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Electrical and elastic properties of Cu-W graded material produced by vibro compaction

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Abstract Self-formed W graded preform was produced by size segregation of weakly vibrated tungsten bimodal granular medium. The bimodal granular media bed was initially set up with larger W agglomerates placed on the bottom and with smaller agglomerates on the top of the container. During the vibro-compaction treatment the granular bed progresses through three distinguished compaction stages: percolation, diffusion like or hopping, and non-equilibrium steady state, which exhibit different packing factor and structures. Shorter vibration time results in a skeleton type of microstructure, while a graded structure was formed when the system reaches a non-equilibrium steady state. The vibrated beds were uniaxially pressed to manufacture sintered W preform with a graded interconnected porosity. High temperature sintering treatments complete the evolution of a steeper gradient in porosity predominantly through coalescence process. Electrical and elastic properties of the final materials, produced by infiltration of Cu into the sintered W preforms, are strongly influenced by the W microstructural evolution. It has been shown that the optimal microstructure for electrical properties consists of a highly 3D interconnected Cu phase (skeleton type of microstructure), while the graded structure exhibits higher E-modulus. This work was undertaken to better understand the nature of the graded structure and to study the relationship between the self-formed microstructure types, electrical and elastic materials properties.

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Introduction

Granular medium (GM) has been usually defined as collection of particles kept together through the action of gravity, with repulsive forces between the particles, and with many different metastable states which can determine static condition of the system. Dynamical properties and flow of GM have long intrigued physicists who studied them, like Faraday, Maxwell, and Reynolds, as reviewed by Jaeger and Nagel [1]. In general, excited GM exhibits very complex relaxation behavior while reaching non-equilibrium steady state. One, among several phenomena occurring in vibrated GM is size segregation, i.e. Brazil Nut Effect. Size segregation is mainly determined by: excitation level, particle size, and friction force and is manifested by different particle velocity and direction of the particle motion. With elapsing time this process enriches a position with lower potential energy with the smaller particles, which move into the gaps between larger particles, leading to rise of the larger particles [2]. Depending on excitation level GM can segregate through convection rolls, geometrical segregation aided by surface convection, and solely by geometrical segregation [3, 4]. In the present work size segregation of the weakly excited W bimodal GM, i.e. regime of geometrical segregation, was used to form graded porous W structures suitable to produce Cu-W functionally graded material (FGM) in a continuous way.

High thermal stability and low thermal expansion of W and high thermal conductivity of Cu, allow application of Cu-W FGM in extreme environmental conditions, like as high flux components in diverter structure for the future nuclear fusion reactor, ITER, high voltage arc contact material, and electrodes for resistance welding and spark erosion [5].

Prediction of thermal and electrical conductivities, as well as elastic constants of graded material, where microstructural field cannot be assumed to be homogeneous, is a very complex case and therefore models and approximations used for traditional composites [6], are not directly applicable. Therefore, in this study the relationship between obtained microstructure and electrical/mechanical properties was considered. Also, to improve a production route for FGM, the possibility to control and enlarge the gradient in porosity of the sintered tungsten preform was examined.

Experimental part

Tungsten powders with two average particle sizes (APS): 1) 1–5 μm and 2) 45–75 μm were used in this study. Initial powders were agglomerated with polyvinylbutiral, giving agglomerate sizes of 45–60 μm (agglomerates A1) and 200–250 μm (agglomerates A2). The agglomerates were layered (50 Vol.% of agglomerates A1 and 50 Vol.% of agglomerates A2) in the following sequence: larger ones at the bottom and the smaller ones at the top of the container. The details of the experimental procedures were presented elsewhere [4]. To study the temporal evolution of segregation the tungsten agglomerates were vibrated at a frequency of 600 Hz, with the acceleration of 6 g for different times (60, 100, and 120 min), under an absolute humidity in the range of 8–10 g/m^3. The vibro-compaction process was monitored through a change of GM-bed height. For that purpose a laser device with a beam spot size of 70 μm and with a resolution of the dimensional measurement of 1 μm was applied. The experimental setup was placed in a closed chamber and connected to the vibrational plate. The humidity in the chamber was controlled by using a humidity source with a Peltier element and a water condensator. Sintered W preforms were subsequently infiltrated with molten Cu at 1523 K, for 3 h in a reducing atmosphere. The microstructure of the final material was examined with optical (OM) and scanning electron microscopy (SEM). The quantification of porosity and phase volume fractions, as well as determination of W–W contiguity, as an indicator of the interconnectivity of W phase, was carried out by image analysis. The concentration profiles were also evaluated by the image analysis to follow the temporal evolution of segregation and microstructure. Electrical resistivity was determined by the four-probe test method from 293 to 973 K under a flow of N_2. The measurements were conducted using a direct current of 100 mA. The samples had the final cross-section dimension: 0.5 × 2.1 mm and the length of 8.5 mm. To improve the contact points, on the polished W-rich sample side a thin W layer (thickness of 200 μm) was deposited by PVD technique. Puls echo ultrasonic test was used for determination of E-modulus and position dependent elastic constant was investigated by B-scan method [7].

Results and discussion

In the following the formation of graded W skeleton via the complex interaction of W agglomerates of different sizes subjected to inertial variable vertical vibrations are reported and analyzed theoretically. Two important criteria have to be met to produce material taking advantages from the size segregation. First of all, agglomerate size difference should be large enough to provoke size segregation. Secondly, initial particles should to have reasonably high surface energies to perform effective sintering (driven by solid state mechanisms). Subsequently, the elastic and electrical properties of graded W-Cu composites (made by initially sintering the above graded W and finally infiltrating with molten copper the sintered W preforms) are reported and discussed.

Self-formed graded structure: nature, microstructural characteristics, and temperature development

Intensity of vibration and particle size ratio are the two main parameters affecting size segregation. The effect of vibration intensity on the segregation process in bimodal Cu-W GM system was studied in our previous work [4], and it was observed that weakly excited bimodal GM segregates in a manner that a gradient in packing was self-formed. In this work, under applied experimental conditions, i.e. constant acceleration and particle size ratio, segregation is predominantly determined by the interparticle friction forces. It has been observed that a variation in ambient humidity (Ha) affects the interagglomerate forces, causing different particle motion under vibration. This motion dynamics depend on the contributions of the electrostatic charge and humidity [8]. Under a low humidity (Ha $<$ 8 g/m^3) inverse Brazil nut effect [9] or single convection roll occur and segregation is dependent on the electrostatic charge in the GM bed [8]. GM bed rotation dominates under a high humidity (Ha $>$ 10 g/m^3), while under a moderate humidity segregation propagates primarily through hopping, which is diffusion-like process or hopping combined with moderate surface toroidal convection [4, 10].

Under an absolute humidity in the range of 8–10 g/m^3 smaller agglomerates A1 diffuse through hopping, thereby changing their configuration in the potential energy gradient [11, 12]. In that way a gradient in particle packing was obtained, that after sintering turns into a porosity gradient and later on, after infiltration, into a concentration gradient. The segregation process itself is explained in more detail elsewhere [4, 10]. Here, it will be pointed out that segregation of the bimodal GM is dominantly controlled by the motion of the smaller particles and progresses through three different stages: percolation, intermediate stage, and non-equilibrium steady stage. In the percolation stage smaller particles fall into cavities between large ones forming a network structure. In the intermediate stage the motion of the smaller agglomerates, through hopping to available positions, drive the motion of the larger agglomerates toward the top of the container. In this stage large particles form a 3D skeleton structure rearranging themselves possibly toward hexagonal close packing, but reaching only random close packing limit, as observed by Breu et al. [13] for spherical particles. Segregation process is completed when the non-equilibrium steady state is reached—where a graded packing is formed. This steady state is reached as a consequence of the competition between the segregation process promoted by the hopping of the smaller agglomerates and the capillary forces acting under the moderate humidity condition. Each of these stages is associated to different microstructure types which determine the material properties. This relationship will be discussed later on.

The most interesting question addressed in this study was: what may be the nature of the graded packing structure? A simulation of density relaxation in a frustrated lattice gas, performed by Nicodemi et al. [14] was used to explain the intrinsic nature of the obtained graded packing structure. Such study showed that for a long-time behavior the diffusion coefficient becomes zero when the density reaches the random close packing limit, signalizing a localization in which particles are confined in local cages and macroscopic diffusion-like process are suppressed. In the current study, the weakly excited bimodal W GM finally reached a steady state. This steady state depends on the competition between the internal force of the granulate, determined by the contact force network and the segregation phenomena. The graded packing observed in this steady state was considered as the most effective packing model. Above this density, attributed to the random close packing limit [13], it is impossible to obtain a further macroscopic rearrangement of the particle without increasing the system volume. This phenomenon seems to correspond to the Reynold‘s transition observed in GM [14, 15] and probably to total segregation. In our previous work [4] it was shown that depending on the humidity and excitation intensity the system was also able to reach the steady state characterized by complete segregation, when the agglomerates were completely separated in the opposite way as in the initial configuration (larger agglomerates at the top and smaller at the bottom of the container).

Microstructure and corresponding concentration profile of the graded structure, obtained in the steady state, after 2 h vibration, are presented in Fig. 1. Also, in the same figure development of the graded structure and the corresponding concentration profiles at higher sintering temperature and two sintering times are shown. With the increase in sintering temperature and time, the concentration profile spreads in the range of a higher gradient. In the case of the W skeleton sintered at the lower temperature (1723 K), concentration gradient is between 100 and 70 Vol.% W (Fig. 1b), while at the high sintering temperature (2073 K) the profile expands in the range between 100 and 15 Vol.% W (Fig. 1f).

Observed microstructural development (Fig. 1a, c, and e) can be assigned to porosity reorganization, as firstly recognized by Kingery and Francois [16]. Only those pores with coordination number lower than critical coordination number, $R < Rc$ (in this work corresponding to-intraagglomerate pores) are able to disappear during sintering. On the other hand, pores with $R > Rc$ (interagglomerate pores) will grow. As a consequence, reduction of the intraagglomerates porosity occurs readily, while the interagglomerate voids become larger. This result is an illustrative example, that thermodynamically driven porosity redistribution can facilitate formation of a profile with extended spatial gradient.

Elastic properties

To study the relationship between the self-formed packing structures during vibro-compaction of the W GM and the properties of the final Cu-W materials, effective Young's modulus of elasticity and position dependent E-modulus were measured. The compaction behavior of all three segregation stages (percolation, intermediate, and steady state) obtained after 60, 100, and 120 min of vibration, respectively, is presented in Fig. 2a, c, and e. Figure 2b, d, and f illustrates the position dependent E-modulus profiles, investigated by B-scan model and the corresponding concentration profiles.

At the beginning of the vibro-compaction, the linear part of diagram (Fig. 2a) corresponds to a high kinetic condition and low dissipation forces, and activated-like hopping description has been proposed as the model to describe particle motion [17, 18]. In this situation the individual and independent particle motion dominated and the network configuration is readily broken. Later on, at the end of the percolation stage (after 2600 s) and in the intermediate stage (till 6000 s) the friction forces increase and the

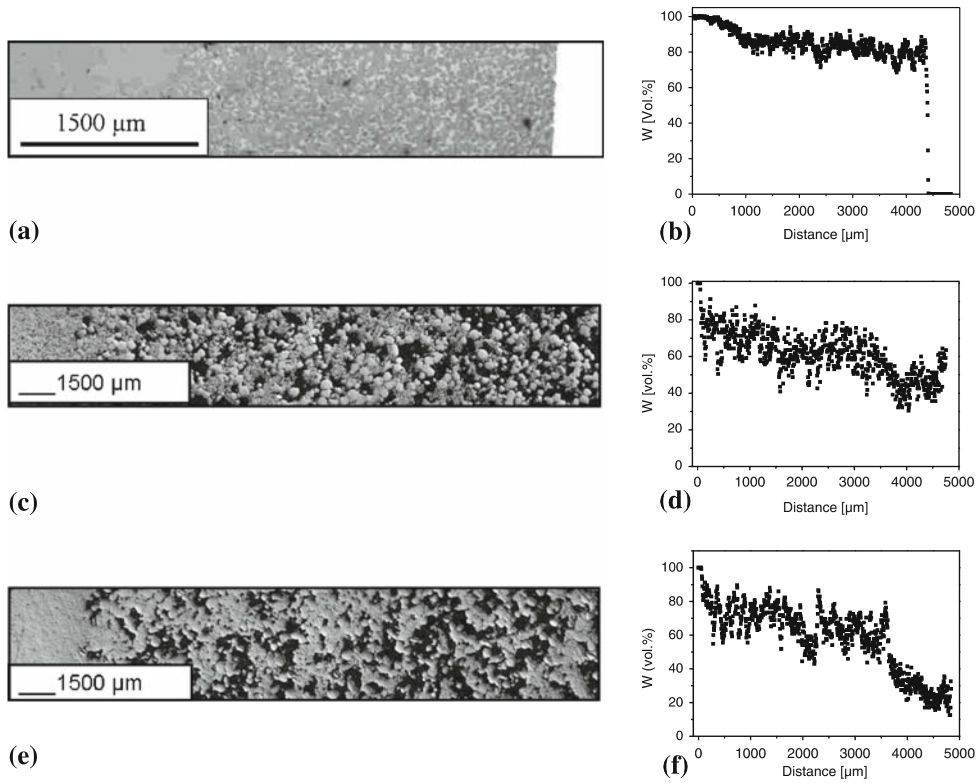

Fig. 1 Microstructure of W-Cu graded material: W skeleton sintered at 1723 K 3 h and infiltrated with Cu (**a**) and corresponding concentration profile (**b**) (white Cu, dark gray W). Microstructures of W skeleton sintered at 2073 K 1 h (**c**); and 3 h (**e**) and corresponding concentration profiles (**d**), (**e**), respectively (black pores, light gray W)

system experiences the competition between individual particle relaxation ("elastic rearrangement") and more complex non-elastic particle rearrangement with collective behavior [17]. This process involves inelastic microscopic processes at the surfaces between the particles such as: plastic and viscoplastic deformation, fatigue, surface fracture, blow out, and other form of localized dissipative process [18]. This compaction stage exhibits a diffusion nature and the macroscopic manifestations of the collective processes are characterized by a nearly homogeneous distribution of large particle and intensive density fluctuation observed in the compaction curve [4]. After 120 min of vibration, through a predominantly slow collective motion of close packed clusters, the system reaches the steady state.

It was observed that E-modulus profiles (Fig. 2b, d, and f, open data points) were largely influenced by several factors: concentration profile, packing characteristics, porosity, pore distribution, number and quality of interfaces. Clear agreement of the E-modulus profile and concentration profile is presented for the sample vibrated for 60 min (Fig. 2b). Samples vibrated for longer times (100 and 120 min) exhibit clear deviations from concentration profiles (Fig. 2d, f). It was assumed that the larger number of local interfaces, more uniform porosity and particle distribution, and better packing density prevail over the effect of concentration; therefore, samples vibrated for longer times show nearly uniform E-modulus profile with higher E-modulus values.

The results corresponding to the microstructural parameters of the self-formed structures, as well as their elastic and electrical properties are summarized in Table 1. The percolation stage (after 60 min of vibration) reveals the poorest packing density, while after 2 h of vibration the obtained graded packing has highest packing density. The sintered graded structure has almost 10% higher density compared to the structure in percolation stage (Table 1). Consequently, the higher density structure has been characterized by the lower content of infiltrated Cu. The higher E-modulus obtained in graded structure is attributed to the higher W-content and the higher W–W contiguity (Table 1). Sintered W skeleton at 2073 K shows an important improvement in elastic constant. These results are in good agreement with commercially available homogeneous Cu-W composites with similar composition, where E-modulus is in the range of 200–225 GPa [19].

Electrical properties

Electrical resistivity (ρ) has been selected in this study to compare the electrical properties of the Cu-W materials. The electrical resistivity is strongly dependent on the W packing structures self-formed after different durations of applied vibro-compaction process. During sintering, due to

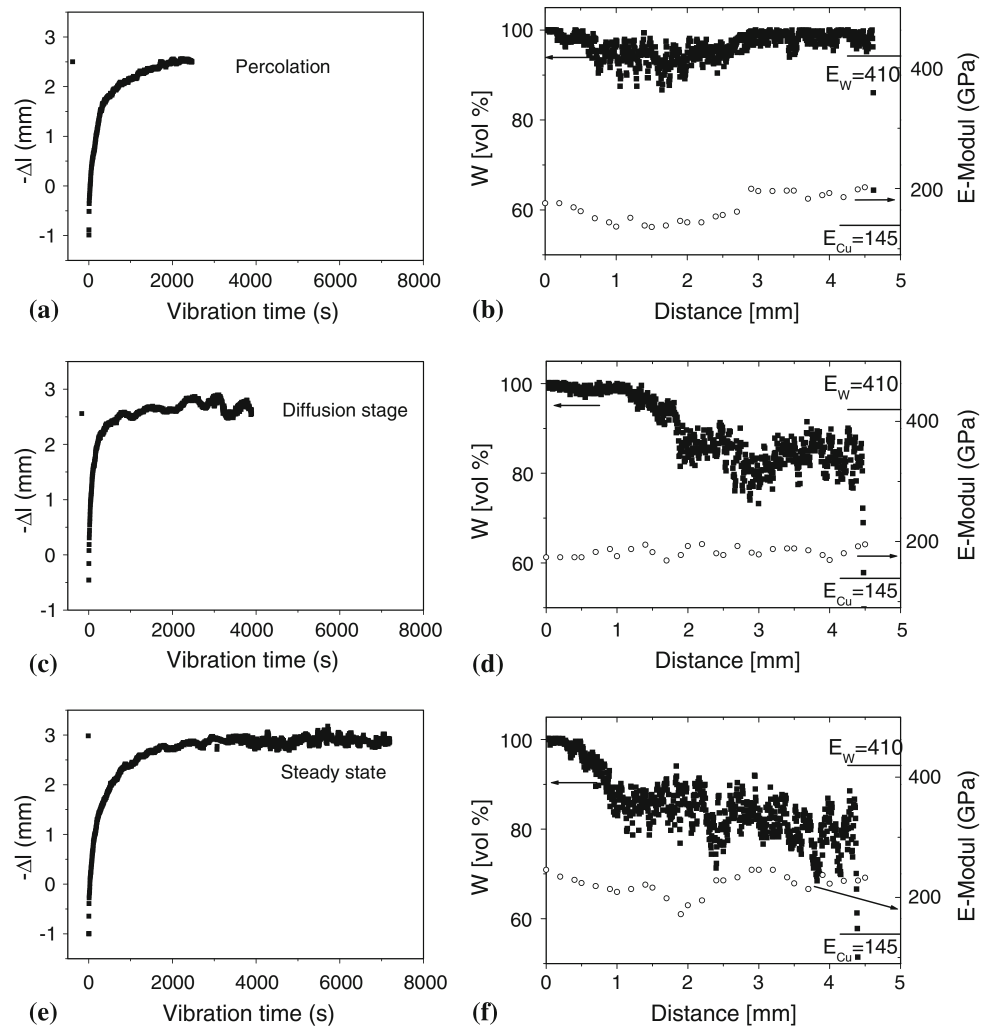

Fig. 2 Compaction curves, as bed contraction ($-\Delta l$) versus vibration time, for W bimodal GM vibrated for different times: 60, 100, and 120 min are presented in **a**, **c**, and **e**, respectively. Concentration profiles and corresponding E-modulus profiles obtained by B-scan ultrasonic method of Cu-W materials made of self-formed W preforms infiltrated with molten Cu are shown in **b**, **d**, and **f**

Table 1 Microstructural characteristics, E-modulus and electrical resistivity of Cu-W composite materials

Vibration time (min)	$\%\rho_t$ (1723 K)	Porosity (%)	Contiguity[a] (%)	wt% C_{inf}	E-modulus GPa[b] (1723 K)	E-modulus GPa[b] (2073 K)	ρ^c (Ωm)
60	50.0	1.85	27.2	37.2	175	241.46	4.635
100	58.3	0.39	32.1	35.2	173	257.27	4.764
120	59.3	0.5	36.5	32.3	229	284.46	5.647

[a] Contiguity was estimated with an error of 2.73%

[b] E modulus was measured with an accuracy of 2.66 GPa, on samples sintered at two temperatures: 1723 and 2073 K

[c] Electrical resistivity (ρ) was measured with an accuracy of 0.12×10^{-8} Ωm

significant neck growth [10, 20] such W packing structures turn into interconnected W networks which dominantly determine the complicated current path through the Cu-W composite structures. The dependence between electrical resistivity and contiguity of W phase with vibration time is shown in Fig. 3. The lowest resistivity was obtained for the shorter vibration duration of 60 min (Table 1). Additionally to the higher Cu content, this may be also attributed to the lower contiguity of the W phase, which limits the current path through the W phase. In the structure with skeleton of the large agglomerates (100 min of vibration) W–W connections are more numerous and therefore the effective resistivity is higher. For the graded structure the highest resistivity is obtained which can be assigned to the larger contribution of current paths through the W phase.

Figure 4 shows the temperature dependence of the electrical resistivity for the various specimens prepared in this work. The electrical resistivity increases nearly linearly with temperature. The Cu-W systems exhibit behavior which is between those for pure Cu and pure W. It should

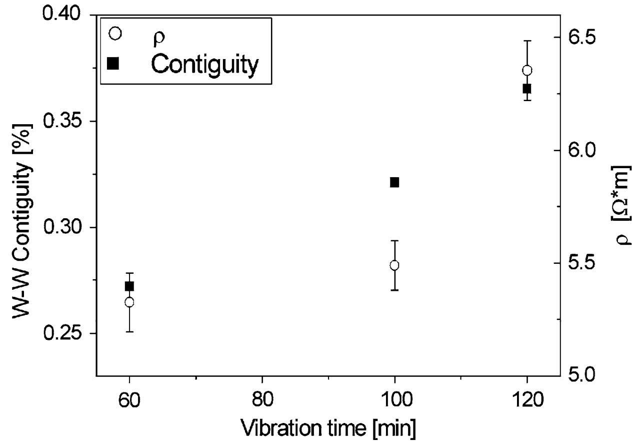

Fig. 3 Electrical resistivity (ρ) and contiguity of W phase as a function of vibration duration in the sample sintered at 1723 K for 3 h

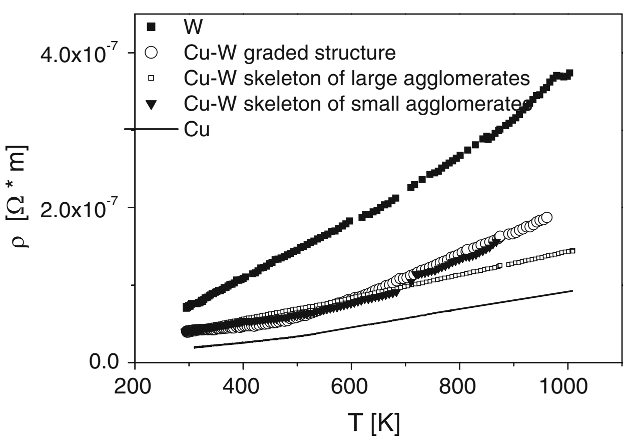

Fig. 4 Electrical resistivity (ρ) as a function of temperature for Cu-W composites, pure Cu, and W

be noted that pure Cu and Cu-W systems are characterized by similar slopes (at least for $T < 673$ K), indicating electron–phonon interaction as the main effect controlling the electrical resistivity. On the other side, above 673 K, the graded sample and sample in the percolation stage (W skeleton of small particle) show similar behavior as pure W phase, which is believed to be a consequence of the W contact network characteristics (Table 1) and attainable residual stresses.

Conclusions

Tungsten skeleton with a gradient in porosity is obtained by vibration of bimodal agglomerate systems. Prior to formation of the graded packing structure, vibrated powder passes through state of skeleton type of microstructure. Firstly, skeleton of small agglomerates is formed, and afterward skeleton of larger agglomerates develops. Particle motion under vibration is strongly influenced by interparticle forces, which vary with intensity of vibration and variation of ambient humidity. Depending on ambient humidity particle motion can be mainly influenced by: (i) single convection or inverse Brazil nut effect—under low ambient humidity, (ii) GM bed rotation—under high humidity, and (iii) hopping or hopping combined with moderate surface toroidal convection—under moderate humidity ($8\ g/cm^3 < Ha < 10\ g/cm^3$). The gradient in packing of bimodal W granular media is self-formed in the steady state which is reached as a consequence of segregation process promoted by the hopping of smaller agglomerates and capillary force acting under moderate humidity condition. Second important contribution coming from vibration is the significant increase in packing density obtained in the graded samples compared to the skeleton ones. Therefore it has been proposed that graded packing model represents the most effective packing configuration. By applying appropriate sintering cycles it is possible to enlarge the obtained gradient in concentration, predominantly through the redistribution of porosity.

The resulting electrical and elastic characteristics of Cu-W materials represent the combined effect of composition and W–W contiguity. The graded sample has a larger E-modulus compared to sample with skeleton type of microstructure. Electrical resistivity of these composites is between those for pure W and Cu, and depends strongly on the vibration time of initial W agglomerates. The resistivity increases nearly linearly with the temperature. The Cu-W composite materials show similar behavior below 673 K to that for pure Cu that indicates electron–phonon interaction as the main effect controlling the electrical resistivity.

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