REFRACTORY MATERIALS

A SERIES OF MONOGRAPHS

VOLUME 2

THE REFRACTORY CARBIDES

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A SERIES OF MONOGRAPHS

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PREFACE

During the last ten years, an increasing interest in the refractory carbide systems has generated a large collection of data, much of which adds little understanding to the subject. It is clear that these systems are a good deal more difficult to investigate than many authors have suspected. This book, therefore, is intended as a guide to the chemist who wishes to undertake a fundamental study of these compounds.

No effort has been made to discuss all of the properties for which information is available. Rather, the selection is intended to give the reader information and some insights which are basic to any measurement. In general, early work which is clearly in error has been ignored except to show the difficulties in these attempts. Some unpublished research done at Los Alamos has been included to give a more complete presentation. In some systems, this work conflicts with accepted, or at least, published notions. In these cases, every effort has been made to present both viewpoints as fairly as possible. Since these measurements have not had the solidifying benefit of publication, minor changes might be made when publication is finally accomplished.

Dr. Melvin Bowman provided the environment wherein this effort could be made and a number of my colleagues at Los Alamos have been most generous with their comments and data. They include Dr. Allen Bowman, Dr. Terry Wallace, Mr. Willard Witteman, Mr. Andrew Yencha, and Mr. Nerses Krikorian. Dr. Allan Bowman and Dr. Aaron Goldman kindly supplied several of the computer programs used. In addition, advantage was taken of the Anifac program created by Dr. A. Larson and Dr. D. Cromer (LA–3335), and of the Herta program developed by Mr. R. E. Vogel and Dr. C. P. Kempter (LA–2317) as modified by Dr. A. Bowman. Mrs. Maxine Lewis and Mrs. Rose Mary Boicourt helped relieve much of the drudgery, which accompanies such an effort, by their good humor and secretarial talents.

E. K. STORMS

July, 1967

TABLE OF CONTENTS

CHAPTER I / The Titanium–Titanium Carbide System

CHAPTER II / The Zirconium–Zirconium Carbide System

CHAPTER III / The Hafnium–Hafnium Carbide System

CHAPTER IV / The Vanadium–Vanadium Carbide System

CHAPTER V / **The Niobium–Niobium Carbide System**

CHAPTER VI / **The Tantalum–Tantalum Carbide System**

CHAPTER VII / **The Chromium–Chromium Carbide System**

CHAPTER VIII / **The Molybdenum–Molybdenum Carbide System**

CHAPTER IX / **The Tungsten–Tungsten Carbide System**

CHAPTER X / **The Thorium–Thorium Dicarbide System**

CHAPTER XI / **The Uranium–Uranium Dicarbide System**

CHAPTER XII / **The Plutonium–Plutonium Dicarbide System**

CHAPTER XIII / **Discussion**

INTRODUCTION

This work includes a number of the more important physical and chemical properties of the nine transition elements included in Groups 4, 5, and 6 of the 4th, 5th, and 6th periods. The three actinide systems, Th–C, U–C, and Pu–C, have also been discussed. While this limited selection does not include all of the high melting carbides (many Group 3 and rare earth systems fall into this category), it does include the more refractory and the more useful ones. Besides, only for these systems has sufficient information been generated to make a critical review worthwhile.

These systems offer a unique collection of properties for an understanding of the chemical bond. They have very high melting points, which provide very wide temperature ranges for property measurements; they contain compounds which exist over a wide composition range; and they exhibit an unusual mixture of metallic, ionic, and covalent behavior. A number of theoretical treatments have been attempted but, as yet, a basic understanding has not been achieved. Part of this failure must result because so many measurements have been made on impure materials. For this reason, emphasis has been placed on the effect of impurities and the methods for their removal. Each system is discussed individually in terms of each property. These include phase relationship, lattice parameter and structure, chemical stability, hardness, and thermochemical properties which include vaporization behavior. In addition, the thermal data for the carbides and many of the associated elements have been reevaluated. Following a description of the various measurements, a general discussion is given of each property. Although no effort has been made to include the various theoretical treatments, a number of trends are revealed which might be useful for a future understanding.

The carbide systems are characterized by compounds which have a wide range of single phase composition. This is caused, in most cases, by defects in the carbon sublattice, and, for this reason, they are called defect compounds. Until this behavior was understood, many workers, starting with Hägg, in 1931, had described the phases as an interstitial solution of carbon in the metal lattice. Atom size considerations and experience with alloys added emphasis to this view. Unfortunately, such a model is rather poor in predicting properties in these systems. In addition, it creates unnecessary confusion, for example, when one wishes to indicate the interstitial sites between both the metal and the carbon atoms. If this description were applied to sodium chloride, which shares a common crystal structure with many of the carbides, one would have interstitial sodium atoms within a chlorine lattice. Most will admit this adds little insight from a chemist's viewpoint. Some authors have treated the nonstoichiometric compounds as a solid solution between the stoichiometric composition and the metal. While this leads, on some occasions, to an apparently correct prediction, it cannot be trusted. It is better to handle such compounds on the basis of the measured composition. Thus, equations must be written involving the actual stoichiometry which will not be integral nor will it, in some cases, be fixed. For this reason, it is important that data be obtained as a function of composition. Many of us will miss the Law of Definite Proportions which still simplifies chemistry in a few dwindling areas.

A number of expressions for composition are found in the literature, the most popular being weight percent, atomic percent, and atom ratio. The first is useful only in engineering, the second if solution theory is used, while the last simplifies the writing of chemical equations and emphasizes the defect nature of the compounds. For these reasons, all reported compositions have been converted to atom ratio in the text. Conversion to atomic percent is easily made through the identity: $\text{at.}\% = (C/M)/[1 + (C/M)]$.

The composition statement does not imply anything about the phases present in the sample. This decision must be based on the phase diagram. Thus, $MC_{0.56}$ might be a mixture of $MC_{0.5}$ and $MC_{0.7}$, both being the respective phase boundary compositions of the adjacent phases. When the general phase, irrespective of composition, must be described, the perfect lattice composition will be used, such as MC, M_2C, MC_2. If the perfect lattice is unknown, the designation MC_{1-x}, for example, will be used. Greek letters will be used only to designate allotropes, beginning with α for the low temperature form.

Thermodynamic quantities are given on the basis of one mole of metal, or, in other words, on the basis of a gram formula weight when written as MC_x.

All lattice parameters are given in angstrom units and the conversion from *kx* units is made by the factor 1.00202. In some cases, when the unit is in doubt, the value which would give the best agreement with later data has been used. In all cases, the original paper was consulted for a clarification of this vexing point.

In addition to the usual journals, an attempt has been made to include information which is found in various reports, both government and private. Many of these can be obtained for a small charge through the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U.S. Department of Commerce, Springfield, Virginia.

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