UNCLASSIFIED

BMI-730

Subject Category: METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

THE CONSTITUTION DIAGRAM OF
MOLYBDENUM-RICH URANIUM-MOLYBDENUM
ALLOYS

By
H. A. Saller
F. A. Rough
D. C. Bennett

March 6, 1952

Battelle Memorial Institute
Columbus, Ohio

Technical Information Service, Oak Ridge, Tennessee

UNCLASSIFIED

This document is
PUBLICLY RELEASABLE
Barry Steele
Authorizing Official
Date: 1-8-07

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

2

Date Declassified: December 7, 1955.

This report was prepared as a scientific account of Government-sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights. The Commission assumes no liability with respect to the use of, or from damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

This report has been reproduced directly from the best available copy.

Issuance of this document does not constitute authority for declassification of classified material of the same or similar content and title by the same authors.

Since nontechnical and nonessential prefatory material has been deleted, the first page of the report is page 7.

Printed in USA, Price 15 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

Contract No. W-7405-eng-92

THE CONSTITUTION DIAGRAM
OF
MOLYBDENUM-RICH URANIUM-MOLYBDENUM ALLOYS

by

H. A. Saller
F. A. Rough
D. C. Bennett

March 6, 1952

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	9
EXPERIMENTAL PROCEDURE	9
Materials and Melting	9
Heat Treatment and Examination	10
RESULTS	11
BIBLIOGRAPHY	17

ABSTRACT

Uranium-molybdenum alloys containing 50 to 100 atomic-per-cent molybdenum have been studied. The results of this work are reported, along with a review of the results of work on alloys from 0 to 50 atomic per cent. The principal feature of high-molybdenum alloys covered in this report is the limited solubility of uranium in molybdenum. Data indicate that about 1.8 atomic per-cent of uranium is soluble at 1200°C.

INTRODUCTION

Uranium-molybdenum alloys have been under study at Battelle for some time. Recently, a report was issued covering findings of work on alloys of 0 to 50 atomic per cent molybdenum.⁽¹⁾ The study of the remainder of the alloy system has been completed, and results are included in this report, along with some details from the previous work. The experimental techniques described include only those worked out for 50 to 100 atomic per cent molybdenum alloys. Complete details of the results and techniques used on 0 to 50 per cent molybdenum alloys are, of course, included in the earlier report.⁽¹⁾

Much of the effort on molybdenum-uranium alloys has involved a study of the metastable characteristics of the gamma-uranium phase. Early work⁽²⁾ showed that the gamma phase was stabilized by molybdenum additions of about 23 to 28 atomic per cent. Experiments indicated that the gamma in these alloys was retained even after long periods of annealing at temperatures of 400 to 600 C. Somewhat similar results were reported in the unclassified literature by Pfeil.⁽³⁾ More recently, a tetragonal product of decomposition of the gamma phase was reported⁽⁴⁾ and was confirmed by work at Battelle.⁽¹⁾ The decomposition has been found to be very sluggish in the range of 20 to 30 atomic per cent molybdenum. The rate of decomposition decreases, qualitatively, with increasing molybdenum composition, so that cold work and four weeks' annealing are required to produce appreciable transformation in a sample of 28 to 30 per cent molybdenum alloy.

The discovery of a new phase, of course, produced considerable alteration in the proposed equilibrium diagram. The revised diagram presented in this report is not precise in all details, but is believed to be adequate for general use. No further work on the diagram as such is planned in the Battelle program, although further studies of the kinetics of decomposition of the metastable gamma are in progress.

EXPERIMENTAL PROCEDURE

Materials and Melting

Good Mallinckrodt biscuit uranium and Fansteel molybdenum were used for this investigation. The analyses of these materials are shown in Table 1.

TABLE 1. MATERIAL ANALYSIS

Mallinckrodt Biscuit Uranium		Fansteel Molybdenum	
Element	ppm	Element	per cent
C	600	Mo	99.9
Fe	20	C	0.015 max.
Ni	50-100	Ni	0.02 max.
Al	10-100	O	0.10 max.
Mo	20		
Cr	20		
V	20		
Si	8-40		
P	50		

The uranium was sectioned into suitable pieces for melting and was examined by macroetching before making up charges. Only the cleanest pieces were used as melting stock.

All alloy ingots for this study were arc melted in a water-cooled copper crucible under an atmosphere of argon. A melting procedure involving three to five turns of the alloy material, and melting after each turn, produced homogeneous small ingots of 10 to 15 grams. Contamination of the alloys with tungsten from the electrode was minor; in most cases, a pickup of less than 0.05 weight per cent was found to be present by spectroscopic analysis.

Heat Treatment and Examination

All alloys were homogenized by annealing for 40 hours at 1200 C under a vacuum of one micron or less. Samples thus treated were quenched and examined before re-treating at other temperatures. After all examinations were completed, the samples were crushed and submitted for chemical analysis.

Specimens were prepared by cutting under a water spray with a carborundum 0.020-inch cut-off wheel. The heat-treated samples were mounted in bakelite and prepared for polishing by grinding wet through 240-, 400-, and 600-grit abrasive papers. This was followed by polishing mechanically on billiard cloth with an abrasive consisting of a suspension of stannic oxide in water. The specimens were then ready to be etched.

The etching technique varied, depending upon the type of structure which was obtained. High-molybdenum alloys which contained primarily single-phase solid-solution material were etched with Murakami's etch to reveal the grain structure. The etch solution consisted of 10 grams potassium hydroxide, 10 grams of potassium ferricyanide, and 100 of milliliters of water. Application was made to the specimens by swabbing with cotton at room temperature. Best results were obtained by alternately polishing and etching, in order to remove cold-worked metal from the surface of the specimens.

Alloy samples containing from 50 to 98 atomic per cent molybdenum, and which contained varying amounts of a high-uranium phase, were etched with a second solution. This etch consisted of equal parts by volume of nitric acid, hydrofluoric acid, and water. After polishing on billiard cloth with the stannic oxide abrasive, the etch was applied by swabbing for a few seconds at room temperature. This procedure brought out phase boundaries readily and produced excellent results with all the alloys of 50 to 98 per cent molybdenum.

RESULTS

The constitutional diagram for molybdenum-uranium alloys is shown in Figure 1. Only data on alloys of 50 to 100 atomic per cent molybdenum are plotted in the diagram, since a detailed report on alloys of 0 to 50 per cent has been published previously.⁽¹⁾

A peritectic reaction occurs at 1285 ± 10 C and extends from 25 to 98 atomic per cent molybdenum, Figure 1.⁽²⁾ The solubility of uranium in molybdenum is limited. Data indicate a solubility of about 1.8 per cent at 1200 C, and a slightly lower solubility at lower temperatures. Because of the sluggish equilibrium in these alloys at the lower temperatures, precise data were not obtained in this region.

The solubility of molybdenum in gamma uranium is a maximum of 42 atomic per cent at 1285 C and decreases with decreasing temperature. At 600 C, the maximum solubility is 30 per cent, and at lower temperatures transformation of the body-centered-cubic gamma phase can be accomplished. The gamma uranium is metastable over a range of compositions. Alloys of 12 per cent molybdenum transform during furnace cooling, although equilibrium is not reached by such a procedure. Gamma of 20 atomic per cent molybdenum does not transform readily, and annealing for four to five days at 5-600 C is required to obtain appreciable transformation. Application of cold work before annealing accelerates the transformation in this alloy. The rate of decomposition of the metastable gamma

FIGURE I. URANIUM-MOLYBDENUM EQUILIBRIUM DIAGRAM

decreases as the molybdenum content is increased. For example, in an alloy of 28 to 29 per cent molybdenum, it is believed that 20 per cent cold reduction and annealing for four weeks did not produce equilibrium, but did accomplish general transformation. An additional useful fact is that rates of transformation are more rapid in annealed filings prepared for X-ray examination than in bulk samples. Because of this fact, the principal data on the gamma-to-epsilon transition were obtained by X-ray methods.⁽¹⁾ The structure of the transition product is tetragonal with c/a ratio of 0.96.

Other features of the high-uranium portion of the diagram, Figure 1, include limited solubilities in both the beta- and alpha-phase regions, with a eutectoid reaction at 658 ± 5 C where beta uranium decomposes. The maximum solubilities in beta and alpha uranium are about 1.0 and 0.5 atomic per cent molybdenum, respectively.

The preceding discussion covers some of the general features of the equilibrium diagram and includes data from the earlier work.⁽¹⁾ With this as background, attention is turned to alloys of 50 to 100 per cent molybdenum for a more detailed discussion of results. In order to illustrate the general nature of these alloys, a series of microstructures of cast alloys is shown in Figures 2 to 11. A 70 per cent molybdenum alloy is shown in Figure 2. It contains white dendrites of high-molybdenum phase which are surrounded by high-uranium gamma material. The dendrites in this alloy are of a finer nature than in alloys of higher molybdenum content. This is presumed to be the result of a narrower solidification range, and perhaps faster cooling during casting. Alloys of 85, 91, 96, and 98 atomic per cent show decreasing amounts of the high-uranium phase, Figures 3, 4, 5, and 6. The remainder of the series of micrographs, Figures 7, 8, 9, 10, and 11, show essentially single-phase structures existing from 98.4 to 100 per cent molybdenum. These structures are not to be interpreted as representing equilibrium conditions.

The solubility of uranium in molybdenum at 1200 C is about 1.8 atomic per cent. This was determined by metallographic examination of quenched samples, as plotted in Figure 1. At lower temperatures, the data were inconclusive, although the solubility is believed to decrease somewhat with decreasing temperature. Partial data are plotted in Figure 1 representing the results of heat treating at 800 C.

The isothermal at 600 ± 10 C, separating the gamma-plus-delta and epsilon-plus-delta phase regions, was determined during the study of 0 to 50 per cent molybdenum alloys. Because of the difficulty of producing and identifying the transformation product of the metastable gamma, this type of test was not performed on alloys of greater than 50 atomic per cent.

250X

78837

FIGURE 2. 70 ATOMIC PER CENT
Mo-U, AS CAST

250X

73282

FIGURE 3. 85 ATOMIC PER CENT
Mo-U, AS CAST

250X

72507

FIGURE 4. 91 ATOMIC PER CENT
Mo-U, AS CAST

250X

72506

FIGURE 5. 96 ATOMIC PER CENT
Mo-U, AS CAST

250X

72505

FIGURE 6. 98 ATOMIC PER CENT
Mo-U, AS CAST

250X

74721

FIGURE 7. 98.4 ATOMIC PER CENT
Mo-U, AS CAST

250X

74722

FIGURE 8. 98.8 ATOMIC PER CENT
Mo-U, AS CAST

250X

74723

FIGURE 9. 99.2 ATOMIC PER CENT
Mo-U, AS CAST

250X

74724

FIGURE 10. 99.6 ATOMIC PER CENT Mo-U, AS CAST

250X

78845

FIGURE 11. 100 PER CENT MOLYBDENUM, AS CAST

BIBLIOGRAPHY

1. Saller, H. A., Rough, F. A., and Vaughan, D. A., "The Constitutional Diagram of Uranium-Rich, Uranium-Molybdenum Alloys", BMI-72, June 1, 1951. (Secret)
2. Ahmann, D., Snow, A. I., and Wilson, A. S., "The Uranium-Molybdenum Binary System", CT-2946, July, 1945. (Secret)
3. Pfeil, P. C. L., "The Constitution of Uranium-Molybdenum Alloys", J. Inst. Metals, Vol 77, pp 553-70 (1950-51).
4. Knolls Atomic Power Laboratory, "Monthly Report for October, 1948", Metallurgy Section, Memo J. P. H.-30. (Secret)