



Article Superior Plasticity of Silver-Based Composites with Reinforcing Pyrochlore

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Abstract: Silver (Ag) has difficult forming strong bonding with oxides due to its deep d band beneath the Fermi level and completely filled 4d orbital. Thus, it is difficult to fabricate silver-based composites with superior plasticity and processability because of the easy debonding at their interface. Herein, La₂Sn₂O₇ pyrochlore was used as a reinforcing phase for a silver matrix. The enhanced interfacial bonding strength of Ag-La₂Sn₂O₇ was confirmed both theoretically and experimentally, indicating that Ag could form more localized ionic bonding with La₂Sn₂O₇ than with SnO₂. The superior plasticity was further confirmed for the Ag-La₂Sn₂O₇ composite, as the uniform elongation (UE) of the Ag-La₂Sn₂O₇ composite was ~19%, i.e., ~14% higher than and 2.8 times that of the conventional Ag-SnO₂ composite. The plasticity enhancement mechanism was also unraveled by calculating the interfacial mobility. This work verified the usefulness of pyrochlore to fabricate silver-based composites with superior plasticity and also provides a new strategy for the construction of advanced silver-based composites for application in the electrical contact field.

Keywords: silver-based composite; plasticity; enhanced localization; interfacial bonding strength; interfacial mobility



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1. Introduction

Silver (Ag) is widely used in many scientific and industrial fields, such as in heat sink materials, conducting components, electrodes, aircraft circuit breakers, motor controllers, pressure controllers and electric switches due to its excellent thermal and electrical conductivity [1,2]. However, its inferior strength, low hardness and thermal stability do not allow meeting the design requirements for practical applications, especially under severe conditions.

Silver–ceramic particle composites, due to their integrated properties of high hardness and strength, a low thermal expansion coefficient, good arc resistance arising from the ceramic particles and high electrical and thermal conductivity arising from Ag, offer excellent thermal, electrical and mechanical performance, allowing a wide range of applications [3,4]. Great efforts have been made to fabricate the desired silver–ceramic particle composites. As reported previously, mono-oxides such as tin oxide (SnO₂) [5], zinc oxide (ZnO) [6] and nickel oxide (NiO) [7] are promising candidates for high-strength silver-based composites obtained by dispersion strengthening [8]. However, the plasticity and deformability of these composites rapidly degrade with increasing amounts of SnO₂, ZnO and NiO [9].

Since metal-based composites consist of metal and ceramic particles, the characteristics of the metal–ceramic interface are a vital factor that affects the monolithic mechanical properties of the composites [10,11]. A decreased bonding strength in metal-based composites may lead to the formation of cracks during the deformation process and thus to a decrease in plasticity. Generally, the charge transfer between the metal matrix and the metal oxides dispersed phase, which increases the oxidation of the interfacial metal, can enhance the bonding strength by electrostatic attraction. Silver, due to its completely filled d orbital, has

difficulty forming a strong interface with metal oxides [12,13]. Typically, the introduction of heteroelements or defects into the metal matrix was considered an effective way to improve the interface properties of metal-based composites. The introduced elements or defects would affect the electronic structure and bond properties of the interfaces, thus improving or weakening the bonding strength. The introduction of chromium (Cr) improved the bonding strength between SiO_2 and a silver matrix [14], that of both titanium (Ti) and Cr improved the bonding strength between SiO_2 and a copper matrix [15], and that of Ni improved the bonding strength between a copper matrix and Tungsten (W) [16]. Meanwhile, introduced defects such as oxygen vacancies can also improve the metal-ceramic bonding strength by regulating the interfacial electrons distribution and enhancing the interaction between metal cations and oxygen anions [17–19]. However, the heteroatoms or defects introduced in a metal matrix can restrain dislocation motions and act as scattering centers, hindering the motion of electrons and thus decreasing plasticity and conductivity. Thus, changing the components of dispersed metal oxides is a more desirable way to enhance the interfacial bonding strength. In addition, it is of great importance to reveal how different incorporated ceramic particles affect the interfacial properties, thus affecting the plasticity of metal-based composites, and their potential positive effects on conductivity, and thereby guide to the discovery of advanced silver-based composites with superior plasticity and deformability.

In addition, for particle-reinforced composites, the thermal mismatch (difference of the coefficient of thermal expansion between the matrix and the reinforcement particles) would induce residual strain and produce a high density of defects that will restrain the dislocations and decrease the plasticity [20,21]. A high thermal mismatch can induce dislocation accumulation and stress concentration around the two-phase interface, which will also decrease the plasticity of the composites and facilitate microcracks nucleation and growth. The coefficient of thermal expansion (CTE) of silver is about $19.0 \times 10^{-6} \text{ K}^{-1}$, while the CTE of SnO₂, a typical reinforcing phase in silver-based composites, is about 3.8×10^{-6} K⁻¹. Thus, Ag–SnO₂ composites usually show poor plasticity and deformability. Bearing the negative effect of thermal mismatch on plasticity in mind, pyrochlore, a typical ceramic with a high CTE of $7-9 \times 10^{-6} \text{ K}^{-1}$ [22], can be a competitive candidate as the reinforcing phase. So far, although Ag-SnO₂ composites fabricated by internal oxidation and powder metallurgy have been widely used as electrical contact materials, their poor plasticity (the elongation is up to 13% for Ag-SnO₂ composites fabricated by internal oxidation, and to 3~7% for those fabricated by powder metallurgy) impedes the process of replacing the toxic Ag-CdO composites.

Herein, La₂Sn₂O₇ pyrochlore was chosen as the reinforcing phase for a silver matrix. We performed calculations based on the density functional theory (DFT) for the Ag-La₂Sn₂O₇ and Ag-SnO₂ composites to establish the theoretical properties of the silverceramic interface for these two composites (e.g., the bonding properties based on the electron localization function, diffusion coefficient, theoretical displacement under shear stress and binding energy) and predict their mechanical performance, especially plasticity. Accordingly, $Ag-La_2Sn_2O_7$ composites were prepared by the powder metallurgy process combined with the extrusion method and demonstrated superior plasticity. The as-prepared Ag-La₂Sn₂O₇ composites showed enhanced plasticity, which was much higher than that of the Ag-SnO₂ composite and other composites. The plasticity enhancement mechanism was also revealed by theoretical calculations and by comparing the experimental values of conductivity with the theoretical values for the Ag-La₂Sn₂O₇ and Ag-SnO₂ composites, respectively. The good conformity between the experimental and the theoretical conductivity of the Ag-La₂Sn₂O₇ composites indicated interfaces with less defects, which can scatter moving electrons, and good interfacial bonding strength, which hinders the formation of cracks.

2. Materials and Methods

2.1. Materials

All chemicals were of analytical grade and were used without further purification. Oxalic acid, stannic chloride, an ammonia aqueous solution and polyethylene glycol (PEG2000) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Lanthanum nitrate hexahydrate was purchased from Aladdin. The silver powder (purity > 99.9% mass%) was purchased from Wenzhou Hongfeng Electrical Alloy Co., Ltd. (Wenzhou, China).

2.2. Material Synthesis

2.2.1. Synthesis of La₂Sn₂O₇ and SnO₂ Powders

In a typical synthesis of $La_2Sn_2O_7$ powders, 0.025 mol $La(NO_3)_3 \cdot 6H_2O$ and 0.025 mmol $SnCl_4 \cdot 5H_2O$ were first dissolved in 500 mL of deionized water, and then 0.98 g of PEG2000 was added as a dispersant. Ammonia was added to the above solution drop by drop until reaching pH 7~8, and then the solution was subjected to vigorous stirring for 3 h. The precursor powders were obtained by centrifugation, washed with deionized water for 3 times and dried at 80 °C for 12 h. $La_2Sn_2O_7$ pyrochlore was obtained by calcinating the precursor powder at 1200 °C for 2 h (XRD and SEM images are shown in Figure S1 in Supplementary Information). The SnO₂ powder was synthesized by the same method.

2.2.2. Composite Fabrication

The mixed Ag-La₂Sn₂O₇ powders were first subjected to ball milling t a rotation speed of 300 rpm for 4 h using a planetary ball milling machine and the mass fraction of La₂Sn₂O₇ of 12%. Then, the milled Ag-La₂Sn₂O₇ powders were added to a die (Φ 40 mm) and uniaxially pressed at a hydraulic pressure of 7 MPa for 10 s. The obtained disks, 33.10 mm in height and 38.11 mm in diameter, were sintered at 900 °C for 6 h in a muffle furnace. Then, hot extrusion was carried out at 900 °C at an extrusion pressure of 10 MPa to help densification. Subsequently, further heat treatment was carried out at 400 °C for 6 h. The Ag-SnO₂ composites were synthesized through the same process. The ceramic volume fraction was 17.2% in Ag-SnO₂ and 17.5% in Ag-La₂Sn₂O₇. The relative densities of Ag-SnO₂ before and after extrusion were 93.96 ± 0.62% and 95.88 ± 0.27%, respectively, while the corresponding values were 95.37 ± 0.76% and 97.86 ± 0.14% for Ag-La₂Sn₂O₇.

2.3. Material Characterization

Transmission electron microscopy (TEM) was carried out on a JEM-1200 TEM (JEOL, Akishima, Japan) at an acceleration voltage of 120 kV and on a JEM-2100 (JEOL, Akishima, Japan) at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) was carried out on a HITACHI S-8010 scanning electronic microscope (HITACHI, Tokyo, Japan).

2.4. Tensile Test

The Ag-SnO₂ and Ag-La₂Sn₂O₇ composites were used for the tensile test along the hot extrusion direction. The length of the scale distance of the tensile samples was 100 mm. The tensile test was carried out on a unidirectional tensile testing machine (CMT5504) (Sansi Yongheng Technology (Zhejiang) Co., Ltd., Ningbo, China) at a loading rate of 0.5 mm/min. Each sample was measured at least three times.

2.5. Computational Method

The compound Ag-SnO₂ was modelled by building the (1 1 1) plane of Ag and the (1 1 0) plane of SnO₂. Similarly, the model of Ag-La₂Sn₂O₇ was built by the (2 2 0) plane of Ag and the (4 0 0) plane of La₂Sn₂O₇. Structure optimization was performed by the Vienna Ab initio Simulation Package (VASP) [23,24] with a force convergence smaller than 0.05 eV/Å. Monkhorst–Pack k-points of $1 \times 1 \times 1$ were used for all structures. Generalized gradient approximation of the Perdew–Burke–Ernzerhof (PBE) functional [25] was used to describe the exchange–correlation effects of the electrons. The projected augmented wave

(PAW) potentials [26,27] were chosen to describe the ionic cores, taking valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 500 eV. In order to calculate the diffusion coefficients, ab initio molecular dynamics (AIMD) studies were carried out. The optimized structures were firstly equilibrated by NVT ensemble at 300 K, then the production run was carried out with NVT ensemble, holding the temperature at 300 K for 10 ps with a timestep 0.2 fs. The shear strength was calculated according to a previous work [28] on the (1 1 1) plane of Ag in Ag-SnO₂ and on the (2 2 0) plane of Ag in Ag-La₂Sn₂O₇. In order to investigate the microscopic origin of the mechanical properties, the electron localization function (ELF) and static electronic potential were calculated based on the optimized structure.

3. Results

3.1. Theoretical Evaluation of Interfacial Bonding Strength

A theoretical calculation of the electron localization function (ELF) and the evaluation of the bonding energy in the interface of the composites were carried out to confirm the enhanced interfacial bonding strength of the Ag-La₂Sn₂O₇ composites. The models of Ag-SnO₂ and Ag-La₂Sn₂O₇ composites on which our calculations were based are shown in Figure 1a,b, respectively. As shown in Figure 1c, the enhanced localization and ionicity induced by charge transfer between metal and metal oxide could be confirmed at the interface of Ag-La₂Sn₂O₇, while less charge transfer was generated at the interface of Ag-SnO₂, indicating a weaker interaction between Ag and SnO₂. Moreover, the bonding energy calculated was -0.8944 eV for Ag-La₂Sn₂O₇ and -0.5537 eV for Ag-SnO₂, showing enhanced structural stability of the Ag-La₂Sn₂O₇ interface. Apparently, the boosted localization at the Ag-La₂Sn₂O₇ interface and the resulting structural stability indicated the enhanced interface bonding strength of the Ag-La₂Sn₂O₇ composite compared to the Ag-SnO₂ composite.



Figure 1. Established models of the (**a**) Ag-SnO₂ and (**b**) Ag-La₂Sn₂O₇ interfaces; (**c**) electronic localization function (ELF) for the Ag-SnO₂ and Ag-La₂Sn₂O₇ interfaces.

3.2. Microstructures of the Ag-SnO₂ and Ag-La₂Sn₂O₇ Composites

Based on the theoretical prediction of the interfacial bonding strength, the Ag-La₂Sn₂O₇ composites were prepared by the powder metallurgy process combined with extrusion methods. Figure 2 presents the TEM morphologies of the as-prepared Ag-SnO₂ composite and Ag-La₂Sn₂O₇ composite. As shown in Figure 2a, a large number of dislocation walls and dislocation cells were observed near the SnO_2 particle. Meanwhile, the debonding of the SnO₂ particles from the Ag matrix was also detected, as shown in Figure 2a. In contrast, as shown in Figure 2b, dislocation slip bands and movable dislocations were observed near the La₂Sn₂O₇ particles, where no dislocation walls were detected. It is often the case that the mismatch of the CTE between the reinforcements and the Ag matrix will generate geometrically necessary dislocations (GNDs) [29]. The larger density of dislocations and dislocation accumulation observed for $Ag-SnO_2$ can be attributed to the larger CTE mismatch between SnO_2 and the Ag matrix, while the lower CTE mismatch between $La_2Sn_2O_7$ and the Ag matrix produced a lower dislocation accumulation and less hardening [30]. Figure 2c,d shows the HRTEM images of the Ag-SnO₂ and Ag-La₂Sn₂O₇ interfaces, respectively. A clear and tight Ag-SnO₂ interface was observed for the Ag-SnO₂ composite, while a blurred interface indicating an interfacial transition layer was observed for Ag-La₂Sn₂O₇. The presence of an interfacial transition layer indicated enhanced interfacial bonding strength in the Ag-La₂Sn₂O₇ composite, which was consistent with the calculated bonding energy of the Ag-La₂Sn₂O₇ interface. The enhanced interfacial bonding strength confirmed by both theoretical calculations and TEM observations will decrease the formation and growth of microcracks and microcavities, which is beneficial to increasing fracture elongation and plasticity.



Figure 2. TEM images of Ag-SnO₂ (a,c) and Ag-La₂Sn₂O₇ (b,d).

3.3. Tensile Test

Furthermore, a tensile test was conducted on both the $Ag-La_2Sn_2O_7$ composite and the conventional $Ag-SnO_2$ composite to confirm the superior plasticity of the $Ag-La_2Sn_2O_7$ composite experimentally. The engineering stress–strain curves of the $Ag-La_2Sn_2O_7$ composite and $Ag-SnO_2$ composite are shown in Figure 3a. The tensile strength (TS) and uniform elongation (UE) are reported in Table 1. It was found that the $Ag-La_2Sn_2O_7$ com-

posite exhibited superior UE of 19%, which was ~14% higher than that of the Ag-SnO₂ composite. Meanwhile, the TS of the Ag-La₂Sn₂O₇ composite was lower than that of the Ag-SnO₂ composite, indicating good dislocation mobility and a lower density of defects that restrain the motion of dislocation (the typical jagged stress–strain curve induced by twinning was absent). Figure 3b–d shows the fracture morphologies of pure silver, Ag-SnO₂ and Ag-La₂Sn₂O₇, respectively. The fracture surface of pure silver consisted of quite coarse dimples, while the fracture surface of the Ag-La₂Sn₂O₇ and Ag-SnO₂ composites consisted of relatively fine dimples, apparently indicating typical plastic fracture features in all samples [31,32]. For the Ag-SnO₂ composite, the dimples became much denser and shallower than those of pure silver and Ag-La₂Sn₂O₇, indicating a much higher density of microcracks or microcavities in the Ag-SnO₂ composite, primarily formed in the early stage of fracture [31], which is consistent with the lower relative density of the Ag-SnO₂ composite.



Figure 3. Engineering stress–strain curves (**a**); fracture morphologies of pure Ag (**b**), Ag-SnO₂ composite (**c**) and Ag-La₂Sn₂O₇ composite (**d**).

Table 1. Mechanical properties of the Ag-SnO₂ composite and Ag-La₂Sn₂O₇ composite.

Materials	Tensile Strength (MPa)	Uniform Elongation (%)
Ag-SnO ₂ composite	296 ± 6	5 ± 1
Ag-La ₂ Sn ₂ O ₇ composite	243 ± 19	19 ± 3

4. Discussion

4.1. Experimental Demonstration of Enhanced Interface Bonding Strength

In order to further confirm the enhanced interfacial bonding strength, the theoretical conductivity of the Ag-La₂Sn₂O₇ and Ag-SnO₂ composites was also calculated and related to its experimental values. A theoretic formula for silver-based composites was defined by theoretic derivation based on the Effective Medium Theory (EMT) [33].

The assumption of this theory is that the second phase disperses well in the matrix phase, and the structure of second phase is spherical. It was assumed that the finely dispersed second-phase particles were well distributed in the Ag matrix and were nearly spherical. Based on the Bruggeman model [34], the function of the electrical conductivity of the Ag-La₂Sn₂O₇ or Ag-SnO₂ composite is:

$$\frac{\phi(k_1 - k_e)}{k_1 + 2k_e} + \frac{(1 - \phi)(k_2 - k_e)}{k_2 + 2k_e} = 0 \tag{1}$$

where ϕ is the volume fraction of Ag in the composites, k_e is the electrical conductivity of Ag-La₂Sn₂O₇ or Ag-SnO₂, k_1 is the theorical electrical conductivity of Ag ($k_1 = 0.6305 \,\mu\Omega^{-1} \cdot \text{cm}^{-1}$), k_2 is the electrical conductivity of La₂Sn₂O₇ or SnO₂, which is six orders smaller than k_1 ; therefore, k_2 could be neglected. Considering k_2 as zero in Equation (1), the linear dependence of k_e on ϕ was obtained:

$$k_e = \frac{3\phi - 1}{2}k_1\tag{2}$$

By connecting ϕ with the mass fraction of Ag, denoted as w, Equation (3) was obtained:

$$\phi = \frac{w}{\rho_1} / \frac{1}{\rho} = \frac{\rho w}{\rho_1} \tag{3}$$

where ρ is the measured density of the Ag-La₂Sn₂O₇ or Ag-SnO₂ composites, and ρ_1 is the theorical density of Ag ($\rho_1 = 10.49 \text{ g/cm}^3$). Then, by combining Equation (3) with Equation (2), the final expressions of the electrical conductivity (Equation (4)) and electrical resistivity (Equation (5)) of the composites were:

$$k_e = \frac{3\rho w - \rho_1}{2\rho_1} k_1 \tag{4}$$

$$R_e = \frac{2\rho_1}{3\rho w - \rho_1} R_1 \tag{5}$$

where R_1 is the theorical electrical resistivity of Ag ($R_1 = 1.586 \ \mu\Omega \cdot cm$), and R_e is the electrical resistance of the Ag-La₂Sn₂O₇ or Ag-SnO₂ composite. It was showed that the electrical conductivity and/or the electrical resistance of the Ag-La₂Sn₂O₇ or Ag-SnO₂ composite were related to its density and the mass fraction of Ag. In contrast to the ideal conditions assumed in the derivation, microcavities, microcracks and severe dislocations accumulating at the Ag–ceramic interface would induce great electron scattering and cause a deviation between the experimental and the theoretical conductivity. As shown in Figure 4, the curve of the experimental conductivity of Ag-La₂Sn₂O₇ fits well with the theoretical curve, while that of the experimental conductivity of Ag-SnO₂ shows an enhanced deviation from the theoretical curve for increasing SnO₂ amounts and decreasing Ag amounts, indicating enhanced electron scattering, increased interfacial defects and weakened interfacial bonding strength in the Ag-SnO₂ composites.



Figure 4. ρ w- k_e curve of (a) Ag-SnO₂ composites and (b) Ag-La₂Sn₂O₇ composites.

4.2. Mechanism of Enhanced Interface Bonding Strength

Silver, due to its deep d band beneath the Fermi level and a completely filled 4d orbital, has difficult forming strong bonding with oxides. Enhancing the Fermi level difference between Ag and the reinforcing phases can produce a strong interfacial bonding, facilitating the charge transfer at the interface [35,36]. Figure 5a,b shows the Fermi level differences between Ag and the reinforcing phases. The Fermi level difference between Ag and SnO₂ was -1.44 eV, and the Fermi level difference between Ag and La₂Sn₂O₇ was -4.75 eV, indicating enhanced charge transfer between La₂Sn₂O₇ and the Ag matrix. Meanwhile, the pDOS for the Ag/La₂Sn₂O₇ interface showed the overlap between the Ag (4d) and O (2p) states below the Fermi level, indicating a strong hybridization between the Ag (4d) and O (2p) orbitals and enhanced bonding [37–39]. Obviously, although silver is inert, the enhanced interfacial bonding strength induced by the enlarged Fermi level difference and resulting charge transfer could also be achieved.



Figure 5. Calculations of the Fermi level difference between Ag and the reinforcing phases: (**a**) SnO₂, (**b**) La₂Sn₂O₇; projected density of the state plots (pDOS) of the O 2p band and Ag 4d band for the Ag-SnO₂ interface (**c**) and the Ag-La₂Sn₂O₇ interface (**d**).

4.3. Geometric Phase Analysis (GPA) around the Interfaces

The higher dislocation density of the Ag-SnO₂ composite around the interface compared to that of the Ag-La₂Sn₂O₇ composite was confirmed with the TEM images shown in Figure 2. The effect of different reinforcing phases on the interfacial microstructures was further characterized by HRSTEM and corresponding strain mapping. As shown in Figure 6, the ε_{xx} difference between the Ag phase and La₂Sn₂O₇ was small, and only a few high strain zones were observed, indicating a small and homogenous strain in the x direction. In contrast, large, high-strain zones were observed for ε_{xx} of the Ag phase in the Ag-SnO₂ composite. The comparison of the ε_{yy} values showed that the strains in the y direction were similar for the Ag-SnO₂ and Ag-La₂Sn₂O₇ interfaces. Therefore, it can be concluded that the introduced SnO₂ particles produced enhanced strain at the interface, which could induce more defects, thus decreasing the plasticity by restraining dislocation motions and dislocation accumulations.



Figure 6. HRSTEM images of the Ag-SnO₂ interface (**a**) and Ag-La₂Sn₂O₇ interface (**d**); strain mapping at the Ag-SnO₂ interface in the x direction (ε_{xx} , (**b**)) and y direction (ε_{yy} , (**c**)) and corresponding strain-distance curves ((**b1,c1**); strain mapping at the Ag-La₂Sn₂O₇ interface in the x direction (ε_{xx} , (**e**)) and y direction (ε_{yy} , (**f**)) and corresponding strain-distance curves ((**e1,f1**). (red and blue in strain mapping indicate large strain in different directions, while the green indicate a area free from strain).

4.4. Enhanced Interfacial Mobility and Plasticity

Other than the interfacial bonding strength and CTE mismatch, the interfacial mobility of the Ag-based composites is also another very important factor that affects the plasticity of metal-based composites because of the high proportion of metal-ceramic interface in the composites [40,41]. As shown in Figure 7, the shear stress needed for a certain displacement at the Ag-La₂Sn₂O₇ interface was lower than that needed for the Ag-SnO₂ interface, signifying enhanced mobility of the Ag-La₂Sn₂O₇ interface. An enhanced mobility of an interface can be beneficial for releasing the stress concentration at the interface to inhibit the formation and growth of microcracks and the debonding phenomenon, which will further improve the plasticity of the composite [40]. Generally, increased interfacial mobility combined with enhanced interfacial bonding strength and decreased CTE mismatch could finally lead to Ag-La₂Sn₂O₇ composites with good plasticity, boosted deformability mechanics and good processability.



Figure 7. Stress-displacement curves at the Ag-SnO2 interface and Ag-La2Sn2O7 interface.

5. Conclusions

In summary, a successful strategy to obtain Ag-based composites based on theoretical bonding energy and bonding type was demonstrated, and a relevant Ag-La₂Sn₂O₇ pyrochlore composite was successfully fabricated.

- The as-prepared Ag-La₂Sn₂O₇ composite showed enhanced plasticity, approximately 2.8 times that of the traditional and widely used Ag-SnO₂ composite.
- (2) The good conformity between the experimental conductivity and the theoretical conductivity of the Ag-La₂Sn₂O₇ composites indicated interfaces with less defects, which can scatter moving electrons, and good interfacial bonding strength, which hinders the formation of cracks.
- (3) The enhanced mobility of the Ag-La₂Sn₂O₇ interface helped to release the stress concentration at the interface, inhibiting the formation and growth of microcracks and the debonding phenomenon.

Generally, the enhanced interfacial bonding strength, decreased mismatch of the CTE and enhanced interfacial mobility can help to improve the plasticity and processability of Ag-La₂Sn₂O₇ composites.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/met13020325/s1, Figure S1: (a) XRD pattern and (b) SEM image of the obtained La₂Sn₂O₇ powder.

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References

- 1. Bahiraei, M.; Heshmatian, S. Thermal performance and second law characteristics of two new microchannel heat sinks operated with hybrid nanofluid containing graphene–silver nanoparticles. *Energ. Convers. Manag.* **2018**, *168*, 357–370. [CrossRef]
- 2. Damle, T.; Varenberg, M.; Graber, L. Electric Contact Material Selection for Medium and High Voltage DC Circuit Breakers. *Trans. Electr. Electron. Mater.* **2020**, *21*, 329–338. [CrossRef]
- 3. Yu, H.; Zhang, L.; Cai, F.; Zhong, S.; Ma, J.; Bao, L.; Jiu, Y.; Hu, B.; Wei, S.; Long, W. Microstructure and mechanical properties of brazing joint of silver-based composite filler metal. *Nanotechnol. Rev.* **2020**, *9*, 1034–1043. [CrossRef]
- Kennes, K.; Martin, C.; Baekelant, W.; Coutino-Gonzalez, E.; Fron, E.; Roeffaers, M.; Hofkens, J.; Van der Auweraer, M. Silver Zeolite Composite-Based LEDs: Origin of Electroluminescence and Charge Transport. ACS Appl. Mater. Inter. 2019, 11, 12179–12183. [CrossRef] [PubMed]
- Wang, J.; Li, D.; Wang, Y. Microstructure and properties of Ag–SnO₂ materials with high SnO₂ content. J. Alloy. Compd. 2014, 582, 1–5. [CrossRef]
- Wei, Z.; Zhang, L.; Yang, H.; Shen, T.; Chen, L. Effect of preparing method of ZnO powders on electrical arc erosion behavior of Ag/ZnO electrical contact material. J. Mater. Res. 2016, 31, 468–479. [CrossRef]
- Hetzmannseder, E.; Rieder, W. Make-and-break erosion of Ag/MeO contact materials. *IEEE Trans. Compon. Packag. Manuf. Technol. Part A* 1996, 19, 397–403. [CrossRef]
- 8. Muñoz-Morris, M.A.; Garcia Oca, C.; Morris, D.G. An analysis of strengthening mechanisms in a mechanically alloyed, oxide dispersion strengthened iron aluminide intermetallic. *Acta Mater.* **2002**, *50*, 2825–2836. [CrossRef]
- 9. Wei, Z.; Zhang, L.; Shen, T.; Qiao, Z.; Yang, H.; Fan, X.; Chen, L. Effects of Oxide-Modified Spherical ZnO on Electrical Properties of Ag/ZnO Electrical Contact Material. *J. Mater. Eng. Perform.* **2016**, *25*, 3662–3671. [CrossRef]
- Liu, G.; Wang, S.; Misra, A.; Wang, J. Interface-mediated plasticity of nanoscale Al–Al₂Cu eutectics. *Acta Mater.* 2020, 186, 443–453. [CrossRef]
- Lou, M.; Chen, X.; Xu, K.; Deng, Z.; Chen, L.; Lv, J.; Chang, K.; Wang, L. Temperature-induced wear transition in ceramic-metal composites. *Acta Mater.* 2021, 205, 116545. [CrossRef]
- 12. Hammer, B.; Norskov, J. Why gold is the noblest of all the metals. *Nature* 1995, 376, 238–240. [CrossRef]
- 13. Norskov, J.; Abild-Pedersen, F.; Studt, F.; Bligaard, T. Density functional theory in surface chemistry and catalysis. *PNAS* **2011**, 108, 937–943. [CrossRef]
- 14. Xilian, S.; Jianda, S. Influence of Cr interlayer on the structure and optical properties of Ag films on glass substrate by magnetron sputtering. *Appl. Surf. Sci.* 2006, 253, 2093–2095. [CrossRef]
- 15. Russell, S.; Rafalski, S.; Spreitzer, R.; Li, J.; Moinpour, M.; Moghadam, F.; Alford, T. Enhanced adhesion of copper to dielectrics via titanium and chromium additions and sacrificial reactions. *Thin Solid Films* **1995**, *262*, 154–167. [CrossRef]
- 16. Hou, C.; Song, X.; Tang, F.; Li, Y.; Cao, L.; Wang, J.; Nie, Z. W–Cu composites with submicron- and nanostructures: Progress and challenges. *NPG Asia Mater.* **2019**, *11*, 74. [CrossRef]
- 17. Matsunaka, D.; Shibutani, Y. Effects of oxygen vacancy on adhesion of incoherent metal/oxide interface by first-principles calculations. *Surf. Sci.* 2010, *604*, 196–200. [CrossRef]
- 18. Ferrari, A.; Pacchioni, G. Metal Deposition on Oxide Surfaces: A Quantum-Chemical Study of the Interaction of Rb, Pd, and Ag Atoms with the Surface Vacancies of MgO. *J. Phys. Chem.* **1996**, *100*, 9032–9037. [CrossRef]
- Liu, Y.; Ning, X. Influence of α-Al₂O₃ (0001) surface reconstruction on wettability of Al/Al₂O₃ interface: A first-principle study. *Comp. Mater. Sci.* 2014, 85, 193–199. [CrossRef]
- Jikihara, A.; Tanaka, C.; Ballester, R.; Meira, J. Zirconia-ceramic versus metal-ceramic: Thermal expansion mismatch and residual stresses. *Dent. Mater.* 2018, 34, e62–e63. [CrossRef]
- Levy-Tubiana, R.; Baczmanski, A.; Lodini, A. Relaxation of thermal mismatch stress due to plastic deformation in an Al/SiCp metal matrix composite. *Mater. Sci. Eng. A* 2003, 341, 74–86. [CrossRef]
- 22. Feng, J.; Xiao, B.; Zhou, R.; Pan, W. Thermal expansion and conductivity of RE₂Sn₂O₇ (RE = La, Nd, Sm, Gd, Er and Yb) pyrochlores. *Scr. Mater.* **2013**, *69*, 401–404. [CrossRef]
- 23. Kresse, G.; Hafner, J. Ab initio molecular-dynamics liquid-metal—Amorphous-semiconductor simulation of the transition in germanium. *Phys. Rev. B* 1994, 49, 14251–14269. [CrossRef]
- 24. Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mater. Sci.* **1996**, *6*, 15–50. [CrossRef]
- Perdew, J.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868. [CrossRef]
- 26. Blöchl, P.; Jepsen, O.; Andersen, O. Improved tetrahedron method far Brilleuin-zane integratians. *Phys. Rev. B* 1994, 49, 16223–16233. [CrossRef] [PubMed]
- 27. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 1999, 59, 1758–1775. [CrossRef]
- 28. Roundy, D.; Krenn, C.R.; Cohen, M.L.; Morris, J.W. Ideal Shear Strengths of fcc Aluminum and Copper. *Phys. Rev. Lett.* **1999**, *82*, 2713–2716. [CrossRef]
- 29. Wegst, U.G.K.; Bai, H.; Saiz, E.; Tomsia, A.P.; Ritchie, R.O. Bioinspired structural materials. Nat. Mater. 2014, 14, 23–36. [CrossRef]

- Yang, P.; Li, Q.; Tsuru, T.; Ogata, S.; Zhang, J.; Sheng, H.; Shan, Z.; Sha, G.; Han, W.; Li, J.; et al. Mechanism of hardening and damage initiation in oxygen embrittlement of body-centred-cubic niobium. *Acta Mater.* 2019, 168, 331–342. [CrossRef]
- 31. Rong, X.; Zhao, D.; He, C.; Shi, C.; Liu, E.; Zhao, N. Revealing the strengthening and toughening mechanisms of Al-CuO composite fabricated via in-situ solid-state reaction. *Acta Mater.* **2021**, 204, 116524. [CrossRef]
- 32. Zhang, J.; Han, W. Oxygen solutes induced anomalous hardening, toughening and embrittlement in body-centered cubic vanadium. *Acta Mater.* 2020, 196, 122–132. [CrossRef]
- 33. Choy, T. Effective Medium Theory; Oxford University Press: Britain, UK, 1999.
- 34. Bruggeman, D.A.G. Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen. *Ann. Phys.-Berl.* **1935**, *416*, 636–664. [CrossRef]
- 35. Verdozzi, C.; Jennison, D.R.; Schultz, P.A.; Sears, M.P. Sapphire (0001) Surface, Clean and with d-Metal Overlayers. *Phys. Rev. Lett.* **1999**, *82*, 799. [CrossRef]
- Bogicevic, A.; Jennison, D.R. Variations in the Nature of Metal Adsorption on Ultrathin Al₂O₃ Films. *Phys. Rev. Lett.* 1999, 82, 4050. [CrossRef]
- Petrie, J.R.; Cooper, V.R.; Freeland, J.W.; Meyer, T.L.; Zhang, Z.; Lutterman, D.A.; Lee, H.N. Enhanced Bifunctional Oxygen Catalysis in Strained LaNiO₃ Perovskites. J. Am. Chem. Soc. 2016, 138, 2488–2491. [CrossRef]
- Duan, Y.; Sun, S.; Xi, S.; Ren, X.; Zhou, Y.; Zhang, G.; Yang, H.; Du, Y.; Xu, Z.J. Tailoring the Co 3d-O 2p Covalency in LaCoO₃ by Fe Substitution to Promote Oxygen Evolution Reaction. *Chem. Mater.* 2017, *29*, 10534–10541. [CrossRef]
- 39. Kuznetsov, D.A.; Naeem, M.A.; Kumar, P.V.; Abdala, P.M.; Fedorov, A.; Müller, C.R. Tailoring Lattice Oxygen Binding in Ruthenium Pyrochlores to Enhance Oxygen Evolution Activity. J. Am. Chem. Soc. 2020, 142, 7883–7888. [CrossRef] [PubMed]
- 40. Ribes, H.; Suéry, M.; L'Espérance, G.; Legoux, J.G. Microscopic Examination of the Interface Region in 6061-Al/SiC Composites Reinforced with As-Received and Oxidized SiC Particles. *Metall. Trans. A* **1990**, *21*, 2489–2496. [CrossRef]
- Van Trinh, P.; Lee, J.; Minh, P.N.; Phuong, D.D.; Hong, S.H. Effect of oxidation of SiC particles on mechanical properties and wear behavior of SiCp/Al6061 composites. J. Alloy. Compd. 2018, 769, 282–292. [CrossRef]

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