Effect of sintering temperatures on the properties of in-situ copper-niobium-titanium di-boride composites

Azunna Agwo Eze¹ · Emmanuel Rotimi Sadiku¹ · Williams Kehinde Kupolati² · Jacques Snyman² · Julius Musyoka Ndambuki² · Tamba Jamiru³ · Mondiu Olayinka Durowoju⁴ · Idowu David Ibrahim³ · Mxolisi Brendon Shongwe¹ · Dawood A. Desai³ · Ronald Machaka⁵ · Khumbulani Mpopu⁶

Received: 17 August 2020 / Accepted: 25 November 2020 / Published online: 30 November 2020
© Springer Nature Switzerland AG 2020

Abstract

This work investigated the effect of the sintering temperatures on the densification of the powders, density, relative density, microhardness, coefficient of thermal expansion, and corrosion resistance in sulphuric acid solution environment of copper-niobium-titanium di-boride composite. A 90% weight of copper, reinforced with a 6% weight of niobium micro-particles and 4% weight of titanium-diboride was prepared in powdered form and sintered in two different temperatures of 650 °C and 700 °C using the spark plasma sintering method. The crystal phases and the morphologies of both the starting powders and the sintered samples were analyzed by the use of X-ray diffraction with copper Alpha-K radiation and scanning electron microscopy with energy dispersive X-ray spectroscopy. The results show that sintering at a temperature of 700 °C reduced the displacement rate of the powders with a higher microhardness value of 941 MPa when compared with the sintering temperature of 650 °C, which prolonged the displacement rate of the powders with a lower microhardness value of 827 MPa. The sintered samples recorded negative thermal expansion values of $-1.375 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$ and $-7.780 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at temperatures of 650 °C and 700 °C, respectively. The sample sintered at 700 °C has better micro-hardness and better corrosion resistance in a sulphuric acid environment when compared to the one sintered at 650 °C. This study has shown that the varying of the sintering temperatures has an effect on the properties of the composite under study. The produced composites can be used to control the mechanical and electrical properties, and the thermal expansion of functional materials, such as superconductors, semiconductors, ferroelectrics, magnetic and Mott insulators, etc.

Keywords Copper-metal matrix composites spark plasma sintering · Microstructure · Negative thermal expansion · Corrosion in sulphuric acid

1 Introduction

Pure copper is a potential material as a substitute for gold (Au) and silver (Ag) to produce metal matrix composites, for electrical contacts. This is because of its excellent

electrical conductivity and low cost. The service lives of electrical contacts decrease due to their low hardness and the low nature of the operational temperatures of pure copper. To overcome this shortcoming of pure copper, the common route of increasing the strength and operational

✉ Azunna Agwo Eze, ezeaaben@gmail.com | ¹Institute for Nano-Engineering Research (INER) and Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa. ²Department of Civil Engineering, Tshwane University of Technology, Pretoria, South Africa. ³Department of Mechanical Engineering, Mechatronics and Industrial Design, Tshwane University of Technology, Pretoria, South Africa. ⁴Department of Mechanical Engineering, Ladoke Akintola University of Technology (LAUTECH), Ogbomoso, Oyo State, Nigeria. ⁵Titanium Centre of Competence, Council for Scientific and Industrial Research, Pretoria, South Africa. ⁶Department of Industrial Engineering, Tshwane University of Technology, Pretoria, South Africa.

temperature of copper, while retaining its excellent conductivity, is to alloy with a member of the body-centered cubic (bcc) structural family of elements, e.g., niobium [1].

Copper-niobium composites have been reported to have excellent mechanical properties [2–4]. It was reported that both the mechanical and electrical conductivity characteristics of copper-niobium, can conveniently and significantly surpass those of its competitive alloys, such as copper-titanium, copper-beryllium, and copper-nickel-magnesium [5, 6]. The increasing research on copper-niobium composites is due to the increasing demand for copper-based composites that have a good combination of excellent mechanical strength, electrical conductivity, and environmentally friendly, unlike copper-cadmium, and copper-beryllium that are harmful to humans and the environment [2]. Copper-niobium alloy has demonstrated a combination of high strength and good electrical conductivity [2, 3, 5] and thermal conductive stability, at temperatures ranging between 400 and 1000 °C, without disruption [4]. The aforementioned properties would make it possible for copper-niobium to be the preferred candidate material for the fabrication of electrical devices that can withstand mechanical and thermal stresses.

On the other hand, there has been great interest in the production of composites with titanium-diboride, as reinforcing phase. Titanium-diboride has excellent mechanical properties, which when added to a matrix, enhances the overall performance of the resulting composites [7, 8]. Titanium-diboride is a ceramic material and its excellent mechanical and good conductive properties, predetermine its potential use in various high-temperature applications, especially those including highly corrosive molten salts [9]. To enhance the strength of copper metal matrix composites, some hard additives, e.g., titanium-diboride had been employed [10–15].

In this study, titanium-diboride is added to copper-niobium as a third phase. The addition is expected to enhance the mechanical properties as well as the corrosion resistance of the composites. There are research works that have shown that titanium-diboride behaves like a passive metal in acid and salt environments, due to the formation of a surface oxide film, whose protective power, decreases with temperature [16, 17].

The admixture of the three material elements (Cu, Nb, and TiB_2), during solid-state mixing, showed significant insolubility, since there are large differences in their specific gravities. However, different powdered materials with immiscibility of phases in their solid states should be prepared/fabricated employing powder metallurgy [2, 18], hence the use of powder metallurgy route, with spark plasma sintering technique in this study. Spark plasma sintering technique has a lot of advantages over the conventional powder consolidation technique, which includes:

fast sintering, lower sintering time with temperature, minimized grain coarsening, prevention of unnecessary reactions between the different phases, effective consolidation, and production of near net-shaped materials [2, 19–23]. In the spark plasma sintering technique, the total punch displacement of the powders is affected by the following parameters such as; the applied pressure, reaction of the products, graphite foil, heating behavior, sintering temperature, and time [24]. In this study, a composite consisting of copper-niobium (Cu-Nb) powders, reinforced with titanium-diboride (TiB_2) powder was produced by using spark plasma sintering technique at two different sintering temperatures of 650 °C and 700 °C. Attention was, focused on the investigation of the effect of those varying sintering temperatures on the densification of the powders, relative density, microstructures, microhardness, and the coefficient of thermal expansion (CTE) and the corrosion performance of the resultant composite, in an H_2SO_4 acid environment, conducted through electrochemical tests. There is no literature information on copper-niobium-titanium-diboride (CuNbTiB_2) fabricated at two different sintering temperatures, via the spark plasma sintering technique, as well as the effects of varying sintering temperatures on their microstructure, mechanical properties, coefficient of thermal expansion, and corrosion resistance, in an acid solution environment. However, the selection criteria of the composition determined in this study were based on the results obtained on good properties of copper-niobium and copper-titanium diboride of the previous works [3, 4, 6, 10–14].

2 Experimental procedure

In the present study, pure copper, niobium, and titanium-diboride were used as the starting powders. The properties, composition of the mixed powders, purity, particle sizes, and the suppliers of the starting materials are contained in Table 1.

The SEM images of the starting powders are shown in Fig. 1. The contents, of the mixed powders (CuNbTiB_2) in weight percent (wt%), were selected to be; 90 wt% of Cu, 6 wt% of Nb, and 4 wt% of TiB_2 . The powders were inserted into a plastic cylinder, together with aluminum balls to enhance the homogenous mixture and reduce agglomeration of the powders. The powders were mixed for two (2) hours in a T2F tubular shaker mixer with a rotational speed of 72 revolutions per minute. After mixing, a spark plasma sintering machine, HPDS model, FCT system made in Germany was then used to sinter the admixed powders. The sintering was done at two different sintering temperatures of 650 °C and 700 °C, with a heating rate of 50 °C/min, holding time (dwell time) of

Table 1 Summary of the properties, compositions, suppliers, purities, and particles size of the starting materials

Elements	Cu	Nb	TiB ₂
Density (g/cm ³)	8.96	8.57	4.50
Melting point (°C)	1083.4	2477	> 3000
Hardness Vickers	369 MPa	1320 MPa	33343 MPa
CTE at 20 °C	$17 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$	$7.1 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$	$8 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$
Composition of CuNbTiB ₂ mixed powders (wt%)	90	6	4
Suppliers	Alfa Aesar	Alfa Aesar	Grade F supplied by Herman C Starck, Belin, German
Purity (%)	99	99.8	99
Particle sizes	44 μm	44 μm	75 μm

Fig. 1 Shows SEM images of the starting powder: **a** TiB₂, **b** Nb and **c** Cu

5 min, and at a pressure of 50 MPa. The displacement of the piston during the heating of the powders created a linear shrinkage, and the recorded values were used in Eq. 1 to obtain the values of the CTE [8].

$$CTE = \frac{\epsilon_{T1} - \epsilon_{T2}}{T1 - T2} \frac{1}{100} \quad (1)$$

Where: ϵ_{T1} represents the shrinkage after cooling in %, ϵ_{T2} represents the shrinkage at the ending of the dwell in %, and

T_1 represents the temperature after cooling in °C and T_2 represents the temperature at the ending of the dwell in °C.

X-ray diffraction (XRD) and the field emission scanning electron microscopy (FESEM, JSM-7600F, Jeol, Japan), equipped with energy dispersive x-ray spectrometer (EDS), were used to characterize the structural and morphological characteristics of the starting powders and the sintered samples.

The densities were measured according to the Archimedes principle. The relative densities were calculated

regarding the theoretical density of $_{90}\text{Cu}_6\text{Nb}_4\text{TiB}_2$ by using the rule of mixture.

The microhardness of the sintered samples was determined by the EMCO Durascan Vickers micro-hardness tester, under a load of 100 gf and a dwelling time of 15 s. The measurement was performed five (5) times from random locations on the central region of the polished cross section, and the average values were then considered.

The corrosion resistance of the sintered CuNbTiB_2 was analyzed. The specimens for corrosion testing were prepared by attaching an insulated copper wire, by using aluminum tape to one face of the specimen, and cold-mounted in an epoxy resin, and the opposite face was ground and polished. The open circuit potential (OCP) and potentiodynamic polarization tests were conducted to obtain information on the corrosion behavior of the sintered samples in a mole of sulphuric acid (H_2SO_4) environment. The corrosion experiments were carried out by using an Auto-lab potentiostat (PasTAT30). All the experiments were carried out by using a 3-electrode corrosion cell setup with Ag/AgCl reference electrode, saturated with 3 mol AgCl, a graphite rod as the counter electrode, and the specimen as the working electrode. Tests were conducted at room temperature ($23 \pm 2^\circ\text{C}$), whereby the open circuit potential stabilization was run for one (1) hour and polarization measurements were carried out at a scan rate of 0.002 V/s, with potential initiated at -1.5 V to $+1.5\text{ V}$.

3 Results and discussion

3.1 Powder characterization

The SEM of the starting powders is shown in Fig. 1. The particle sizes of the starting powders are shown contained in Table 1, and the particle shapes of the powders are presented in Figs. 1 and 2. The TiB_2 particles shape are irregular (Figs. 1a and 2a), Nb powders have flak-like shapes (Figs. 1b and 2b), while Cu powders have agglomeration with some rounded shape particles distributed among them (Figs. 1c and 2c). The elemental composition of the starting powders is presented in the table attached to Fig. 2. The EDS result (Fig. 2) shows that all the powders of the starting powders were pure as-received materials with a little amount of oxygen present in each of them. In Fig. 2a, the TiB_2 powder is found to be composed of: boron (B: 39.08 wt%), oxygen (O: 11.69 wt%), and titanium (Ti: 49.23 wt%). In Fig. 2b, the niobium powder is found to be composed of; oxygen (O: 4.32 wt%), and niobium (Nb: 95.68 wt%), while the copper powder is found to be composed of oxygen (O: 2.99 wt%), and copper (Cu: 97.01 wt%). The presence of oxygen might have resulted in the partial oxidation of the elements of the starting powders, to form their respective oxides.

Fig. 2 SEM images and EDS analysis of the starting powders with their elemental compositions: **a** TiB_2 , **b** Nb and **c** Cu

3.2 Displacement rate as a function of the temperature of the admixed powder during sintering

The CuNbTiB₂ admixed powders were sintered at two different sintering temperatures, while the other sintering parameters, such as pressure, holding time, and heating rate, were constant of 50 MPa, 5 min, and 50 °C/min, respectively. The displacement rate, as a function of temperature, for the CuNbTiB₂ composites, is shown in Fig. 3. The variation of the sintering temperatures has a perceptible effect on the densification rate of the composite. According to the work of Diouf and Molinari [25], which stated that under the application of low initial pressure, the densification is due to particle rearrangement, localized deformation, bulk deformation, and neck growth, and these phenomena were presented as four peaks. In this study, one weak peak at 350 °C is observed (Fig. 3a) from the sample sintered at 650 °C. This peak can be identified as the point, where there was particle rearrangement, which occurred with the maximum displacement rate at a low temperature of 350 °C. Rearrangement occurs through the relative movement of the particles and this is opposed by the inter-particle friction at the contact points [25]. In Fig. 3b, densification occurred between 400 °C and 700 °C. The phenomena that are responsible for densification, according to Diouf and Molinari [25] are overlapped in Fig. 3b, where one broad peak at 400–700 °C, was observed. In Fig. 3, the arrow that pointed rightward indicates the path of heating (displacement rate with an increase in temperature). While the arrow pointing leftward indicates the cooling of the sample after the maximum sintering temperatures. However, the extinction of the peaks in this study, which are responsible for the

Fig. 3 Densification rate as a function of temperature for CuNbTiB₂ composite: **a** sample sintered at 650 °C and **b** sample sintered at 700 °C

Fig. 4 XRD analysis of CuNbTiB₂ sintered composite at 650 °C and 700 °C

proper densifications, according to the work of Diouf and Molinari [25], could be attributed to the presence of dissolved oxygen in the samples, as can be seen in the SEM and EDS images (Figs. 5, 6, 7, 8, 9, 10). The presence of oxygen in the sintering samples, during the spark plasma sintering process, hinders the densification mechanism [26]. The poor densification observed in this study, due to the presence of oxygen, was the prime cause of the low density and relative density obtained. Also, it is seen that the selected temperature and sintering time are also effective among the factors that determined the densifications and densities of the sintered samples. Also, the presence of Nb and TiB₂ as the reinforcement agents to Cu, in this study, is believed to be the cause of the low densification experienced, during the sintering of CuNbTiB₂ composite. Other researchers had confirmed that the higher the reinforcement content, the higher the probability of clusters

Fig. 5 SEM image of CuNbTiB₂ composite sintered at 650 °C

Fig. 6 SEM images and EDS analysis of CuNbTiB₂ composite, sintered at 650 °C showing 1 and 2 peaks

and particle defects and consequently, the reduction in the composite densification and hence, in its density [8, 27].

3.3 X-ray diffraction of the sintered samples

To classify the phases present or formed when 90 wt% of Cu, 6 wt% of Nb and 4 wt% of TiB₂ were sintered as CuNbTiB₂ composite, at the sintered temperatures of 650 °C and 700 °C, the XRD analysis was carried out and it is shown in Fig. 4. The XRD results show the distribution of the phases observed as the composite was sintered at 650 °C and 700 °C. There are five (5) phases observed in the samples that were sintered at both temperatures, with the peaks of Cu and Nb occurring at high intensity. There was no significant shift in the peaks of Cu and Nb, but oxygen and titanium were observed to have occurred at higher 2theta of the sample sintered at 700 °C. The phases observed in the XRD results (Fig. 4), are the same as the phases in the starting powders (Fig. 2), which are: Cu, Nb, B, Ti, and O. These show that the composite was not contaminated with any other foreign material, except oxygen during the spark plasma sintering at both temperatures.

3.4 SEM and EDS of the sintered samples

Figures 5, 6, 7, 8, 9, 10 show the SEM images and EDS analysis of the CuNbTiB₂ composite, sintered at temperatures of 650 °C and 700 °C. The EDS spectra were used to analyze the chemical composition of dissimilar regions of the CuNbTiB₂ composites. The results are summarized in the tables, attached to each EDS graph. Figures 5 and 8 present the high magnification, the SEM images of the sintered composites at 650 °C and 700 °C, respectively. Figure 6 shows the EDS analysis, indicating the elemental composition, as summarized in a tabular form, for the CuNbTiB₂ composites sintered at 650 °C. In Fig. 6, there are two spectra (1 and 2) that identify the phases that are present at those points in the matrix. Spectrum 1 in Fig. 6, identifies the thick black colors that are dispersed in the matrix to be TiB₂, which contains: B (49.30 wt%), and Ti (50.70 wt%). In spectrum 2 in Fig. 6, it confirms the white dispersed colors to be a high amount of Nb particles (94.65 wt%), with little presence of Cu (1.68 wt%), and O (3.67 wt%). Figure 7 shows spectrum 3 EDS analysis of CuNbTiB₂ composite, sintered at 650 °C. Spectrum 3 in Fig. 7 confirms the fact that Cu (96.61 wt%), with a little amount of O (3.39 wt%), were present in that region. Figure 8 shows

Fig. 7 SEM image and EDS analysis of CuNbTiB₂ composite sintered at 650 °C, showing 3 peaks

Fig. 8 SEM image of CuNbTiB₂ composite sintered at 700 °C

the SEM image of CuNbTiB₂ composite, sintered at 700 °C. The EDS analysis with spectra 1 and 2 of the CuNbTiB₂ composite, sintered at a temperature of 700 °C, is shown in Fig. 9, while Fig. 10 shows the EDS analysis with spectra 3 and 4 of the CuNbTiB₂ composite, sintered at 700 °C. Spectrum 1 in Fig. 9 identifies a large whitish phase to be

a high amount of Nb (95.44 wt%) and little amounts of Cu (1.47 wt%) and O (3.09 wt%). Spectrum 2 in Fig. 9 identifies the dispersed black pigment to be TiB₂ with a little amount of Cu, Ti (52.37 wt%), B (46.76 wt%), and Cu (0.87 wt%). Spectrum 3 in Fig. 10 identifies a whitish spot to be a high amount of Nb (93.74 wt%) with little amounts of Cu (2.07 wt%) and O (4.18 wt%), while spectrum 4 in Fig. 10 identifies a tiny black dispersion to be a high amount of Cu (94.83 wt%), with little amounts of Nb (2.88 wt%) and O (2.29 wt%).

In the sintered composites, sintered at two different temperatures (650 °C and 700 °C), it was observed that oxygen was present everywhere there is the presence of Nb and Cu. These results confirmed the possibility of having niobium oxide(s) (NbO_x) and copper oxide(s) (CuO_x) in the composites, sintered at both temperatures, where *x* could range between 1 and 5. However, this is strong evidence that confirms the negative thermal expansion (NTE) behavior, found in the CuNbTiB₂ composites produced, in this work. It had been reported that NbO_x and CuO_x are strong candidates for NTE materials [28–31]. The SEM micrographs of the sintered samples sintered at 650 °C and 700 °C show uneven dispersion of Nb and TiB₂ particles in the Cu matrix. The clustered particles of Nb and TiB₂ in the matrix are attributed to the different particle sizes, as well as the different specific gravity of the starting powders. These could make it difficult to have a homogeneous mixture of the starting powders during turbulence mixing. However, the admixed powders of the elements, which have different specific gravities, are liable to separate during vibration, flow, or movement [4]. Therefore, this might be the cause for the poor densification (Fig. 3), of the composite, observed during sintering. This effect could as well be attributed to the low density and relative density values obtained (Table 2).

3.5 Density, relative density, and microhardness of the sintered samples

The values of the final density, relative density, and microhardness of the sintered CuNbTiB₂ composites, are summarized in Table 2. In this study, 90 wt% Cu was reinforced with 6 wt% Nb and 4 wt% TiB₂ powders. With high mass fractions of the reinforcement phase (6 wt% Nb, and 4 wt% TiB₂), it is predictable that there will be a high likelihood of powders agglomeration, unsuitable binding of the matrix phase, and possibly for crack development within the sintered composites. From Table 2, it can be seen that the sample that was sintered at 650 °C, has higher density and relative density values of 7.605 g/cm³ and 88.4%, respectively, when compared with the sintered sample at 700 °C, which has a density and relative density values of 7.556 g/cm³ and 87.9%,

Fig. 9 SEM images and EDS analysis of CuNbTiB₂ composite sintered at 700 °C showing 1 and 2 peaks

respectively. However, the sample (2 specimens) was sintered at two different sintering temperatures. The sample sintered at 700 °C recorded a higher microhardness value of 940.8 MPa when compared with the one that was sintered at 650 °C, which recorded 827.3 MPa. The higher density and relative density values recorded by the sample sintered at 650 °C might have been influenced by Cu particles. At the lower temperature of 650 °C, Nb and TiB₂ particles might not have been precipitated out in the Cu matrix, to create more pores. The higher microhardness value observed in the sample sintered at 700 °C is expected to be influenced by the precipitation of Nb and TiB₂, as hard materials. The precipitation of Nb and TiB₂ at the sintered temperature of 700 °C might have formed closely parked particles that could hinder dislocations. Thus, the Orowan strengthening, caused by the resistance of the closely parked hard particles to the passing of dislocations, is widely acknowledged as the strengthening mechanism in metal matrix micro/nanocomposite [8, 17].

3.6 Coefficient of thermal expansion (CTE)

Figure 11 shows the CTE of the sintered sample (CuNbTiB₂) at two different temperatures of 650 °C and 700 °C. Both samples sintered at 650 °C and 700 °C, showed negative thermal expansion (NTE). At a sintering temperature of 700 °C, CuNbTiB₂ recorded a NTE value of $-7.780 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and $-1.375 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$ at a temperature of 650 °C. The negative thermal expansion values indicate contractions of materials when subjected to heat, rather than expansion. In this study, the NTE values obtained showed that the CuNbTiB₂ composite contracted upon heating. The presence of Nb–O–Nb bonds, O–Cu–O bonds, and TiO_x ($x=6$) in the CuNbTiB₂ composite (Figs. 5, 6, 7, 8, 9, 10) are believed to be responsible for the NTE observed in this study. The greater parts of the crystal structures of NTE materials, have a general feature of two organize metal–oxygen–metal bonds (M–O–M bond) for the positive ion polyhedral that builds a 3-dimensional lattice. The transverse vibration about an M₁–O–M₂ linkage is the key

Fig. 10 SEM images and EDS analysis of CuNbTiB₂ composite sintered at 700 °C showing 3 and 4 peaks

Table 2 Summary of the final density, relative density, theoretical density, and microhardness of the CuNbTiB₂ sintered composite

Sintered Temp. °C	Final density g/cm ³	Relative density (%)	Micro-hardness value (MPa)
650	7.605	88.4%	827.3
700	7.556	87.9%	940.8

factor for the occurrence of NTE with open-frame-work structure and form a strong bond of M₁–O–M₂ linkage; the length of the M₁–M₂ contracts by the transverse vibrations of oxygen [32]. For approximately linear M–O–M linkages, this process leads to a reduction of the second-nearest-neighbor distances and this can result in linear or volume NTE [33]. There have been reports of materials where the NTE takes place by using the oxygen–metal–oxygen (O–M–O) configuration, instead of the metal–oxygen–metal (M–O–M) bond, and an example of such materials is CuO₂ (Cuprite), which has an NTE value of $-8 \times 10^6 \text{ K}^{-1}$ at a temperature below 225 K [29, 31]. In the cuprite structure and with its linear O–Cu–O bonds, the bridging copper has the potential of performing transverse ‘guitar string’

Fig. 11 Negative thermal expansion (NTE) of CuNbTiB₂ at 650 °C and 700 °C

vibrations that give rise to the rotation of OCu₄ tetrahedral and hence, leading to the shortenings of the O–O distances (negative thermal expansion) [31]. There is another

report that at room temperature, the TiO_6 polyhedral bonds are distorted (and thus, the bonds are weaker and longer), but they start to become more regular as heat is applied and this will result in a thermal contraction, which occurs along the crystal axis [29]. However, the presence of niobium oxides (NbO_x), copper oxides (CuO_x), and titanium oxides (TiO_x) contributed, immensely, to the NTE of the CuNbTiB_2 composite (Figs. 5, 6, 7, 8, 9, 10) in this study. It was recorded in the work of Amos [34] that at 327 °C, niobium was displaced in length by $\sim 0.318 \text{ \AA}$ from the octahedron centered structure and the dilatometer measurement showed negative thermal expansion, associated with temperatures above 200 °C. There are previous works that also demonstrated the NTE behavior of Nb_2O_5 in the temperature range of between 20 °C and 1000 °C [35, 36]. Besides, another report demonstrated a negative thermal expansion of Nb_2O_5 at relatively high temperatures, even as high as 500 °C [28, 30], which was attributed to the recombination of the micro-crack network, formed during cooling [37]. The new CuNbTiB_2 composite produced in this work has many relevancies; as an NTE material. It can be used to control both the physical properties and the thermal expansion of functional materials, such as superconductors, semiconductors, ferroelectrics, magnetic, and Mott insulators [32]. This is so since difficulties attributed to thermal expansion control are universal. These challenges are difficult to resolve and the core technology of thermal expansion control is the negative thermal expansion (NTE) of the materials in question [38].

3.7 Corrosion studies of sintered samples, in 1 mol H_2SO_4 acid

Figure 12 shows the potentiodynamic polarization curves, which were determined for the CuNbTiB_2 composites

Fig. 12 Polarization curves in 1 mol of H_2SO_4 acid of CuNbTiB_2 sintered composite

sintered at 650 °C and 700 °C. In Fig. 12, it can be seen that the sintered sample at 700 °C, exhibits a reduction in both the current density and the active-zone-line slope when compared with the sintered sample at 650 °C. From the electrochemical theories, it is known that the corrosion rate is directly proportional to the corrosion current density and that a reduction of the corrosion current density will enhance the passivity of the alloys or composites [39]. Based on these facts, it can be inferred that the CuNbTiB_2 composite, sintered at 700 °C, exhibited better corrosion resistance than that sintered at 650 °C, due to the possible formation of protective oxide films, which hindered the instigation of pitting.

Figure 13 shows the variation in open circuit potential (OCP) as a function of time for the CuNbTiB_2 composites, sintered at 650 °C and 700 °C, in a 1-mol sulphuric acid environment. The OCP measurement shows the reactivity or tendency of the sintered samples to corrode in 1 mol H_2SO_4 acid environment with time. The variation in the OCP values of the sintered composite at 650 °C and 700 °C was examined at zero applied currents without delay after the immersion of the sintered composites in the acid solution for one hour (1 hr). The potential of the sample sintered at 700 °C was observed, at the initial stage, to have shifted toward positive values, which later started dropping toward a negative direction with time. On the other hand, the potential of the sample sintered at 650 °C was observed to shift towards the negative values at the initial stage and was observed to have maintained relative stability as time progressed. After the initial stages, with time, stable passive films were formed on the surface of the samples for composites sintered at both temperatures. At the initial stages, the samples showed that there was a breakdown in the films on their reacting surfaces, followed

Fig. 13 OCP in 1 mol of H_2SO_4 acid of CuNbTiB_2 sintered composite

by the creation of new passive films, after dissolution. Sample sintered at 700 °C was observed to show the higher potential values, which established why it exhibited the lowest corrosion rate in the potentiodynamic polarization examination (Fig. 12). Niobium (Nb) and titanium-diboride (TiB_2) have been known to have good corrosion resistance properties. At a sintering temperature of 700 °C, it is assumed that more Nb and TiB_2 would have precipitated out in the matrix more than experienced at the sintering temperature of 650 °C. This is likely the reason why the sample sintered at 700 °C performed better in corrosion resistance than the sample sintered at 650 °C.

4 Conclusions

This study has investigated the effect of varying the sintering temperatures (650 °C and 700 °C) on the microstructure, corrosion resistance in a 1 mol H_2SO_4 acid, thermal expansion, and mechanical properties of an in-situ $_{90}\text{Cu}-_6\text{Nb}-_4\text{TiB}_2$ powdered composite by using the spark plasma sintering technique. This was studied in detail with the following concise results:

- The study shows that the sintering at a temperature of 700 °C, reduced the displacement rate of the powders with lower density and relative density values when compared with the 650 °C sintering temperature.
- The microhardness value of the sample sintered at 700 °C was higher when compared with the one sintered at 650 °C; this is expected due to the precipitation of Nb and TiB_2 particles in the matrix of Cu.
- It was found that the novel composite produced in this work, resulted in a negative thermal expansion (NTE) material at both temperatures of 650 °C and 700 °C.
- The corrosion resistance of the sample sintered at 700 °C was better when compared with that sintered at 650 °C.

This study has shown that the varying of the sintering temperatures has an effect on the properties of the composites under study.

A novel composite material of high technological/scientific value was produced. It can be used to control the mechanical and electrical properties, and the thermal expansion of functional materials, such as superconductors, semiconductors, ferroelectrics, magnetic, and Mott insulators, etc.

However, further studies are recommended to explore more the vital properties of this novel composite material.

Acknowledgements The authors acknowledge the Department of Science and Technology (DST), South Africa for financial support.

Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Morris D, Morris M (1990) Mechanical alloying of copper-BCC element mixtures. *Scr Metall Mater* 24:1701–1706
2. Eze A, Jamiru T, Sadiku E, Diouf S, Durowoju M, Ibrahim I et al (2017) Electrical conductivity of Cu and Cu-2vol.% Nb powders and the effect of varying sintering temperatures on their mechanical properties using spark plasma sintering. *Silicon* 9:855–865
3. Eze AA (2016) Production of binary copper-titanium and copper-niobium alloys for trolley wire applications using spark plasma sintering techniques spark plasma sintering techniques. Tshwane University of Technology, Pretoria
4. Eze AA (2019) Development of a new copper-niobium based composite trolley cable for electric trains. Tshwane University of Technology, Pretoria
5. Eze AA, Jamiru T, Sadiku ER, Durowoju MO, Kupolati WK, Ibrahim ID (2019) Considering the use of niobium and titanium to enhance electrical and mechanical properties of copper at higher operational temperature application. *SN Appl Sci* 1:74
6. Raabe D, Heringhaus F, Hangen U, Gottstein G (1995) Investigation of a Cu-20 mass% Nb in situ composite, part I: fabrication, microstructure and mechanical properties. *Zeitschrift fur Metallkunde* 86:405–415
7. Balaji R, Babu SVS, Channankaiah D (2014) Wear behaviour of sintered titanium diboride reinforced graphite aluminium composites. *Int J Eng Res Technol*. 3
8. Durowoju M, Sadiku E, Diouf S, Shongwe M, Makena I, Ramakokovhu M et al (2019) Wear and corrosion studies of graphite-aluminum composite reinforced with micro/nano- TiB_2 via spark plasma sintering. *Mater Werkst* 50:126–139
9. Pavlík V, Boča M (2012) Corrosion of titanium diboride in molten FLiNaK (eut). *Chem Pap* 66:1073–1077
10. Guo Z, Li N, Hu J (2015) Cu- TiB metal matrix composites prepared by powder metallurgy route. *Sci Sinter* 47:165–174
11. Legoux J, Dallaire S (1993) Copper-titanium diboride coatings obtained by plasma spraying reactive micropellets. *J Therm Spray Technol* 2:283–286
12. Park J, Yun J, Park YD, Park YH, Cho KM, Park IM (2007) Effect of cooling rate on mechanical and electrical properties of Cu- TiB_2 by turbulent in-situ mixing process. *Solid State Phenom Trans Tech Publ* 119:135–8
13. Tu JP, Rong W, Guo SY, Yang YZ (2003) Dry sliding wear behavior of in situ Cu- TiB_2 nanocomposites against medium carbon steel. *Wear* 255:832–835
14. Xu L, Han JC, Zhang XH (2007) Defect and its influence on mechanical property of titanium diboride-copper matrix composite. *Key Eng Mater Trans Tech Publ* 336:1414–6
15. Xu Q, Zhang XH, Han JC, Pan W (2005) Effect of copper content on the microstructures and properties of TiB_2 based cermets by SHS. *Mater Sci Forum Trans Tech Publ* 475:1619–22
16. Balbo A, Monticelli C, Bellosi A, Pagnoni A (2002) Corrosion of alumina/titanium diboride composites in neutral and acidic chloride solutions. *Mater Corros* 53:471–478
17. Monticelli C, Frignani A, Bellosi A, Brunoro G, Trabanelli G (2001) The corrosion behaviour of titanium diboride in neutral chloride solution. *Corros Sci* 43:979–992

18. Ankem S, Margolin H, Greene CA, Neuberger BW, Oberson PG (2006) Mechanical properties of alloys consisting of two ductile phases. *Prog Mater Sci* 51:632–709
19. Bellosi A, Monteverde F, Sciti D (2006) Fast densification of ultra-high-temperature ceramics by spark plasma sintering. *Int J Appl Ceram Technol* 3:32–40
20. Durowoju M, Sadiku E, Diouf S, Shongwe M, Olubambi PA (2015) Spark plasma sintering of graphite–aluminum powder reinforced with SiC/Si particles. *Powder Technol* 284:504–513
21. Hungria T, Galy J, Castro A (2009) Spark plasma sintering as a useful technique to the nanostructuring of piezo-ferroelectric materials. *Adv Eng Mater* 11:615–631
22. Saheb N, Iqbal Z, Khalil A, Hakeem AS, Al Aqeeli N, Laoui T et al (2012) Spark plasma sintering of metals and metal matrix nanocomposites: a review. *J Nanomater*. <https://doi.org/10.1155/2012/983470>
23. Zhang F, Reich M, Kessler O, Burkel E (2013) The potential of rapid cooling spark plasma sintering for metallic materials. *Mater Today* 16:192–197
24. Ghasali E, Palizdar Y, Jam A, Rajaei H, Ebadzadeh T (2017) Effect of Al and Mo addition on phase formation, mechanical and microstructure properties of spark plasma sintered iron alloy. *Mater Today Commun* 13:221–231
25. Diouf S, Molinari A (2012) Densification mechanisms in spark plasma sintering: effect of particle size and pressure. *Powder Technol* 221:220–227
26. Walker LS, Pinc WR, Corral EL (2012) Powder processing effects on the rapid low-temperature densification of ZrB₂–SiC ultra-high temperature ceramic composites using spark plasma sintering. *J Am Ceram Soc* 95:194–203
27. Fogagnolo J, Robert M, Ruiz-Navas E, Torralba J (2004) 6061 Al reinforced with zirconium diboride particles processed by conventional powder metallurgy and mechanical alloying. *J Mater Sci* 39:127–132
28. Choosuwan H, Guo R, Bhalla A, Balachandran U (2002) Negative thermal expansion behavior in single crystal and ceramic of Nb₂O₅-based compositions. *J Appl Phys* 91:5051–5054
29. Grima JN, Zammit V, Gatt R (2006) Negative thermal expansion
30. Palatnikov M, Shcherbina O, Frolov A, Pavlikov V, Karpets M, Makarova O et al (2010) Effect of high-intensity light on the micro- and nanostructuring and thermal expansion of Ta₂O₅ and Nb₂O₅ ceramics. *Inorg Mater* 46:683–690
31. Schäfer W, Kirfel A (2002) Neutron powder diffraction study of the thermal expansion of cuprite. *Appl Phys A* 74:s1010–s1012
32. Chen J, Hu L, Deng J, Xing X (2015) Negative thermal expansion in functional materials: controllable thermal expansion by chemical modifications. *Chem Soc Rev* 44:3522–3567
33. Lind C (2012) Two decades of negative thermal expansion research: where do we stand? *Materials* 5:1125–1154
34. Amos TG. Negative thermal expansion in AOMO₄ compounds. 2000.
35. Douglass D (1963) The thermal expansion of niobium pentoxide and its effect on the spalling of niobium oxidation films. *J Less Common Metals* 5:151–157
36. Dwivedi G, Subbarao E (1973) Thermal expansion of monoclinic (alpha) Nb₂O₅. *J Amer Ceram Soc* 56:443–444
37. Rani RA, Zoofakar AS, O'Mullane AP, Austin MW, Kalantar-Zadeh K (2014) Thin films and nanostructures of niobium pentoxide: fundamental properties, synthesis methods and applications. *J Mater Chem A* 2:15683–15703
38. Takenaka K (2018) Progress of research in negative thermal expansion materials: paradigm shift in the control of thermal expansion. *Front Chem* 6:267
39. Popoola A, Pityana S, Popoola O (2011) Microstructure and corrosion properties of Al (Ni/TiB₂) intermetallic matrix composite coatings. *J South Afr Inst Min Metall* 111:345–353

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.