HOT EXPLOSIVE CONSOLIDATION OF NANOSTRUCTURED TUNGSTEN–SILVER PRECURSORS

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Different precursors of refractory nanostructural tungsten-silver (W-Ag) composites were consolidated into cylindrical billets by hot explosive consolidation (HEC) method. Different types of compositions with a nanoscale W phase (100 nm) and coarse matrix phase of Ag were consolidated to near theoretical density under and above of melting point of silver (940 – 1050°C). The intensity of loading in all experiments was around 10GPa. The combination of high temperatures and two stage explosive densification processes was found to be beneficial to the consolidation of the nanostructural W based composites, resulting in high densities, good integrity, and good electronic properties. The structure and property of the samples depends on the value of consolidation temperature and dimension of consolidated particle. It was observed that for the W-Ag based composites, application of high temperature and consolidation of precursors near melting point of silver 940 °C gives samples without cracking with high value of density and uniform distribution of two phases. The features of structure/property relationship depending on phase content and consolidation conditions have been discussed.

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Introduction

In recent years, tungsten (W)-based heavy alloys have received increased use in both commercial and industrial spheres. Most heavy alloys consist of W particles embedded in matrix of other metals or their alloys such as iron, nickel, or copper.[1] In particular, W–silver (Ag) composites may have potential uses as heat dissipation materials in the microelectronic devices that are prone to failure at high operating temperatures,[2] as diverter plates in fusion reactors,[3] or in special industrial (e.g., aerospace) applications.

Experimental studies relating the mechanical properties of samples formed from nanocrystalline precursor powders show that these ultra-fine grained materials are fundamentally different from their normal, coarse-grained counterparts. These materials often have very unusual properties for instance, they are ultra-hard and wear-resistant, have an ideal compatibility of strength and elasticity, and are characterized by super-plasticity. When the average grain size is less than or equal to the wavelength of visible light, the material will also have unique optical, thermal, electrical and magnetic properties as well. Therefore, a decrease of the grain size and concomitant control of the defect substructure of the grains seems to be a promising way to improve properties of these materials. At present, there are various methods (e.g., cold or hot isostatic compaction in vacuum or in other media) for the manufacturing of monolithic specimens using precursor powders ranging from micro- to sub micrometer- to nanometer-sized powders (i.e., covering the visible-light spectrum from infrared to ultraviolet wavelengths).

All existing conventional technologies, alongside with imparting positive properties, introduce certain negative features. Nanometer-scale grains are very sensitive to heating, with increasing temperatures, these powders begin to grow rapidly. Typically, this grain growth is non-uniform and its overall impact causes imperfections and non-uniformity in the nanostructure and, as a result, monolithic materials formed under such conditions do not have the unique physical and mechanical properties that are otherwise would be intrinsic to nanostructural materials.

Usually, decreasing the compaction or sinter temperature during low-temperature processing does not lead to a desirable outcome. In this case, the relatively large free surface area of the powder precludes the attainment of high-density samples. Additionally, at low temperatures, the required interfacial grain-to-grain boundaries do not form and this is especially true during the compression and consolidation of refractory and ceramic powders. Thus, such samples are characterized with high level of porosity and, therefore, inadequate physical or mechanical properties.

Nevertheless, sufficient experience has been accumulated to provide solutions to some of the aforementioned problems. The idea is to apply high temperatures, up to 1200 °C, to the samples and carry out rapid consolidation at the hot, elevated temperature, conditions. Heating of the powders or alloys before loading assists in increasing the sample's plasticity. As a result, common boundaries, interfacial solid solutions, intermediate layers (in the case of joining of bulk alloys), and other beneficial features are formed. The high value of recrystalization temperature of W prevents or suppresses grain growth processes.

A further novelty of the proposed, non-conventional approach is that the consolidation of solid samples in a cylindrical geometry from sub micrometer- and nanometer-sized W-Ag blend powders is performed in two stages:

(a) First stage: preliminary explosive compression of the precursor powder blend is carried out at room temperature with a loading intensity of 5 – 10 GPa to increase the initial density and to activate the particle surfaces in the blend;

(b) Second stage: the same, already densified cylindrical sample is loaded again by a primary explosive shock wave with a loading intensity of 10GPa, but at a temperature between 20 – 1100 °C.

It is expected that the effect of the first consolidation stage is to primarily compact the precursor powder without causing a change in its microstructure. The second, hot consolidation stage is performed on the pre-compacted samples by heating in an electrical furnace. The high recrystalization temperature of W significantly decreases the probability of the thermally activated grain growth process (as it was demonstrated in the preliminary experiments), while the high intensity shock wave compression imparts fluidity to the grain surfaces thereby increasing their plasticity and, thus generate the particle-particle bonds that would otherwise not form under the quasistatic conditions.

In this study we undertook the consolidation of tungsten–(10–50) wt. % silver (W–(10–50)Ag) powder mixtures into cylindrical rods using hot explosive consolidation (HEC) processes. Two types of nanometer-scale W–Ag blend compositions with 100 nm W, and 10 & 50 % 5 μm Ag were consolidated to near theoretical density at different temperatures up to 1100 °C. The shockwave loading intensity was about 10 GPa.

The intent of the investigations were to determine if the use high temperatures and the two-stage shock wave processing resulted in acceptable homogeneity, good bonding between the metal particles and absence of voids. These micro-structural features would provide an indication of the degree of mechanical and thermal property uniformity. Of further interest was a determination of the mechanical properties (elastic modulus and internal friction losses) as a function of Ag content, processing method, and processing temperature. Lastly, the electromagnetic properties (electrical resistivity and diamagnetic susceptibility) were measured. These results are described.

Experimental

In these experiments, we have used nominally nanometer-sized W powders from US Research Nanomaterials, Inc., USA and coarse Ag powders from Inframat "Advanced Materials", Manchester, USA

The W–(10–50)%Ag precursor powder blends were prepared from commercially available elemental powders. In turn these powders were consolidated into cylindrical rods using hot explosive consolidation (HEC) methods. Three types of W–Ag were consolidated to near theoretical density. The coarse Ag powders used in experiments have dimensions around 5μm. The shock wave loading intensity was about 10GPa, The temperatures during compaction were different and maximum value was under 1100 °C.

The explosive compaction process is carried out using a cylindrical scheme of dynamic loading described earlier.[4]

Typically, the shock waves are initiated with the use of industrial explosives and their mixtures with varying amounts of ammonium nitrate.

After consolidation, the HEC samples were subjected to micro-structural characterization and micro-hardness measurements. Coefficient of Thermal Extension (CTE) was measured to determine compatibility of the W–Ag composite to other materials, such as semiconductors and ceramics that would be part of the electronic assembly in need of heat dissipation. The electro-magnetic properties (electrical resistivity and magnetic susceptibility) along with, the mechanical properties (elastic modulus and internal friction) were also measured.

Results and Discussion

Using scanning electron microscopy (SEM) it was found that while the nanometer powders did indeed contained nanometer-scale particles, they were heavily agglomerated into multi-micrometer agglomerates.

Cross-section view of the sample of W–Ag billets fabricated by two-stage HEC at 1050 °C with nanometer-sized W–10%Ag and the W–50%Ag are presented in Figure 1a and 1b respectively. A comparative examination of the samples revealed major differences in their macrostructures. Both samples contain radial cracks but sample with high content of silver (1b) contains an additional zone formed along the whole length in the central part of billet. Macrostructure (Figure 1b) of the newly-formed zone in the central part of HEC sample has definite structure that differs from another part in colour and could be result of over compression and collision of shock waves in the central part of sample. This effect is popularly known as Mach's effect.
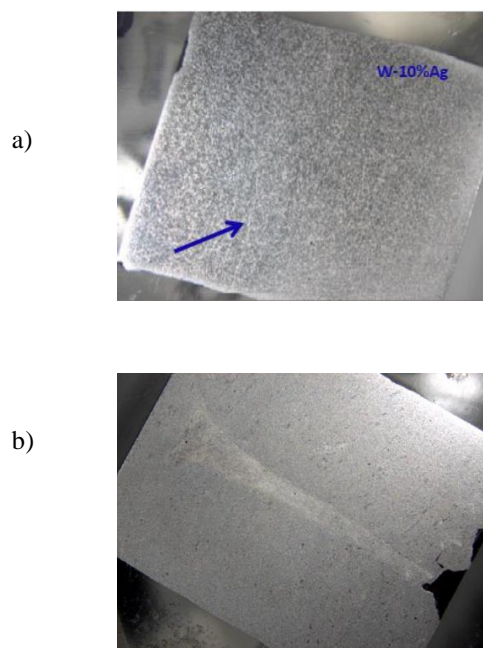
a)

b)

Figure 1. The Optical micrographs view of HEC W–Ag samples consolidated at 1050 °C with 10GPa. a) W–10%Ag at 6×. Radial cracking is observed b) W–50%Ag at 6×. Compositional segregation and radial cracking are observed.

Figure 2 illustrates the microstructures of different parts of the W−10%Ag composition presented in the Figure 1. Extensive radial cracking was observed in samples of the W−10%Ag composite (Figures 2a). The explosive forming of the dense W−10%Ag composite achieved good bonding between W and Ag particles. This is shown in Figures 2b, taken at 100× and 1000× correspondently. As expected, the Ag particles, initially of 8 − 10μm in size, tended to agglomerate in nodules of approximately 30μm in size in average around large areas of W in the W−10%Ag sample.
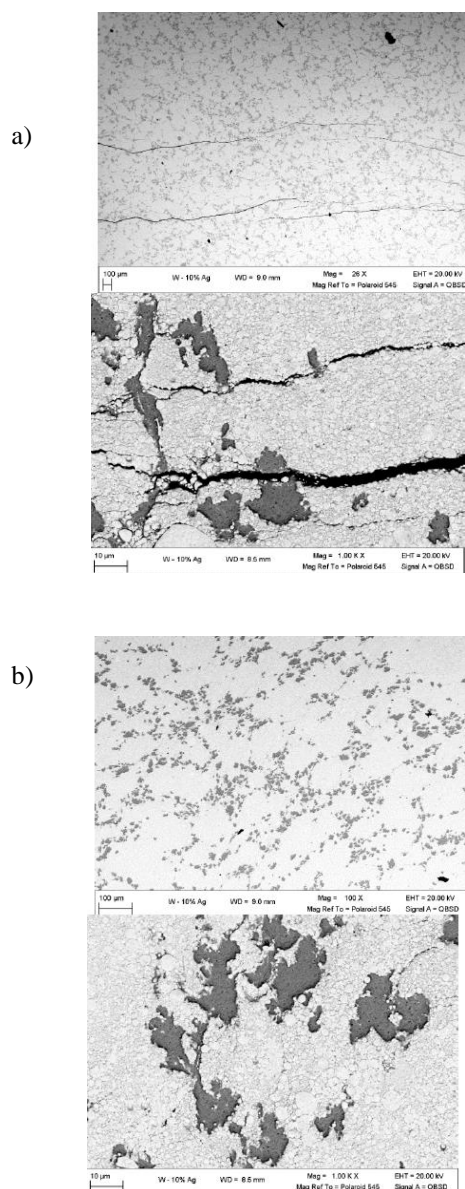

a)

b)

Figure 2. Microstructures of W−10%Ag HEC sample obtained at 1050 °C temperature with intensity of loading 10GPa. (a) Significant radial cracking is observed. (b) Distribution of Ag particles (in dark colour) – good bonding between W and Ag particles.

The formation of radial cracks in high density W−10%Ag composites after hot explosive consolidation at1050 °C, when bonding phase is in liquid state, seems to have both advantages and disadvantages. As a matter of fact liquid phase consolidation, when the bonding phase is liquid, provides extrusion of Ag phase on the shock wave front during the compression process and better densification of

consolidated precursors in contrast to processes in solid state when consolidation mechanism works through plastic flow of particle surfaces with further formation of joint boundaries.

Undoubtedly existence of liquid bonding phase during consolidation under shock wave compression facilitates the formation of solid solutions and new chemical compounds under similar loading conditions. On the other hand, liquid phase shock wave consolidation gives opportunity to use low detonation velocity explosives with higher pulse duration and to easily fabricate high density billets. Figure 3 illustrates compositional mapping of HEC W−10%Ag sample presented on Figure 1a.
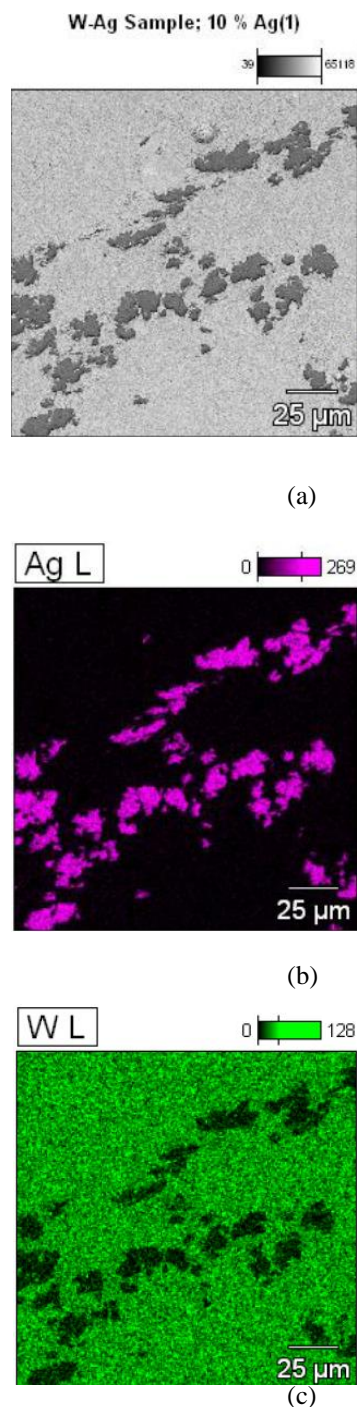

(a)

(b)

(c)

Figure 3. The location and distribution Ag (lavender color) and W (green color) in the matrix (grey colour) is shown.

As mentioned above, distribution of phases of W−10%Ag showed that Ag precursor, initially of 8 – 10 μm in size, agglomerates into nodules of average size of approximately 15 to 30 μm.

The appearance of agglomerates of silver phase in some regions of HEC W–10%Ag may be explained as an influence of high temperature and low intensity of compression that may not provide good extrusion and uniform distribution matrix of silver phase in whole volume of obtained billets.

In order to evaluate influence of silver content in W−Ag phase on consolidation process, HEC method was applied under similar experimental conditions on W−50%Ag composites also. Figure 4 illustrates the microstructures of different parts of the W−50%Ag composition presented in the Figure 1b.
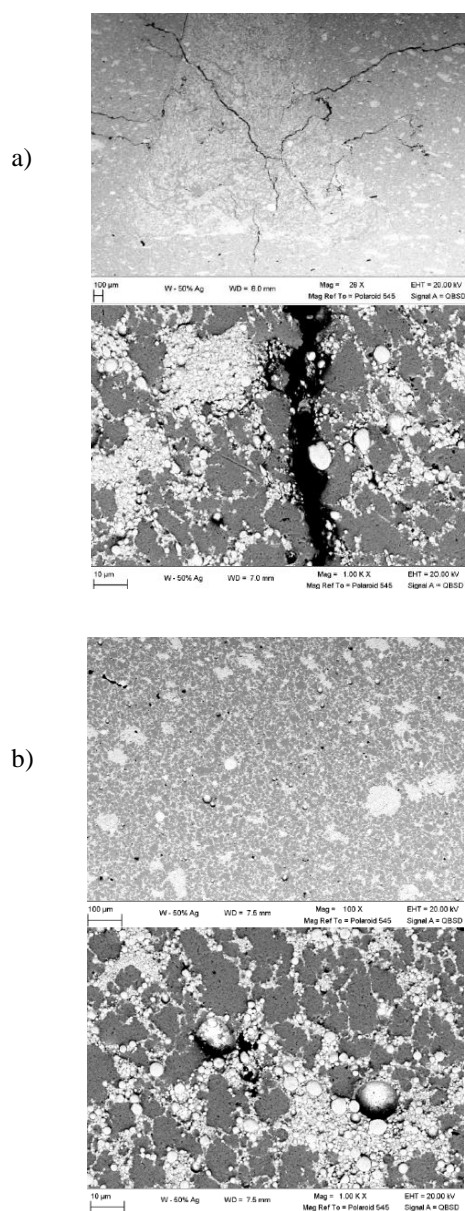
As it is seen from microstructure the increase in of silver content in W–Ag composition has substantial influence on quality of HEC samples. Under similar experimental conditions, the obtained billets are characterized with compositional segregation accompanied with intensive cracking in the central part of sample.

The formation of tungsten rich central zone that is different from other parts may be explained by assuming transportation of heavy W phase by shock wave front during of movement to central part during the explosive compression. As for the observed intensive cracking in the same central region, it must be result of "Makh's" steam effect. The intensive collision of shock waves in central part of billets causes an increase of the internal temperature and thermal stresses during the rapid cooling results in formation of intensive cracking.
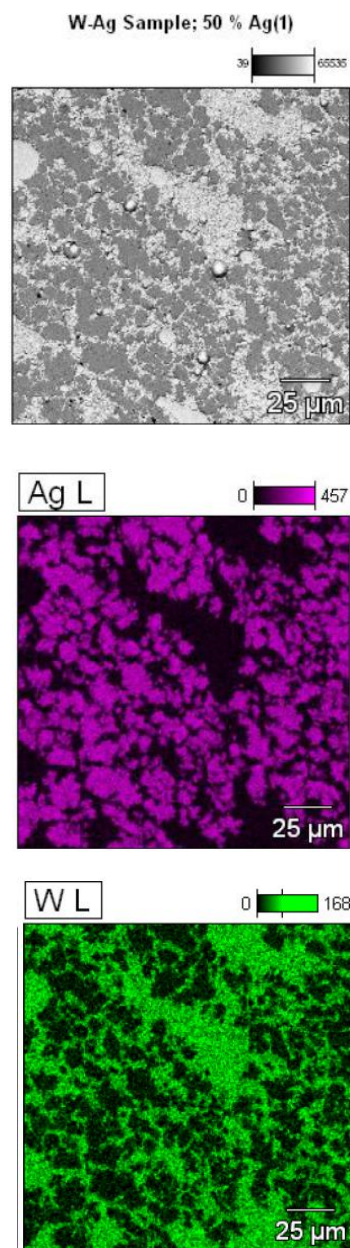

Figure 4. Microstructures of W−50%Ag HEC sample obtained at 1050 °C temperature with intensity of loading 10 GPa. (a) A large area of compositional segregation is visible at the centre of sample. This area is W rich and shows in light grey colour. Numerous cracks are also visible. (b) Distribution of Ag particles (in dark colour) –good bonding between W and Ag particles.

Figure 5. The location and distribution Ag (lavender colour) and W (green colour) in the matrix (grey colour) is shown. The Ag powder, initially of 8 – 10μm in size, agglomerates into nodules of average size of approximately15 to 30μm .

The Figure 5 illustrates compositional mapping of HEC W–50%Ag sample presented in Figure 1(a).

It is seen from the distribution of the combining phases that in the W–50%Ag also, Ag phase, initially of 8–10μm in size, agglomerates into nodules of average size of approximately 15 to 30μm. Similar observations were recorded for W–10%Ag case.

The presence of numerous cracks in the W–10%Ag samples would be detrimental to a uniform heat dissipation path. Non-uniform heat dissipation could create hot spots and potentially damage an electronic component or assembly. The presence of a W rich area at the centre of the W–50%Ag sample could also contribute to uneven heat conduction and heat dissipation from the assembly.

Therefore the fabrication of crack free W–Ag composites of near theoretical density with good bonding and uniform distribution of consisting phases is necessary for further successful application W–Ag composites in the modern microelectronics.

In order to reduce thermal stresses and cracking during the consolidation process and to evaluate the role of temperature on the consolidation process of W–Ag precursors, the HEC was performed under melting point of silver at 940 °C with loading intensity up to 10 GPa. Figure 6 illustrates the microstructures of different parts of the resulting consolidate of W–10%Ag composition.

As it's seen from microstructures the central part and whole volume of HEC sample are free from cracks and no traces of compositional segregation are observed. The agglomerated separate W particles with internal micro cracks might be observed at higher magnification that could be result of bad mixing and matching of sizes between the W and Ag phases.

The results of hardness testing of HEC W–Ag samples depending on consolidation conditions are presented in Table 1.

Table 1. The value of hardness for HEC W–Ag composites depending on consolidation temperature obtained at intensity of loading 10 GPa.

Compacted Composites	Temp. of compaction, °C	Loading, g	Microhardness HV, kg mm^{-2}
W–5%Ag	1000	50	331.5
W–10%Ag	940	50	248.5
W–10%Ag	1050	50	208.2
W–50%Ag	1050	50	47.5

As it is seen from table the content of silver phase in composition influences the value of hardness and sample with 5 % Ag content has the best value of hardness at 331 HV. The high consolidating temperature with increased Ag content in composition leads to reduced hardness value, it might be result of intensive cracking and compositional segregation. As stated above W–Ag materials could be used for heat dissipation from electronic devices that are prone to failure at high operating temperatures. Currently, materials such as copper–tungsten (Cu–W) and aluminum–silicon carbide (AlSiC) are used in industry for heat dissipation.

The above-mentioned characterizations were to determine if explosive consolidation resulted in acceptable homogeneity, good bonding between the metal particles, and absence of voids. These microstructural features provide an indication of the degree of uniformity in mechanical and thermal properties.
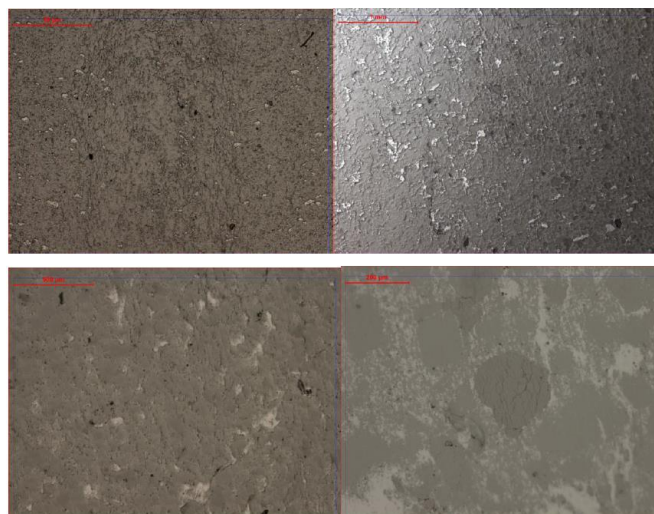

Figure 6. Microstructures of different regions of W–10%Ag HEC sample obtained at 940 °C temperature with loading intensity under 10 GPa. The sample is free from cracks in whole volume of billet and good bonding between W and Ag was observed.

CTE was measured to determine compatibility of the tungsten–silver (W–Ag) composites to other materials, such as semiconductors and ceramics that would be part of the electronic assembly in need of heat dissipation. CTE was determined by Thermal Mechanical Analysis (TMA) from –60 to 350 °C at 10 °C min^{-1} with three cycles (heat–cool–heat). Two heating cycles were used: from –60 to 20 °C and from 50 to 350 °C. The CTE from the two heating cycles is averaged from each lot of material. These values are shown in Table 2 below.

Table 2. Measurements of coefficient of thermal expansion, μm/m °C.

Composition	Coefficient of thermal expansion	
	–60 to 20 °C	50 to 350 °C
W–10%Ag	5.5	7.5
W–50%Ag	9.5	13.7

Conclusions

Cracking on both of the W–Ag samples consolidated above melting point of silver were observed. The cracking is severe and can compromise the mechanical integrity of the sample as well as the uniformity of the heat dissipation. In actual applications, this lack of mechanical integrity and non-uniformity may lead to hot spots which could damage the devices in need of heat dissipation.

The CTE of the W–Ag samples, shown in Table 2, compares well with the CTE of other materials commonly used by industry for this application, namely Cu–W and AlSiC. Reported CTE values for Cu–W are 6.5 for W–10%Cu and 8.3 for W–20%Cu. The CTE for the W–10%Ag

sample of 5.5 to 7.5 (μm m°C^{-1} or ppm K^{-1}) is within this range. CTE values for AlSiC range from 8.0 to 15 (ppm K^{-1}) depending on the composition ratios. Cu–Mo, another material used for its high thermal conductivity has a CTE of 7.2 to 11 (ppm K^{-1}) depending of the ratio of Cu to Mo. The CTE, 9.5 to 13.7 (μm m°C^{-1}), of the W–50%Ag sample measured in this investigation is within this range. The CTE of a low temperature co-fired ceramic, measured under the same conditions as the W–Ag samples was 4.4 to 6.4 (μm m°C^{-1}).

Compositional segregation was observed in the centre of the W–50%Ag sample. A large area, rich in W is visible around the longitudinal axis. This segregation raises concern about the uniformity of properties, such as thermal conductivity, of the sample.

The measurement of the thermal conductivity of the samples was not in the scope of this initial evaluation, but the presence of numerous cracks in the samples would be detrimental to a uniform heat dissipation path. Non-uniform heat dissipation could create hot spots and potentially damage an electronic component or assembly. The presence of a W rich area at the centre of the W–50%Ag sample could also contribute to uneven heat conduction and heat dissipation from the assembly.

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