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Thermal properties of micro- and nano- structured W-Cu functional gradient materials

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Abstract

High temperature investigations on thermo-physical properties of W-Cu composites with different compositions, are used in conjunction with microstructural investigations to define the best solution to produce a functional gradient material (FGM) acting as a functional joint between W armor and Cu-based heatsink materials in the divertor of the DEMO fusion reactor. The study is focused on materials with 1:3, 1:1 and 3:1 W-Cu volume proportions created with nano-metric and micrometric metallic powders consolidated by spark plasma sintering (SPS) at about 900 °C, below the Cu melting temperature. Since at such temperature there is no W-W sintering possible, agglomeration of W grains, arising during both mixing and sintering, creates W islands with poorly connected grains and therefore lower thermal conductivity. The best results are obtained for micrometric particle dimensions. For these compositions the density, specific heat, thermal diffusivity and thermal expansion coefficient are close to the expected theoretical values. A resulting 1 mm thick, 3 layers W-Cu FGM produced by this simple method shows a remarkable almost constant thermal conductivity value of 200 W/m/K from room temperature 1000 °C

Keywords: W-Cu FGMs, fusion materials, spark plasma sintering, high temperature thermo-physical properties, laser flash analyzer

1. Introduction

Functional gradient materials (FGMs) can provide useful interfaces between materials with different melting temperatures, different thermal expansion coefficients and different thermal properties [1-5]. In particular, as application for fusion energy materials, connecting W armor with Cu based heat sink materials is a challenging task [6-7] and one of the possible options considered is the use of W-Cu FGMs with 1-2 mm thickness. W is the main choice for fusion reactor armor materials due to its highest melting temperature among metals (~ 3420 °C), low activation and low sputtering rate. Also W has a high thermal conductivity for a refractory material (~175 W/m/K at room temperature) and low thermal expansion coefficient ($4.5 \times 10^{-}$

^{6}/K). On the other side, Cu based materials are traditionally used as heat sink materials and already employed in various test reactors design, including ITER. Cu and Cu alloys materials benefit from a high thermal conductivity (up to above 400 W/m/K for Cu) but they have a low melting temperature, low softening temperature and also a high thermal expansion coefficient (16.8×10^{-6}/K for Cu), about 4 times greater than the W coefficient. Thus, directly joining W and Cu in, e.g. divertor components for a fusion reactor, will generate a high stress on the interface when the temperature is repeatedly raised an decreased, which is a normal working behavior of tokamak reactor. As a result, an interface material is needed to mitigate for the thermal coefficient mismatch. The DEMO fusion reactor design requires that all used materials fulfil the low activation criteria, which further restrict the materials' choices to only a few elements [7]. W and Cu are already included in this restricted list and since they are not miscible metals [8], they are from this point of view well suited components for composite materials. Moreover, like all other fusion reactor materials, they should limit the tritium retention, and withstand high heat (~10-20 MW/m^2)and consistent neutron fluxes (starting with the equivalent of ~ 5 dpa in the divertor). A W-Cu gradient material interface should provide a gradual increase of the thermal expansion coefficient and thermal conductivity from W to Cu and can be realized by superposing several composite layers with different W-Cu proportions. The composite layers can be realized by various methods, involving solid state consolidation [2,4,9-14], liquid Cu – solid W interaction [15-17], or various deposition methods[1,5]. In the case of a solid state reaction, at normal processing temperatures (which must be below the Cu melting temperature), W-W connections can not be realized in a reasonable amount of time and accidental agglomerations of not joined W grains or pieces will detriment the mechanical strengths of the composite. To avoid this, for high W content, in the second route, a preformed W matrix is realized using W powder mixed with a resin type binder, followed by thermal removal of the resin and high temperature sintering of the matrix [18]. After that, molten Cu can be infiltrated in the preformed matrix by various methods [16-18]. Such composites with various concentrations, usually and incorrectly termed as "WCu alloys" are now produced on a large scale and commercially available. However, this route requires many steps and unfilled voids can persist in the matrix, allowing for gas accumulation (including T). An elaborated solution to use the solid state reaction was proposed by L. Zang et al [13] who used hot pressing of Cu coated W grains and obtained dense highly thermal conductive materials with a well formed network of Cu inside the specimens. Unfortunately, since the Cu coating process has itself limits in terms of the Cu thickness, this limits also the compositional range. A possible alternative to reduce the above problems might be provided by using an electrical field (or

current) assisted sintering technique, also known as spark plasma sintering SPS. The main benefit of this technique relays in the heating system. For classical sintering furnaces the heating of the material is made by heat convection that came from the material's holder and/or by radiation from the inner surface of the furnace. In SPS the heating process is happening through direct energy transfer to sample. This procedure is possible sending trains of high electric dc current pulses of the kA order. The electric current pulses are propagated through the material through grains if these are electrical conductive or on the grains surfaces if they are electrical insulators. In both cases, the contact areas between the grains are strongly heated leading to a local increase of temperature. In these areas, due the distribution of electric field there are electric sparks produced which have a contribution to the mass transfer between grains. The spectacular fact of this method are the huge compression of sintering process time, very fast heating and cooling times and, essential, sintering of materials at much lower mean temperatures. As a result it is possible on one side to preserve the nanometric size of grains, creating bulk nanostructured materials, and on the other side to sinter very different types of materials.

In this work, we have used SPS process to consolidate different mixtures of nanometric and micrometric W and Cu powders as composite layers to create a W-Cu FGM. Thermo-physical properties investigations of the resulted composites have been used to evaluate both the proposed sintering process feasibility and the resulting composite application potential as a fusion interface material.

2. Experimental

Mixtures of W micrometric powders (APS = 1 μm) with Cu micrometric powders APS = 1 μm and nanometric powders (APS 40-60 nm) as well as W nanometric powders (APS = 60-80 nm) with the same Cu powders have been prepared in protective Ar atmosphere by mechanical mixing (20 minutes, 50 rpm) with weight concentrations corresponding to 1:3, 1:1 and 3:1 final volume ratio assuming a full densifications and no solubility between W and Cu. The nanometric powders with a purity of at least 99.9% were provided by Skyspring Nanomaterials Inc. (USA) while the micrometric powders (99.95% purity for Cu and 99.99% purity for W) were provided Smart-elements GmbH (Austria). The powder mixtures were placed in graphite molds with a diameter of 12,5 mm protected on the inside with Sigraflex© graphite thin foils. The entire manipulation process was performed in a glove box under Ar atmosphere with both

O_2 and H_2O content smaller than 0.5 ppm. To create a FGM, 3 different layers of micrometric W and Cu mixtures were placed successively in the mold and cold pressed up to 5 MPa. The resulting specimens have been consolidated using a SPS equipment (FCT, Germany) in vacuum using a simple cycle with heating and cooling rates of 90 K/min and 5 min at 890 °C sintering plateau. The pressure was increased first at room temperature up to 25 Mpa and then together with the temperature further increased up to 65 Mpa. This value was preserved on the entire sintering plateau and then gradually decreased together with the temperature.

The resulting samples morphology was analyzed by scanning electron microscopy (SEM) using an EVO 50 CARL ZEISS microscope with a LaB_6 cathode enabling 2 nm spatial resolution for a maximum voltage of 30 kV and equipped with EDX (Energy-dispersive X-ray analysis) and a backscattering detector (BSD) used to evaluate the distribution of the elements in the sample. The thermo-physical properties have been investigated using Laser Flash Analyzer (Netzsch LFA 457 Microflash) up to 1000 C and the expansion coefficients have been determined in the same temperature range using a Netzsch 402 C dilatometer. The LFA equipment allows the direct measurement of the thermal diffusivity, α, by analyzing the temperature variation of one surface of the sample when a calibrated laser pulse is applied on the other surface. The specific heat of the materials, C_p can be determined by a differential method using a reference sample (in this case Mo, NIST certificate SRM 781). The thermal conductivity was calculated by $\lambda = \alpha \times \rho \times C_p$, where ρ is the density of the sample. The samples' density was measured by Archimedes method using a high resolution balance.

3. Results and discussion

To create a functional gradient material from 2 metallic powders, i.e. to obtain a gradual variation of some properties means creating in the first place a material with a gradual change of compositions, from one of the metals to the second one. However, sintering metallic powders from W and Cu is limited by the Cu low melting temperature. In a SPS equipment, which can generate hot points with consistently much higher temperatures as the overall desired sintering temperature, this upper temperature limit is even lower as in the case of classic sintering, in particular for Cu-W being at about 100 K below the Cu melting temperature. This limit is further decreased when using smaller Cu grain sizes. On the other side, at this temperature values one can not expect W-W sintering. Therefore, it is not reasonable to expect to realize a continuous compositional gradient on the W side.

To determine experimentally the concentration limit for W, up to 10 different layers FGMs specimens have been produced at decreasing temperatures until samples without visible Cu melting have been obtained. On these samples, by removing the un-sintered part, the concentration of the last well sintered layer was determined by EDX. For samples produced from about 1 micron Cu grains this limit is at about 20% Cu volume concentration (about 10 wt.%). An elemental map of such a test specimen is presented in Figure 1 a. To quantify the thermal properties of the W-Cu composites in this work, we have selected a upper W volume concentration limit at 75% (further designed as W:Cu 3:1), and symmetrical a lower W volume concentration at 25% (further designed as W:Cu 1:3). An intermediate layer with 50% volume concentrations was also included in the analyses (further designed as W:Cu 1:1). Mixing, manipulating and sintering of W-Cu mixtures is already known to produce agglomerations of similar grains, which in the case of un-sintered W grains might lead to poorer mechanical and thermal properties. Using as start materials powders with smaller grains might improve the homogeneity of the composites and the resulting physical properties. Thus we have tested various combinations of micrometric and nanometric W and Cu powders, to test both the mixing behavior and the consolidation by SPS sintering. Using nanometric sized powders in combination with micrometric powders is expected to increase the density of samples, at least taking into account volume filling considerations.

A survey of the density data presented in Table I shows that this is not happening. While for the mixture of W and Cu micrometric grains it can be observed that the relative density decreases with increasing W content, no trend can be determined in connection with the nanometric powders used. For the mixture of W and Cu micrometric grains the highest relative density is obtained for low W content (1:3) and this value is in fact one of the highest obtained yet, including the reported values from literature for SPS [11], higher values (~98%) being obtained with Cu coated W grains by SPS [13]. The decrease of density with increasing W content can be ascribed to pores created between un-sintered W grains (see for example the morphology of the 1:1 sample depicted in Figure 1 b).

Following this reasoning, using nm grain sizes for W should increase the density by decreasing the pores' size. the highest density is achieved for the mixture of W and Cu micrometric grains. However this can be observed only for 1:1 nm W – μm Cu composition, which gives also the highest density for this grains' size combination. A possible explanation might be found in the morphological particularities of these samples, as shown in Figure 1 c. In the EBS image can be seen that W agglomerates in some spherical structures with

dimensions up to ~20 μm. Such structures can be observed also for composites made from nm W and nm Cu powders (see Figure 1 d). A detailed SEM image (Figure 2 e) shows that indeed the W agglomerations are constituted from small nm W particles, while a EDX quantitative analysis performed on such structures (see Figure 2 f) shows a large presence of Cu inside them. One can assume that during the SPS processing Cu was melted locally and due to its surface tension has created these almost spherical structures, trapping the nm W on the surface. An unclarified yet balance in local distribution of W and Cu might be responsible in this case for the density variation in specimens containing nm W powders.

A similar void filling reasoning can be applied to nm Cu powders in a μm W matrix. In this case optimum filling is expected to be in a crude model of spherical particles in a cubic or tetrahedral network between 47% nm spheres volume and 26% nm spheres volume, respectively. Thus, the maximum densifications will be expected at highest nm Cu content and the minimum densification at lowest nm Cu content. Data presented in Table I for μm W – nm Cu composites follow indeed this trend.

Thermal diffusivity is a direct measure of the thermal response of a material to a heat flux, characterizing its thermal inertia and is directly proportional to its thermal conductivity. Generally thermal conductivity can be separated in the electron and phonon contributions. In metals, at high temperatures, the electron contributions to thermal conductivity is related to electrical conductivity by Wiedemann-Franz law. Thus electronic thermal conductivity is at high temperatures constant. The phonon contribution at these temperatures is mostly determined by the so-called umklapp scattering processes and consequently has a temperature dependence proportional to 1/T. As a result, a metal should exhibit a total thermal conductivity slowly decreasing with 1/T. In real materials, additional facts like impurities (pores, precipitates, trapped gases) and grain boundaries affect this behavior. In a composite material with constituents exhibiting different transport properties, contiguity reasons should also be taken into account [19]. The later factor depends on concentrations and sample morphology.

Figure 2 shows the thermal properties of W-Cu 1:3 composites with nanometric and micrometric grains. Including nanometric sized grains in a material implies increasing the grain boundaries' surface and therefore introducing additional scattering for charge and energy carriers. As a result it is expected that the thermal diffusivity decreases with increasing nm grains content. This is remarkably well shown by the 1:3 composites. A more pronounced decrease of thermal diffusivity for the μm W - nm Cu composite at temperature above the sintering temperature might be explained by further temperature driven material consolidation.

This can also be correlated with the specific heat behavior of the samples (see the inset of Figure 2). While for the other 3 composites the specific heat values at room temperature are very close below the expected value resulting from the mixing rule (i.e. 0.2808 J/g/K) for the μm W - nm Cu composite a much higher value is obtained (~ 0.31 J/g/K). This sample has in fact also a very low density, pointing to a poorly sintered sample. It is also interesting to observe that the specimens containing nm W grains have a different specific heat slope, and this fact appears to be independent of the W concentration (compare Figures 2-4). Although we don't have a definite explanation from this difference, one can speculate that is related to the nm W grains agglomerations which might act as heat accumulation points. A similar behavior was observed in W-SiC composites [20]. The highest values obtained for thermal conductivity of 1:3 composites reach 250 W/m/K for both samples containing μm Cu grains, albeit in slightly different temperature intervals (see the online supplementary figure 1). For the 1:3 μm W - μm Cu composite a CTE value of 16.42 × 10-6 K-1 was obtained by dilatometry measurements between room temperature and 1000 °C.

Figure 3 shows the thermal properties of W-Cu 1:1 composites with nanometric and micrometric grains. As the W content is increased, the thermal diffusivity decreases, as expected from the different materials transport properties. Similar to the previous case, including nanometric sized grains produces a thermal diffusivity decrease with increasing nm grains content. Obviously, the different sintering behavior of W and Cu results in a difference between specimens containing nm W grains. They have the lowest diffusivity values. The specific heat behavior for the 1:1 samples (see the inset of Figure 3) shows the same features as in the case of 1:3 composites, with room temperatures values close to the mixing rule derived value (i.e. 0.2115 J/g/K). Here the only exception is provided by the nm W - nm Cu composite with a much lower value (~ 0.17 J/g/K). We ascribe this difference to the increased number of spherical W formations. Without an in deep investigation of the morphology and structure of these formations it is difficult to provide a more specific assessment. The highest value obtained for thermal conductivity of 1:1 composites reaches ~220 W/m/K at room temperature and ~ 175 W/m/K at 1000 °C for the sample produced with μm W and Cu grains. (see the online supplementary figure 2). For the 1:1 μm W - μm Cu composite a CTE value of 16.42 × 10-6 K-1 was obtained by dilatometry measurements between room temperature and 1000 °C.

Figure 4 shows the thermal properties of W-Cu 3:1 composites with nanometric and micrometric grains. The same considerations can be applied to these composites. The lowest

diffusivity values are obtained for samples containing nm W grains. One should however note that here the highest diffusivity values are obtained for the sample containing μm W grains and nm Cu grains. The small difference compared to the μm W – μm Cu samples can be easily explained by the increased density of the former one, which in turn can be ascribed to a better filling of the W inter-spaces. Concerning the specific heat behavior for the 3:1 samples (see the inset of Figure 4) it can be observed that, for the samples containing μm W grains, the room temperatures values are close to the mixing rule derived value (i.e. 0.1645 J/g/K), while for samples containing nm W grains the room temperature values are much lower (~ 0.14 J/g/K), consistent with the increased number of spherical W formations. The highest values obtained for thermal conductivity of 3:1 composites is around 75 W/m/K at room temperature for samples with μm W grains (see the online supplementary figure 3). This value is about half of the pure W value and in the case of a FGM will have a local thermal barrier effect. However one should note that the thermal diffusivity it is about 50% higher than that one reported in [1], the low specific heat value being the main responsible for the reduced thermal conductivity value. Thus a needed improvement can be obtain by a better mixing procedure, at least for high W content. For the 3:1 μm W - μm Cu composite a CTE value of 16.42 × 10-6 K-1 was obtained by dilatometry measurements between room temperature and 1000 °C.

As the highest thermal conductivity values are obtained for micrometric powder mixtures, in Figure 5 the thermal diffusivity from room temperature to 1000 °C is plotted for a 1 mm thick, 3 layer W-Cu FGM. For comparison the plot includes data for high temperature SPS-ed W and a 890 °C SPS-ed micrometric grains Cu, as well as the result for a commercial W60Cu40 (wt.%) sample with a close composition to the mean value of the presented FGM. It is interesting to observe that the diffusivity values are very close to the values obtained for 1:3 W-Cu composites. A possible explanation resides in the single step processing mode, which might induce a strong mixing between layers. The corresponding specific heat values are plotted in the inset of Figure 5 and the FGM values follow the mixing rule calculations. As a result, the thermal conductivity (see the online supplementary figure 4) is almost constant in the whole temperature range with a value of about 200 W/m/K. This value is similar and even grater at high temperatures that those obtained by microwave sintering above Cu melting temperature [4] and much higher than those reported for SPS sintering [2]. In fact is comparable to the values reported for molten Cu infiltration, Which is a remarkable fact taking into account the lower densities obtained in general by SPS.

4. Conclusions

A survey of the thermal properties was performed for SPS-ed W-Cu composites with different compositions and grain sizes. The data was analyzed in conjunction with microstructural investigations and indicates a clear dependence on the morphological features, which in turn are defined by the mixing quality of powders. Since there is no W-W sintering possible, different types of W grains agglomerations, created both during mixing and sintering. The best results are obtained for micrometric particle dimensions. Using these results, a 1 mm thick, 3 layers W-Cu FGM was produced by this simple method. The thermal transport properties investigation of this material shows a remarkable almost constant thermal conductivity value of 200 W/m/K from room temperature to 1000 °C

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Table I. Densities for W-Cu composites with different volume proportions.

Sample	**Volume proportions**	**Density ρ [g/cm^3]**	**Teoretical density ρ [g/cm^3]**	**Relative density ρ_{rel} [%]**
μW - μCu	1-3	11.05	11.48	96.23
nW - μCu		10.94		91.45
μW - nCu		9.94		86.54
nW - nCu		10.26		89.37
μW - μCu	1-1	13.36	14.07	94.95
nW - μCu		13.42		95.37
μW - nCu		12.58		89.41
nW - nCu		12.13		86.17
μW - μCu	3-1	15.09	16.66	90.60
nW - μCu		15.36		92.20
μW - nCu		15.20		91.20
nW - nCu		15.54		93.25
μW - μCu	FGM 3 layers	13.04	14.07	92.68

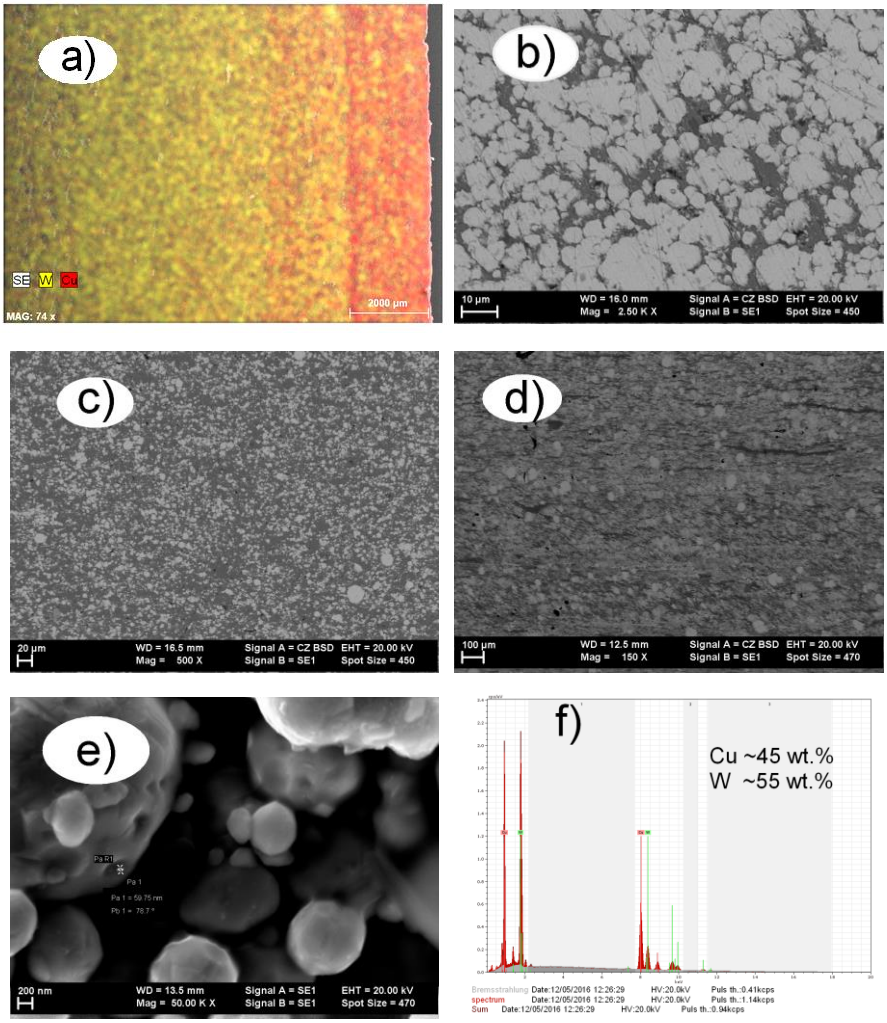

Figure 1. Morpho-compositional investigations of W-Cu composites: a) elemental map obtained by EDX in a multilayer FGM used to determine the compositional limits for SPS sintering; b) EBS image of µm W-µm Cu 1:1 composite; c) EBS image of nm W-µm Cu 1:3 composite: some rare spherical agglomerations of W particles can be seen; d) EBS image of nm W-nm Cu 1:3 composite: more spherical agglomerations of W particles can be seen; e) detail SEM image of the nm W-nm Cu 1:3 composite: the W agglomerations are made from small W grains with ~60 nm grain size; f) EDX analysis result on a W agglomeration, showing that the nm sized W grains are in fact covering Cu agglomerations. (color online)

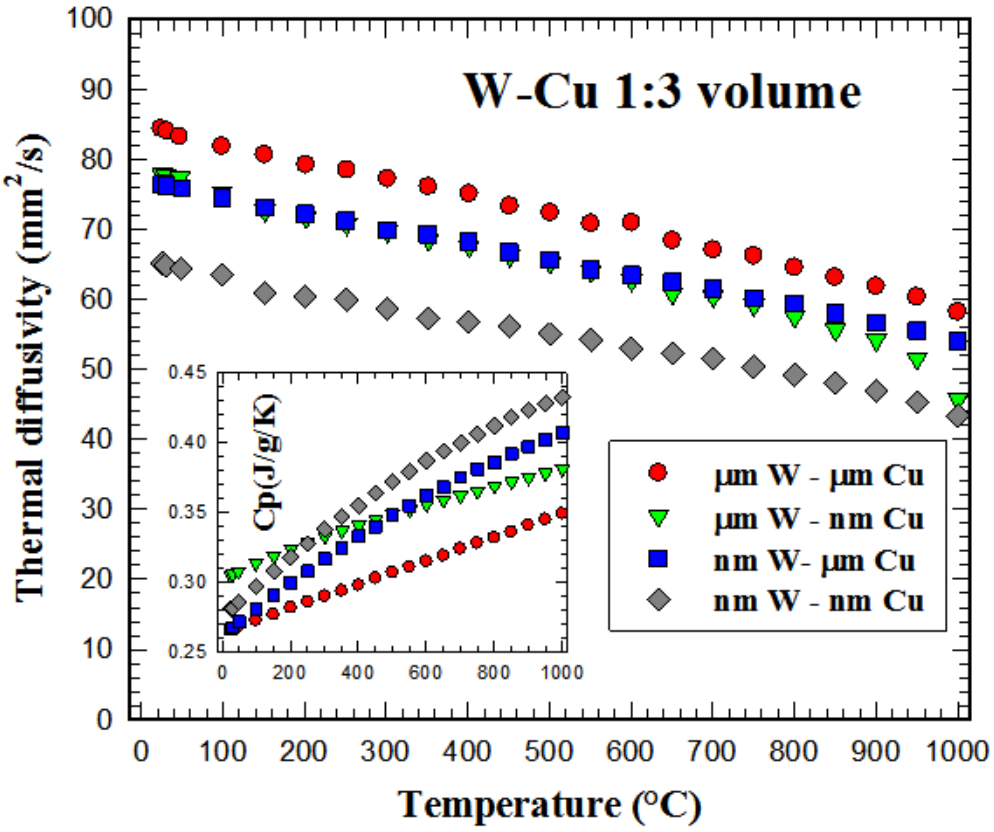

Figure 2. Thermal diffusivity of W-Cu 1:3 composites with nanometric and micrometric grains (main plot) from room temperature to 1000 °C; The inset shows the specific heat behavior in the same temperature range. (color online)

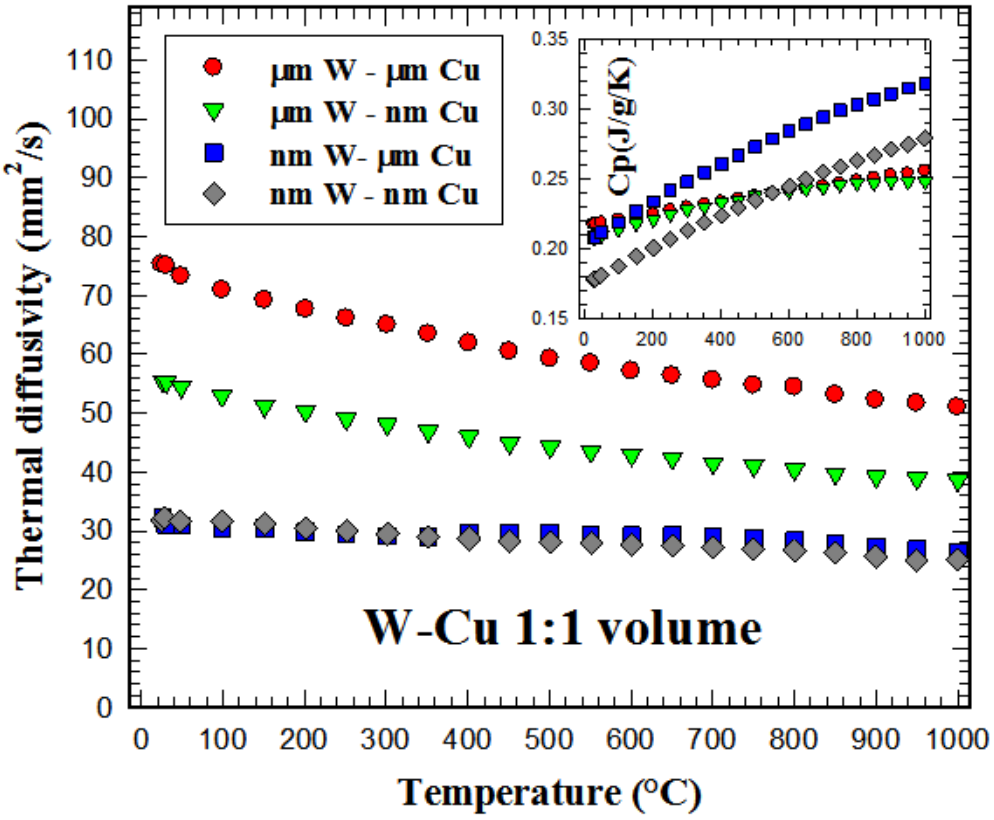

Figure 3. Thermal diffusivity of W-Cu 1:1 composites with nanometric and micrometric grains (main plot) from room temperature to 1000 °C; The inset shows the specific heat behavior in the same temperature range. (color online)

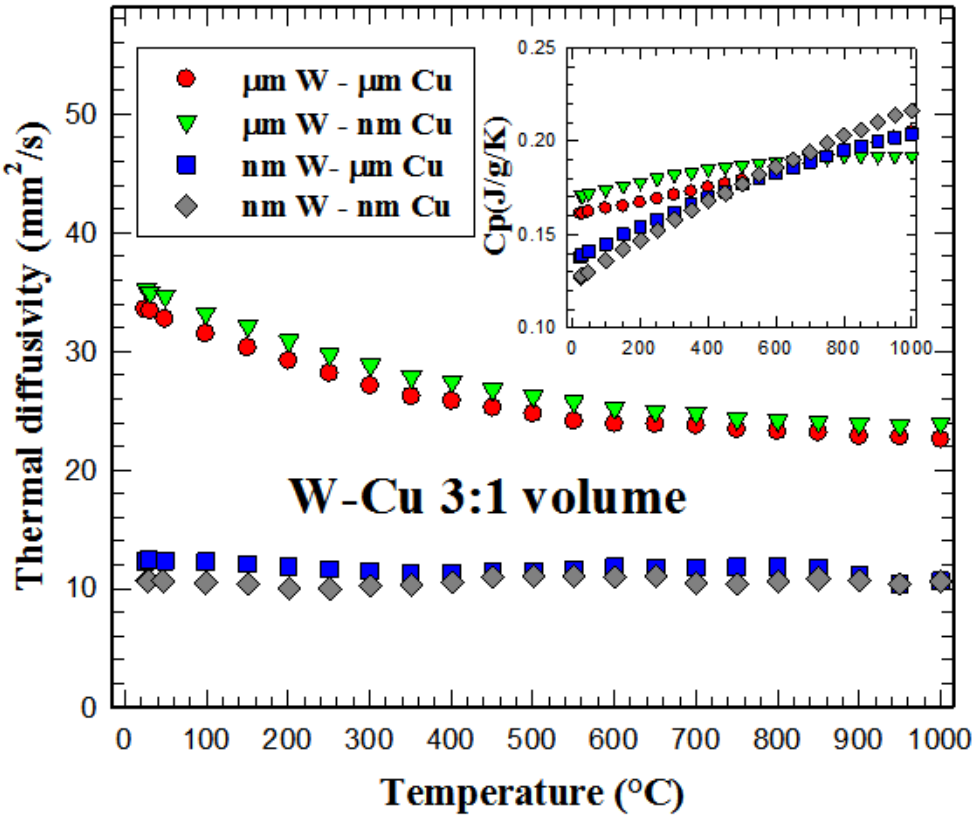

Figure 4. Thermal diffusivity of W-Cu 3:1 composites with nanometric and micrometric grains (main plot) from room temperature to 1000 °C; The inset shows the specific heat behavior in the same temperature range. (color online)

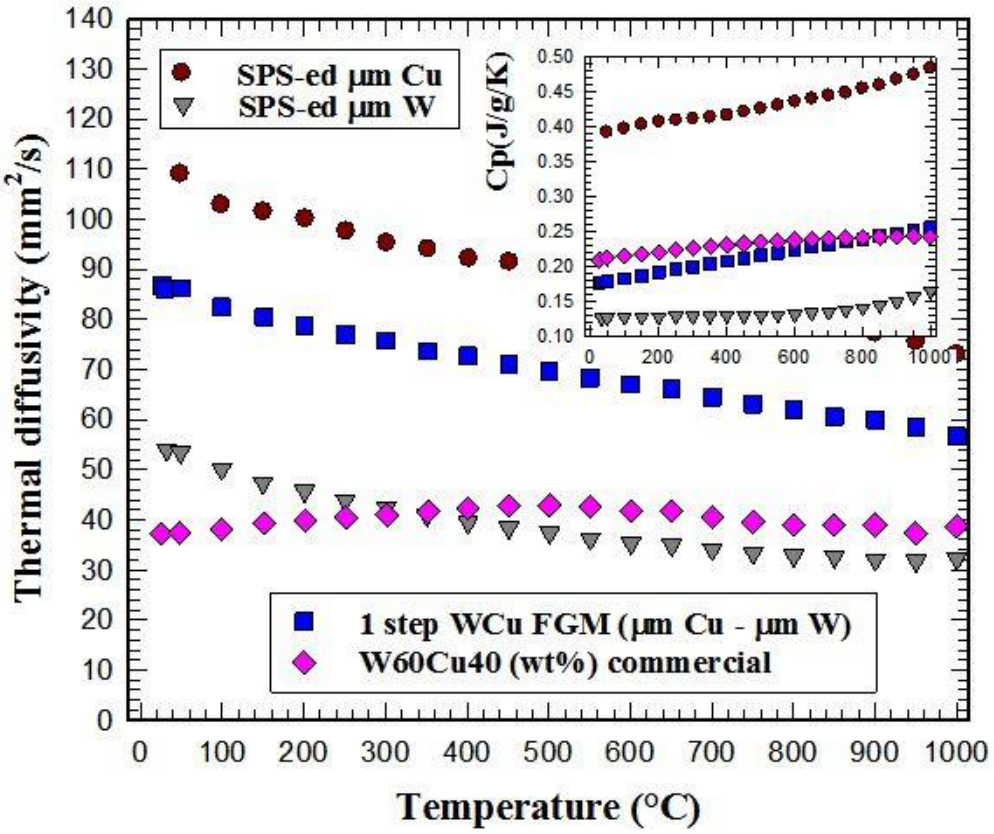

Figure 5. Thermal diffusivity from room temperature to 1000 °C for a 1 mm thick, 3 layer W-Cu FGM produced with micrometric powders (main plot). For comparison the plot includes data for high temperature SPS-ed W and a 890 °C SPS-ed micrometric grains Cu, as well as the result for a commercial W60Cu40 (wt.%) sample; The inset shows the specific heat behavior for the same materials. (color online)