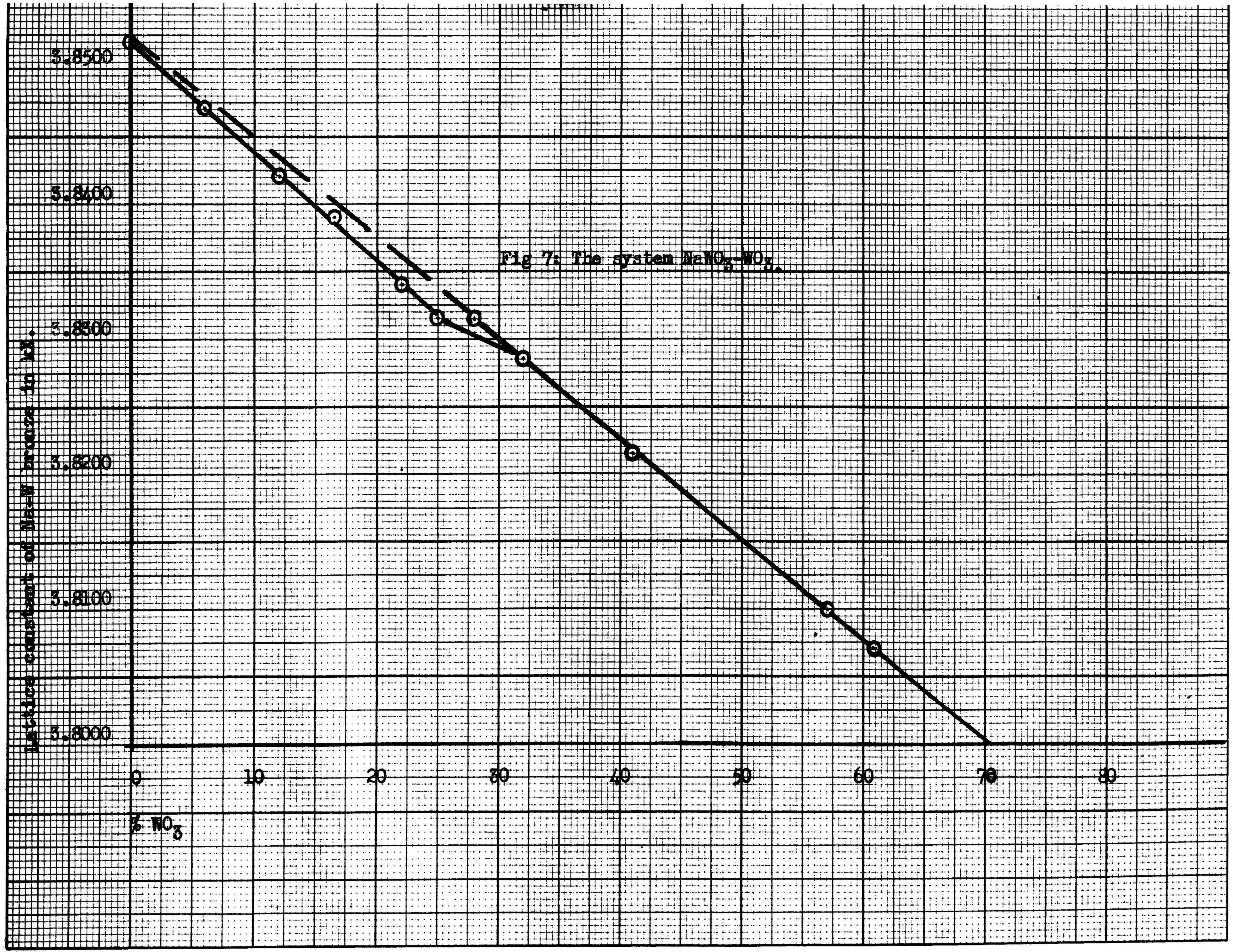


Fig 7: The system NaWO$_3$-WO$_3$.

of 0.1% by weight.

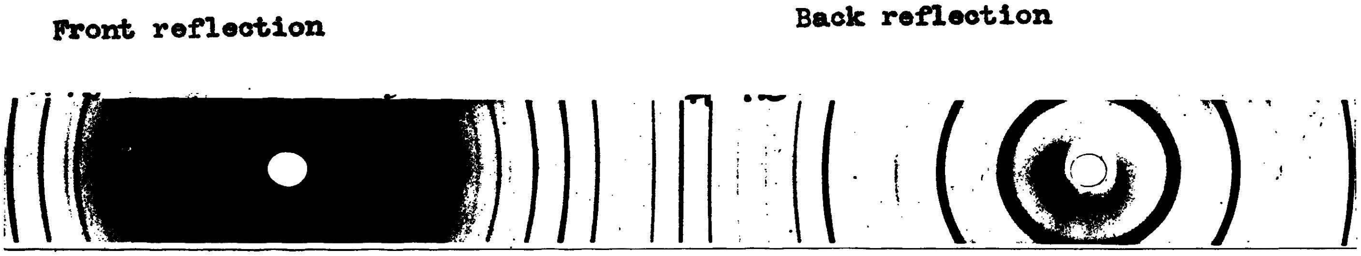


Fig. 8: The X-ray Powder Photograph of Na-W Bronze Co-radiation

The Reaction of Molybdenum Trioxide with Sodium-Tungsten Bronze

The main purpose of this part of the work was to study the reaction of molybdenum trioxide with sodium-tungsten bronze and to find out the solubility limit, if any. In order to achieve this aim, samples of Na-W bronze were weighed in the proper proportions with different amounts of MoO_3, from 5 percent to 30 percent by weight, and heated in a vacuum at 800°C. The resulting products were examined under the microscope; powder patterns of every sample were made, and the lattice parameter of each sample was determined.

The theoretical basis for this determination lies in the fact that the lattice constant of Na-W bronze will have to change if MoO_3 dissolves in it. The solu-

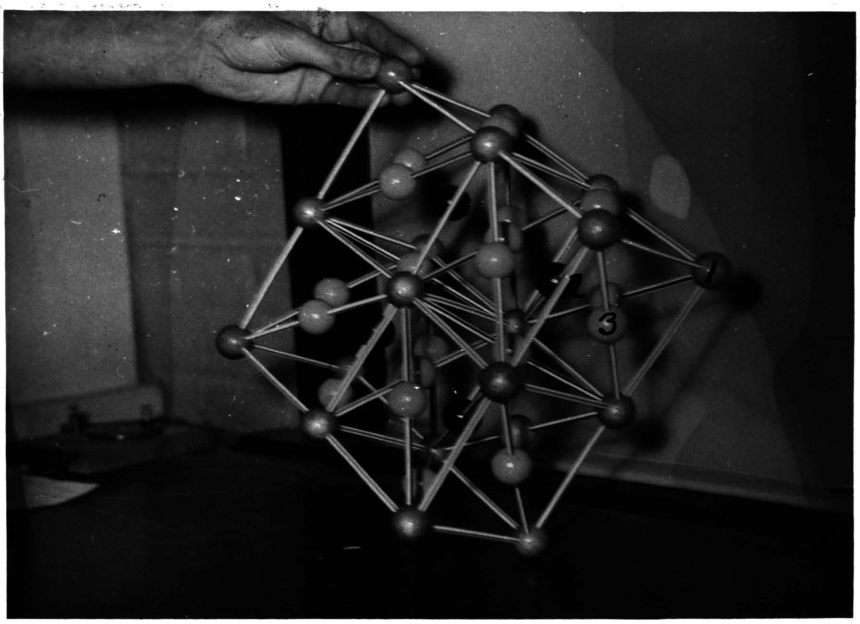


Fig. 9: The Four-Unit Cells of the Crystal of Na-W Bronze: 1) Sodium ion; 2) Tungsten ion (in black); 3) Oxygen ion. The ionic radii are not in proportion.

bility limit will be at the point where new lines appear and the lattice of Na-W bronze does not change any more. If that is not the case, then there is an indication of non-equilibrium and that other processes are occurring.

Chemically pure molybdic anhydride was heated in air for some time, till it was certain that all the entrapped moisture had been driven out. This MoO_3 was used for the subsequent experiments.

Experiment 7

Na-W bronze (Sample 16) and MoO_3 were thoroughly mixed in the proportion given below, and the mixture was transferred into a porcelain crucible and heated in a vacuum at 820°C for two hours. The composition of the charge was as follows:

Na-W bronze	475 mg.	95%
MoO_3	25 mg.	5%

The product (Sample 30) so obtained was reddish in color, quite different from that of Na-W bronze. An x-ray picture was made (Film 524), and the diffraction pattern of this sample revealed strange, faint lines on the front reflection region of the bronze pattern. The lattice constant was measured, showing an appreciable decrease as compared with Na-W bronze number 16. The lattice constant a was equal to 3.8393 kX.

Experiment 8

The decrease in lattice constant in Experiment 7 was satisfactory, but the appearance of the strange lines wss puzzling. Here a higher percentage by weight of MoO_3 was added. The composition of the charge was as follows:

Na-W bronze	450 mg.	90%
MoO_3	50 mg.	10%

The heating temperature was 820°C. for two hours. In this case, the product, Sample 28, was brilliantly red in color. Examined under the microscope, the powder looked unhomogeneous; it seemed that there were two phases present - one a violet-reddish one and the other a darkish brown one. An x-ray diffraction pattern revealed still more new lines in the front reflection region of the bronze. The lattice constant decreased still more and was $\underline{a}$ = 3.8392 kX.

Experiment 9

The deepening of the color of the samples in the previous experiments, 7 and 8, and the contraction of the lattice of the sodium bronze, with increasing amounts of MoO_3 added, was very satisfactory, but due to the appearance of an increasing number of strange lines in Sample 8, it was decided also to increase the proportion of MoO_3 in this experiment and to try to identify the new lines. The composition of the charge was as follows:

Na-W bronze	425 mg.	85%
MoO_3	75 mg.	15%

The heating temperature was 820°C., and the heating time was two hours. The product obtained (Sample 27) looked more intense in color and appeared unhomogeneous. The intensity of the strange lines increased still more

(Film 519), and the lattice constant continued to contract, a = 3.8392 kX. In the next experiments, 10 and 11, the MoO_3 content was increased still more.

Experiment 10

The composition of the charge was as follows:

Na-W bronze	- 400 mg.	- 80%
MoO_3	- 100 mg.	- 20%

The heating temperature was 820°C. for two hours. The sample, No. 31, obtained, appeared chocolate brown in color, very uniform in composition. The intensity and the number of the new lines continued to increase on the diffraction pattern of the sample. The lattice constant of Film 525 appreciably decreased: a = 3.8310 kX.

Experiment 11

The composition of the charge was as follows:

Na-W bronze	- 350 mg.	- 70%
MoO_3	- 150 mg.	- 30%

The heating conditions were the same as in the previous cases. The product (Sample 29) appeared reddish violet. Under the magnifying microscope, there was an intermingling of reddish-violet crystals with bluish crystals, and on top of the powder were deposited slender, long, greenish-blue crystals. The sample was washed with distilled water; the solution was colored bluish. The decanted solution was preserved for further investigations. To the precipitate to be washed was added NaOH solution; the solution appeared greyish tinged. After two to three washings and neutralization by hydrochloric acid, the precipitate was dried. The product appeared blackish grey. X-ray film 523 revealed a diffraction pattern which was different from the old pattern of Na-W bronze. The copper lid of the crucible was heavily attacked and corroded, and fine, reddish-violet crystals were deposited on the lid of the crucible. The results of the experiments are tabulated in Table 3.

TABLE 3

Reaction of Molybdenum Trioxide with Na-W Bronze at 820°C., for two Hours

Sample Number	Film Number	Na-W brnz. wt. %	MoO_3 wt. %	a in kX
14	497	100	0	3.8436
30	524	95	5	3.8393
28	522	90	10	3.8392
27	519	85	15	3.8392
31	525	80	20	3.8310
29	523	70	30	

It was quite interesting to observe the steady decrease of the lattice of Na-W bronze and the appearance of new lines while the content of the MoO_3 in the samples was increased. In order to find out the new products formed (also on the copper lid), the following experiments were performed, also in connection with the intention of preparing the so-called "molybdenum bronze", all of which are related to the reaction of Na-W bronze with MoO_3.

In an attempt to prepare the "molybdenum bronze", the equation which would lead to the formation of the sodium-molybdenum bronze was:

$$\begin{array}{lllll} 3Na_2MoO_4 & + \; 2MoO_3 & + \; Mo & = \; 6NaMoO_3 & \\ 617.832 \text{ gm} & 143.950 & 95.95 & & \text{(in grams)} \\ 0.62 & 0.29 & 0.096 & & \text{(in grams)} \end{array}$$

This is the same equation which was used for the preparation of Na-W bronze, the element tungsten being changed for molybdenum.

Experiment 12

The theoretical amounts of sodium molybdate and molybdenum were used for this experiment, but the amount of MoO_3 added to the charge was twice the calculated one. The composition of the charge was as follows:

Molybdenum	- 0.1 gram
MoO_3	- 0.58 "
Na_2MoO_4	- 0.62 "

The heating temperature in a vacuum was 820°C., and the time of heating was two hours. The product so obtained consisted of fine, brownish-violet crystals, quite homogeneous. They were washed in the manner already described. An x-ray picture was made (Film 529) of Sample 34, but the pattern was quite different from the Na-W bronze pattern. The sublimate and the attack on the copper lid of the crucible were the same as noticed and already mentioned in Experiment 11 and in the samples of Table 3.

Similar further experiments were performed as above, but with MoO_3 contents being three times and four times the calculated amount. The samples, 36 and 37, obtained, were identical in all respects with Sample 34. Their x-ray diffraction pattern of Films 530 and 531 were also the same when compared to Film 529. These results proved conclusively that the product formed in all the samples remained the same, even though the additions of MoO_3 were made in greater than calculated amounts. The next step was taken in order to determine other ways of preparing the same unknown product, so that an answer might be given concerning its identity.

Experiment 13

The three starting materials for the preparation of Na-W bronze in experiments 1 through 6 were Na_2WO_4, WO_3, and W. In this experiment, the same two original substances were used, but Mo was substituted for W in the belief that the addition of molybdenum might throw a light on the unknown product. The composition of the charge was as follows:

Mo - 0.2 grams
WO_3 - 0.5 "
Na_2WO_4 - 1.0 "

The charge was heated for two hours, at 820°C., in a vacuum. The product, Sample 4, was a dark reddish powder. It was treated in the usual way. An x-ray diffraction pattern (Film 483) revealed the Na-W bronze pattern, with strange lines on its front-reflection region. This experiment confirmed the fact that the so-called "molybdenum bronze" samples prepared in Experiment 12 could not be identified in this manner because the diffraction pattern obtained was that of Na-W bronze while that of the molybdenum bronze had no similarity with the Na-W bronze pattern.

Experiment 14

An effort was also made to substitute MoO_3 and Na_2MoO_4 for WO_3 and Na_2WO_4 in order to determine the nature of the strange lines in the molybdenum bronze. Because the atomic weight of tungsten is twice that of molybdenum, two times the weight of tungsten was taken. The composition of the charge was as follows:

W - 0.1 x 2 = 0.2 x 3 = 0.6 gm
MoO_3 - 0.87 x 3 = 2.61 gm
Na_2MoO_4 - 0.62 x 3 = 1.86 gm

The conditions of heat treatment were the same as in the previous experiment, No. 13. The product (Sample 47) so obtained was completely fused, looked brownish violet and crystalline on top. When washed with distilled water, the solution was colored bluish. It was observed that there was no sublimate on the copper lid. The x-ray diffraction pattern (Film 544) of Sample 47 was identical in some respects with that of Film 529 and 523 of Experiments 11 and 12 (p. 30, 32). In order to find the composition of the compounds giving the strange lines, the x-ray diffraction of MoO_2[8, 9, 4] was determined first. MoO_2 was prepared according to the following equation:

$$\underset{288}{2MoO_3} + \underset{96}{Mo} = 3MoO_2$$

Experiment 15

The charge consisted of Mo - 0.96 gram
MoO_3 - 2.88 gram

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8 Oskar Glemser and Gertrud Lutz. Zeit. Anorg. und Allg. Chemie: 263: 1-13. (1950)

9 ------------------------------ Kolloid Zeitschrift 119: 99-102. (1950)

and was heated to 820°C. for two hours, in a vacuum. Reddish violet crystals were obtained (Sample 50), appearing quite homogeneous under the microscope. An appreciable quantity had sublimed on the copper lid.

The x-ray diffraction pattern (Film 546) revealed identity to those of Films 523, 530, and 531 (see Table 3) in all respects. Film 546, when compared with Film 523 of Experiment 11, showed that the lines of Film 546 appeared on the front- as well as the back-reflection of Film 523 (30% MoO_3), but in addition, there were strange lines on Film 523 which were unaccounted for. Probably they were due to the formation of a new product, for instance, the tetragonal Na-W bronze. Therefore, the next step lay in preparing this tetragonal bronze.

Experiment 16

The tetragonal Na-W bronze had been prepared by adding a large excess of WO_3 to Na-W bronze. The composition of the charge was as follows:

WO_3	- 475 mg.	- 95%
Na-W bronze	- 25 mg.	- 5%

and was heated in a vacuum at 900°C. for two hours. A bluish product, Sample 63, was obtained. The x-ray picture (Film 554) was quite different from the Na-W bronze pattern. This film was compared with Film 523 (30% MoO_3) of Experiment 11, and it was observed that the lines of Film 554 appeared on Film 523, hence the lines on the diffraction pattern, No. 523. So the lines on the diffraction pattern were those due to molybdenum dioxide and the tetragonal sodium tungsten bronze. Still, it was suspected that in the samples there might have formed a soluble product which dissolved when the sample was digested with water for the purpose of washing. For this reason, the washed water of Sample 29 was preserved for further investigation.

Experiment 17

The decanted solution of Experiment 11 (Sample 29 - 30% MoO_3) was evaporated to dryness. A dirty whitish residue in a quite appreciable amount was obtained. An x-ray diffraction pattern (Film 550) was taken. The picture had a large number of lines and looked quite complex. It was unlike the sodium-tungsten bronze pattern and the MoO_2 pattern. Because it was suspected that the residue was a "paramolybdate", since such compounds are very soluble in water, two attempts were made to determine the substance obtained in Experiment 17.

Experiment 18

$Na_2MoO_4 \cdot 2H_2O$, from the reagent bottle, was heated in an open crucible to drive off the hydrated water, and an x-ray picture was taken of Sample 59 (Film 551). This diffraction pattern did not correspond with Film 550 when both were compared and observed in the light of a fluorescent lamp.

Experiment 19

Experiment 19

Next, a polymolybdate, $Na_2Mo_2O_7$, was prepared, according to the following equation:

$$\underset{206}{Na_2MoO_4} + \underset{144}{MoO_3} = Na_2Mo_2O_7$$

The charge consisted of Na_2MoO_4 - 0.412 gram
MoO_3 - 0.288 gram

and was heated in a porcelain crucible, in air, till the mixture became liquid. The charge was then cooled. A crystalline, shiny white mass was obtained. The x-ray diffraction pattern (Film 552 of Sample 60) was identical with the residue obtained in Experiment 17. Therefore, it was definitely proved that, in experiment 11, the soluble product formed was $Na_2Mo_2O_7$.

Discussion and Conclusions

The values of lattice constants of Na-W bronze versus percentage of MoO_3 from the experiments on p. 28-31 and Table 3 are plotted, and a curve, Fig. 11 (p. 39) is obtained.

In the case of the solution of MoO_3 in Na-W bronze, the plot of lattice constant versus percentage concentration of MoO_3 should be as shown in Fig. 12 (p. 40), but, actually, the diagram was obtained as shown in Fig. 11. The appearance of the new, faint lines was already visible on the films of the sample containing 5 percent of MoO_3, and their intensities increased with increasing amounts of MoO_3. At 30 percent of MoO_3, the

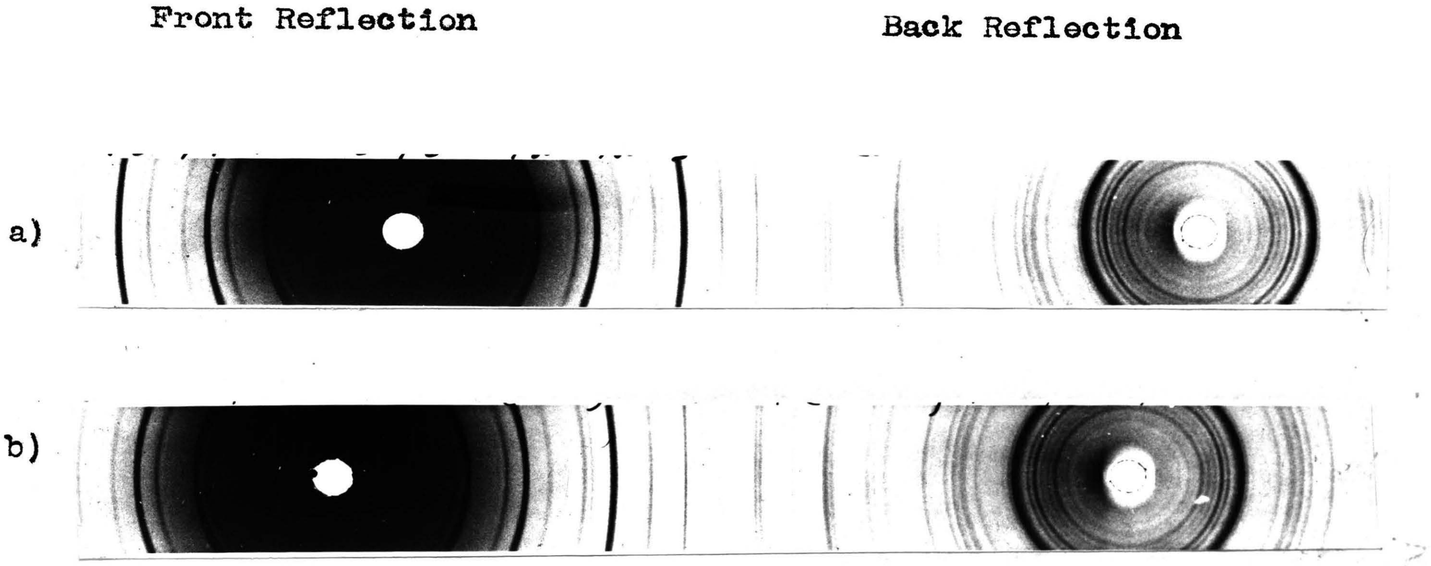

Fig. 10: a) The X-ray Powder Photograph of MoO_2.
b) The X-ray Powder Photograph of the so-called "molybdenum bronze".
The diffraction patterns of a) and b) are similar.

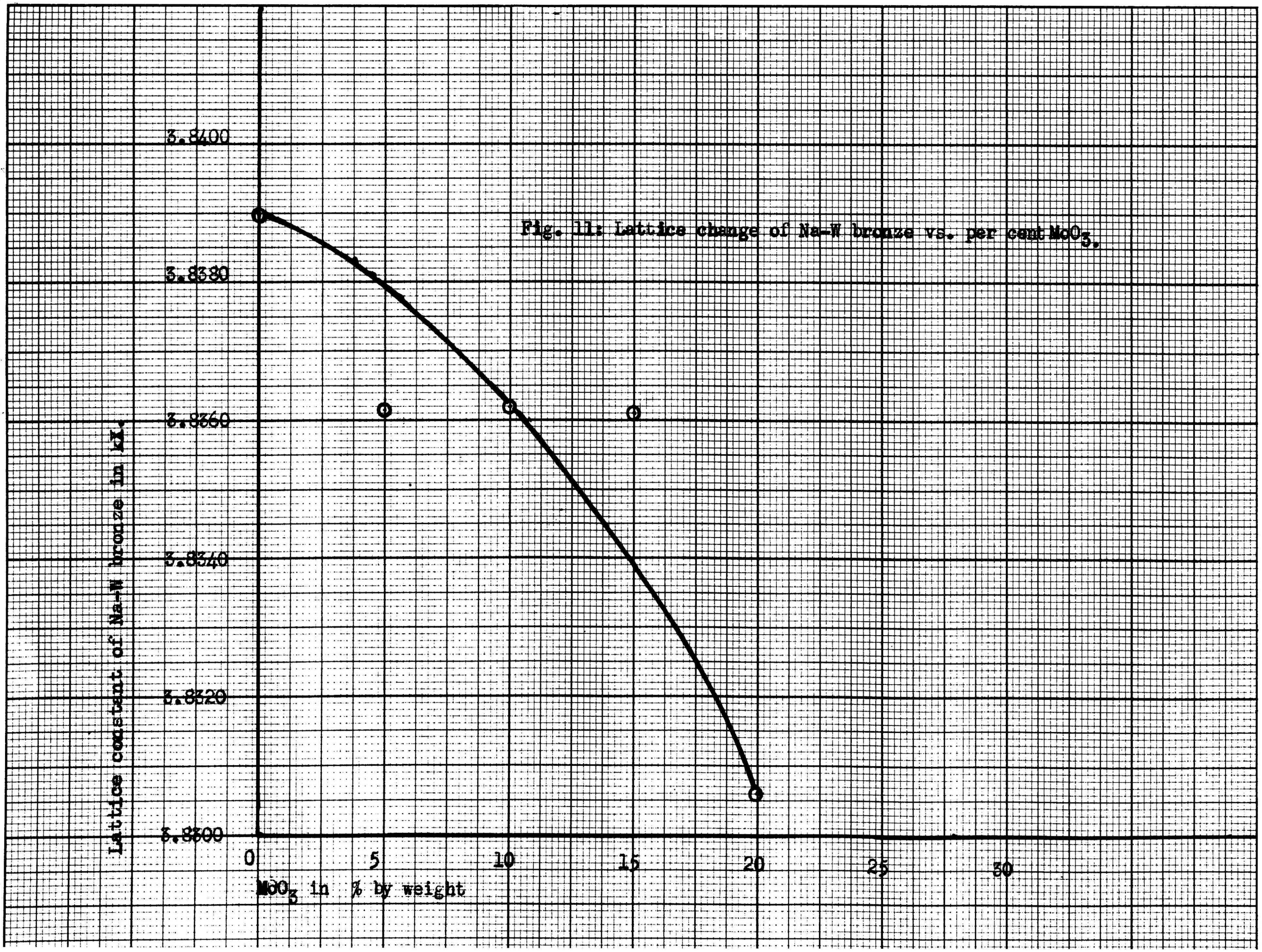

Fig. 11: Lattice change of Na-W bronze vs. per cent MoO_3.

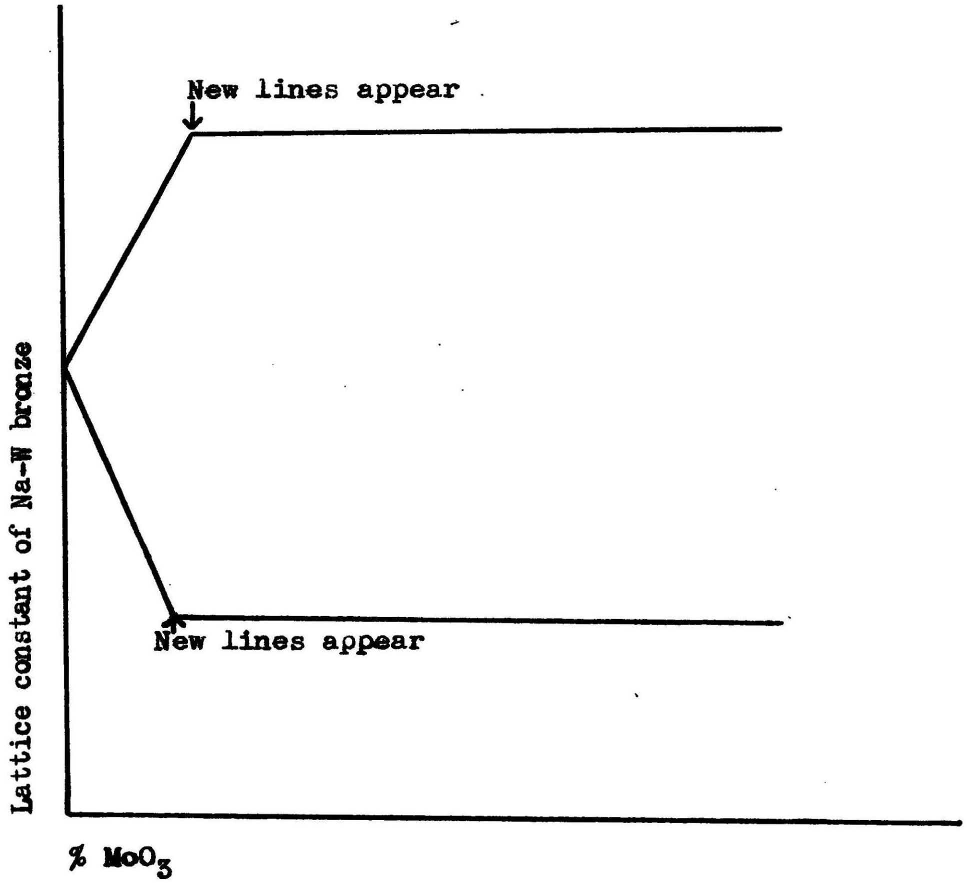

Fig. 12: Lattice Change of Na-W Bronze *versus* Percentage of MoO_3 by Weight, according to the theoretical concept.

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diffraction pattern was quite different from that of the Na-W bronze; there were no Na-W bronze lines, and the new lines were present in the largest number. All this indicates that there is no solubility, but rather a reaction between Na-W bronze and MoO_3. The reaction between MoO_3 and Na-W bronze should result in a new product or products, the lines of which would be observed on the films.

The same strange lines were identified

1) on the diffraction patterns of samples in the preparation of molybdenum bronze in Experiment 12 (p. 32), $Na_2MoO_4 + MoO_3 + Mo$;

2) on patterns of samples obtained in Experiment 13, $Na_2WO_4 + WO_3 + Mo$;

3) on patterns of samples obtained in Experiment 14, $Na_2MoO_4 + MoO_3 + W$.

In order to establish the identity of these new lines, MoO_2 was prepared at first according to the following reaction:

$$2MoO_3 + Mo = 3MoO_2$$

The lines on the diffraction pattern of MoO_2 matched perfectly with the strange lines on the above patterns just described. Therefore, it was definitely proved that MoO_2 is one of the products formed in the above experiments.

The reaction between the sodium-tungsten bronze and molybdenum can be written as an unbalanced equation:

$$2NaWO_3 + xMoO_3 = (2-\underline{\alpha})NaW^{V}O_3(W^{VI}O_3)x + xMoO_2 + xNa_2W_2O_7$$

The interpretation might be as follows: the result of the reaction of sodium-tungsten bronze with MoO_3, at high temperatures, is the formation of MoO_2, a sodium-tungsten bronze with a high WO_3 content, and of $Na_2W_2O_7$ or related products. The explanation is that MoO_3 releases its oxygen atom, which oxidizes the Na-W bronze to $Na_2W_2O_7$, whereby the excess WO_3 dissolves in the remaining sodium-tungsten bronze. This bronze, now with a high WO_3 content, has a smaller lattice constant and is responsible for the contraction of the lattice dimensions observed in the samples and shown in Table 3. The successive steps of the reaction may be written as follows:

$$MoO_3 = MoO_2 + O \qquad (1)$$

$$2NaWO_3 + O = Na_2W_2O_7 \qquad (2)$$

and $$Na_2W_2O_7 + 2MoO_3(\text{excess}) = Na_2Mo_2O_7 + 2WO_3 \qquad (3)$$

and remainder of

$$NaWO_3 + xWO_3 = NaW^{V}O_3(W^{VI}O_3)x \qquad (4)$$

The WO_3 formed dissolves in the Na-W bronze (Equation 4), forming the deeper colored sodium bronzes, red to blue in color. If a large quantity of MoO_3 (30%) is added, the liberated WO_3 (Equation 3) is sufficient to form the deep blue, tetragonal sodium bronze, several lines of which were observed on the films of the reaction products with 30% of MoO_3. In order to compare the x-ray patterns, the tetragonal bronze was prepared from the bronze containing 10% of WO_3, as in Experiment 16, and some of the lines on the film of tetragonal sodium-tungsten bronze were found to correspond to the film of the reaction products with 30% of MoO_3. The sodium paramolybdate of Reaction 3 dissolved when the product was digested with water (for washing purposes) and, therefore, was not detected in the washed bronze powder. The formation of the molybdates was proved in this way. The decanted water solution from Experiment 11, containing the soluble sodium salts, was evaporated to dryness, and its x-ray diffraction pattern was compared with the pattern of $Na_2Mo_2O_7$, prepared in Experiment 19 (p. 37) by the following reaction:

$$Na_2MoO_4 + MoO_3 = Na_2Mo_2O_7$$

Both x-ray patterns were identical, proving the formation of $Na_2Mo_2O_7$ in Reaction 3. Reaction 2 proceeds because of the oxidation power of MoO_3, as a consequence of which MoO_2 was observed on the copper lid of the crucible. The the sublimate on the copper lid was MoO_2 could definitely be proved by the x-ray diffraction pattern. The formation of MoO_2 on the copper lid might be explained as follows:

$$Cu + MoO_3 = CuO + MoO_2 \quad \text{at } 800^{o}C.$$

The gray-black CuO was observed on the lid, together with MoO_2. The ability of MoO_3 to act as an oxidizer at elevated temperatures was also confirmed by other authors. Rathenau and Meijering[10] demonstrated in their paper the strong oxidizing property of MoO_3, where copper and heat-resisting copper alloys, iron and heat-resisting iron alloys, nickel and nickel-chromium alloys, silver and silver-aluminum were oxidized at elevated temperatures in the presence of MoO_3 and air. Thus, a solid solution of a type such as $NaW^{V}O_3(Mo^{VI}O_3)_{\alpha}$ or $NaW^{V}O_3(W^{VI}O_3, Mo^{VI}O_3)_{\alpha}$ cannot exist because of the oxidation power of MoO_3, whereas, at the elevated tem-

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[10] G. W. Rathenau and J. L. Meijering, *Metallurgia* 42: 167-172. (Sept. 1950)

peratures of bronze formation, MoO_3 destroys the bronzes and converts itself into MoO_2.

On the diffraction pattern of Experiment 13 (p. 33) $Na_2WO_4 + WO_3 + Mo$, it was observed that there were lines of MoO_2 on the front-reflection region of the diffraction pattern and the lines of the red or blue Na-W bronzes. The reaction to explain this can be written as follows:

a) $2Na_2WO_4 + 2WO_3 = 4NaWO_3 + 2O$

b) $Mo + 2O = MoO_2$

Mo acted as a reducing agent; as a result Na-W bronze was formed and MoO_2.

In the case of Experiment 14 (p. 33), $Na_2WO_4 + MoO_3 + W$, the diffraction pattern of the washed product was identical with that of MoO_2. Here the only product, insoluble in water, to form, was MoO_2. The reaction could simply be written as follows;

$$3MoO_3 + W = WO_3 + MoO_2$$

and $Na_2WO_4 + WO_3 = Na_2W_2O_7$, which was washed off. The not-reacted MoO_3 also dissolved in Na_2WO_4, forming compound $Na_2WO_4(MoO_3)$, soluble in water. This was proved as follows: Na_2WO_4 and MoO_3 were heated together; a white product resulted which was found to be very soluble in water.

In Experiment 12 (p. 32), $Na_2MoO_4 + MoO_3 + Mo$, an attempt was made to synthesize the so-called "Molybdenum bronze". But the product obtained was identified as MoO_2, by comparison of its diffraction pattern with that of the MoO_2 prepared. This reaction can be written as follows:

$$2MoO_3 + Mo = 3MoO_2$$

because the sodium molybdate dissolved in water during the washing operation. If an excess of MoO_3 were used, sodium paramolybdate and MoO_2 would be formed, according to this reaction,

$$Na_2MoO_4 + MoO_3 = Na_2Mo_2O_7$$

which also is soluble in water.

The formation of MoO_2 instead of the so-called "molybdenum bronze" could be explained on the ground that MoO_3 is a very strong oxidizing agent at elevated temperatures and that it oxidized the molybdenum to MoO_2. The existence of a molybdenum bronze is connected with the question of stability of Mo^{5+} in the presence of Mo^{6+} at elevated temperatures, since the bronzes contain pentavalent W or Mo. Because of the oxidation power of MoO_3, Mo^{5+} cannot exist -

$$Mo_2O_5 + MoO_3 = 2MoO_3 + MoO_2$$

and no molybdenum bronzes can be formed, at least not at 800°C.

In his papers, Canneri has described the possibility of preparation of molybdenum bronze only when the ratio of $Na_2O : MoO_3$ was very high. At intermediate proportions, only MoO_2 was formed.

As has already been pointed out in Experiment 12, even the amount of MoO_3, multiplied to four times the calculated amount, was without success in obtaining the molybdenum bronze. Only MoO_2 was produced. This is in accordance with the statements of van Liempt and Hägg.

PART II

PREVIOUS WORK AND INTENTION OF THE PRESENT WORK

The Solid Solutions of Li-W Bronze and K-W Bronze

In 1888, W. Feit[11] prepared a product consisting of violet needles with blue ends, by fusing a mixture of one gram mole of $K_2W_2O_7$ and one gram mole of $Li_2W_2O_7$ and reducing with tin. By analysis, he arrived at the formula $Li_2W_5O_{15} + 3K_2W_4O_{12}$. In those times, there was not much known about mixed crystals and solid solutions, so Feit was not certain about the nature of the compound obtained. It might be that the product $Li_2W_5O_{15} + 3K_2W_4O_{12}$ was a solid solution of the lithium- and potassium-tungsten bronzes. In order to clarify this point, it was decided to approach the problem by carrying out a series of tests in which different proportions of K-W bronze were added to the Li-W bronze and then heated in a vacuum at different temperatures, as already described. X-ray diffraction photographs were made of the products obtained, and, from the pattern, the lattice constants were calculated. The contraction or expansion, if any, of the lattice would indicate the mutual solid solubility of the two bronzes.

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[11] W. Feit, "Zur Kenntniss der Wolframverbindungen". Ber. Deutsche Chem. Ges. 21: 133-137. (Jan., 1888)

The Preparation of Lithium-Tungsten Bronzes

Previous workers have fully investigated the preparation and properties of Li-W bronze. The lithium-tungsten bronzes were prepared by reducing a mixture of lithium tungstate and tungstic oxide with metallic tungsten, at high temperatures, in a vacuum.

The sample was placed in a porcelain crucible and heated in the vacuum furnace, the same one used for the preparation of Na-W bronze.

Experiment 20

The following starting materials were used:

W	- 0.05	gram
WO_3	- 0.58	gram
Li_2WO_4	- 0.80	gram
Total	1.43	grams

The mixture was heated to 800°C. for four hours and cooled down slowly to room temperature. The product was composed of pure blue crystals without any WO_2 present. X-ray powder photographs shows sharp diffraction lines of the bronze pattern.

The Experimental Procedure

The Li- and K-W bronze were weighed out in proper proportions, mixed thoroughly, ground to a fine powder in a mortar; the mixture was transferred into a quartz vial and heated in the same way as in the series Na- and K-W bronze. The results obtained were tabulated Table 4 and Table 5.

TABLE 4

Mixtures of K-W Bronze and Li-W Bronze, Heated at 840°C. for Two Hours

Sample Number	Film Number	K-W Bronze wt. %	Li-W Bronze wt. %	a in kX
		0	100	3.7142
77	568	1	99	3.7148
78	569	2	98	3.7149
72	565	2.5	97.5	3.7146
73	564	5	95	3.7146
74	563	10	90	3.7146
75	562	15	85	3.7144
76	567	25	75	3.7145

Remarks:

1) The WO_3 (W in six-valent form) content in the Li-W bronze corresponded approximately to $LiWO_3 \cdot WO_3$.

2) No distinction could be made regarding the color of different samples. They were all dark blue after heating.

3) K-W bronze lines were identified in the front-reflection region of the Li-W bronze pattern, Film 562.

4) Since the accuracy of determination of the lattice constant of the Li-W bronze is approximately 3.7142 ± 0.0005 kX, the lattice of the heated samples did not show any increase. Thus, the next series of tests was made at 900° and 950°C.

TABLE 5

Mixtures of K-W Bronze and Li-W Bronze for Two Temperatures, 900°C. and 950°C.

Sample Number	Film Number	K-W Bronze wt. %	Li-W Bronze wt. %	a in kX	Temperature
		0	100	3.7142	
124	618	5	95	3.7153	900°C.
125	619	10	90	3.7150	900°C.
126	620	20	80	3.7150	900°C.
127	621	10	90		950°C.
128	622	20	80		950°C.

Remarks:

1) The time of heating the samples was two hours in all cases.

2) The samples at 900°C. again did not show any change in color: all were bluish black.

3) The expansion of lattice of the samples obtained at 900°C. was slightly greater than that at 840°C.

4) Lines of K-W bronze appeared on Film 620; it is very possible that the limit of solubility of K-W bronze in Li-W bronze is about 5 percent.

5) At 950°C., the samples 127 and 128 obtained, were red in color. Under the microscope, slender, long, red crystals were observed embedded in a blue-black mass.

6) The patterns of Samples 127 and 128 were entirely different from the old pattern of Li-W bronze.

Discussion and Conclusion

At 840°C., all the samples obtained had the same blue color of the Li-W bronze. Measurement of their lattice constants shows a very small increase, nearly within the error limits in the fourth place. From these results, it followed that the solubility of K-W bronze in Li-W bronze was very low. The exact determination of the solubility limit of K-W bronze was very difficult, because the lattice constants differed in the fourth place, by a small amount, in a very irregular manner. This irregularity might be caused by experimental measurement errors. From the appearance of K-W bronze lines on the front-reflection region of the Li-W bronze diffraction pattern (Film 562), it was possible to conclude that the limit of solubility of K-W bronze was below 15 percent.

Again at 900°C., no change of the color of the samples was observed. The lattice constant values had increased slightly from the values obtained at 840°C. The appearance of K-W bronze lines, observed in Film 620, containing 20% of K-W bronze, might indicate that the solubility limit of K-W bronze was below 20 percent.

Quite a complete change in the colors of the samples heated at 950°C. was noticed. The samples were reddish in color, and, under the microscope, the product looked quite unhomogeneous, with slender, reddish crystals dispersed between the bluish-black mass. The diffraction pattern was different from the pattern of the old Li-W bronze - although the lines of Li-W bronze and K-W bronze had been identified in the front-reflection region - but there also were strange lines. Therefore, a new phase was formed.

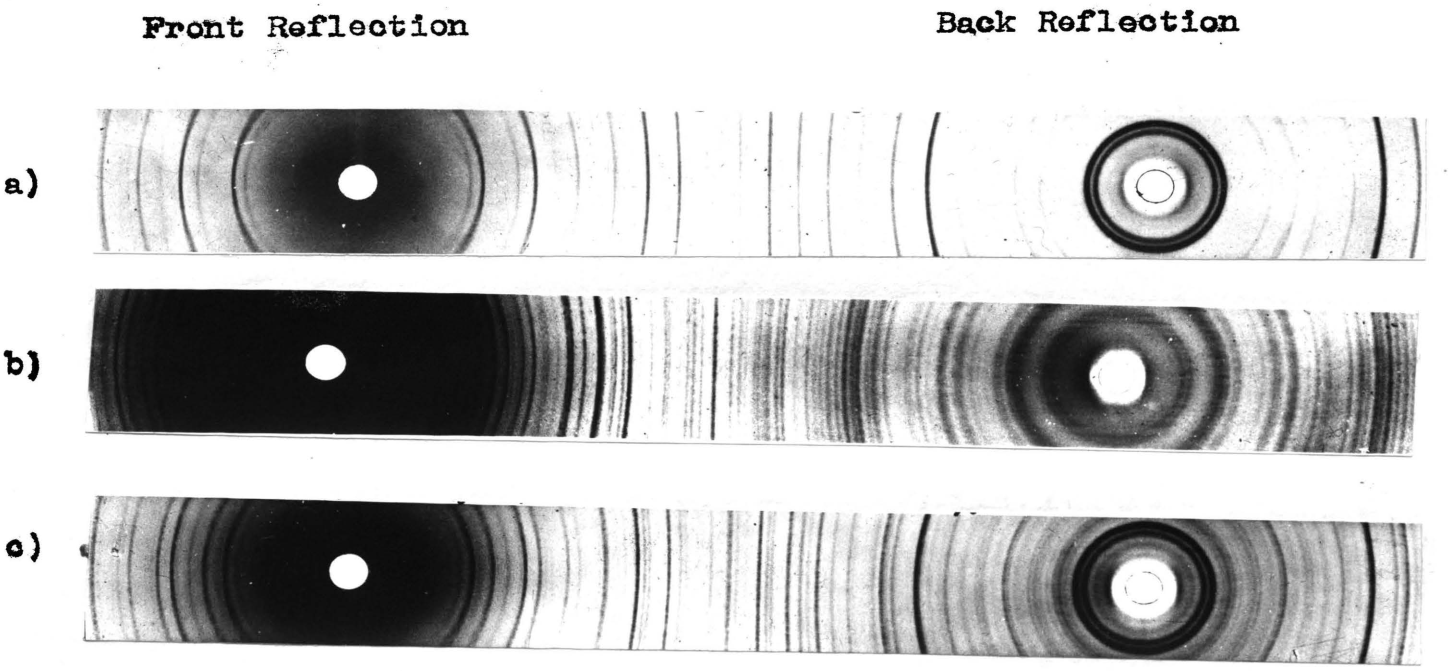

Fig. 13: a) The X-ray Powder Photograph of Pure Li-W Bronze.

b) The X-ray Powder Photograph of Pure K-W Bronze.

c) The X-ray Powder Photograph of Li-W Bronze plus K-W Bronze (20 percent) at 900°C. showing the appearance of K-W bronze lines.

PART III

PREVIOUS WORK AND INVESTIGATION OF THE PRESENT WORK

Solid Solutions in the System Sodium-Tungsten Bronze (10% of WO_3) - Potassium-Tungsten Bronze

Potassium-sodium-tungsten bronzes of the composition $5K_2W_4O_{12} \cdot 2Na_4W_5O_{15}$ and $3K_2WO_4 \cdot 2Na_2W_3O_9$ had been prepared earlier by von Knorre[12] and W. Feit[11] by fusing together equimolar proportions of sodium and potassium paratungstates and heating the mixture to redness in hydrogen. This experiment showed that there exists a solid solubility of Na-W bronze in K-W bronze, or vice versa.

In order to check this and to investigate the limit of solid solubility of K-W bronze in Na-W bronze, a series of samples of different composition was prepared by heating them in a vacuum at various temperatures.

The reason for choosing the Na-W bronze and not the K-W bronze as the starting point was that the sodium bronze possessed a simple, cubic structure, the diffraction pattern of which did not contain many lines, and also that it was very easy to measure the expansion or contraction of the lattice parameter of such a bronze; however, the K-W bronze possessez a tetragonal lattice

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[12] G. V. von Knorre. J. Prakt. Chem. 27: 65. (1883)

which is very complex and difficult to treat.

The Experimental Procedure

The Na- and K-W bronzes were weighed in the required amount, mixed thoroughly, and crushed in a mortar to a fine-grained size. The mixture was then transferred into a small quartz vial. The open end of the quartz vial was next inserted into a narrow, glass tube connected to the vacuum pump, and the two ends were connected in an airtight manner by sealing with wax. Then the quartz vial was evacuated and sealed off with a gas-oxygen flame. The vial was placed in a resistance furnace and heated to the desired temperature for the proper time. It was next quenched in air; microscopic examinations followed, x-ray photographs were made, and lattice constants were determined. The starting material used was a Na-W bronze containing 10.9% of WO_3. The lattice constant was a = 3.8440 kX. The K-W bronze used was the one prepared by Ma[13]; the initial heating temperature chosen was 620°C. The results obtained have been tabulated in Table 6.

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[13] Ma, . Potassium-Tungsten Bronzes. Missouri School of Mines. (1950)

TABLE 6

Samples of the Mixtures of K-W Bronze and Na-W Bronze for the Heating Temperature of 620°C. and Time of Heating of Four Hours

Sample Number	Film Number	Na-W Brnz wt. %	K-W Brnz wt. %	a in kX	Color
80	579	97	3	3.8439	yellow
81	574	94	6	3.8434	yellow
82	572	90	10	3.8434	yellow
83	573	85	15	3.8434	deep yellow
84	575	80	20	3.8434	deep yellow
85	576	70	30	3.8434	deep yellow

Remarks:

1) The samples at 620°C. did not show a great change in color.

2) The contraction of the lattice continued up to six percent of K-W bronze and thereafter ceased to change.

3) Lines of K-W bronze appeared in the front-reflection region of Film 572.

4) All these results showed that the solubility limit of K-W bronze in Na-W bronze at the low temperature of 620°C. was not great.

How the solubility increases with increasing temperature will be shown in the next series of experiments, to be carried out at elevated temperatures.

TABLE 7

Samples of the Mixtures of K-W Bronze and Na-W Bronze for the Heating Temperature of 720°C. and Time of Heating of Three Hours

Sample Number	Film Number	Na-W Brnz. wt. %	K-W Brnz wt. %	a in kX	Color
86	582	97	3	3.8429	deep yellow
87	583	94	6	3.8428	deep yellow
88	584	90	10	3.8427	deep yellow
89	585	85	15	3.8427	deep yellow
90	586	80	20	3.8427	deep yellow
91	587	70	30	3.8427	deep yellow

Remarks:

1) The sample at 720°C., in each instance, was deep yellow in color.

2) The lattice contraction continued up to ten percent of K-W bronze and, from there onward, ceased to change.

3) The contraction of lattice of samples obtained at 720°C. was slightly greater than at 620°C.

4) Lines of K-W bronze appeared on the front reflection region of Film 585.

This table shows that there is a definite increase in solubility of K-W bronze in Na-W bronze with increasing temperature; therefore, it was decided to go to a still higher temperature, 820°C.

TABLE 8

Samples of the Mixtures of K-W Bronze and Na-W Bronze for the Heating Temperature of 820°C. and Time of Heating of Two Hours

Sample Number	Film Number	Na-W Brnz wt. %	K-W Brnz wt. %	a in kX	Color
92	589	97	3	3.8415	deep yellow
93	590	94	6	3.8395	deep yellow
94	591	90	10	3.8379	deep yellow
95	592	85	15	3.8381	yellow red
96	593	80	20	3.8381	red
97	594	70	30	3.8381	intense red

Remarks:

1) The contraction of the lattice continued up to 15 percent of K-W bronze and, from there onward, it stayed constant.

2) As compared to the samples at 620°C. and 720°C., the change of color was clearly noticeable.

3) The lines of K-W bronze appeared on the front-reflection of the Film 593.

Table 9 shows the results obtained at 900°C. Since the quantity of Na-W bronze was exhausted, a fresh amount of Na-W bronze was prepared in the usual manner, at 810°C. The lattice constant was measured, $\underline{a}_0$ = 3.8439 kX, corresponding to ten percent of WO_3.

TABLE 9

Samples of the Mixtures of K-W Bronze and Na-W Bronze for the Heating Temperature of 900°C. and Time of Heating of One Hour

Sample Number	Film Number	Na-W Brnz wt. %	K-W Brnz wt. %	a in kX	Color
107	630	98.5	1.5	3.8358	yellow
99	600	97.	3.	3.8349	deep yellow
100	596	94.	6.	3.8340	deep yellow
101	597	90.	10.	3.8330	red
102	595	85.	15.	3.8316	deep red
103	598	80.	20.	3.8312	very deep red
104	599	70.	30.	3.8304	deep dark red
105	601	60.	40.	3.8290	chocolate
106	602	50.	50.	3.8313	chocolate

Remarks:

1) The contraction of the lattice continued up to 40 percent of K-W bronze.

2) The colors of the samples varied from yellow to red to chocolate.

3) The lines of K-W bronze were observed on the front-reflection region of Film 599.

4) All these results indicated a greater solubility of K-W bronze in Na-W bronze at 900°C. than at the temperatures 620°C., 720°C., and 820°C.

In order to complete the investigation, the temperature of 1000°C. was resorted to, to determine whether the solubility limit still increased.

Experiment 21

Na-W bronze - 485 mgs.
K -W bronze - 15 mgs. - 3% of K-W bronze

The heating temperature was 1000°C., and the time of heating half an hour. A highly fused mass was obtained; the color of the product was yellow, and, under the illuminator, well formed, shiny yellow crystals were observed. Pieces of silica particles were heavily dispersed in the yellow mass. The lattice constant showed a very great contraction. No attempt was made to measure the film. Strange lines, in addition to the lines of K-W bronze, were observed on the front-reflection region of Film 607 of Sample 108.

Experiment 22

Na-W bronze - 470 mgs.
K -W bronze - 30 mgs. - 6% of K-W bronze

The time of heating was half an hour, and the heating temperature 1000°C. Sample 109, obtained, was the same as Sample 108. Their diffraction patterns looked the same.

Experiments 23, 24, 25, and 26, containing 10 percent, 15 percent, 20 percent, and 30 percent of K-W bronze, respectively, were performed at the same temperature and time. Samples 110, 111, 112, and 113 were obtained, respectively; all had the same characteristic appearance. When the quartz vials were opened, all that was observed in them were a few deep yellowish particles, firmly embedded in the matrix of the quartz vial. The quartz vials were very brittle and thin lamellaes of silica, sheared off the lining of the quartz tube. On one side of the disintegrated pieces, there were deep yellowish particles, and on the reverse side there were shiny, tiny, greyish-black particles. It was practically impossible to single out the different substances, and the diffraction pattern obtained from these mixtures was a completely new one. It was possible by comparison to recognize the lines of Na-W bronze, K-W bronze, and metallic tungsten.

The data of the tables have been plotted in Fig. 14 (p. 61): Lattice constants of different Na-W bronze - K-W bronze samples as ordinates, versus the percentage of K-W bronze. Four curves were drawn on the basis of experimental measurements. All these curves and the tables showed that the lattice of Na-W bronze contracted with the addition of K-W bronze.

For the curve at 620°C., the lattice contraction continues up to six percent of K-W bronze. After this amount, the lattice of Na-W bronze ceased to change, although more and more K-W bronze was added. The lines of K-W bronze appear in the patterns of the samples containing more than six percent.

For the curve at 720°C., the lattice contraction continues up to ten percent of K-W bronze. After this contraction had been reached, the lattice of Na-W bronze ceased to change, although more and more K-W bronze was added. The lines of K-W bronze appeared in the patterns of the samples containing more than ten percent.

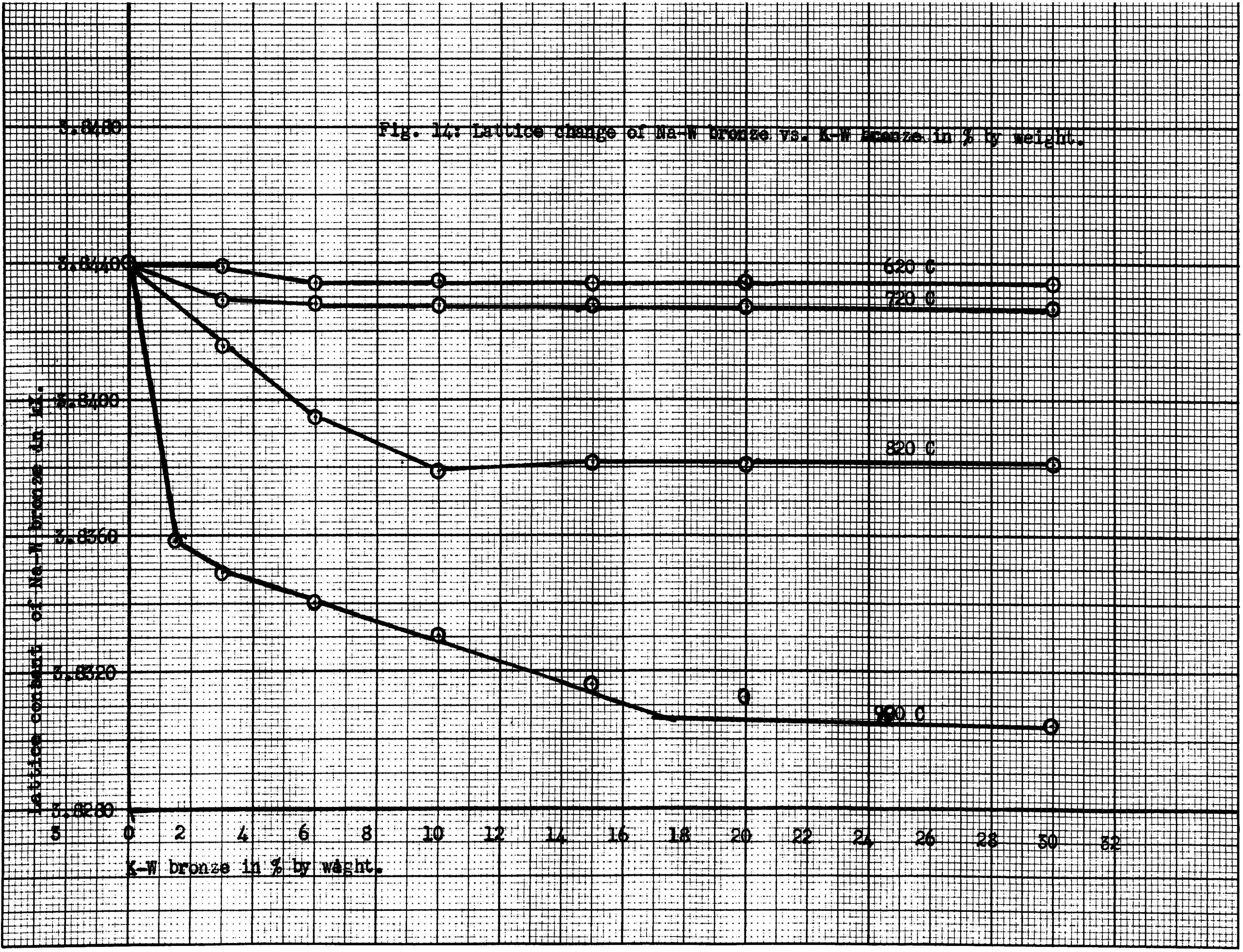

Fig. 14: Lattice change of Na-W bronze vs. K-W bronze in % by weight.

In the case of the curve at 800°C., the lattice constant continues to decrease up to 15 percent of K-W bronze. Beyond this amount, the lattice parameters ceased to change, although the concentration of K-W bronze in other samples was increasing. The lines of K-W bronze appeared in the patterns of the samples containing more than 15 percent.

For the curve at 900°C., the lattice constant continues to decrease, up to a high concentration of K-W bronze, namely 40 percent of K-W bronze. It was very difficult to determine the concentration of K-W bronze at which the lattice ceased to contract. At 50 percent of K-W bronze, it was found that the lattice constant had increased appreciably. The lines of K-W bronze appeared in the patterns of the samples containing more than 20 percent of K-W bronze.

No curve was plotted for the samples heated at 1000°C. because only the diffraction patterns, Numbers 108 and 109, showed the patterns of Na-W bronze; in addition, they showed new lines which were probably those of cristobalite, since the samples were heavily attacked by the silica from the quartz. The samples (110, 111, 112, and 113), obtained, were all identical, and the diffraction patterns of these samples were very complex, with the lattice of Na-W bronze indistinguishable.

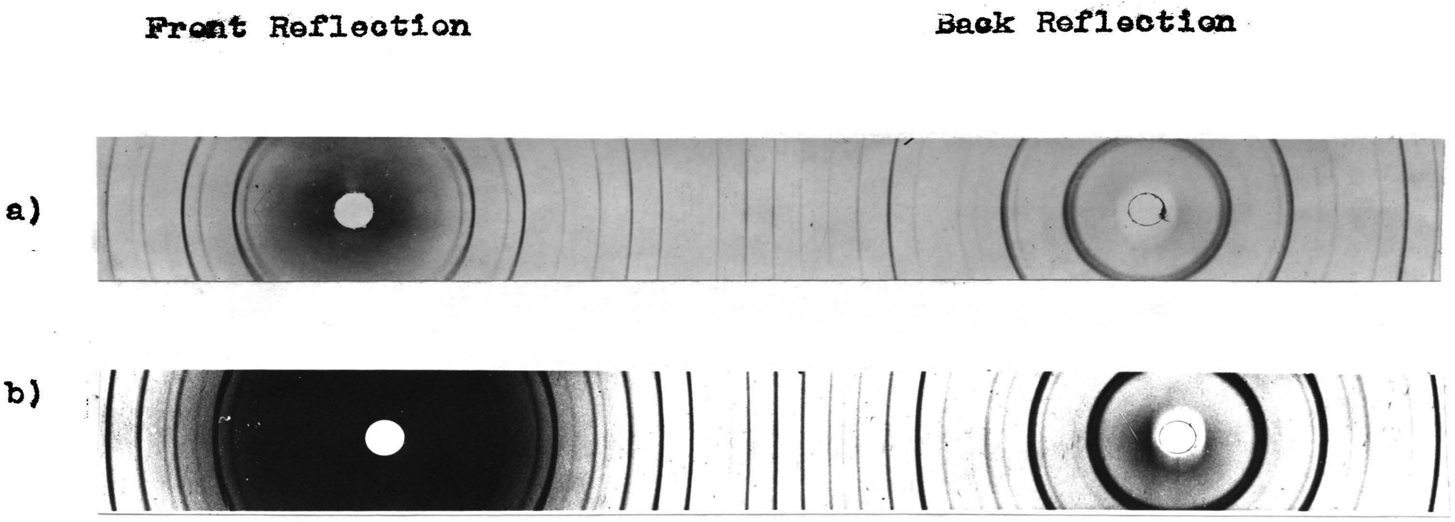

Fig. 15: a) The X-ray Powder Photograph of Na-W Bronze plus K-W Bronze (30 percent) at 800°C., showing the contraction of the lattice Co-radiation.

b) The X-ray Powder Photograph of Na-W Bronze Co-radiation.

Conclusion and Discussion

The curves show clearly that the solubility of K-W bronze in Na-W bronze depends on the heating temperature. At 620°C., the solubility limit for K-W bronze lies below six percent, since, at this concentration, the lattice constant ceases to change, so that a constant value is reached.

Since the flat slope of the curve does not permit an exact determination of the solubility limit, the films were examined under the fluorescent illuminator. If the percentage of K-W bronze was over the solubility limit, new lines would appear on the films. Under the illuminator, the new lines could be seen first at a concentration of ten percent of K-W bronze. This result confirmed that the solubility limit of K-W bronze in Na-W bronze at 620°C. was below six percent, as found above.

At 720°C., the solubility limit of K-W bronze lies below ten percent. This also is a curve similar to the one at 620°C. New lines on the diffraction pattern were observed at a concentration of 15 percent K-W bronze, so it can be said that the solubility limit of K-W bronze in Na-W bronze had been reached at ten percent.

At 820°C., the solubility limit of K-W bronze lies below 15 percent. In contrast to the curves for 620°C. and 720°C., this curve has an appreciable slope up to ten percent of K-W bronze, and then the curve flattens out. From the slope of this curve, it is possible to say that the solubility limit is also in the vicinity of 15 percent. K-W bronze lines were observed under the illuminator at a concentration of approximately 20 percent of K-W bronze. From these observations, it is safe to say that, at 20 percent, the solubility limit of K-W bronze in Na-W bronze had already been passed.

The curve at 900°C., shows that the solubility of K-W bronze in Na-W bronze had considerably increased with higher temperatures. The solubility limit of Na-W bronze lies below 20 percent, although the constant value for the lattice constant was not reached in this case. It was suspected that, at high temperatures, some of the sodium of Na-W bronze was absorbed by the quartz tube, thereby resulting in a bronze with higher WO_3 content and a lower lattice constant. This might be one of the reasons why, even at one and one-half percent, a sample was obtained with a too-low lattice constant. Under the illuminator, lines of K-W bronze were observed at a concentration of 30 percent of K-W bronze. This result therefore indicated that the solubility limit had already been exceeded. Besides, it was observed that strange lines appeared on the front reflection region of the diffraction pattern of samples containing higher percentages of K-W bronze, namely 40 percent and 50 percent. These lines might be due to the formation of a new phase.

It was observed that the color of the products become deeper with increasing heating temperature. At

620°C and 720°C., the color of the samples containing up to 30 percent of K-W bronze was deep yellow, while at 820°C. the shade of red appeared on samples containing 15 percent of K-W bronze. At 900°C., the color of the product containing ten percent of K-W bronze was reddish, and at 30 percent, it was deep, dark red. All these results once again showed that K-W bronze dissolved in Na-W bronze, the amount increasing with higher temperatures.

From the condition of the quartz tube, it was evident that at 1000°C. a reaction had occurred between the products and the quartz tube. Its wall was stained black, and it had become so brittle that it sheared off into this pieces of silica. On one side of these silica pieces there were embedded the yellow-brownish particles, and on their reverse side were tiny, grey, shiny-black particles. An attempt was made to dissolve the silica in hydrofluoric acid, but with little success. The x-ray diffraction patterns conclusively showed the lines of Na-W bronze, K-W bronze, and metallic tungsten, by comparison with their individual diffraction patterns. It was suspected that there was silicon present, but on the diffraction pattern it was almost impossible to identify silicon lines.

It is apparent that at higher temperatures samples containing larger concentrations of K-W bronze reacted with the quartz of the tube. The sodium of the bronze reduced the silica, and the remaining WO_3 dissolved in the bronze, lowering its lattice constant. It is also probable that the K-W bronze and Na-W bronze attacked the silica, resulting in the decomposition of silica to silicon and of the bronzes to metallic tungsten.

Solid Solutions in the System Na-W Bronze (40% of WO_3) - K-W Bronze

Na-W bronze and WO_3 form a series of solid solutions with contraction of the bronze lattice. The relationship between the WO_3 dissolved in Na-W bronze and the lattice change in the latter have been worked out be previous investigators. The graph drawn in Fig. has been discussed in chapter . The Na-W bronze, used for the determination of the limit of solubility of K-W bronze therein, had a lattice constant of 3.8440 kX, corresponding to ten percent of WO_3 by weight. Now it is very interesting to find out what will be the effect on the solubility limit of K-W bronze in the Na-W bronze containing a higher percentage of WO_3 than ten percent. This time - on this line of thought - the series was prepared with the use of a Na-W bronze containing 40 percent of WO_3.

Preparation of Na-W Bronze Containing 40% of WO_3

The Na-W bronze already prepared contained 11.5 percent of WO_3; the problem to be solved now was to prepare from it a bronze containing 40 percent of WO_3.

Let us suppose that we started with 100 grams of

Na-W bronze, containing 11.5 percent of WO_3. The following relation can be written: From a bronze with 11.5 percent of WO_3, we want a $\underset{28.5}{\underline{\text{bronze}}}$

with 40 percent of WO_3, $\underset{60}{\underline{\text{starting from 100 grams.}}}$

11.5%   40%   100 gms

28.5   60

Difference: 100 - - - x, hence $\frac{100}{x} = \frac{60}{28.5}$

Therefore, $x = \frac{142.5}{3} = 47.5$ grams

Therefore, if we start from 100 grams of bronze, containing 11.5 percent of WO_3, and add 47.5 grams of WO_3, we will obtain a bronze with 40 percent of WO_3.

For instance, if we begin with 5.29 grams of bronze containing 11.5 percent of WO_3, the amount of WO_3 to be added is $\frac{47.5 \times 5.29}{100} = 2.51$ grams of WO_3

Two and fifty-one hundredths grams of WO_3 was the required amount, needed to prepared Na-W bronze containing 40 percent of WO_3.

Experiment 27

The charge consisted of

5.29 grams of Na-W bronze (11.5% of WO_3)
2.51 grams of WO_3

and was heated for three hours at 800°C. The two constituents were mixed intimately together, ground in a mortar; the mixture was transferred to a porcelain crucible and heated in a vacuum in the same furnace which was used for the preparation of Na-W bronze (10% of WO_3). The sample was purple in color. An x-ray picture was made, and the lattice constant corresponded to a bronze containing 38 percent of WO_3. This sample was used as a starting material for subsequent tests.

This series of experiments was carried out in a furnace similar to the one which was used for the determination of the solubility limit of Na-W bronze (10% of WO_3) in K-W bronze. Since it was observed before that the solubility limit of K-W bronze increased with higher temperature, it was decided to start with 800°C.

TABLE 10

Samples of Mixtures of Na-W Bronze (38% of WO_3) - K-W Bronze

Sample Number	Film Number	Na-W Bronze (38% WO_3) wt. %	K-W Bronze wt. %	a in kX
115	609	95	5	3.8240
116	610	90	10	3.8237
117	612	85	15	3.8237
118	613	80	20	3.8237
119	614	70	30	3.8240

Remarks:

1) The samples were all heated for two hours at 800°C.

2) There were no changes in the colors of the samples; all samples were purple.

3) There was no change in lattice dimension measurements.

4) These results indicated that K-W bronze did not dissolve in Na-W bronze containing 38 percent of WO_3 at 800°C. There was a possibility that at higher temperatures K-W bronze might dissolve; therefore, a higher temperature, 900°C., was chosen for the next experiments. The results of these experiments are tabulated in Table .

TABLE 11

Samples of Mixtures of Na-W Bronze (38% of WO_3) - K-W Bronze

Sample Number	Film Number	Na-W Brnz (38% WO_3) wt. %	K-W Brnz wt. %	Temperature	a in kX
121	615	90	10	900°C.	3.8241
122	616	80	20	900°C.	3.8246
123	617	85	15	950°C.	------

Remarks:

1) The samples obtained at 900°C. were reddish purple in color.

2) There was no change in their lattice dimensions.

3) The Sample 123 obtained was a brownish-yellow product, heavily impregnated with the silica from the quartz vial.

4) The diffraction pattern of Sample 123 was different from that of the Na-W bronze containing 38 percent of WO_3.

Discussion and Conclusions

The samples (numbers 115, 116, 117, and 119) containing 5 percent, 10 percent, 15 percent, and 30 percent, respectively, of K-W bronze, all heated at 800°C. for two hours, were all observed to have the same reddish-violet color under the microscope. Lattice constants of the samples just mentioned, Tables 10 and 11, showed no change in lattice dimensions within the error limits, proving that K-W bronze did not dissolve in Na-W bronze (38% of WO_3) at 800°C. Films with 15 percent and 30 percent of K-W bronze revealed the appearance of new lines, and when they were compared with those of pure K-W bronze, the lines in the front-reflection region were found to be identical with those of the K-W bronze, but there were certain lines which might indicate a possibility of the formation of a new phase, for instance, tetragonal solid solution of Na-W and K-W bronzes.

In the case of samples 121 (10 percent of K-W bronze) and 122 (20% of K-W bronze) at 900°C., the products showed a definite change in color. Large, beautiful, shiny-red crystals were observed in bright light. Lattice parameters of these two films, 615 and 616, were the same as those for the samples heated at 800°C. (see Table 10).

Comparing the films of the samples of Na-W bronze (38 percent of WO_3), heated at 800°C. and 900°C., (numbers 612, 614, and 615 and 616), with each other, showed a complete resemblance in all respects. Hence, the change of color of the crystals was thought to be due to the fact that at higher temperatures the crystals recrystallized with the formation of large, well defined crystals of slightly different color.

At 1000°C., Sample 123 was highly fused, and the silica of the vial was strongly attacked. The x-ray picture in the front-reflection region revealed a strong resemblance to the K-W bronze, with the lines of Na-W bronze fading, while in the back reflection the pattern was quite different.

All these results conclusively proved that there was no solubility of K-W bronze in Na-W bronze containing a 38-percent amount of WO_3 up to 900°C. At still higher temperatures, the outcome would be uncertain and a new lattice would be formed. Besides, there would be the possibility of reaction of silica of the tube with the bronze, accompanied by the formation of a new product.

SUMMARY

1) The sodium-tungsten bronzes, containing approximately ten percent of WO_3, have been prepared by reducing sodium tungstate and tungstic oxide with metallic tungsten at 800°C. in a vacuum. A bronze with a lower percentage of WO_3 in content was impossible to obtain.

2) The reactions between MoO_3 and Na-W bronze have been studied.

3) The results showed that, at concentrations of MoO_3 from 5 to 25 percent by weight, the Na-W bronze was decomposed into a bronze containing a greater amount of WO_3 and $Na_2Mo_2O_7$.

4) At 30 percent of MoO_3, by weight, a new phase, probably the tetragonal Na-W bronze, and the products mentioned in 3) above were formed.

5) An attempt to prepare sodium-molybdenum bronze according to the following equation

$$3Na_2MoO_4 + 2MoO_3 + Mo = 6NaMoO_3$$

resulted in MoO_2. Thus, the results obtained were in agreement with those of Hägg and of Burgers and van Liempt.

6) MoO_2, for identification purposes, was prepared by reducing MoO_3 with Mo.

$$2MoO_3 + Mo = 3MoO_2$$

7) The solubility of K-W bronze in Li-W bronze at different temperatures had been investigated. The results showed that the solubility limit of K-W bronze

in Li-W bronze is below 2.5 percent of K-W bronze at 830°C. and below 5 percent of K-W bronze at 900°C. The expansion of the $LiWO_3$ lattice was noticed with increasing additions of K-W bronze.

8) The solubility of K-W bronze in Na-W bronze at different temperatures had been investigated. The results showed that at 720°C. the solubility limit of K-W bronze in Na-W bronze was below that of 5 percent of K-W bronze; at 820°C., the solubility was below 10 percent of K-W bronze, and at 900°C., it was below 20 percent of K-W bronze. The contraction of the $NaWO_3$ lattice was noticed with increasing additions of K-W bronze.

9) The solubility of K-W bronze in Na-W bronze containing 38 percent of WO_3 in solid solution had been investigated at various temperatures. It was found that there was practically no solid solubility.

BIBLIOGRAPHY

1. Buerger, M. J., "X-ray Crystallography". John Wiley and Sons, New York, 1942.

2. Burgers, G. W. and J. A. M. van Liempt. Zeit. Anorg. Chem. 202: 325-328. (1931)

3. Canneri, G. Gazz. Chim. ital., 60: 113. (1930)

4. Feit, W. Ber. 21: 133. (1888)

5. Glemser, O. and Lutz, G. Z. Kolloid. 119: 99-102. (1950)

6. ------------------------ Zeit. Krist. 263: 1-13. (1950.

7. Knorre, G. V. von. J. prakt. Chem. 27: 65. (1883)

8. Magneli, A., "Crystal Structure Studies of Molybdenum and Tungsten Oxides and Related Compounds". Acta Chem. Scand. 14: 1-19. (1949)

9. Rathenau, G. W. and J. L. Meijering. Metallurgia 42: 167-172. (1950)

10. Sproull, W. T., "X-ray in Practise". McGraw-Hill, New York, 1946.

11. Straumanis, M. E. Zeit. Krist. (H): 104, 167. (1942)

12. ----------------- and A. J. Dravnieks. Am. Chem. Soc. 71: 683-687. (1949)

13. ----------------- J. Am Chem. Soc. 71: 679-683. (1949).

VITA

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