

Tungsten Heavy Alloy Handbook:

Applications, Compositions, Fabrication, Properties, Microstructures, and Modeling of Sintered Tungsten Heavy Alloys

Randall M. German, FAPMI

Professor, College of Engineering, San Diego State University Consultant, German Materials Technology

Cover image – This micrograph is taken from a 93W-5Ni-2Fe composition, sintered at 1500 °C for 120 minutes in vacuum; interference phase contrast on a polished cross-section.



Copyright © 2021 Metal Powder Industries Federation 105 College Road East Princeton, New Jersey 08540-6692 USA

ISBN: 978-1-943694-26-6

All rights reserved. No part of this publication is to be reproduced, stored, or transmitted in any form or by any means, electronic, optical, acoustic, or mechanical, including photocopying, scanning, recording, or made available by any information storage, on-line posting, broadcasting, or retrieval system, without the written permission of the Metal Powder Industries Federation.

Comments, corrections, and updates are welcomed and encouraged. Please e-mail Professor Randall M. German at randgerman@gmail.com.

FOREWORD

The standard abbreviation for tungsten heavy alloys is WHA, where W is the chemical symbol for tungsten. These high density compositions arose in the 1930s to provide radiation protection in a machinable tungsten-based material. From that start came an array of applications combining tungsten's density and stiffness with the formability afforded by transition metal alloying additions. Applications for tungsten heavy alloys now span from wristwatches to nuclear fusion plasma barriers. The high density creates a sweet spot useful in golf clubs, bowling balls, birdshot, fishing sinkers, and competitive throwing darts. The thermal-electrical properties match to the needs for semiconductor heat sinks, electro-discharge machining tools, and plasma containment structures. The arc erosion resistance and electrical conductivity of tungsten plus silver or copper make for heavy duty electrical contacts. High temperature die casting tools are another application for W-Mo-Ni-Fe alloys. A significant use is in high strain-rate penetrators, munitions, projectiles, and perforation tools. Thus, WHA compositions are focused on various property combinations of density, strength, hardness, stiffness, and conductivity.

My involvement with tungsten heavy alloys started with the fabrication of transpiration cooled tungsten-copper missile reentry nose tips. My doctoral thesis with Zuhair Munir created a model for predicting sintering densification. Subsequent WHA research support came from private industry, national laboratories, and research foundations on a global basis. A few of these efforts lasted decades. This handbook builds on the learning from that student-based research. The current efforts are exploring microgravity liquid phase sintering, where the WHA high density accentuates gravity effects on densification and distortion, but without gravity there is reduced densification.

Everything is important with respect to WHA processing. Powder purity interacts with processing to influence the microstructure. In turn, microstructure along with impurity segregation dramatically change properties. Heat treatments modify segregation, residual strain, and microstructure, while deformation and strain aging trade ductility for strength. The early portion of this handbook covers the compositions and the underlying thermodynamics (solubility, wetting, and phase diagrams). Processing-microstructure-property links constitute the bulk of the handbook. Issues such as toxicity, fracture origins, notch sensitivity, hydrogen embrittlement, and age hardening are a part of the story and are treated in several sections.

Computer simulations are predicting final component size, shape, microstructure, and properties. Some models require identification of an effective viscosity that includes time-dependent microstructure changes during processing. These are focused on prediction of sintered component size. Thus, practical and computational aspects of dimensional control are included in the latter sections.

In this handbook, many citations are given to enable location of source documents. Unfortunately, much of the WHA literature is in the form of conference reports. A problem with conference reports is the lack of peer review, resulting in only partial details and mixed reliability. Also, patents are often missing details. Even some peer reviewed publications lack sufficient detail to allow replication. Thus, care is exercised in culling though the literature. In the end considerable help was provided by a few experts.

Handbooks are used to answer specific questions. A reader expects to jump into relevant data using either the table of contents or index, without reading the surrounding text. Accordingly, this handbook is designed to provide solutions to typical challenges. That means a certain level of repetition, anticipating a reader is not starting at the beginning. Both the table of contents and index help find specific data, relations, models, and correlations. A difficulty is that the ideas are interrelated, so a user will have to jump back and forth between sections to fully grasp key relations.

Valuable draft manuscript reviews were provided by Steven Caldwell, John Johnson, Pavan Suri, Yoko Pittini-Yamada, Vinay Choudary Chilakapati, and Animesh Bose. I much appreciate the assistance of these individuals. The project gained momentum due to the isolation from the Covid-19 pandemic. It was a massive undertaking. The final draft was finished soon after my second inoculation.

May 2021 Del Mar, California

CONTENTS

Title, 1	
Foreword,	3

Contents, 5

- 1. Introduction, 10
 - 1.A. Composition Fidelity and Notation, 11
 - 1.B. Tungsten Benefits, 12
 - 1.C. Structure and Microstructure, 14
 - 1.D. Property Combinations, 14
- 2. Historical Highlights, 17
- 3. Applications, 21
- 4. Powders, 29
 - 4.A. Tungsten Powder Options, 29
 - 4.B. Additive Powder Options, 33
 - 4.C. Particle Modifications, 37
 - 4.D. Nanoscale Powder, 39
- 5. Compositions, 42
 - 5.A. Introduction, 42
 - 5.B. Ni-Fe Alloying, 43
 - 5.C. Refractory Metal Alloying, 46
 - 5.D. Tungsten Wetting, 48
 - 5.E. Limitations, 50
 - 5.F. Typical Alloys, 51
 - 5.G. Additives, 52
 - 5.H. Impurities, 53
 - 5.I. Summary, 54
- 6. Solubility, 56
 - 6.A. Wetting, 56
 - 6.B. Mass Transport, 57
 - 6.C. High Solubility, 58
 - 6.D. Filling and Densification, 60
 - 6.E. Coarsening, 61
 - 6.F. Nickel Role, 62
 - 6.G. Tungsten Alloying, 65
- 7. Phase Diagrams, 66
 - 7.A. Desirable Features, 66
 - 7.B. W-Ni-Fe System, 67
 - 7.C. Alloying Goals, 69
- 8. Processing Overview, 70
 - 8.A. Summary Best Practices, 70
 - 8.B. Processing Options, 71

- 8.C. Dominant Processing Factors, 76
- 9. Powder Modification, 78
 - 9.A. Milling Techniques, 78
 - 9.B. Mechanical Alloying, 80
 - 9.C. Coated Powder, 81
- 10. Binder, Lubricant, and Feedstock, 82
 - 10.A. Definitions, 82
 - 10.B. Binder Variants, 83
 - 10.C. Binder Formulations, 86
 - 10.D. Binder-Assisted Agglomeration, 87
 - 10.E. Slurry Forming Binders, 88
 - 10.F. Lubricants, 89
 - 10.G. Feedstock, 90
 - 10.h. Mixing, 92
- 11. Shaping, 96
 - 11.A. Shaping Options, 96
 - 11.B. Uniaxial Die Compaction, 97
 - 11.C. Cold Isostatic Pressing, 102
 - 11.D. Powder Extrusion, 103
 - 11.E. Powder Injection Molding, 105
 - 11.F. Powder Rolling, 108
 - 11.G. Slurry Processes, 108
 - 11.H. Additive Manufacturing, 109
 - 11.I. Summary Comments, 109
- 12. Binder and Lubricant Removal, 111
 - 12.A. Overview, 111
 - 12.B. Removal Cycles, 111
- 13. Measurement Tools, 118
 - 13.A. Property Scatter, 118
 - 13.B. Composition and Phases, 119
 - 13.C. Density and Porosity Tests, 122
 - 13.D. Archimedes Technique, 123
 - 13.E. Pycnometry Technique, 124
 - 13.F. Hardness, 126
 - 13.G. Elastic Properties, 128
 - 13.H. Tensile Testing, 129
 - 13.I. Rupture and Compression Testing, 130
 - 13.J. Fatigue Testing, 132
 - 13.K. Impact and Fracture Toughness, 133
 - 13.L. Thermal Properties, 134
 - 13.M. Testing Standards, 136
- 14. Sintering Process, 138

- 14.A. Overview, 138
- 14.B. Outline of Sintering Mechanisms, 139
- 14.C. Solid-State Activated Sintering, 144
- 14.D. Liquid Induced Capillarity, 147
- 14.E. Solution-Reprecipitation Densification, 148
- 14.F. Solid Skeletal Shrinkage, 149
- 14.G. Mass Transfer Factors, 151
- 14.H. Composition Effects, 151
- 14.I. Microstructure Relations, 153
- 14.J. Sequential Sintering Steps, 157
- 14.K. Particle Size Role, 162
- 14.L. Green Density Role, 164
- 14.M. Heating Rate, 165
- 14.N. Peak Temperature, 166
- 14.0. Hold Time, 168
- 14.P. Sintering Atmosphere, 171
- 14.Q. Swelling and Blisters, 172
- 14.R. Vacuum and Partial Pressure Sintering, 173
- 14.S. Cooling Rate, 174
- 14.T. Sintering Substrates, 176
- 14.U. Sintering Furnaces, 177
- 14.V. Microwave Heating, 178
- 14.W. Impurity Reactions, 180
- 14.X. Integral Work of Sintering, 182
- 14.Y. Post-Sintering Processes, 185
- 14.Z. Process Optimization, 186
- 15. Pressure-Assisted Consolidation, 190
 - 15.A. Uniaxial Hot Pressing, 190
 - 15.B. Spark Sintering, 192
 - 15.C. Hot Isostatic Pressing, 194
- 16. Embrittlement, 196
 - 16.A. Property Changes, 196
 - 16.B. Embrittlement Factors, 196
 - 16.C. Pores, 201
 - 16.D. Precipitates, 203
 - 16.E. Hydrogen, 204
 - 16.F. Impurities, 206
- 17. Heat Treatment, 208
 - 17.A. Introduction, 208
 - 17.B. Precipitation Control, 208
 - 17.C. Impurities, 210
 - 17.D. Strength and Ductility Adjustment, 212

- 17.E. Cycles, 214
- 18. Deformation and Strain Aging, 216
 - 18.A. Concept, 218
 - 18.B. Property Changes, 221
 - 18.C. Summary, 224
- 19. Microstructure, 226
 - 19.A. Accessing Microstructure, 228
 - 19.B. Solid Volume Fraction, 229
 - 19.C. Dihedral Angle, 233
 - 19.D. Contiguity, Coordination Number, and Connectivity, 236
 - 19.E. Grain Size, 249
 - 19.F. Pore Size and Liquid Lake Size, 253
 - 19.G. Grain Shape, 255
- 20. Grain Growth, 259
 - 20.A. Context for Coarsening, 259
 - 20.B. Porosity Effect, 264
 - 20.C. Size of Tungsten Grains, 266
 - 20.D. Grain Growth Kinetics, 268
 - 20.E. Growth Rate Parameter, 272
 - 20.F. Master Grain Growth Curve, 277
 - 20.G. Size Distributions, Grain and Pore, 279
 - 20.H. Grain Growth Summary, 283
- 21. Physical Properties, 285
 - 21.A. Density, 285
 - 21.B. Elastic Modulus, 289
- 22. Mechanical Properties, 293
 - 22.A. Tensile Curves, 294
 - 22.B. Sintered Strength, 295
 - 22.C. Strain Hardening, 303
 - 22.D. Thermomechanical Effects, 304
 - 22.E. Hardness-Strength Correlation, 306
 - 22.F. High Strain Rate Properties, 307
 - 22.G. Test Temperature Effects, 309
 - 22.H. Constitutive Models, 311
 - 22.I. Fracture Path, 313
 - 22.J. Fracture Toughness, 317
 - 22.K. Impact Toughness, 318
 - 22.L. Fatigue, 321
 - 22.M. Summary Comments, 321
- 23. Thermal Properties, 324
 - 23.A. Heat Capacity, 325
 - 23.B. Thermal Expansion, 327

- 23.C. Conductivity, 328
- 23.D. Summary Comments, 335
- 24. Other Properties, 336
- 25. Industrial Practices, 341
 - 25.A. Standards, 341
 - 25.B. Design Considerations, 343
 - 25.C. Manufacturing Guides, 345
 - 25.D. Cost Considerations, 346
- 26. Dimensional Control, 349
 - 26.A. Situation, 349
 - 26.B. Stress Versus Strength, 352
 - 26.C. Models, 357
 - 26.D. Effective Viscosity, 358
 - 26.E. Calculations, 359
 - 26.F. Key Learning, 364
- 27. Research Recommendations, 366
- 28. Acknowledgements, 374
- 29. References, 376
- 30. Author, 439
- 31. Abbreviations, 440
- 32. Index, 445

1. INTRODUCTION

Tungsten heavy alloys (abbreviated WHA, where W is the chemical symbol for tungsten) are two-phase metallic composites. Mostly they are fabricated by melting the matrix phase to assist in sintering the solid tungsten grains. This liquid phase sintering process forms a three-dimensional body-centered cubic tungsten solid skeleton interwoven with a face-centered cubic matrix. Alloys include several matrix variants (Ni-Fe, Ni-Cu, Ni-Fe-Co, Ni-Cu-Mn, Cu-Co, Cu, Ag, and such). A common characteristic of the alloys is a tungsten grain structure enmeshed in a transition metal matrix.

Tungsten is a high density refractory metal with characteristics listed in Table 1.1 [88, 198, 426, 492, 677, 736, 811, 845]. Throughout this handbook the square brackets [###] indicate cited literature, collected by reference number in Section 29 References. The references are sorted and numbered by publication date. Patents are generally ignored, since they often fail to disclose information required for replication.

Table 1.1. Properties of Tungsten (W).

Abundance = 1.2 - 1.6 mg/kg of earth's crust

Atomic diameter = 0.274 nm

Atomic mass = 183.85 g/mol

Atomic number = 74

Atomic volume = $9.53 \text{ cm}^3/\text{mol}$

Boiling temperature = 5660°C

Crystal structure = body-centered cubic

Density = $19.3 \text{ g/cm}^3 \text{ or } 19300 \text{ kg/m}^3$

Elastic modulus = 400 to 405 GPa

Electrical conductivity = $18 \text{ to } 19 \cdot 10^6 \text{ S/m}$

Elongation to fracture (as-sintered) = nil

Fusion enthalpy = $138 \, \text{kJ/mol}$

Global consumption = 146.000.000 kg/v

Hardness Vickers = 340 - 430 HV

Lattice constant = 0.3168 nm

Melting temperature = 3422°C

Poisson's ratio = 0.28 to 0.29

Specific heat = 120 to 130 J/(kg °C)

Surface energy = 2.8 J/m^2

Thermal conductivity = 164 to 172 W/(m °C)

Thermal expansion coefficient = 4.2 to $4.4 \cdot 10^{-6}$ 1/°C

Ultimate tensile strength = 560 MPa

Vaporization enthalpy = 824 kJ/mol

Yield strength (as-sintered) = 550 MPa