International Journal of Refractory Metals & Hard Materials 73 (2018) 22–28

Contents lists available at ScienceDirect

International Journal of Refractory Metals & Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Traditional and additive manufacturing of a new Tungsten heavy alloy alternative

Animesh Bose[d,*], Christopher A. Schuh[a,d], Jay C. Tobia[d], Nihan Tuncer[a,d], Nicholas M. Mykulowycz[d], Aaron Preston[d], Alexander C. Barbati[b,d], Brian Kernan[d], Michael A. Gibson[a,d], Dana Krause[d], Tomek Brzezinski[d], Jan Schroers[c,d], Ricardo Fulop[d], Jonah S. Myerberg[d], Mark Sowerbutts[d], Yet-Ming Chiang[a,d], A. John Hart[b,d], Emanuel M. Sachs[b,d], Ester E. Lomeli[e], Alan C. Lund[e]

[a] *Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*
[b] *Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*
[c] *Department of Materials Science and Mechanical Engineering, Yale University, New Haven, CT 06520, USA*
[d] *Desktop Metal, Inc., 63 Third Street, Burlington, MA 01803, USA*
[e] *Veloxint Corporation, 125 Newbury Street, Framingham, MA 01701, USA*

ABSTRACT

A new class of rapid-sintering, fine-grained alloys recently developed is being commercially scaled through both traditional and additive manufacturing approaches. This paper discusses the scientific underpinnings of these new alloys and their processing, specifically for a W-based alloy as an alternative to Tungsten Heavy Alloy (WHA). This new alloy offers similar density and sintering temperatures to traditional WHA, but with a fine, thermally-stable microstructure that has the potential for higher temperature operation and significantly higher strength as compared to WHAs. The new alloy can be manufactured through established traditional approaches (e.g. press and sinter) and also through a recently developed 3D printing approach.

1. Introduction

Tungsten is one of the earliest powder metallurgy (PM) refractory material characterized by its high melting temperature (around 3422 °C which is among the highest in metals) and high density (19.3 g/cm^3). Due to its extremely high melting point, tungsten and its alloys are mainly processed using the PM route [1]. The PM process of making ductile tungsten wire (first used as light bulb filaments) originated from the work of Coolidge more than a century ago. The ductility was primarily achieved by taking a sintered tungsten bar and hot swaging it to effect a large reduction in area, with the smaller sizes exhibiting increasing ductility. The commercialization of this process led to the widespread use of tungsten PM technology. Efforts to impart high strength and ductility to tungsten through the use of lower temperature alloying elements led to the development of tungsten heavy alloys (WHA) or heavy metal alloys around the mid to late 1930s [2,3]. This development was spurred by the use of alloying elements such as nickel, iron, cobalt, and/or copper to form a liquid phase sintered tungsten alloy. These alloys are still processed by liquid phase sintering (with more controls and sophistication) and this class of material serves as the basis for its use in numerous applications with a major thrust coming from the ordnance sector which found these alloys to be a candidate material for the replacement of Depleted Uranium (DU) as kinetic energy penetrators [4–9]. Since then, this early PM liquid phase sintered alloy has found numerous applications including kinetic energy (KE) penetrators, specialty golf clubs, balancing weights in race cars as well as in aerospace, rotors for the watch industry, heat sinks (W—Cu), radiation shields, heavy duty electrical contact materials, and more recently as plasma-facing materials in fusion reactors [10]. The popularity of tungsten heavy alloys stem from their unique combination of physical and mechanical properties. The alloys typically have high density (usually 50% higher than lead), high strength and ductility, high hardness, desirable electrical and thermal conductivity, low thermal expansion, good corrosion resistance, and vibration dampening capability.

Properties of WHAs are significantly influenced by the amount of tungsten versus the alloying additives. The chemistry of the alloying additives also plays a critical role in influencing the properties of these

---

[*] Corresponding author.
E-mail address: animeshbose@desktopmetal.com (A. Bose).

https://doi.org/10.1016/j.ijrmhm.2018.01.019
Received 18 October 2017; Received in revised form 19 December 2017; Accepted 20 January 2018
0263-4368/

materials. Most of the WHAs are currently processed using nickel and iron as the sintering additives typically in the ratio of 7:3 or 8:2 of Ni:Fe [11]. However, many other alloying additives have been used which includes the additions of some Co along with Ni and Fe. For heat sink type applications, generally Cu is the additive of choice though sometimes for improving the densification, minor additions of nickel have been used (although this results in the loss of thermal conductivity). WHAs are also extremely sensitive to the processing history and the overall chemistry of the material [12–15]. Improper processing of the material can lead to formation of internal porosity, embrittlement due to impurity segregation, and hydrogen embrittlement, all of which can lead to significant lowering of the mechanical properties of the material. Material processing is often carried out in a hydrogen atmosphere to reduce the oxides. The possibility of entrapped water-vapor can be mitigated by control of the dew point of the sintering atmosphere while hydrogen embrittlement, impurity segregation, and intermetallic phase formation can be reduced through the use of proper heat treatment.

Conventional tungsten heavy alloys exhibit a classic two-phase composite microstructure where large almost pure bcc tungsten grains are embedded in a ductile matrix material consisting of the alloying elements (such as nickel, iron, cobalt) with some amount of tungsten taken into solution. This matrix phase is generally responsible for the ductility and toughness that is exhibited by this class of alloy. As discussed earlier, with increasing tungsten content (from 88 to around 93 or 94 wt% of tungsten) the strength (UTS) of the alloy increases. Continuing to increase the tungsten content results in a decrease in the strength of the alloy. With high tungsten contents, the microstructure starts to exhibit an increase in contiguity, which in turn results in a drop in the strength of the alloy. However, generally when using the same liquid phase forming elements in the same ratio, the elongation shows a constant decrease with increasing tungsten content.

The conventional tungsten heavy alloys have, however, not proven to be very successful in replacing DU as KE penetrators. WHAs tend to form a mushroom shape near the penetrator nose area following the impact event. This behavior is unlike that of DU, where the nose undergoes self-sharpening due to shear localization. Extensive R&D efforts have been conducted to rectify these differences and impart the shear localization characteristics in WHAs similar to those of DU. Efforts in this area include: processing of higher strength and higher hardness WHAs through thermomechanical treatments (as very high strength steels are shown to be prone to shear localization), use of alternate matrix materials that are known to be more susceptible to shear localization (intermetallic compounds) under high strain rate, microstructural manipulations to allow an easy path for the shear band to easily form and propagate, substituting a small amount of the tungsten with an alternate material that can alloy with the tungsten to make the material prone to shear localization, attempts to create ultrafine microstructures, solid state sintering of the material instead of the conventional liquid phase sintering, and using alloying elements that can result in significantly lower liquid phase sintering temperatures [16–22]. While a great deal of effort has been directed to the above areas to try and modify the tungsten-based materials, an equally important effort was also in progress to try and devise alternate processing techniques (in place of conventional press and sinter) that can be used to shape the tungsten based alloys into useful components. One of the techniques that have become the process of choice for making small complex shaped tungsten alloy components is powder injection molding [23–25].

Grain structure refinement has advanced significantly in tungsten-based composites. WHAs typically have tungsten grain sizes that are in the range of 20 to 50 μm. The aim of grain refinement is to target higher strength and hardness with a concomitant goal that the finer grains will increase the tendency of the material to undergo adiabatic shear localization. Various processing and alloying techniques have been used to achieve the finer grain sizes including: (1) solid state sintering of the material to try to preserve the original grain size of tungsten, (2) doping with elements such as Mo, Ta, Re [26,27], and (3) limiting grain growth in liquid phase sintering by suppressing the solidification-reprecipitation step through choice of the binder phase such as Co—Cu [28]. A novel approach combines shaping with dopants, utilizing powder injection molding with and Mo and Re additives with conventional WHA compositions. This final approach enables the processing of higher strength and higher hardness heavy alloys into complex shapes.

1.1. Nano duplex structure

More recently, fine grained tungsten alloys have been produced via powder metallurgy. PM has long been considered a possible route to the production of nanostructured metals as powders with internal nanoscale grain sizes are routinely produced by high energy milling methods. The ability of producing such powder, however, does not directly translate into bulk PM components with nanostructure. Grain growth proceeds rapidly in nanostructured metals, and the consolidation cycle typically results in coarsening well beyond the conventional nanostructure range (< 100 nm). One popular approach to overcoming this coarsening problem is to engage in a kinetic race between densification and grain growth. Rapid consolidation methods such as field-assisted sintering, with their shorter times at temperature, can avoid some coarsening and retain fine or even ultrafine grains. However, to retain truly nanoscale grain sizes in bulk P/M components through a full consolidation cycle remains somewhat of a challenge, and other popular methods to accelerate sintering such as liquid-phase sintering or activated sintering also tend to encourage coarsening during the cycle. Recently, Park and Schuh [29] proposed a strategy using alloying elements that favor both stability of nanostructure and accelerated sintering. Their approach was built upon thermodynamic calculations of alloy mixing systems with nanocrystalline grain sizes [30] where alloying elements that favor a grain boundary environment were shown to stabilize the nanostructure against coarsening. Whereas some elements prefer to segregate to grain boundaries as compared to occupying any other site in the alloy, Chookajorn et al. [31] observed that some alloying elements favor a so-called "nano-duplex" structure. Such alloys feature both grain boundary segregation as well as nanoscale second phase precipitation, both of which contribute to stabilizing a nanoscale structure. As an example, the W—Cr system exhibits such thermodynamics; Cr decorates grain boundaries in W, while also precipitating out as a second Cr-rich phase. The work of Park and Schuh used the concept of stable nano-duplex alloys to effect a rapid powder consolidation cycle in the W—Cr system. Beginning with mechanically alloyed powders, they showed that cold-pressed pellets sintered rapidly at low temperatures (below 1500 °C) without the need for applied pressure. They traced the sintering acceleration to the nano-duplex structure, which evolves upon heating. As the solid solution decomposes, Cr becomes enriched at grain boundaries and also emerges as a second (nano-duplex) phase. Because the second phase has access to particle surfaces and is a rapid diffusing element, it quickly evolves inter-particle necks which support rapid sintering thereafter. The advantage of the Park and Schuh concept is that the alloying addition is designed to both accelerate sintering and retain fine grain sizes. In the binary W—Cr system, those authors reported full density compacts with ~1 μm grain sizes, roughly an order of magnitude below what would be typical for rapid sintering methods in the same temperature range. With further addition of stabilizers, they extended the concept to produce 100 nm grains at full density. This technology is currently being commercialized by Veloxint Corporation.

In this investigation, W—Cr material that has been milled to produce suitable powders will be subjected to both conventional press and sinter treatment as well as used in a novel metal additive manufacturing (AM) technique known as Bound Metal Deposition (BMD).