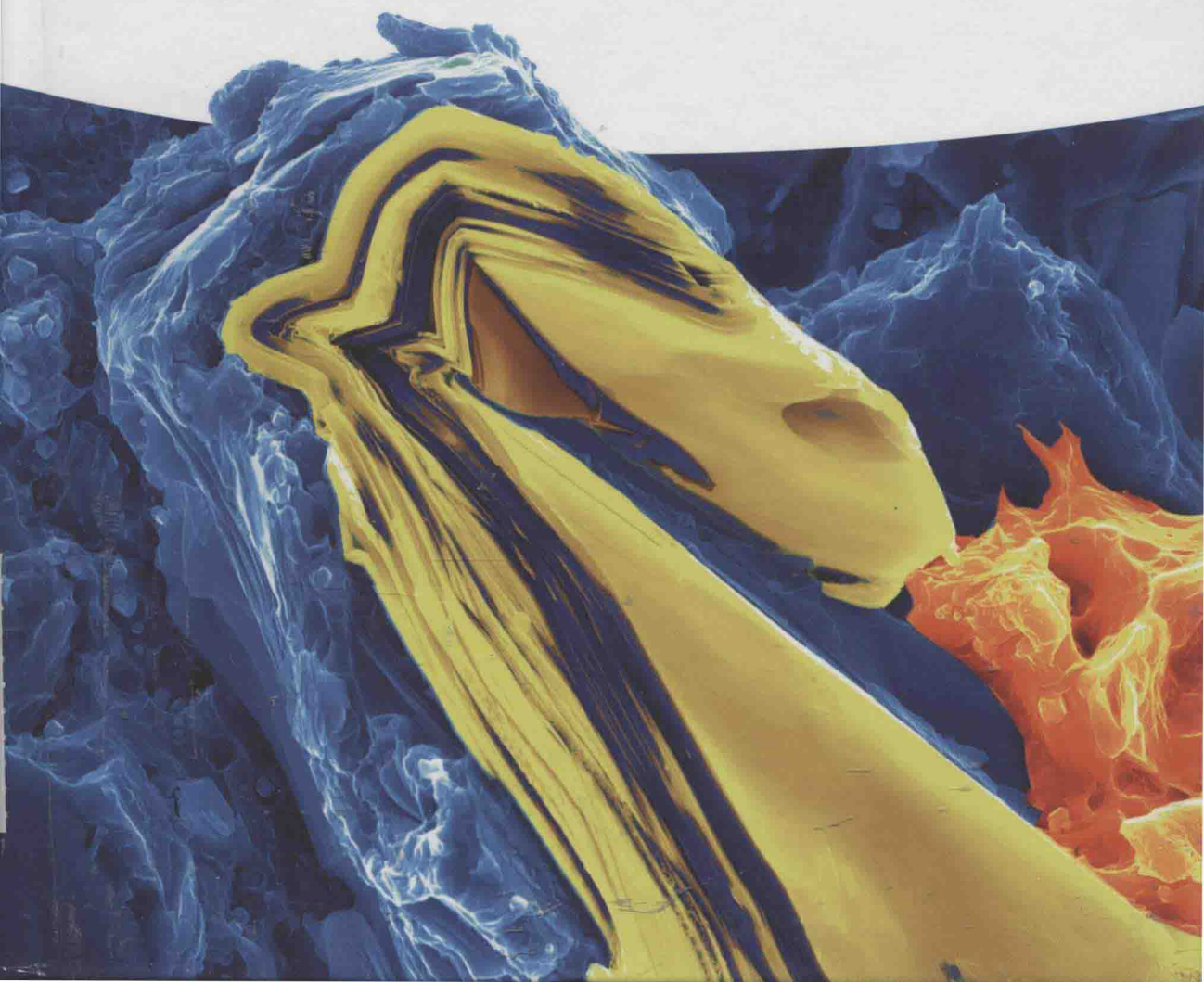


Michel W. Barsoum

MAX Phases

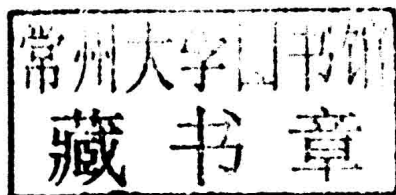
Properties of Machinable Ternary Carbides
and Nitrides



Michel W. Barsoum

MAX Phases

Properties of Machinable Ternary Carbides and Nitrides



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The Author

Prof. Michel W. Barsoum

Drexel University
Department of Material Science &
Engineering
3141, Chestnut Street
Philadelphia, PA 19104
USA

Cover

This colorized scanning electron micrograph is of a fractured surface of a Mg/MAX composite material. The micrograph highlights the propensity of the MAX phases to kink upon deformation. The micrograph was taken and colorized by Mr. Babak Anasori of Drexel University.

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Dedicated to my wonderful wife, close confidant, and best friend, Patricia.

Preface

The MAX phases are a fascinating class of layered solids that are relatively young. Interest in these 50+ phases has increased recently because they combine an unusual and very often unique combination of properties. For example, some are stiff and light and yet are readily machinable. Some are oxidation and creep resistant while also being metallic conductors and exceptionally thermal shock resistant. At this time, there are a number of good review articles on the MAX phases. However, the articles either focus on a few MAX phases, most notably Ti_3SiC_2 , Ti_3AlC_2 , Ti_2AlC , and Cr_2AlC , or try to tackle the entire subject in which much per force has to be glossed over. Said otherwise, there is no comprehensive compact monograph that renders these phases justice.

In this book, I attempt to summarize and explain, from both an experimental and a theoretical viewpoint, all the features that are necessary to understand the properties of these new materials. The book covers elastic, electrical, thermal, chemical, and mechanical properties in different temperature regimes. As much as possible, I tried to emphasize the physics.

One of the joys of working with the MAX phases is the ease by which one can change chemistry, while keeping the structure the same. As I anticipated many years ago, this has proven to be a real boon; I have a hunch, with no data to back me up, that the progress the MAX phase community has made in understanding their properties, in the past decade or so, can be traced directly to this feature. The range of experimental and theoretical techniques currently available has also indubitably made a big difference. In today's world, like much else, we have Science on steroids. We are quickly reaching the point – if we have not it already – at which the rate of data generation far exceeds our capability to make sense of them. In this book, I tried to buck the tide and make sense of what we currently know. The reader of this book will quickly realize from the sheer volume of data tabulated and plotted that this was not a trivial task. I do believe, however, that to truly understand properties and what influences them, one needs, every now and then, to step backward and make out the forest from the trees.

As shown in this book, this systemic approach, while tedious, is quite gratifying and edifying. For example, one of the leitmotifs of this book is the idea that above a certain concentration of valence electrons per unit volume, n_{val} , the MAX phases

are somehow destabilized. While plotting one set of properties versus n_{val} does not necessarily make a compelling case, but when this destabilization is repeated and recognized in several different properties, the idea becomes harder to dismiss. Another important idea of this book is that we can roughly subdivide the MAX phases into four categories: (i) those with exceptionally low c -parameters, such as Ti_2SC ; (ii) those with large atoms, such as Sn, Hf, Zr; (iii) those in between but with low n_{val} values; and (iv) those in between, but with high n_{val} values that are relatively unstable, such as some of the Cr-containing MAX phases. Hopefully, this idea comes across.

The other joy of working with the MAX phases is their two-dimensional nature, especially when it comes to mechanical properties. The fact that dislocations are, for the most part, confined to 2D and that the orientation of the basal planes on which these dislocations glide are in many cases readily determined from optical microscope micrographs has rendered understanding their mechanical response rather straightforward. In solid-state physics, the pedagogy is well established; first you solve the one-dimensional problem, move on to the 2D, and then, and only then, generalize to the most complicated 3D situation. In dealing with the deformation of solids, however, the hapless metallurgy or materials science undergraduate is immediately asked to deal with more than five independent slip systems, a daunting task that certainly biased me toward ceramics, where I thought I would be safe. That I can now talk somewhat intelligently about dislocations is, in my case, not a mark of any intellectual prowess, but rather a reflection of the simplicity of the problem at hand. Basically, dislocations in the MAX phases, and in the much larger class of solids that we identified as kinking nonlinear elastic (KNE), appear either in dislocation pileups (DPs) and/or dislocation walls normal to the pileups or arrays. Confining the dislocations to 2D also helped us identify a new micromechanism in solids, namely, incipient kink bands (IKBs). As discussed in Chapters 8 and 9, IKBs are the yin to the yang of DPs. IKBs absorb significant amounts of energy at low strains; DPs result in large strains, but little stored energy. It follows that Nature's first line of defense in the case of KNE solids is to nucleate IKBs.

By bringing together, in a unified, self-contained manner, all the information on MAX phases hitherto only found scattered in the journal literature, I hope to help move the field along to the next stage. I have also tried to critically assess the now voluminous literature. The number of papers in the field has increased recently and the task of anybody attempting to review this body of work is becoming daunting. In 2000, when I wrote an early review article on the subject, the situation was significantly easier.

In addition to outlining the contents of this book, it is important to stress what it is not about and what it does not cover. This book is geared to understand the physics of the MAX and hence the synthesis of these phases is not discussed. Thin films are for the most part not covered. A recent review has done this topic justice. When thin films are discussed, it is only to make an important point for which the information is lacking in bulk solids. Composites of MAX phases with other compounds and second phases are also mostly not discussed, except in instances

where comparing the properties of the composites with the pure bulk materials sheds light on the properties of the latter, which is the main focus of this book.

A perusal of the figures in this book will quickly establish that most of the figures originate from papers we wrote. This does not imply that other work is less important. It simply reflects the fact that the information was more easily accessible. In many cases, results and data have been grouped/replotted and in that case having access to the raw data is invaluable and time saving. I have assiduously tried to assign credit where credit is due. It follows that to the best of my abilities, I carefully combed the literature to make sure that when new information on the behavior of the MAX phases was reported, the original paper was cited. The record is out there and I tried my best. If at any time, such attribution is incorrect or lacking, I sincerely apologize and please contact me and I will try to set the record straight in any future editions of this book or any papers I write.

This book is divided into 11 chapters. The first chapter is an introductory chapter where the history of the MAX phases is outlined. Chapter 2 reviews the atomic structures and bonding commonalities and trends in these phases. This chapter also summarizes *ab initio* or density functional theory (DFT) calculations that, for the most part, capture the essence of the bonding in these solids. Chapter 3 deals with their elastic properties, both experimental and those calculated from DFT. Chapter 4 summarizes the thermal properties, including thermal expansion, conductivity heat capacities, atomic displacement parameters, and stability. Chapter 5 deals with the electrical transport, including conductivity, and Hall and Seebeck coefficient measurements. Their optical and magnetic properties are also touched upon.

Chapter 6 deals with the reactivity of the MAX phases with oxygen and other gases. The reactivities of the MAX phases with solids and liquids, including molten metals and common acids and bases, are reviewed in Chapter 7.

Chapters 8–10 deal with the mechanical properties. Chapter 8 deals with kinking nonlinear elasticity and damping. How the MAX phases respond to stresses – compressive, shear, tensile, and so on – at ambient temperature are discussed in Chapter 9. Chapter 10 deals with their response to stresses at elevated temperatures, including creep. Chapter 11 summarizes some of the outstanding scientific issues and outlines some of the potential applications and what needs to be done, research-wise, for these solids to be more widely used.

The quality and quantity of the papers one publishes in academia depend critically on the quality, resourcefulness, imagination, and hardwork of one's students. I would thus like to sincerely thank all my students who have worked with me on the MAX phases over the past 15 or so years. In rough chronological order, they are: T. El-Raghy, D. Brodtkin, M. Radovic, S. Chakraborty, A. Procopio, J. Travaglini, L. H. Ho-Duc, I. Salama, P. Finkel, A. Murugaiah, T. Zhen, A. Ganguly, E. Hoffman, S. Gupta, S. Basu, A. Zhou, S. Amini, T. Scabarosi, J. Lloyd, I. Albaryak, C. J. Spencer, M. Shamma, N. Lane, D. Tallman, B. Anasori, M. Naguib, G. Bentzel, and J. Halim. It was a distinct pleasure to work with each and every one of them. Their productivity and contributions to the field cannot be overemphasized.

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I like to collaborate and I have sought out collaborators in many countries and on many continents. In that vein, I would like to profusely thank the following colleagues and friends with whom I have worked with over the years on the MAX phases and from whom I learned quite a bit. I am greatly indebted to G. Hug, M. Jaouen, L. Thilly, S. Dubois, M. Le Flem, J.-L. Béchade, and J. Fontaine in France; J. Hettinger and S. Loffland at the Rowan University; L. Hultman, M. Magnuson, P. Eklund, J. Rosen, J. Lu, and R. Ahuja in Sweden; and J. Schneider in Germany.

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1

Introduction

1.1

Introduction

The $M_{n+1}AX_n$, or MAX, phases are layered, hexagonal, early transition-metal carbides and nitrides, where $n = 1, 2$, or 3 “M” is an early transition metal, “A” is an A-group (mostly groups 13 and 14) element, and “X” is C and/or N. In every case, near-close-packed M layers are interleaved with layers of pure group-A element with the X atoms filling the octahedral sites between the former (Figure 1.1a–c). The M_6X octahedra are edge-sharing and are identical to those found in the rock salt structure. The A-group elements are located at the center of trigonal prisms that are larger than the octahedral sites and thus better able to accommodate the larger A atoms. The main difference between the structures with various n values (Figure 1.1a–c) is in the number of M layers separating the A layers: in the M_2AX , or 211, phases, there are two; in the M_3AX_2 , or 312, phases there are three; and in the M_4AX_3 , or 413, phases, there are four. As discussed in more detail in later chapters, this layering is crucial and fundamental to understanding MAX-phase properties in general, and their mechanical properties in particular. Currently, the MAX phases number over 60 (Figure 1.2) with new ones, especially 413s and solid solutions, still being discovered.

Most of the MAX phases are 211 phases, some are 312s, and the rest are 413s. The M group elements include Ti, V, Cr, Zr, Nb, Mo, Hf, and Ta. The A elements include Al, Si, P, S, Ga, Ge, As, Cd, In, Sn, Tl, and Pb. The X elements are either C and/or N.

Thermally, elastically, and electrically, the MAX phases share many of the advantageous attributes of their respective binary metal carbides or nitrides: they are elastically stiff, and electrically and thermally conductive. Mechanically, however, they cannot be more different: they are readily machinable – remarkably a simple hack-saw will do (Figure 1.3) – relatively soft, resistant to thermal shock, and unusually damage-tolerant. They are the only polycrystalline solids that deform by a combination of kink and shear band formation, together with the delaminations of individual grains. Dislocations multiply and are mobile at room temperature, glide exclusively on the basal planes, and are overwhelmingly arranged either



(b)



312 Phases

*Ti ₃ AlC ₂	*Ti ₃ SiC ₂
*V ₃ AlC ₂ (or (V,Cr) ₃ AlC ₂)	*Ti ₃ GeC ₂
	*Ti ₃ SnC ₂
Ta ₃ AlC ₂	

413 Phases
 Ti_4AlN_3 , V_4AlN_3
 Ti_4GaC_3 ; Nb_4AlC_3
 Ta_4AlC_3 .