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Preparation of 3YSZ/Cu composite by in-situ chemical route

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Abstract To improve electrical and mechanical properties of electrodes for contact welding, a 3 mol% yttria stabilized zirconia (3YSZ) to reinforced copper matrix composite was developed by an in-situ chemical process. The microstructure and properties of the in-situ composite were investigated. The results showed that in-situ nanoscale particles were uniformly dispersed in the copper matrix by dispersed nano-particle and its cluster. Due to their reinforcement, the hardness of the in-situ 3YSZ/Cu composite significantly increased. Moreover, the electrical conductivity of the in-situ composite decreased with the increase of 3YSZ content.

Introduction

Copper matrix composites have a wide range of application as electrical materials for lead wires, relay blades, contact supports and electrode materials for spot welding because of the combination of high mechanical strength and electrical conductivity [1–3]. Therefore, great attention has been paid to the copper matrix composites with good characteristics. Nano-crystalline yttria stabilized zirconia (YSZ) is a superplastic material, which has made it possible to form different YSZ components using the conventional forming techniques generally applied to metals and alloys. The thermal expansion coefficient is close to that of metals, which makes nano-crystalline YSZ a promising choice as a reinforcement for copper matrix composites [4–7].

To get an excellent composite, the main requirement for structure of dispersion-strengthened materials is a homogeneous distribution and small size of oxide particles in the copper matrix. Conventional melting and casting techniques are unable to give good uniformity of the dispersoid [8]. A few trials such as mechanical alloying or rapid solidification have been used to try to overcome such problems, but often result in contamination and poor economical efficiency. The in-situ chemical method has its particular advantages in dispersing reinforcement particles homogeneously in the copper matrix.

In this paper, the in-situ chemical process was used to produce the 3YSZ/Cu nano composite with a homogeneous distribution and small size of zirconia particles. All steps of the present processes were investigated in detail to optimize the production of the final composite.

Experimental

3ZSY/Cu composite synthesis

The 3ZY/Cu composite was prepared by an in-situ chemical method. Zirconium chloride ($ZrOCl_2 \cdot 8H_2O$) and yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$) were used as precursors for the alcohol solution. Glycol 20000 was used as dispersive agent for the process. The preparation processes of the composite have adopted as the following procedures.

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(1) A known amount of $ZrOCl_2\cdot 8H_2O$ and $Y(NO_3)_3\cdot 6H_2O$ was solved by alcohol solution with a small amount of dispersant to acquire a homogeneous mixed solution, which took place at about 80 °C.

(2) Titrating 25% $NH_3\cdot H_2O$ to the solution until the pH was more than 9.0 to get mixing sol gel solution, deposited for more than 12 h. The reaction can be expressed as:

$$Zr^{4+}(0.1\,\mathrm{mol/L}) + Y^{3+}(0.003\,\mathrm{mol/L}) + 7OH^{1-} \rightarrow Zr(OH)_4 \downarrow + Y(OH)_3 \downarrow$$

and $Zr(OH)_4$,$Y(OH)_3$ sol gels were formed in the solution. To ensure a complete reaction, excess ammonia was used and the pH value of the solution was maintained to about 9. An appropriate diluted polyethylene glycol 20000 was added in order to prevent aggregation.

(3) Add a certain amount of $Cu(NO_3)\cdot H_2O$ to the mixture and mix equably. Then heat to dry and calcine at 500 °C with 10 °C/min heat rate to obtain the precursor CuO and 3YSZ composite powder.

(4) Deoxidize the precursor composite powder at 650 °C in H_2 atmosphere at a rate of 2.5 mL/min for 45 min to acquire the final Cu–3YSZ composite powder.

(5) The composite powder made by the above processes was compressed at 500 MPa, sintered at 975 °C for 1.5 h with a heating rate of 10°C/min in vacuum atmosphere, and finally repressed at 1,000 MPa into cylindrical specimens of about 12 mm in diameter and more than 2 mm in height.

Characterization of the composite and 3YSZ particles

To ascertain the actual content, phase structure and the morphologies of different phases in the composite, the zirconia was extracted by nitric acid. The results of analysis showed that the weight of final 3YSZ powder approaches the theoretically predicted content. Here the small difference of about 2% 3YSZ was neglected in this paper. Phase constituents of composite powder and 3YSZ particles extracted from the composite powder by nitric acid in different phases were identified by a Rigaku X-ray diffract meter with CuK_α radiation at 40 kV and 150 mA. The morphologies of composite powder and nano zirconia were observed using a field-emission scanning electron microscope (SEM; Jeol JSM-6700F) and transmission electron microscope (TEM; PHILIPS TECNAI G^2F20). To analyze the characteristics of the 3YSZ–Cu composite, the composite was etched with the etchant shown in Table 1. After etching the composite microstructure was observed by SEM (Model: Jeol JSM-6340F).

Table 1 The volume constitution of etchant

Etchant constitution	HF	HCl	HNO_3	H_2O
Volume content (mL)	2	3	20	175

The hardness of the 3YSZ/Cu composite was tested using a Vickers hardness tester (model: MH-6) with 50 kg load. The comparative conductivity was tested in whirlpool conductivity (Model: FQR7501).

Results and discussion

Figure 1 shows the DSC/TG data of the composite precursor powders. Endothermic peaks are present at about 200 and 500 °C corresponding respectively to the loss of NO_3 and OH from the decomposition of $Cu(NO_3)_2$ and $Zr(OH)_4$.

The composite powders prepared by the in-situ chemical route before and after deoxidation were analyzed using XRD (Fig. 2). It can be seen that only CuO and tetragonal ZrO_2 peaks exist after calcinations (Fig. 2a). But in Fig. 2b, it can be seen that neither residual metal oxide nor reaction phase were observed after deoxidation in a H_2 atmosphere at 650 °C. At the same time, the peaks of monoclinic ZrO_2 emerged in addition to tetragonal ZrO_2 and Cu (Fig. 4). The results indicate that a tetragonal-monoclinic (t–m) transformation in ZrO_2 takes place during increasing temperature of deoxidation.

Figure 3 shows the morphologies of both deoxidized and non-deoxidized composite powders. The dried CuO and 3YSZ precursor powders have irregular size particles and are spherical in shape (Fig. 3a). After deoxidation

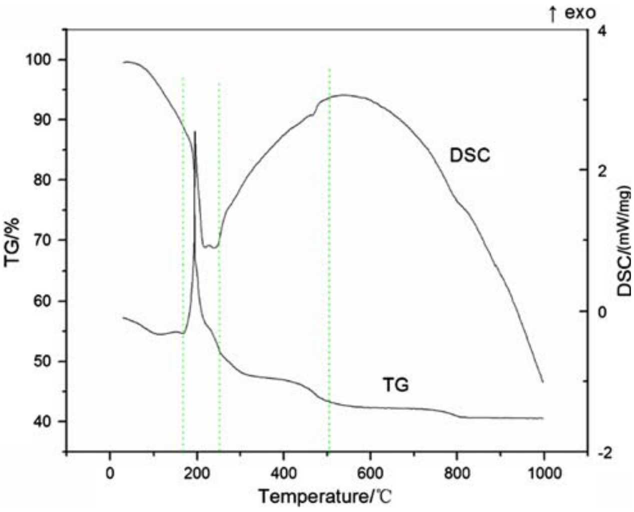


Fig. 1 TG/DSC results for the $Cu(NO_3)_2$ and $Zr(OH)_4$ precursor composite powders

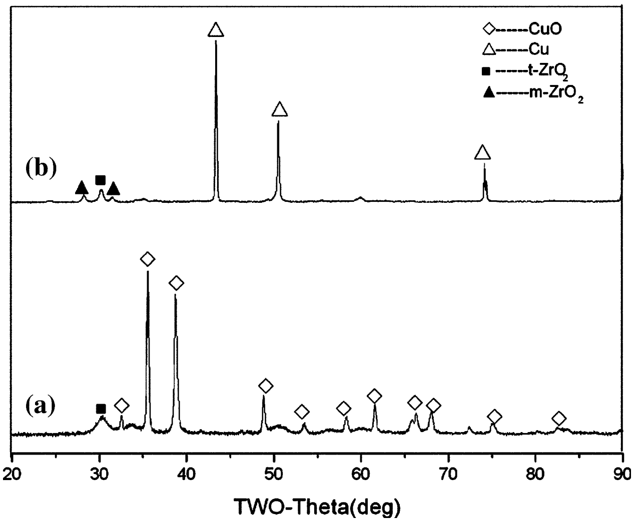


Fig. 2 X-ray patterns of the 8 wt.%3YSZ of (**a**) CuO/3YSZ composite powder after calcinations at 500 °C for 1 h. (**b**) Cu/3YSZ nano composite powder after deoxidation of 650 °C for 45 min

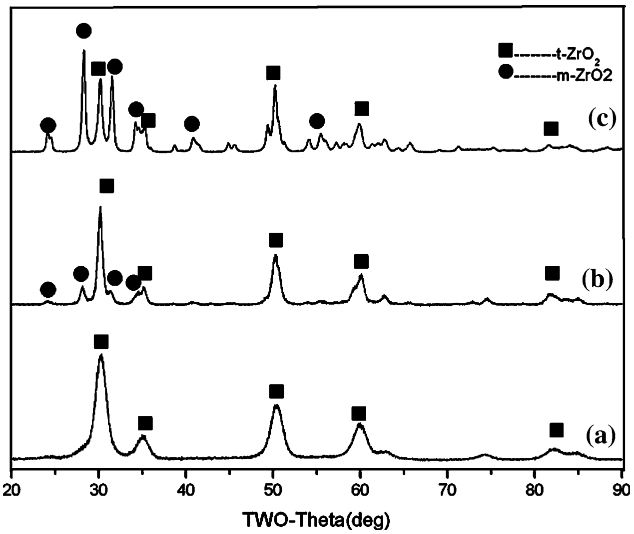


Fig. 4 X-ray diffraction patterns of zirconia extracted from (**a**) CuO/3YSZ composite powder after calcination; (**b**) Cu/3YSZ composite powder after deoxidation; and (**c**) final 3YSZ–Cu composite

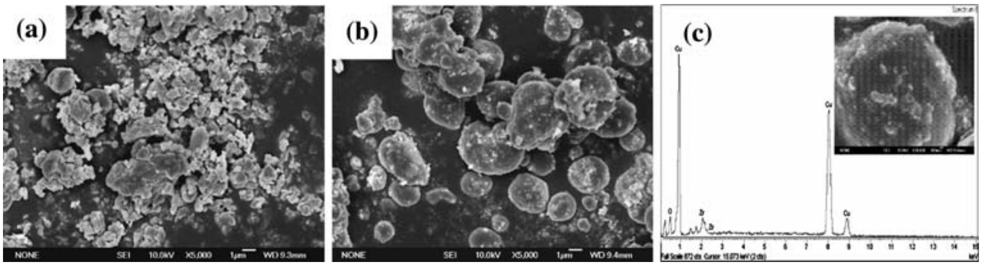
under H_2 atmosphere, the composite powders have a spherical shape and glazed surface particles with a mean size of 3 µm (Fig. 3b). 3YSZ particles, light in contrast with a granular irregular morphology dispersed on copper particles and a high-magnification morphology is presented in Fig. 3c. It has an agglomerated structure of fine particles with the mean size of 20 nm, and these must be Zirconia particles (Fig. 3c).

To analyze and characterize the 3YSZ particles in the different phases of the composite fabrication, the 3YSZ particles were analyzed using XRD in which different zirconia structures were detected, as shown in Fig. 4. It can be seen that monoclinic zirconia exists besides tetragonal zirconia when the 3YSZ–CuO precursor composite powder was deoxidized at 650 °C (Fig. 4b) and the content of monoclinic zirconia increased when the zirconia was extracted from the final composite (Fig. 4c). This indicated that the outside physical influence caused the zirconia crystal transformation (Fig. 4c) and its size also increased (Fig. 5).

Figure 5 shows the morphologies of the 3YSZ particles extracted from the different phases of the composite fabrication. The zirconia particles extracted from the CuO–3YSZ precursor powder were regularly spherical as apparent from Fig. 5. The average diameter of the round zirconia was less than 8 nm. Quadrate zirconia appeared after deoxidation at 650 °C for 45 min because of the crystal transformation to monoclinic. The size of the zirconia particles increased with the fabricating process.

Figure 6 shows the influence of 3YSZ content on the 3YSZ–Cu composite structure. It is noted that the in-situ nano-scale particles were uniformly dispersed in the copper matrix by dispersed nano-particle and its cluster. 3YSZ nano-particles tended to cluster and could not be dispersed adequately in the copper matrix because of the effect of small size. More holes and loose regions existed in the copper matrix. With the increase of 3YSZ content, the loose regions increased but the pores decreased. Meanwhile, EDS analysis of the loose region of 8% 3YSZ–Cu composite as shown by white circle mark in Fig. 6, which shows that there exists a high amount of Zr element, in addition to Cu element. Corresponding to the XRD and EDS analysis results, it was confirmed that the in-situ nano-scale particles in the copper matrix were ZrO_2.

Fig. 3 SEM microstructure consist of (**a**) CuO and 5%3YSZ (**b**) Cu and 5%3YSZ nano composite (**c**) EDS analysis of the large spherical particle of reduced Cu/3YSZ composite powder



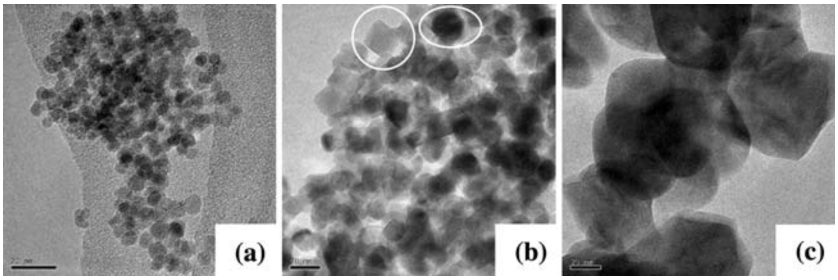


Fig. 5 TEM micrographs of 3YSZ particles extracted from (**a**) 3YSZ–CuO composite powder calcined at 500 °C for 1 h; (**b**) 3YSZ–Cu composite powder reduced at 650 °C for 45 min; (**c**) final composite

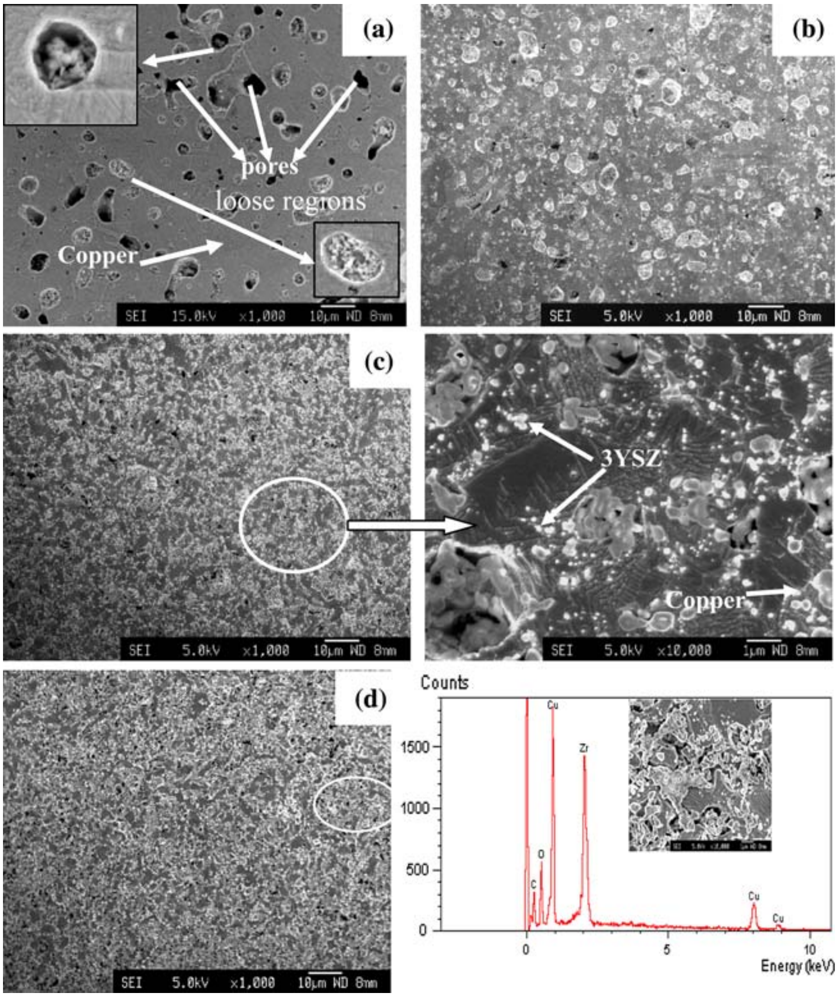


Fig. 6 SEM images of 3YSZ/Cu composite with different 3YSZ content of (**a**)1 wt.%, (**b**) 3 wt.%, (**c**) 5 wt.%, and (**d**) 8 wt.%

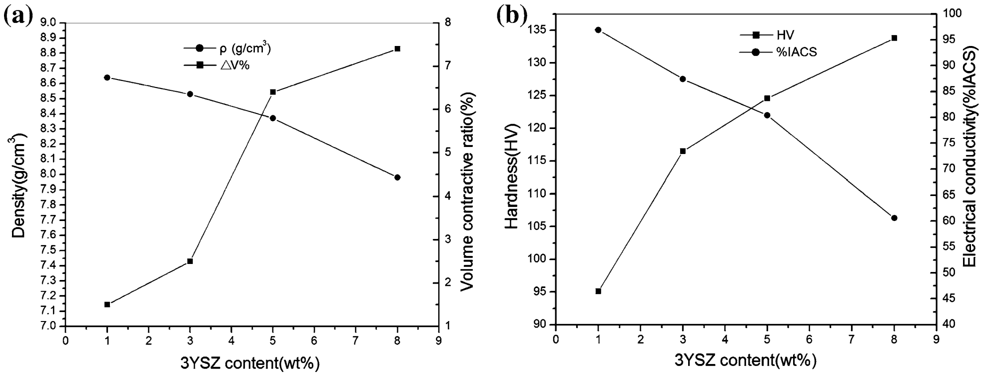
In this work, the hardness and electrical conductivity of in-situ composite cylindrical specimens were tested at room temperature. The results of hardness and electrical conductivity are listed in Table 2.

From Table 2 and Fig. 7, it can be seen that the hardness and the volume contractive ratio of the composite were significantly improved with the increase of 3YSZ content, which can be attributed to the dispersion strengthening by nano-scale 3YSZ. The volume contractive ratio of the composite increased and the pores decreased because the zirconia particle size increased with the temperature increase because of the crystal transformation of tetragonal to monoclinic zirconia as seen in Fig. 5. Compared with the earlier reports [3], it indicates that the in-situ nano-scale particles play a significant role in the contribution of the strength enhancement. However, the presence of 3YSZ nano-particles increased the scattering surfaces for the conduction electrons in the copper matrix and the electrical

Table 2 The influence of 3YSZ content on composite performance

Materials	Density (g/cm^3)	Volume contractive ratio (ΔV%)	Hardness (HV)	Electrical conductivity (%IACS)
Cu-1 wt.%3YSZ	8.64	1.5	95.1 ± 5	96.9 ± 1
Cu-3 wt.%3YSZ	8.53	2.5	116.5 ± 5	87.4 ± 1
Cu- 5 wt.%3YSZ	8.37	6.4	124.6 ± 5	80.4 ± 1
Cu-8 wt.%3YSZ	7.98	7.4	133.8 ± 5	60.6 ± 1

Fig. 7 The influence of 3YSZ content on composite (**a**) density and volume contractive rate; (**b**) electrical conductivity and hardness



conductivity of the copper matrix composite was decreased.

Conclusions

Nanostructured 3YSZ–Cu composite were successfully synthesized by the in-situ chemical method. The size of in-situ formed 3YSZ particles and monoclinic zirconia content increased with the process of composite preparation.

It is noted that the in-situ nano-scale particles were uniformly dispersed in the copper matrix as dispersed nano-particles and clusters. With the increase of 3YSZ content, the loose regions increased and the pores decreased because nano 3YSZ particles tended to cluster and could not be dispersed adequately in the copper matrix. Based on all the previous analysis, it can be concluded that it is necessary to deal with the dispersion problem of nano 3YSZ particles.

From the analysis of the composite performances, the volume contraction ratio and hardness of the in-situ 3YSZ–Cu composite significantly improved with the increase of 3YSZ content because of the nano 3YSZ particles reinforcement effect. But the electrical conductivity decreased because the presence of 3YSZ nano-particles increased the scattering surfaces for the conduction electrons in the copper matrix.

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