REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	June 1998	Final: Aug. 1994–March 1998

4. TITLE AND SUBTITLE
Mechanical Alloying Processing with Applications to Structural Materials

5. FUNDING NUMBERS
DAAH04-94-G-0315

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO 33174.17-MS

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

19981222 075

13. ABSTRACT *(Maximum 200 words)*

Relationships among the synthesis, processing, structure and properties of materials generated through mechanical alloying (MA) or mechanosynthesis are described. Several materials classes - cermets, particulate metal matrix composites (MMC), and tungsten heavy alloys (WHA) - have been produced, and their properties and structures evaluated. Niobium carbide and tungsten carbide cermets can be conveniently generated either through room temperature synthesis (NbC cermets) or by room temperature milling followed by elevated temperature exposure (WC cermets). Cermet microstructures following consolidation are fine, and the materials demonstrate exceptional hardnesses albeit their fracture toughnesses are generally low. Al-based MMC can be synthesized similarly. The composites we have studied utilize aluminum carbide as a reinforcement. The yield strengths of these MMC are approximately twice those of high strength aerospace Al alloys. Noncrystalline WHA can be generated via MA. During consolidation, these alloys are prone to crystallization. Nonetheless, because of their fine structure the crystalline products manifest high hardnesses relative to conventional WHA. Current efforts are focusing on retaining the noncrystalline phase during consolidation so as to produce materials having particularly desirable mechanical properties.

14. SUBJECT TERMS	15. NUMBER IF PAGES
Mechanical Alloying, Powder Processing, Cermets, Metal Matrix Composites, Tungsten Heavy Alloys	9
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

MECHANICAL ALLOYING PROCESSING WITH APPLICATIONS TO STRUCTURAL MATERIALS

FINAL REPORT

JUNE, 1998

U. S. ARMY RESEARCH OFFICE

GRANT NO: DAAH04-94-G-0315

MICHIGAN TECHNOLOGICAL UNIVERSITY

FINAL REPORT

MECHANICAL ALLOYING PROCESSING WITH APPLICATION TO STRUCTURAL MATERIALS

RESEARCH AGREEMENT: DAAH04-94-G-0315

I. OVERVIEW

This report summarizes work performed on this program for the period August, 1994-March, 1998. The report capsulizes work that has been published, emphasizing the more important results of the research. The report provides more detailed descriptions of work that has not yet been published.

The emphasis of the program has been on synthesis of materials via mechanical alloying and mechanochemical reactions. The materials classes investigated fall into three broad categories; W-based alloys, cermets, and particulate metal matrix composites. We have investigated these materials in terms of the processing require to develop particular structures, the mechanical properties of these structures, and how both the structure and the properties of the composites respond to elevated temperature exposure. The report contains separate sections devoted to the several material classes. This is done for convenience, for it is clear there are a number of common threads to the processing and structure of the different material classes.

II. CERMET-LIKE MATERIALS

A. NbC Cermets (Brian Murphy, Ph.D. Student)

Murphy investigated the relationships among processing, structure, and properties of NbC cermets. As noted in previous reports, Murphy was able to synthesize NbC by room-temperature SPEX milling of particulate Nb and either graphite or hexane. The crystallite size of the NbC so produced is on the order of 10 nm. When hexane is used as the milling agent, considerable wear debris accompanies carbide synthesis. In distinction, when graphite is the carbon source mill abrasion is minimal. Thus, two "types" of NbC are produced. One (coming from the hexane treatment) contains about 18 vol. % of Fe dispersed in the NbC. The other (deriving from the treatment with graphite) contains only about 4 vol. % of dispersed Fe particles.

Copper was also added to the initial mill charge. Its presence does not affect NbC synthesis during milling. Murphy investigated two different Cu levels, resulting in milled powder containing (9 vol. % Fe/11 vol. % Cu) and (2 vol. % Fe/34 vol. % Cu). Thus, four different types of cermet powders were room-temperature synthesized.

The milled powders are readily consolidated to full density via hot isostatic pressing at 1000-1200 C (the specific temperature depending on whether Cu is present or not). These temperatures are on the order of one-third of the absolute melting temperature of NbC, indicating the

potential of the processing route followed. The microstructure coarsens during consolidation, but its scale remains less than about 100 nm. Further elevated temperature exposure results in additional coarsening. In Murphy's study, such exposure allowed us to investigate cermets having a microstructural scale ranging from 100 nm to several μms. Consolidation resulted in uniform microstructures, for the most part. An exception was for the most Cu-rich cermets. In these, Cu segregation to preexisting powder particle boundaries took place during consolidation and, to a much greater extent, during subsequent high temperature exposure.

Murphy investigated the properties of hardness and fracture toughness of these cermets. As expected, hardnesses are high and fracture toughnesses are low. For example, a hardness of close to 20 GPa is obtained in the as-consolidated cermet containing only 4 vol. % Fe, but the fracture toughness of this material is only about 2.0 $MPa \cdot m^{1/2}$. Hardness values decrease (and fracture toughness increases) with increasing metal content and elevated temperature exposure time. Thus, a cermet containing ca. 10 vol. % each of Cu and Fe and heat-treated for six weeks at 1000° C subsequent to consolidation has a hardness of 6.7 GPa and a fracture toughness of 6 $MPa \cdot m^{1/2}$.

Murphy extensively characterized the microstructure of several heat-treated cermets. He was able to correlate their fracture toughnesses to the size and volume fraction of their dispersed metal component. The correlation is in concert with current models of toughening of brittle materials by ductile particles. Murphy has published some of these results, and two other papers are in the final stages of preparation (see Appendix B).

B. WC Cermets (Shan Mi, M.S. Student)

Mi studied the synthesis of WC cermets by mechanical alloying and subsequent consolidation. In distinction to what transpires during milling of Nb and graphite, milling of W and graphite does not lead to formation of WC. However, when the milled powder is consolidated by hot isostatic pressing, WC spontaneously forms. In addition to making "pure" WC (the material is not "pure," because it appears there is remnant W in the as-consolidated material), Mi added Co to the mill powder charge resulting in WC-Co cermets following the consolidation operation.

The hardnesses (on the order of 18 GPa) of these materials are exceptional, likely as a result of their fine microstructural scale (on the order of 0.1 μm or less). (Typical cemented carbides exhibit microstructural scales on the order of ten micrometers.) Further, the fracture toughnesses of the materials we have fabricated are reasonable, on the order of 10 $MPa \cdot m^{1/2}$ or higher. Mi has published the results of this study, as indicated in Appendix B.

III. Al Metal Matrix Composites (Jeffrey Molnar, M.S. Student)

Because of our success in synthesizing NbC and WC cermets, we decided to investigate mechanical alloying for the purposes of synthesizing Al-based metal matrix composites (MMC). Our original idea was to take Al-Si metal powders, mix them with graphite (or hexane) and mill them. We believed the graphite would react with the Si, either during milling or subsequent consolidation. Thus, a very fine scale Al-SiC MMC would be synthesized. Further, this fine scale might lead to improved properties. And, since commercially available Al-SiC MMC are expensive, this alternate processing route might have commercial potential.

When Al-Si powders are room-temperature milled with hexane, "nothing" happens. X-ray diffraction of milled powder reveals only the presence of the original phases. However, copious amounts of Al_4C_3 form during hot-isostatic consolidation. The amount of Si apparently does not vary during densification; i.e., SiC does not form. Heat-treatment subsequent to consolidation results in more formation of aluminum carbide. Indeed, while our quantitative analysis of the structure is still incomplete, it appears that this carbide can constitute about 40% by volume of consolidated materials. The microstructure of this material is very fine; it can only be resolved at the transmission electron microscope level. Further, the structure is very resistant to coarsening even at temperatures on the order of 500^{o} C. Hardness equivalent yield strengths of these composites are on the order of 1100 MPa, a strength about twice that of the higher strength Al aerospace alloys. Fracture toughnesses, though, are low. They could likely be improved by reducing the material carbon content, although this would be accomplished at the expense of strength. Molnar is in the process of writing his M.S. thesis based on this work. Following that, the salient parts of it will be prepared for publication.

IV: W-BASE MATERIALS (HEAVY METALS)

We have conducted several studies involving aspects of mechanical alloying of W-heavy metal alloys. The studies have commonalties, as is evident below, even though the emphases of the several studies are different.

A. Surface Energy Driven Microstructural Changes in W-Ni-Fe Alloys (C. G. Mukira, Ph.D. Student)

When W-Ni alloys with compositions in excess of about 30 at. % W are mechanically alloyed in a SPEX mill, a noncrystalline metallic phase forms. Because metallic glasses have interesting properties we have made efforts to maintain this amorphous phase during consolidation, but have not yet been successful at this. (See later discussion for amplification of this matter.) Nonetheless, while the amorphous phase crystallizes during consolidation the microstructural scale that develops thereby is much finer than that in conventional heavy metals made by liquid phase sintering. So we investigated the properties of heavy metals fabricated via the mechanical alloying route.

Three crystalline phases form from the amorphous phase during consolidation. The phases are an essentially pure bcc W phase, a Ni-rich

phase, and an intermetallic phase isomorphous to NiW. Iron that is present in the material as a result of mill abrasion is not found in the bcc phase. Fe partitions itself to the other two phases, slightly preferring the intermetallic. Consolidated structures resemble the three-phase equivalent of duplex structures in two-phase materials. That is, the phases are essentially equiaxed in shape, they are situated randomly in the microstructure, and their sizes scale with their respective volume fractions. Since duplex structures are known to be quite stable at high temperature, we thought the triplex structures might be even more so. Thus, to investigate this thermal stability and to assess how thermal exposure affects the properties of these initially fine-scale structures, we exposed them to high temperature following consolidation.

A remarkable thing happens when we do this. The initially random three-phase arrangement is replaced by two (what we term) microconstituents. One microconstituent is NiW rich, but can contain minor amounts of either or both of the other phases. The second microconstituent is an fcc matrix containing a dispersion of W particles; the intermetallic essentially is not present in this microconstituent. Further, the sizes of these microconstituents can be quite large, having diameters as great as 100 μm. Since the initial particle sizes are on the order of micrometers, this change in microstructural scale corresponds to an "affected" volume about a million times larger than the initial particle volume.

We have traced this behavior, never before observed in solid systems to the best of our knowledge, to surface energy effects. Specifically, the intermetallic phase "wets" the tungsten phase. As it does, an interfacial reaction - involving W and the fcc phase - proceeds and more intermetallic phase is locally formed. Equilibrium among the phases (i.e., the requirement that the phase volume fractions are fixed at a specified composition for three-phase equilibrium) is satisfied by dissolution of the intermetallic in other regions of the structure. Thus, intermetallic rich and intermetallic lean microstituents develop. This massive phase segregation is unaccompanied by any chemical segregation to speak of. For example, microchemical analysis of the two different microconstituents shows that they have the same composition, with this composition being that of the overall alloy composition.

Mukira documented the causes of the phenomenon and the mechanisms for it in a paper that has been published. More recent work of his delineates the compositions in the ternary triangle resulting in microconstituent formation. This aspect of his work is described in a paper being readied for submission (Appendix B).

B. Properties of W Heavy Alloys Prepared by Mechanical Alloying (Shan Mi, M.S. Student)

Mi also studied the processing and properties of W heavy metal alloys prepared via the mechanical alloying route. In order to avoid powder amorphization during alloying, Mi employed an attritor mill for powder processing. The energy intensity of this mill is much less than that of

a SPEX mill, and we anticipated that the microstructure of the milled powder would resemble the characteristic "Damascus steel" (layered) morphology found when two immiscible (or slightly miscible) ductile metals are mechanically alloyed.

The layered morphology is observed in attritor milled W-Ni alloys of relatively lean W contents. However, to our surprise, relatively W-rich alloys amorphize during attritor milling. Both types of powders were consolidated by hot-isostatic pressing. As-milled crystalline powder is two-phase (fcc and bcc) following consolidation. As-milled amorphous powder after consolidation contains the three phases (fcc, bcc and NiW) observed during the Mukira study. Hardnesses of heavy alloys prepared in this manner exceed significantly those of heavy alloys made by LPS. As described in the paper resulting from this work (Appendix B), this is likely due to the finer microstructural scale (micrometers vs. tens of micrometers in LPS WHA) generated via the MA processing route.

C. Consolidation of Amorphous W Heavy Alloys (Xi He, Ph.D. Student)

This aspect of our work is "high risk." Specifically, we attempt to consolidate W metallic glasses, maintaining their noncrystalline nature while doing so. The objective is that such a structure may perhaps manifest multiple shear banding in tension. (Possible reasons for this are described below.) Ordinary metallic glasses display one shear band in tension prior to fracture; this limits their macroscopic toughness. Multiple shear banding would promote much tougher metallic glasses, perhaps permitting their high intrinsic yield strengths to be utilized in structures subject to positive mean pressures.

There are two reasons we believe it possible that multiple shear banding might be found in these materials. First, the amorphous particles always contain remnant crystalline W particles of nanometer size. Such a dispersion might interfere with shear band propagation. (The dispersion might be more beneficial in this respect were the W particles of a size closer to that of the shear band width.) The concept is similar to that used for toughening noncrystalline polymers such as polystyrenes (PS). Adding a colloidal elastomeric dispersion to PS produces high impact polystyrene, which has a greater ductility and toughness than ordinary PS.

Second, we plan on bonding the amorphous particles by utilizing a low melting braze with a melting temperature below the particle crystallization temperature (ca. 1000 K). The bonding agent, situated between the particles, would act as an obstacle to shear band propagation across particles. This feature might facilitate multiple shear banding.

We have prepared several low-melting(Cu-Ag-Zn-P) brazes. However, the braze materials we have used do not fully wet the amorphous W material. Nonetheless, evidence of partial wetting is found and the porosity level of "consolidated" compacts is only on the order of 5%. Such a level remains unacceptable for our purposes, though. We are currently

developing additional brazing alloys and alternative schemes for consolidation.

IV: SUMMARY AND CONCLUSIONS

We have further demonstrated that mechanical alloying is a robust process tool for fabricating fine scale structural materials and for low temperature synthesis of high melting temperature phases. In this section, we place these results in perspective.

First, mechanical alloying is an expensive process, even more so than most powder material processes. Nonetheless, the costs of developing structural materials using MA are likely in the same range (perhaps less) as those associated with manufacture of aligned fiber, metal or ceramic matrix composites. Thus, the mechanical alloying processing route may be economically viable for production of materials for which performance is the overriding consideration. [1]

The following comments are pertinent to mechanical synthesis of ceramics (e.g., NbC) and cermet-like structures. The low synthesis (and consolidation) temperatures are both beneficial from an economic standpoint. Further, the fine microstructural scale attendant to MA generated material yields greater material hardness and, for "pure" ceramics, the fine microstructure also is beneficial to fracture toughness. However, a fine microstructure is not beneficial to cermets from the standpoint of fracture toughness. Specifically, increases in fracture toughness attributed to a dispersion of malleable particles scale (for a given particle volume fraction) with particle size. Particle size is finer in MA generated microstructures and, thus, the beneficial effect of the particle dispersion is mitigated.

Tungsten heavy alloys are used as armor material. These materials do not perform as well as depleted uranium as penetrators. The latter material is "self sharpening" due to its propensity to manifest adiabatic shear bands at high strain rates. However, depleted uranium is radioactive and, because of this, interest in WHA as penetrator material remains high. In our work we have attempted to produce amorphpus WHA prone to multiple shear band formation. We have not yet been able to consolidate these materials to full density absent crystallization of the amorphous phase. This matter will be the main focus of our coming year's work.

1- Nickel base superalloys, made via MA, are commercially available and have a market niche. The performance of these alloys derives from generation of a fine microstructure and formation of dispersoids during processing. This is accomplished through extended milling in a low energy density mill. Use of such a mill permits batch runs of significant powder amounts. However, materials synthesis of the type discussed in this report, and to which the comments just made apply, rely on high energy density mills. The amount of material per batch is limited in high energy mills and this is partly responsible for the high cost of the materials.

APPENDIX A: STUDENTS SUPPORTED AND DEGREES GRANTED: SEPTEMBER 1, 1994-JUNE, 1, 1998

Charles G. Mukira, Ph.D., Michigan Technological University, 1996
Brian R. Murphy, Ph. D., Michigan Technological University, 1996
Shan Mi, M.S., Michigan Technological University, 1997
Xi He, Ph.D., Michigan Technological University (in progress)
Jeffrey Molnar, M.S., Michigan Technological University (in progress)

APPENDIX B: PUBLICATIONS; SEPTEMBER 1, 1994 TO PRESENT

A. Archival Journals

R. J. Comstock, Jr. and T. H. Courtney, "Elevated Temperature Stability of Mechanically Alloyed Cu-Nb Powders," Metall. and Mater. Trans. A, vol. 25A, 2091, (1994)

T. H. Courtney, "Modeling of Mechanical Milling and Mechanical Alloying," Reviews in Particulate Materials, vol. 2, 63, (1994)

D. Maurice and T. H. Courtney, "Modeling of Mechanical Alloying II. Development of Computational Programs," Metall. and Mater. Trans. A, vol. 26A, 2431, (1995)

D. Maurice and T. H. Courtney, "Modeling of Mechanical Alloying III. Applications of Computational Programs," Metall. and Mater. Trans. A, vol. 26A, 2437, (1995)

T. H. Courtney, "Process Modeling of Mechanical Alloying (*Overview*)," Materials Transactions, Japanese Institute of Metals, vol. 36, 108, (1995)

T. M. Cook and T. H. Courtney, "The Effect of Ball Size Distribution on Attritor Efficiency," Metall. and Mater. Trans. A, vol. 26A, 2389, (1995)

T. H. Courtney and D. Maurice, "Process Modeling of the Mechanics of Mechanical Alloying," Scripta Mater., vol. 34, 5, (1996)

G. C. Mukira and T. H. Courtney, "Microconstituent Development and Coarsening in Certain Three-Phase Systems," Acta Mater., vol. 44, 3321, (1996)

T. H. Courtney, "Gravitational Effects on Microstructural Development in Liquid Phase Sintered Materials," Scripta Mater., vol. 35, 567, (1996)

D. Maurice and T. H. Courtney, "Milling Dynamics: Part II. Dynamics of a SPEX Mill and a One-Dimensional Mill," Metall. and Mater. Trans. A, vol. 27A, 1973, (1996)

D. Maurice and T. H. Courtney, "Milling Dynamics: Part III. Integration of Local and Global Modeling of Mechanical Alloying," Metall. and Mater. Trans. A, vol. 27A, 1981, (1996)

S. Mi and T. H. Courtney, "Synthesis of WC and WC-Co Cermets by Mechanical Alloying and Subsequent Hot Isostatic Pressing," Scripta Mater., vol. 38, 171, (1997)

S. Mi and T. H. Courtney, "Processing, Structure and Properties of Ni-W Alloys Fabricated by Mechanical Alloying and Hot-Isostatic Pressing," Scripta Mater., vol. 38, 637, (1998)

B. Refereed Proceedings and Conference Publications

T. H. Courtney, "In Situ Processing of Metal Matrix Composites," Advances in Science and Technology, 7 - Advanced Structural Fiber Composites, Proc. 8th CIMTEC-World Ceramics Congress and Forum on New Materials, ed., P. Vincenzini, Techna, Faenza, Italy, 267, (1995)

B. R. Murphy and T. H. Courtney, "Structure-Property-Processing Relationships in Nanocrystalline and Fine-Grained NbC and Cu-NbC Composites," Novel Techniques in Synthesis and Processing of Advanced Materials, ed., J. Singh and S. M. Copley, TMS, Warrendale, PA., 433, (1995)

C. G. Mukira and T. H. Courtney, "The Structure and Properties of Mechanically Alloyed and Consolidated Ni-W(Fe) Alloys," Proc. 2nd Intl. Conference on Tungsten and Refractory Metals, Metal Powder Industries Federation, Princeton, N.J., 157, (1995)

C. Papers in Preparation

The following three papers are in the final stages of preparation. They should be submitted this summer.

B. R. Murphy and T. H. Courtney, "Mechanochemically Synthesized NbC Cermets: Part I. Structure."

B. R. Murphy and T. H. Courtney, "Mechanochemically Synthesized NbC Cermets: Part II. Properties."

C. G. Mukira and T. H. Courtney, "Microconstituent Development in W-Ni-Fe Alloys."