

## Comparison of the effects of microwave and spark plasma sintering on the electrical, thermal, and mechanical properties of Cu-LaB<sub>6</sub> nanocomposites

*Mikrodalga ve kıvılcım plazma sinterlemenin Cu-LaB<sub>6</sub> nanokompozitlerin elektriksel, ısı ve mekanik özellikleri üzerindeki etkilerinin karşılaştırılması*

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### Abstract

The effects of lanthanum hexaboride (LaB<sub>6</sub>) nano-particles on the electrical, thermal, and mechanical properties of copper-based nanocomposites (Cu-LaB<sub>6</sub>) produced using microwave sintering (MS) and spark plasma sintering (SPS) processes were investigated in this study. Nano LaB<sub>6</sub> particles reduced the electrical conductivity of Cu matrix nanocomposites produced via MS and SPS by 20% and 13%, respectively. Cu-LaB<sub>6</sub> nanocomposites had lower thermal conductivity than unreinforced Cu. The electrical and thermal conductivities of the Cu-LaB<sub>6</sub> nanocomposite produced by the SPS process were higher than those of the Cu-LaB<sub>6</sub> nanocomposite produced by the MS process. An equation that takes particle volume ratio and porosity into account was developed to predict the thermal conductivity of nanocomposites from their electrical conductivity. The calculated thermal conductivity values for Cu-LaB<sub>6</sub> nanocomposites were very close to the experimental results. Cu-LaB<sub>6</sub> nanocomposites had much higher hardness and compressive strength by 49% and 38%, respectively, compared to those of unreinforced Cu. The hardness and compressive strength of the Cu-LaB<sub>6</sub> nanocomposite produced by SPS were higher than those of the Cu-LaB<sub>6</sub> nanocomposite manufactured via MS. Although nano LaB<sub>6</sub> reinforcement particles reduced the electrical and thermal conductivities of Cu, Cu-LaB<sub>6</sub> nanocomposite having high hardness and compressive strength were produced by combining the positive influences of nano LaB<sub>6</sub> reinforcement particles and the SPS process.

**Keywords:** Copper, Electrical and thermal conductivity, Microwave sintering, Nanocomposite, Nano-LaB<sub>6</sub>, Spark plasma sintering

### Öz

*Çalışmada, nano lantan heksaborid (LaB<sub>6</sub>) partiküllerinin, mikrodalga sinterleme (MS) ve kıvılcım plazma sinterleme (SPS) işlemleri kullanılarak üretilen bakır esaslı nanokompozitlerin (Cu-LaB<sub>6</sub>) elektriksel, ısı ve mekanik özellikleri üzerine etkileri araştırılmıştır. Nano LaB<sub>6</sub> partikülleri, MS ve SPS ile üretilen Cu matrisli nanokompozitlerin elektrik iletkenliğini sırasıyla % 20 ve % 13 oranında azalmasına neden olmuştur. Cu-LaB<sub>6</sub> nanokompozitleri, takviyesiz Cu'dan daha düşük termal iletkenliğe sahip olmuştur. SPS metodu ile üretilen Cu-LaB<sub>6</sub> nanokompozitinin elektriksel ve ısı iletkenlikleri, MS ile üretilen Cu-LaB<sub>6</sub> nanokompozitinden daha yüksek olmuştur. Nanokompozitlerin ısı iletkenliğini elektriksel iletkenliklerinden hesaplayabilmek için partikül hacim oranını ve gözenekliliği dikkate alan bir denklem geliştirilmiştir. Cu-LaB<sub>6</sub> nanokompozitler için hesaplanan ısı iletkenlik değerleri deneysel sonuçlara oldukça yakın sonuçlar vermiştir. Cu-LaB<sub>6</sub> nanokompozitleri, takviye edilmemiş Cu malzemelere göre sırasıyla % 49 ve % 38 oranında daha yüksek sertliğe ve basma dayanımına sahip olmuştur. SPS yöntemi ile üretilen Cu-LaB<sub>6</sub> nanokompozitinin sertliği ve basma dayanımı, MS ile üretilen Cu-LaB<sub>6</sub> nanokompozitinden daha yüksek olmuştur. Nano LaB<sub>6</sub> partiküllerinin, Cu'nun elektriksel ve ısı iletkenliklerinin bir miktar düşmesine neden olmasına rağmen, nano LaB<sub>6</sub> partikülleri ile SPS işleminin olumlu etkileri biraraya getirilerek, yüksek sertlik ve basma dayanımına sahip Cu-LaB<sub>6</sub> nanokompozit üretilmiştir.*

**Anahtar kelimeler:** Bakır, Elektriksel ve ısı iletkenlik, Mikrodalga sinterleme, Nanokompozit, Nano-LaB<sub>6</sub>, Kıvılcım plazma sinterleme

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## 1. Introduction

Copper is one of the most common metallic materials used in a variety of applications such as electronics and machinery due to its high electrical and thermal conductivities and remarkable mechanical properties (Schipper et al., 2018; Li et al., 2020). Although copper has such good properties, its high thermal expansion and low wear resistance restrict its use in some applications. Copper (Cu) matrix composites are potential materials for overcoming these drawbacks of copper and allowing it to be used in applications such as brushes of DC motor and fusion heat sinks (Raj et al., 2018; Tejado et al., 2018).

Cu matrix composites have been developed by reinforcing Cu with various reinforcement particles such as TiB<sub>2</sub> (Ren et al., 2019), TiC (Afzal and Harish, 2020), WC (Dias et al., 2019), ZrO<sub>2</sub> (Fathy et al., 2019), SiC (Somani et al., 2018), Al<sub>2</sub>O<sub>3</sub> (Strojny-Nędza et al., 2018), and NbC (Bian et al., 2021). The electrical, thermal, and mechanical properties of Cu matrix composites vary depending on factors such as reinforcement particles and production processes. For example, the hardness, tensile strength, and wear resistance of Cu matrix composites are improved by adding reinforcement particles to the Cu matrix and increasing their volume or weight fractions (Singh et al., 2019; Shaik and Golla, 2020; Yin et al., 2020). However, due to the low electrical conductivity of reinforcement particles, the electrical conductivity of Cu matrix composites decreases. Satishkumar et al. produced Cu matrix composites by adding WC and SiC particles at the volume fractions ranging from 2.5 to 7.5% and suggested that the electrical conductivity of Cu-WC/SiC composites decreased as the amount of WC/SiC particles increased due to the non-conducting effect of the reinforcement particles (Satishkumar et al., 2021). Kumar et al. studied the electrical and mechanical properties of Cu-TiB<sub>2</sub> composites and reported that adding TiB<sub>2</sub> particles to the Cu matrix improved the strength of Cu-TiB<sub>2</sub> composites by up to 5 wt.% TiB<sub>2</sub>, whereas the electrical conductivity of Cu-TiB<sub>2</sub> composites decreased as the weight fraction of TiB<sub>2</sub> particles increased (Kumar et al., 2017). In a study on Cu matrix composites reinforced with ZrO<sub>2</sub> particles, it was found that increasing the weight fraction of ZrO<sub>2</sub> increased the hardness of the Cu-ZrO<sub>2</sub> composites while decreasing their electrical resistivity (Fan et al., 2019). The thermal conductivity of Cu-matrix composites was found to behave similarly to electrical conductivity with regards to the effects of reinforcement volume or weight fractions (Wang et al., 2011).

Cu matrix composites are manufactured using a variety of methods such as casting and powder metallurgy (Sridhar et al., 2020). During the production of these conventional methods, porosity or undesirable interface reactions might occur, resulting in an additional decrease in the electrical and thermal conductivities and mechanical properties of Cu matrix composites. Microwave sintering and spark plasma sintering (SPS) outperform conventional methods in improving the properties of metal matrix composites. Microwave sintering has benefits such as enhanced diffusion and lower sintering temperatures (Oghbaei and Mirzaee, 2010), while SPS has advantages such as high densification and restriction of undesired reactions. (Cavaliere et al., 2019). Chmielewski et al. compared the effect of SPS with the influence of conventional hot pressing method on the thermal conductivity of Cu matrix composites reinforced with 5, 10, 15, 20, and 25 vol.% of SiC. It was found that while the thermal conductivities of Cu-SiC composites manufactured by SPS and hot pressing methods decreased with an increase in the amount of SiC particles, the thermal conductivity of specimens produced by the SPS method was higher than that of specimens produced by the hot pressing method (Chmielewski et al., 2017). Ayyappadas et al. investigated the effects of microwave-assisted sintering versus conventional sintering on the electrical conductivity and hardness of Cu-SiC composites (2.5, 5, and 7.5 wt.%) (Ayyappadas et al., 2017). It was reported that as the weight fraction of SiC particles increased, hardness increased but electrical conductivity decreased, and it was shown that the electrical conductivity and hardness of Cu-SiC composites produced by microwave sintering were higher than those of conventional sintering specimens.

Nano-sized reinforcement particles are much more efficient in enhancing the mechanical properties of Cu matrix composites than micro-sized particles (Panda et al., 2014). However, reducing the size of the reinforcement particles lowers the electrical and thermal conductivities of Cu matrix composites (Kargul et al., 2018). While maintaining the positive effect of nanoparticles on mechanical properties, their negative effect on electrical and thermal conductivity can be eliminated by using reinforcement particles with higher conductivity. As compared to other types of reinforcement particles used in Cu matrix composites, lanthanum-based particles such as LaB<sub>6</sub> and La<sub>2</sub>O<sub>3</sub> have a high electrical conductivity. For this reason, recent studies on Cu matrix composites have focused on lanthanum-based

particle reinforced Cu matrix composites (Cong et al., 2019; Solodkyi et al., 2020).

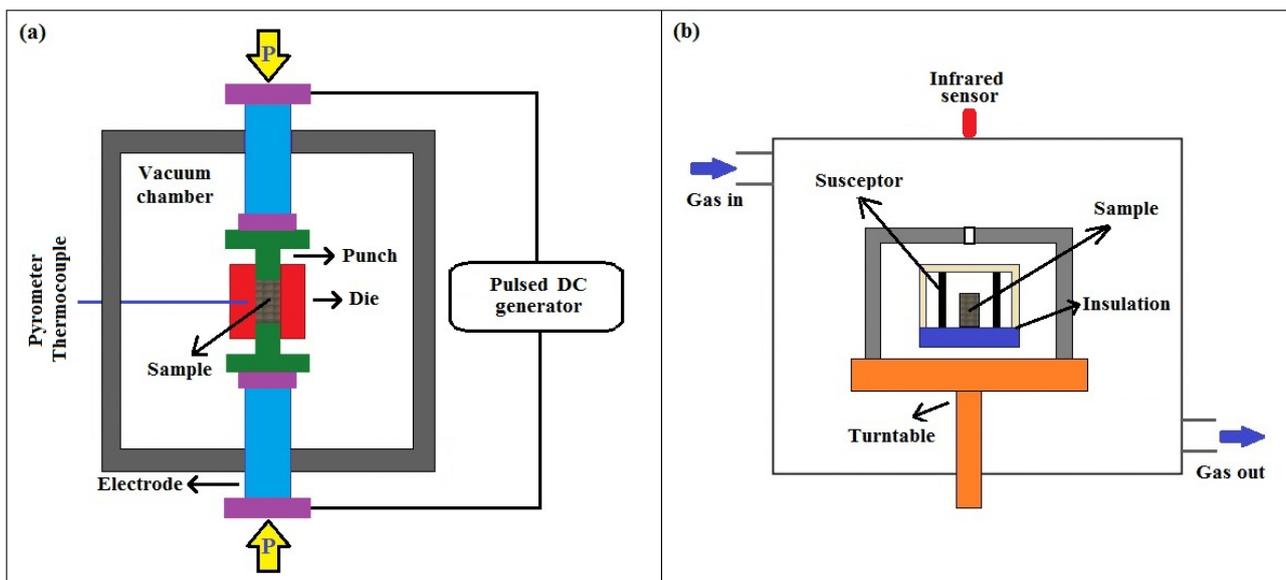
Considering the positive effects of nano-sized particles, LaB<sub>6</sub> particle, and microwave sintering and SPS on the mechanical and electrical and thermal conductivities of Cu matrix composites, in this study, Cu matrix nanocomposites were produced by reinforcing with nano-sized LaB<sub>6</sub> particles using microwave and SPS methods, and electrical, thermal, and mechanical properties of Cu-LaB<sub>6</sub> nanocomposites were investigated.

## 2. Materials and methods

Copper (Cu) (33±7 μm) with a purity of 99.1% and lanthanum hexaboride (LaB<sub>6</sub>) particles (45 nm) were used to produce Cu-LaB<sub>6</sub> nanocomposites.

Taking into consideration the amount of ceramic reinforcement particles in which the maximum

(better) values of physical and mechanical properties of Cu matrix composites, such as electrical conductivity and compressive strength, were obtained in the studies found in the literature (Taha and Zawrah, 2017; Lakshmanan et al., 2019; Moustafa and Taha, 2021), the volume fraction of nano-LaB<sub>6</sub> reinforcement particles in this study was determined to be 2%. To distribute the nano-LaB<sub>6</sub> particles uniformly in Cu powders, a mechanical milling process was performed in a high-energy ball milling machine at a rotational speed of 350 rpm, a ball/powder ratio of 30:1, and an argon atmosphere, for 24 hours. Milling balls and jars were made of 304 stainless steel. Stearic acid was used as a process control agent to avoid excessive cold welding and bonding between powders and balls, and also to minimize powder agglomeration during the high-energy ball milling process.



**Figure 1.** Schematic figures of (a) spark plasma sintering (SPS) and (b) microwave sintering (MS)

Mechanically milled Cu-LaB<sub>6</sub> powders were consolidated using microwave sintering (MS) and spark plasma sintering (SPS) to produce specimens with a diameter of about 13 mm and a height of about 25 mm (Figure 1). According to a literature review (Ngai et al., 2013; Ayyappadas et al., 2017; Sathish et al., 2019; Pellizzari and Cipolloni, 2020), in this study, the optimum values for the production parameters in MS and SPS methods used to produce ceramic particle-reinforced Cu matrix composites were determined, and these values were taken as high as possible in order to achieve higher density, which leads to better mechanical and physical properties such as compressive strength and electrical conductivity,

as well as to avoid excessive grain growth, which has a negative effect on the properties of the materials. Prior to the microwave sintering process, powders were pressed at a pressure of 400 MPa in a steel mold. The compacted specimens were sintered in a microwave furnace (2.45 GHz) to 900 °C at a heating rate of 25 °C/min, a holding time of 30 min, and a 95%N<sub>2</sub>-5%H<sub>2</sub> atmosphere. SiC susceptor (microwave-absorbing element) was used to assist heating and sintering of the compacted specimens. Prior to the SPS process, powders were pressed at a pressure of 40 MPa in a steel mold. Because of the high number, large, and non-uniform distribution of the voids between the powders, loose powders poured into the die cavity

cause the current not to be homogeneously distributed in the powder sample throughout the SPS process, resulting in a temperature gradient during discharging. Inhomogeneous temperature distribution can also cause local discrepancies in Joule heating (Leich et al., 2020). However, in a compact structure formed by pre-compaction, this can make discharging and Joule heating more efficient during the SPS process since the contact points and areas of powders with each other will increase (Balice et al., 2021). For all of these reasons, in this study, pre-compaction was applied to the powders in order to make the powders more compact and then perform more effectively in the SPS process. Following the pre-compaction process of the powders, the SPS process was applied to the pre-compacted powders in a graphite die, at a compaction pressure of 50 MPa, a temperature of 900 °C, and a heating rate of 100°C/min under vacuum for 5 min. After dwelling at maximum temperatures for a set period of time in the SPS and MS processes, the specimens were cooled at a rate of 25 °C/min.

Since pores and voids in the microstructure have a significant impact on the electrical and thermal conductivities, and the mechanical properties of the materials, both experimental and theoretical densities of the specimens were determined in this study. The experimental density ( $\rho$ ) of specimens was measured according to Archimedes' principle using a high accuracy balancer ( $\pm 0.01$  mg). The theoretical density was calculated using the following equation:  $\rho_{th} = V_m \cdot \rho_m + V_r \cdot \rho_r$  (where  $V_m$  and  $V_r$  are the volume fractions of the matrix and the reinforcement particles, respectively, and  $\rho_m$  and  $\rho_r$  are the densities of the matrix and the reinforcement particles, respectively). Theoretical densities of Cu and LaB<sub>6</sub> were assumed to be 8.96 g/cm<sup>3</sup> and 4.72 g/cm<sup>3</sup>, respectively. The porosity percentage of the specimens was calculated as follows: Porosity (%) =  $(\rho_{th} - \rho) / \rho_{th}$ . The thermal conductivity ( $\lambda$ ) of the specimens was determined using the following equation:  $\lambda = \alpha \cdot \rho \cdot C_p$ , where  $\alpha$  is the thermal diffusivity,  $\rho$  is the density, and  $C_p$  is the specific heat capacity.  $\alpha$  and  $C_p$  were measured using a laser flash apparatus (NETZSCH-LFA 467 HyperFlash). The electrical resistivity of the specimens was measured by utilizing a high-precision micro-ohmmeter (Omega-CL8400). The measured electrical resistivity was then converted into the international annealed copper standard conductivity (%IACS) unit. The thermal conductivity, electrical conductivity, and density of the specimens were measured at room temperature. Measurements for electrical and thermal conductivities were repeated

five times for each specimen to obtain a more accurate result, and an average value was taken. Hardness testing of the specimens was conducted using a Vickers hardness tester (Shimadzu HMV-2) with a load of 0.3 kgf (2.942 N) for a dwell time of 10 s. Compression tests of the specimens were conducted at room temperature at a strain rate of 0.005 min<sup>-1</sup> (Shimadzu AG-IS-100 kN). The elemental analyses of the specimens were determined by XRD (X-ray diffraction) and XPS (X-ray photoelectron spectroscopy) analysis. SEM (scanning electron microscopy) was used to show the microstructures and the fracture surfaces of the specimens.

### 3. Results and discussion

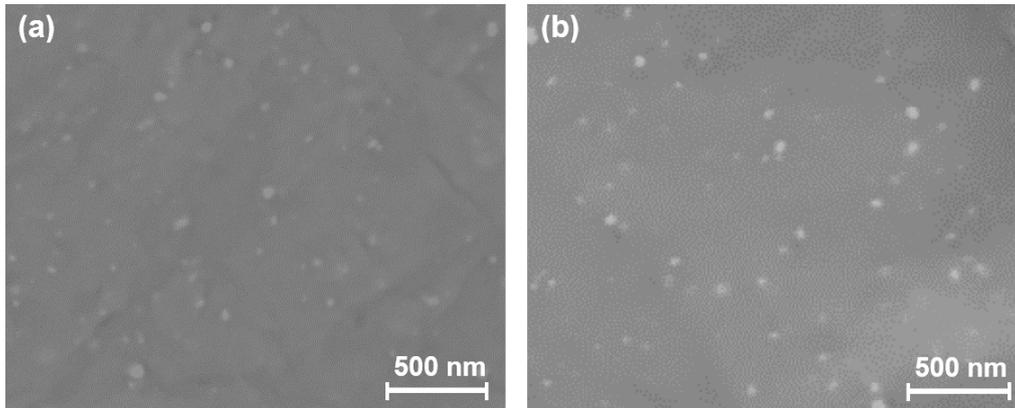
#### 3.1. Microstructure

Figure 2 shows the microstructures of Cu-LaB<sub>6</sub> nanocomposites produced using microwave sintering (MS) and spark plasma sintering (SPS) processes. As seen in Figure 2, nano Cu-LaB<sub>6</sub> reinforcement particles were distributed uniformly in the copper matrix through the high-energy ball milling process. XRD analysis of a Cu-LaB<sub>6</sub> nanocomposite specimen is shown in Figure 3. Three peaks were detected at  $2\theta$  values of 43.7°, 50.8°, and 74.4° degrees corresponding to (111), (200), and (220) of copper, respectively, while two peaks were identified at  $2\theta$  values of 20.7° and 30.2° degrees corresponding to (100) and (110) of LaB<sub>6</sub>, respectively.

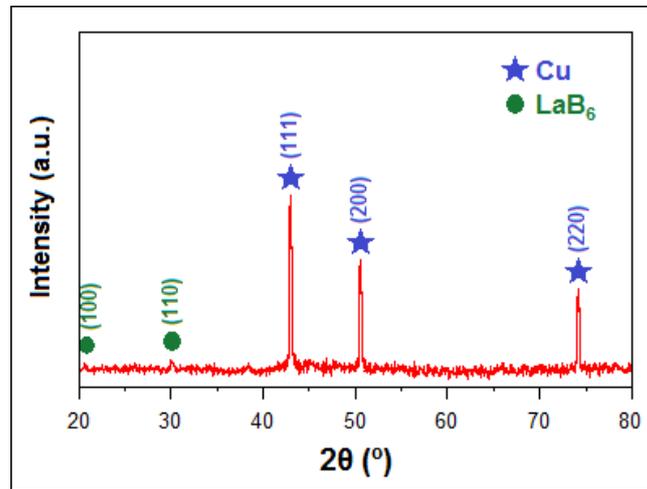
Table 1 shows the elemental compositions of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites produced using MS and SPS methods. In addition to the elements Cu, La, and B, XPS analyses revealed the elements C and O in relatively considerable amounts and Fe, Cr, and Ni in trace amounts in the specimens. It can be attributed to the following reasons. The elements of C, Fe, Cr, and Ni may have contaminated the powders during the high-energy ball milling process due to jar and ball wear. Because of the abrasive impact of reinforcement particles, this may have been more active in Cu-LaB<sub>6</sub> nanocomposites; therefore, the amount of these contaminants was higher in Cu-LaB<sub>6</sub> nanocomposites than in unreinforced Cu, as seen in Table 1. It should be noted that stearic acid, which was used in the high-energy ball milling process, may have caused a significant amount of C to be found in the specimens. The O contamination found in the specimens may have been resulted from the oxidation of powders before and during the manufacturing processes (particularly the high-energy ball milling process).

A higher amount of O in the specimens produced using the MS method, which can be attributed to the longer processing time in the MS method compared to the SPS method. These contaminants

may have an influence on material properties such as electrical conductivity (Ayyapadas et al., 2017; Degroh and Balachandran, 2018).



**Figure 2.** SEM images of Cu-LaB<sub>6</sub> nanocomposites produced using (a) microwave sintering (MS) and (b) spark plasma sintering (SPS) processes



**Figure 3.** XRD analysis of Cu-LaB<sub>6</sub> nanocomposite

**Table 1.** XPS elemental compositions (wt.%) of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites produced using MS and SPS

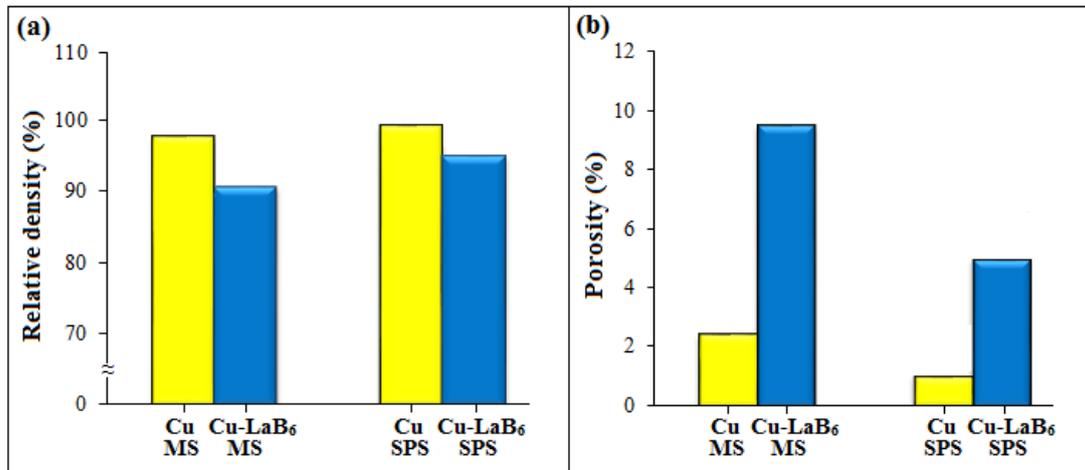
	Weight (%)							
	Cu	La	B	C	O	Fe	Cr	Ni
<b>Microwave sintering</b>								
Cu	Bal.	–	–	0.10	0.05	<0.01	<0.01	<0.01
Cu-LaB <sub>6</sub>	Bal.	0.69	0.32	0.09	0.04	<0.01	<0.01	<0.01
<b>Spark plasma sintering</b>								
Cu	Bal.	–	–	0.08	0.03	<0.01	<0.01	<0.01
Cu-LaB <sub>6</sub>	Bal.	0.71	0.33	0.09	0.03	<0.01	<0.01	<0.01

Compared to MS and SPS processes with each other, while the only temperature is efficient on pre-compacted specimens during MS, the

simultaneous application of temperature and pressure in the SPS process results in higher density. For all of these reasons, the relative density

of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposite produced by SPS was higher than that of manufactured through the MS process (Figure 4a);

in other words, the porosity level in the specimens produced by SPS was lower as seen in Figure 4b.

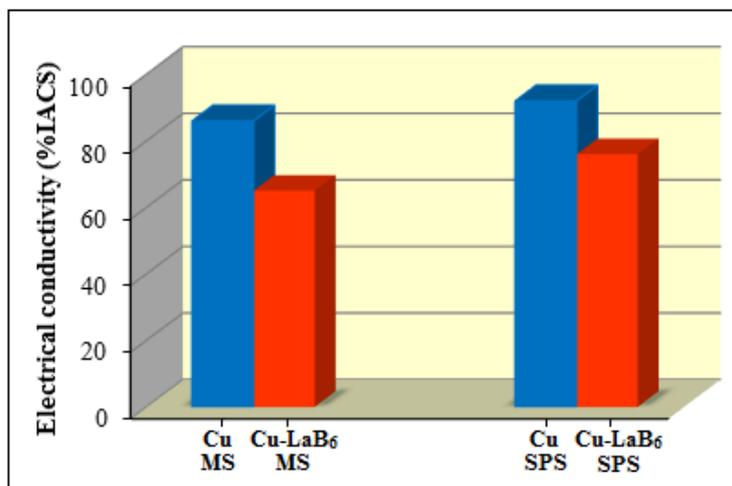


**Figure 4.** Relative densities and porosities of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites produced using MS and SPS

### 3.2. Electrical conductivity

Figure 5 shows the electrical conductivities of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites. The electrical conductivities of nanocomposites produced by MS and SPS were 20% and 13% lower, respectively, than those of unreinforced Cu manufactured using MS and SPS. The electrical

conductivity of unreinforced Cu produced through SPS was 8% higher than that of the specimen produced via MS. Similar behaviour was observed in Cu-LaB<sub>6</sub> nanocomposites. The electrical conductivity of the Cu-LaB<sub>6</sub> nanocomposite manufactured using the SPS method was 14% higher than that of the Cu-LaB<sub>6</sub> nanocomposite produced through MS.



**Figure 5.** Electrical conductivities of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites produced by MS and SPS

Electrical conductivity in a metallic material is determined by the mobility of charge carriers such as electrons, which is highly influenced by pores and voids in the microstructure. Pore and void can restrict the movement of charge carriers. In SPS, the DC pulse discharge generates spark plasma, spark impact pressure, Joule heating, and an

electrical field diffusion (Suárez et al., 2013). The formation of plasma during SPS has a direct impact on powder sintering. Spark discharge occurs in the space between the powders, which increases the diffusion rate due to the melting formed on powder surfaces, resulting in high density in SPS method (Saheb, 2013). It should also be noted that, as

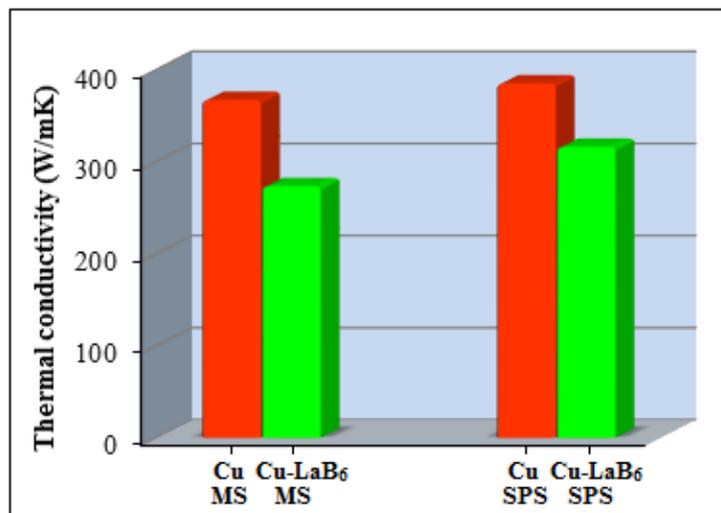
mentioned above, depending on the production method, the porosity level in the specimens produced by SPS was lower than that in the specimens manufactured through MS (Figure 4b), resulting in higher electrical conductivity in the specimens produced using the SPS (Figure 5).

The electrical conductivity of Cu-LaB<sub>6</sub> nanocomposites was lower than that of unreinforced Cu, as seen in Figure 5. It can be due to a number of factors caused by the addition of reinforcement particles. First, ceramic-based reinforcement particles such as LaB<sub>6</sub> have low electrical conductivity than metals such as Cu. Second, hard reinforcement particles resist the densification of powders during the compaction process. Third, if a mechanical milling process is applied to the powders prior to MS and SPS, this process will harden the powders, which leads to retarding the compaction of powders during pressing. The second and third factors result in a reduction in electrical conductivity by causing pores to form in the microstructure. In addition to these factors, elements found in copper metal, such as C and O, may tend to enhance the scattering rate of conducting electrons, resulting in a reduction in the electrical conductivity of the copper (Li et al., 2016; Ayyapadas et al., 2017; Degroh and Balachandran, 2018). Although the amount of Fe, Cr, and Ni contaminants in this study was insufficient to alter the electrical conductivity, C and O may have had a modest effect on the

reduction of electrical resistance. Furthermore, as seen in Table 1, the amount of O in the specimens produced using the MS method was higher than that in the specimens manufactured through the SPS method due to the longer processing time in the MS method. When compared to the SPS method, the relatively high amount of contaminants formed in the specimens produced by the MS method may have contributed to the reduction in electrical conductivity of the specimens. For all of these reasons (ceramic LaB<sub>6</sub> particles, pores, and contaminations), the electrical conductivity of Cu-LaB<sub>6</sub> nanocomposite produced using the MS method was lower than that of the SPS method.

### 3.3. Thermal conductivity

Thermal conductivities of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites are shown in Figure 6. Cu-LaB<sub>6</sub> nanocomposites had lower thermal conductivity than unreinforced Cu. Nano LaB<sub>6</sub> particles reduced the thermal conductivity of the specimens manufactured through MS and SPS as compared to that of unreinforced Cu specimens produced using the same processes. Heat in ceramics is only conducted by phonons while thermal conduction in metals is provided by both phonons and free electrons. This is one of the reasons why the thermal conductivity of LaB<sub>6</sub> particle reinforced nanocomposites was lower than that of unreinforced Cu specimens.



**Figure 6.** Thermal conductivities of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites produced by MS and SPS

Unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites produced by SPS had higher thermal conductivity than those manufactured through MS, which could be attributed to lower porosity in the specimens produced by SPS. It should be also noted that in

addition to negative effects of pore and reinforcement particles with low thermal conductivity, the interface between matrix and reinforcement is another factor that resists heat flow due to the scattering of phonons and electrons

in this region. Thermal conductivity of ceramic-particle reinforced metal matrix composites such as Cu-LaB<sub>6</sub> composite can further decrease as a result of these interfaces, which can be more important in nano-particle reinforced composites due to the greater number of nano-particle interfaces.

The Wiedemann-Franz law given in Equation (1) describes the relationship between the thermal conductivity ( $\lambda$ ) and the electrical conductivity ( $\sigma$ ) of a material containing freely moving electrons.

$$\frac{\lambda}{\sigma} = L T \tag{1}$$

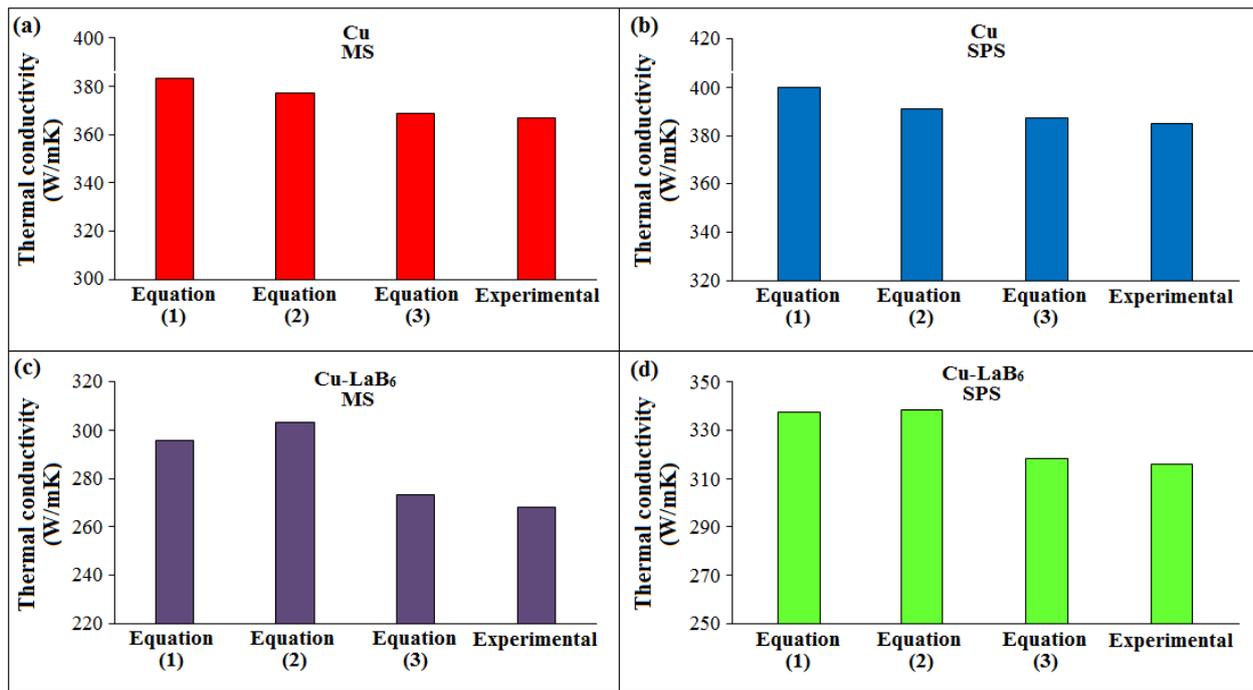
where  $L$  is the Lorenz number and  $T$  is the temperature. By taking into account phonons, which transport thermal energy but not electrical energy, the relationship between  $\lambda$  and  $\sigma$  can be altered by using a constant nonmetallic part ( $k$ ) of the thermal conductivity as follows (Raab et al., 2016):

$$\lambda = k + \sigma L T \tag{2}$$

However, as the porosity in the specimens increases, the reliability of Equation (2) decreases. The amount of porosity in metal matrix composites varies depending on the manufacturing process and also the reinforcements used and their proportions, particularly nano-sized particles. Ceramic-based reinforcement particles have very low conductivity and may cause an increase in porosity, which results in a reduction in conductivity. In this study, Equation (2) has been modified to account for the volume fraction of reinforcement particles and the porosity levels in the composite specimens in order to determine the relationship between thermal conductivity and electrical conductivity in particle-reinforced metal matrix composites as follows:

$$\lambda = (1-V-P) (k + \sigma L T) \tag{3}$$

where  $V$  is the volume fraction of reinforcement particles and  $P$  is the fraction of the pores.



**Figure 7.** Prediction of thermal conductivities from experimental electrical conductivities with different approaches (equations) and comparison with experimental thermal conductivities of (a) and (b) unreinforced Cu produced by MS and SPS respectively, and (c) and (d) Cu-LaB<sub>6</sub> nanocomposites manufactured through MS and SPS, respectively.

Figure 7 shows thermal conductivities calculated from experimental electrical conductivities using various methods (Equations (1)-(3)). The constant  $k$  was assumed to be 53.1 W/mK in Equations (2) and (3) by using the linear fitted value found in a study (Raab et al., 2016). The Lorenz numbers were  $2.07 \times 10^{-8} \text{ W}\Omega/\text{K}^2$  (Raab et al., 2016) and

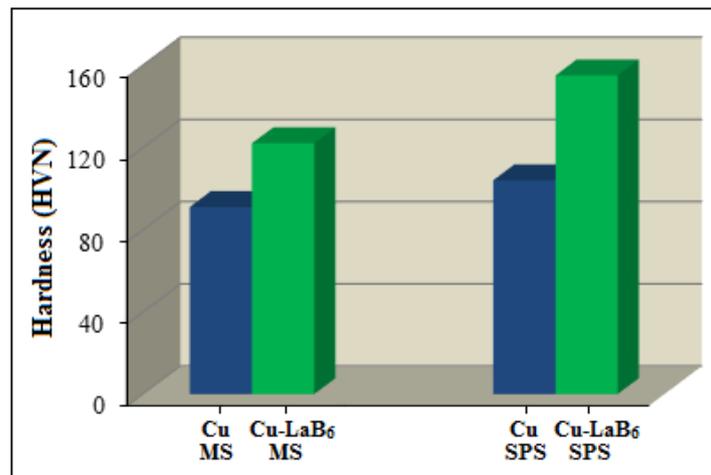
$2.45 \times 10^{-8} \text{ W}\Omega/\text{K}^2$  (White and Tainsh, 1960) for Equation (1) and Equations (2) and (3), respectively. In comparison to Equations (1) and (2), Equation (3) developed for particle-reinforced metal matrix composites predicted results that were very close to the experimental results, as seen in Figure 7. These findings indicate that the negative

effects of porosity and reinforcement particle volume ratios are highly effective on the thermal conductivity of particle-reinforced metal matrix composites such as Cu-LaB<sub>6</sub>, and that these factors must be considered when calculating (predicting) thermal conductivity from experimental electrical conductivity.

### 3.3. Hardness and compressive strength

The hardness values of Cu-LaB<sub>6</sub> nanocomposites produced using MS and SPS were 34% and 49% higher, respectively than that of unreinforced Cu manufactured with MS and SPS (Figure 8). Reinforcement particles have significant effects on

the hardening of the metal matrix to which they are added, both directly and indirectly. Firstly, the hardness of LaB<sub>6</sub> particles is greater than that of Cu. Secondly, reinforcement particles in metal matrix composites inhibit the movement of dislocations in the matrix (Lin et al., 2021). Thirdly, dislocation density increases due to the mismatch of thermal expansion coefficients between matrix and reinforcement particles (Matvienko et al., 2021), resulting in additional inhibition of dislocation movements. For all of these factors, Cu-LaB<sub>6</sub> nanocomposites were harder than unreinforced Cu.

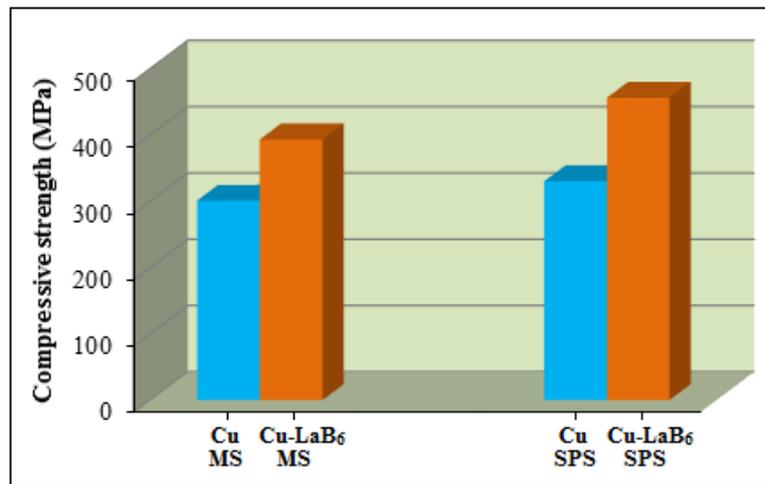


**Figure 8.** Hardness of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites manufactured through MS and SPS

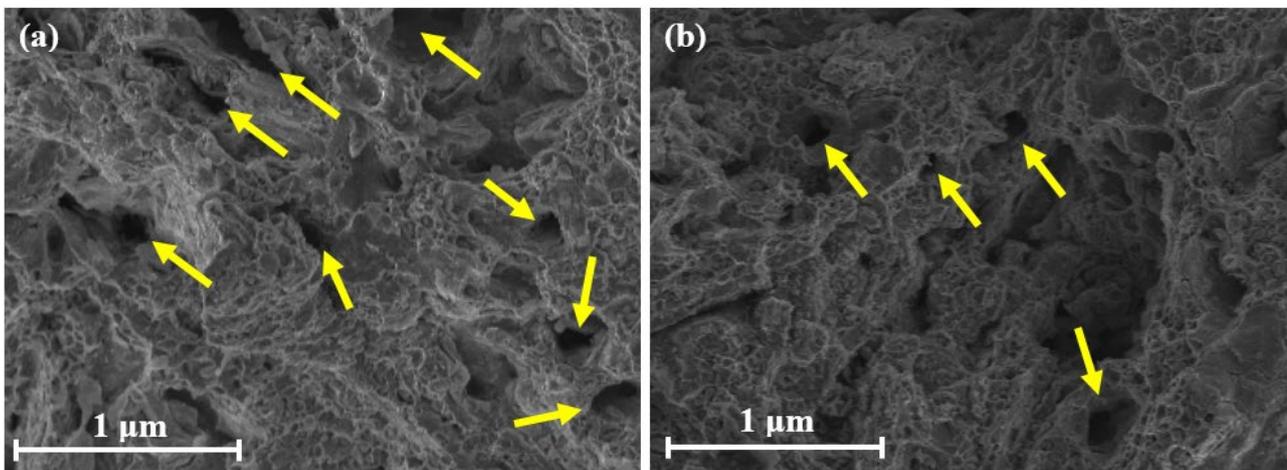
The hardness of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposite produced by MS was lower than that produced by SPS. This is due to the higher porosity of specimens manufactured through the SPS compared to those produced with the MS because porosity has a negative influence on the hardness of particle-reinforced metal matrix composites (Hossein et al., 2014).

Figure 9 shows the compressive strengths of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites. The addition of reinforcement particles into a metal matrix improves mechanical properties such as compressive strength due to the following strengthening mechanisms (Ye et al., 2018): (I) load-bearing effect of reinforcement particles, (II) grain boundary strengthening (Hall-Petch), (III) Orowan strengthening, and (IV) enhanced dislocation-based strengthening mechanisms resulted from the mismatches of thermal expansion coefficients and elastic modulus between the reinforcement particles and the metal matrix. The

addition of nano LaB<sub>6</sub> particles in the Cu matrix increased the compressive strength of Cu-LaB<sub>6</sub> nanocomposite produced by SPS by 38% as compared to unreinforced Cu specimen produced using the same method (Figure 9). Nano LaB<sub>6</sub> particle reinforced Cu-LaB<sub>6</sub> nanocomposite manufactured through MS had a 29% higher compressive strength than unreinforced Cu specimens produced by MS. These findings clearly showed that nano LaB<sub>6</sub> particles and SPS had a strong influence in improving the compressive strength of Cu matrix nanocomposites. Porosity, on the other hand, had a negative effect on the compressive strength of Cu-LaB<sub>6</sub> nanocomposites, depending on the manufacturing process, with a greater negative influence in the Cu-LaB<sub>6</sub> nanocomposite produced using the MS process. As seen in Figure 10, the pores formed in the Cu-LaB<sub>6</sub> nanocomposite manufactured via MS were more numerous and greater than those formed in the Cu-LaB<sub>6</sub> nanocomposite specimen produced with SPS, resulting in lower compressive strength.



**Figure 9.** Compressive strengths of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites produced by MS and SPS



**Figure 10.** SEM images of fracture surfaces of Cu-LaB<sub>6</sub> nanocomposites produced by (a) MS and (b) SPS

#### 4. Conclusions

Copper was reinforced with nano LaB<sub>6</sub> particles using microwave sintering and spark plasma sintering to produce Cu-LaB<sub>6</sub> nanocomposites, and the electrical, thermal, and mechanical properties of unreinforced Cu and Cu-LaB<sub>6</sub> nanocomposites were investigated. The nano LaB<sub>6</sub> particles reduced the electrical conductivities of Cu. Cu-LaB<sub>6</sub> nanocomposites produced with MS and SPS had lower electrical conductivity than unreinforced Cu by 20% and 13%, respectively. Similarly, Cu-LaB<sub>6</sub> nanocomposites had lower thermal conductivity than unreinforced Cu. The electrical and thermal conductivities of Cu-LaB<sub>6</sub> nanocomposite manufactured through SPS were higher than those of Cu-LaB<sub>6</sub> nanocomposite produced using MS since lower porosity was achieved in production with the SPS process. To calculate the thermal conductivity of nanocomposites from their electrical conductivity, an equation that takes particle volume ratio and porosity into account was

developed. The predicted thermal conductivities of Cu-LaB<sub>6</sub> nanocomposites were very close to the experimental results. Cu-LaB<sub>6</sub> nanocomposites produced via MS and SPS had much higher hardness by 34% and 49%, respectively, compared to those of unreinforced Cu manufactured using the same processes. The compressive strength of Cu-LaB<sub>6</sub> nanocomposites produced by MS and SPS were 29% and 38% higher than those of unreinforced Cu manufactured through MS and SPS. SPS process had a greater positive effect on the electrical, thermal, hardness, and compressive strength of Cu-LaB<sub>6</sub> nanocomposites than MS process. In conclusion, despite the fact that nano LaB<sub>6</sub> reinforcement particles reduced the electrical and thermal conductivities of Cu, Cu-LaB<sub>6</sub> nanocomposite having high hardness and compressive strength were produced by combining the positive influences of nano LaB<sub>6</sub> reinforcement particles and the SPS process.

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