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ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 1773−1778
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Application of face centred cubic TiB powder as conductive filler for electrically conductive adhesives

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Received 8 May 2013; accepted 12 May 2014

Abstract: Face centred cubic (FCC) TiB ceramic powder synthesized by Ti-boronizing method was used as conductive filler to make ceramic electrically conductive adhesives (ECAs) with the polymer matrix. Electrically conductive properties of the ceramic ECAs were studied. The bulk electrical resistivity varied with the powder content of the FCC-TiB in ECAs. The FCC-TiB filled ECAs also showed the percolation behavior that usually occurred for the metal-filled ECAs, the percolation threshold was located at the content of 60% FCC-TiB. A minimum value of 0.1 Ω·cm was obtained at a content of 75% FCC-TiB. In order to check the reliability of mechanical property, tensile test was done to measure the shear strength, and the shear strength dropped with increasing the content of FCC-TiB powders. It is about 12.26 MPa at the content of 70% TiB powders. The Cu filled ECAs were also prepared for comparison. The properties of the oxidation resistance of the two ECAs were evaluated. The results show that the ceramic ECAs have excellent oxidation resistance and better stability compared with the Cu filled ECAs.

Key words: ceramic powder; face centred cubic; TiB; electrically conductive adhesives; bulk resistivity; oxidation; shear strength

1 Introduction

It is well known that many applications of conductive ceramic powders, such as BN, TiC, SiC, TiB_2, TiN and TiB, are realized due to their advanced properties. Usually, they are used as enhancements for substrate, also can be used as electrical conductive particles to improve cutting property of electrical discharge machining (EDM) of ceramic cutting tool materials [1,2]. But now, there is little attention focused on FCC-TiB, mainly because it had never been fabricated purely since it was first reported [3]. The attention to TiB employed as enhancements is almost its in situ synthesis of TiB whisker in titanium matrix composites [4−6]. Recently, we fabricated relatively pure TiB powder with face centred cubic structure by boronizing Ti [7], and made it possible to study the structure, properties and the other applications of TiB powder. In this work, we developed a new ceramic conductive adhesive using the FCC-TiB powder as conductive filler.

ECAs have played an important role in electrical industry [8−10]. They are usually fabricated with the polymer matrix and various conductive particles which are referred to as fillers. The task of the filler is to make ECAs possess electrical conductivity. Such metal particles as Ag [11] and Cu [12] were frequently used as fillers for various ECAs because of their good electrical conductivity. The problem for the present ECAs made with such metal fillers is that they have tendency to be oxidized at elevated temperatures. The FCC-TiB is a kind of electrical conductive ceramic whose electrical resistivity is similar to some of metals and has never been used as filler in ECAs. Although some electrical ceramic compounds, such as BN, TiB_2, TiN and SiC, were used as the second filler to improve the electrical and thermal conductive properties of ECAs [13], the main fillers are still metals and nano carbon particles which are most commonly used [14−16] in ECAs. Compared with using those conductive ceramic powders mentioned above as filler for fabricating ECAs, our

Foundation item: Project (51172088) supported by the National Natural Science Foundation of China
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DOI: 10.1016/S1003-6326(14)63252-0

study of using conductive Ti-boronizing FCC-TiB ceramic powder mainly as filler is a originative way which seems to be fast, simple, and economical.

In this work, we take FCC-TiB powder as filler to make ceramic ECAs with polymer matrix. The effects of the content of FCC-TiB filler on electrically conductive properties, shearing strength and stabilities of the FCC-TiB ECAs are investigated.

2 Experimental

2.1 Preparation of ECAs sample

The epoxy resin (E51), curing agent (T31) and antifoamer were used to make the polymer matrix. The particle size of conductive FCC-TiB powders used as filler ranged from the nano-size to micro scale. The contents of FCC-TiB powders used for fabricating ECAs were selected to be 50%, 55%, 60%, 65%, 70% and 75% (mass fraction), respectively. The Cu-filled ECAs were also prepared for comparison, but only a content of 70% Cu was chosen (Cu ≥99.85%, Fe <0.02%, Pb <0.05%, As <0.005%, Sb <0.01%, O <0.15%, Bi <0.004%, S <0.004%, impurity <0.3%); the particle size of Cu powder was less than 48 μm. For making both the FCC-TiB filled and Cu-filled ECAs, the powders were mixed with polymer matrix (m(E51):m(T31)=100:25, 0.5% antifoamer) by the acetone and the mixtures were subsequently smeared on the glass plates, according to the Chinese standard (GJB548A−1996). The dimensions of the coated ECAs films were 65 mm × 2.54 mm × 0.1 mm. Then some of the coated films were aged in a furnace at 80−160 °C for 200 h in order to investigate the oxidation resistance of ECAs. The others were naturally aged in air for 2000 h.

2.2 Characterization of ECAs sample

The aged ECAs were checked by X-ray diffraction (XRD), operated at voltage 40 kV and current 40 mA, using Cu K_α radiation (model D/max 2500pc, Rigaku, Japan). Microstructures of FCC-TiB powders and ECAs were examined by a scanning electron microscope (SEM) (model JSM−5310, JEOL, Japan) equipped with energy dispersive spectroscopy (EDS) (model INCA Energy 250, Oxford, UK).

2.3 Measuring of bulk resistivity

The resistance was measured by 4-point probe method. The data given in this work were the average values of three measurements. The bulk electrical resistivity was calculated with the following equation:

$$\rho=R(wt)/L$$

where ρ is the bulk electrical resistivity; R is the electrical resistance; w is the width; t is the thickness; L is the length.

2.4 Shear strength testing

The sample preparation and testing method for shear strength accorded to the Chinese standard GB7124−86. The structure of shearing sample is shown in Fig. 1. Two pieces of LY12CZ were used in one sample, and purification treatment should be done in order to remove the film of Al_2O_3. ECAs were smeared on one end of the two pieces of LY12CZ, and then glued at a certain pressure. After curing 1 h at 150 °C, tensile test was done on MTS 810 after aging, and tensile rate was 1 mm/min. The maximal load was recorded when rupturing. The shear strength was calculated with the following equation:

$$\tau=P/(BL)$$

where τ is the tensile shear strength; P is the maximal load; B is the width of bonding surface; L is the length of bonding surface.

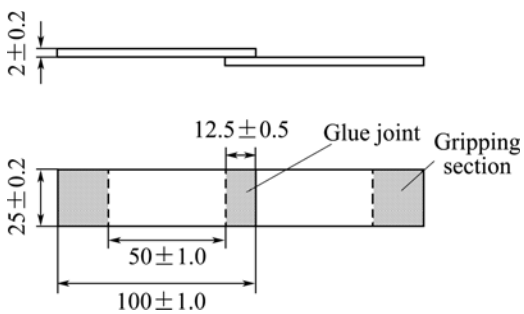

Fig. 1 Schematic diagram of sample for shear strength test (unit: mm)

3 Results

3.1 Physical properties and microstructure of FCC-TiB powders

The physical properties of FCC-TiB powders are shown in Table 1. The distribution of particle size of FCC-TiB powders is shown in Table 2. The particles with nano size are included in a group of 26.2%. Morphology of FCC-TiB powder is shown in Fig. 2.

Table 1 Properties of FCC-TiB powders

Purity/%	Melting point/°C	Crystal structure	Space group	Crystal constant/nm	Hardness (HV_{100})	Bending strength/MPa	Sintered density/($g\cdot cm^{-3}$)	Relative density/%	Electrical resistivity/($\Omega\cdot cm$)
≥95	≥2200	NaCl-type structure	$Fm\bar{3}m$	0.245	1000	240−300	4.9−5.1	93.1	3.4×10^{-7}

Table 2 Particle size distribution of FCC-TiB powders

Particle size/μm	>74	61	43	40	38	25	<25
Mass fraction/%	20.6	7.3	9.3	6.3	12.3	18.1	26.2

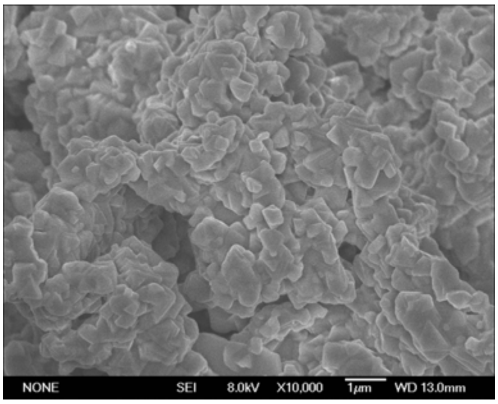

Fig. 2 SEM image of FCC-TiB powder

3.2 Influence of FCC-TiB powder content on bulk electrical resistivity

Figure 3 shows the relationship between the bulk electrical resistivity (sorted for bulk resistivity in following sections) and content of FCC-TiB for the FCC-TiB filled ECAs aged at 150 °C for 1 h. The maximum value of 70.47 Ω·cm appeared at a content of 55% FCC-TiB and the value dramatically dropped to about 3.02 Ω·cm at the content of 60%. The electrical resistivities are 2.13 Ω·cm and 0.19 Ω·cm at the content of 65% and 70%, respectively, and then gradually decrease to about 0.064 Ω·cm at the content of 75%. According to Refs. [11,17], the variation of the bulk resistivity with the content of the filler for ECAs filled with metal fillers usually presents a turning point at which the bulk resistivity drops suddenly and this turning point is referred to the percolation threshold. Apparently, the percolation threshold for the FCC-TiB filled ECAs were located at the 60% FCC-TiB as shown in Fig. 3. The fact that FCC-TiB filled ECAs shows the same behavior as the ECAs made from metal fillers indicates that FCC-TiB particles may play the same role like the metal particles.

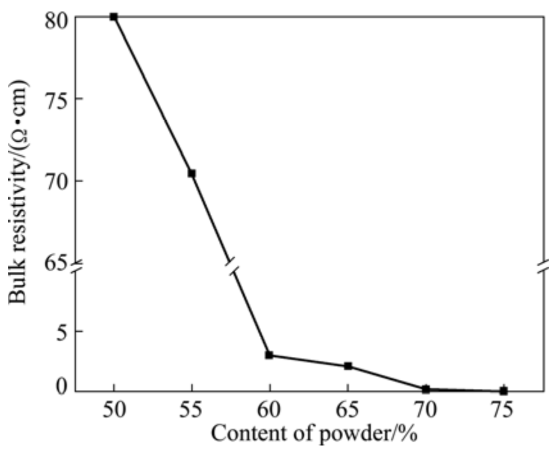

Fig. 3 Relationship between bulk resistivity and content of FCC-TiB powder

SEM observations revealed that the FCC-TiB particles were reunited and coated with the epoxy resin, which are not well connected with each other in ECAs at the content of 50% FCC-TiB from Fig. 4(a), and some big holes still exist. The thickness of insulating layer is too large to form conductive path, so enough conductive networks are not formed. There are two main reasons: first, the FCC-TiB particles are too little to form conductive path; second, the distribution of FCC-TiB particle is not homogeneous. In view of the limitations of the test method, adding more FCC-TiB powders into ECAs increases conductive path without considering the dispersion degree. As a result, a desirable content for a good distribution of the FCC-TiB in ECAs is found to be 75% at which the minimum resistivity of 0.064 Ω·cm is obtained as shown in Fig. 3. Meanwhile, it can be found that FCC-TiB particles are homogeneously dispersed as shown in Fig. 4(b). Network structure of ECAs becomes closed-packed in spite of a few holes.

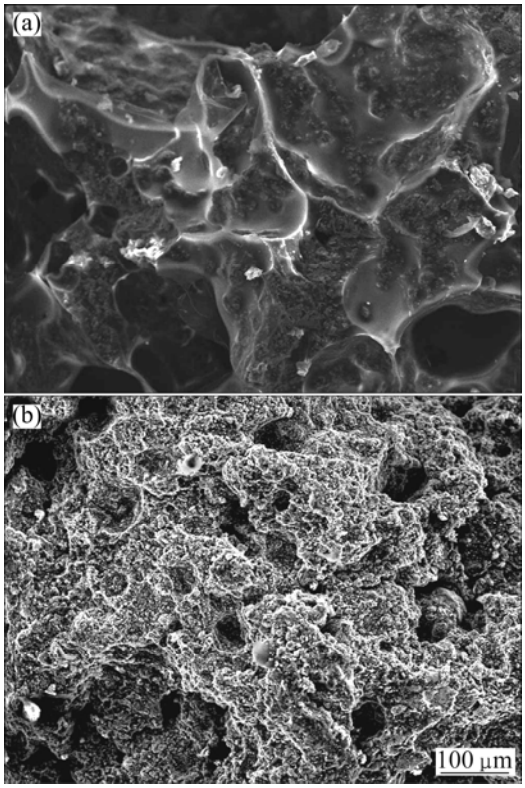

Fig. 4 SEM images of ECAs filled with 50% (a) and 75% (b) FCC-TiB powders

Figures 5(a) and (c) show SEM images of polished surface for ceramic ECAs in which the contents of FCC-TiB powders are 65% and 75%, respectively.

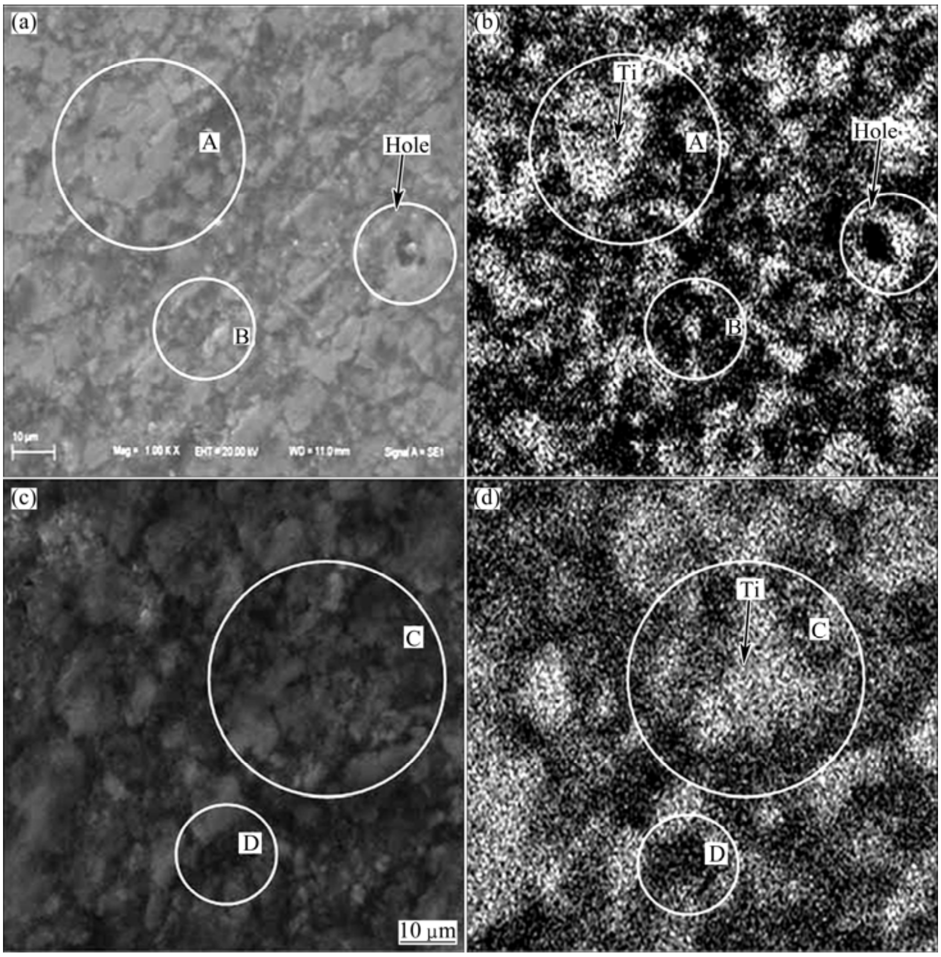

Fig. 5 SEM images (a, c) and EDS (b, d) images of ECAs filled with 65% (a, b) and 75% (c, d) FCC-TiB powders

Figures 5(b) and (d) show element face-distribution EDS mapping images of Ti corresponding to Figs. 5(a) and (c), respectively. Ti-containing regions in ECAs can be recognized as the positions occupied by FCC-TiB particles. It can be seen from Figs. 5(a) and (b) that the FCC-TiB particles reunite (white part), and there are too much epoxy resin(black part) and a few holes because the content of powders is lower. In Figs. 5(c) and (d), the volume of the epoxy resin decreases, the area of the reunited powders expands, the holes basically disappear, and insulting layer is thinner. It is clear that FCC-TiB particles are more homogeneously dispersed in ECAs filled with 75% FCC-TiB powders as shown in Fig. 5(d), which is the sufficient result of increasing electro-conductibility.

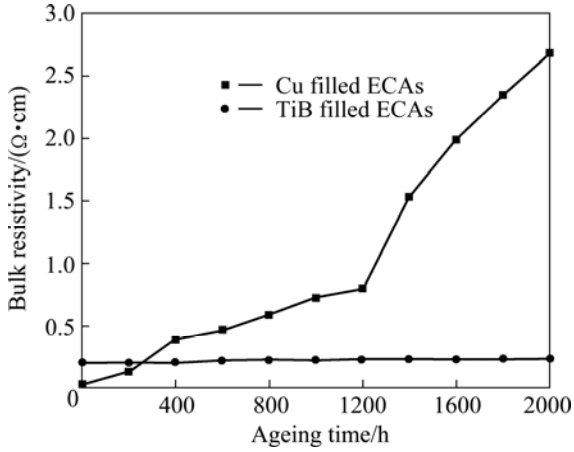

Fig. 6 Variation of bulk electrical resistivity with ageing time for both FCC-TiB filled and Cu filled ECAs aged at room temperature for 2000 h

3.3 Oxidation resistance of FCC-TiB filled ECAs

Figure 6 shows the variation of bulk resistivity with ageing time for both the FCC-TiB filled ECAs and Cu filled ECAs at room temperature. All the values of bulk resistivity of the Cu filled ECAs are lower than those of FCC-TiB filled ECAs within 200 h, but they increase significantly after 200 h. On the other hand, the bulk resistivity of the FCC-TiB filled ECAs remains almost unchanged during ageing for 2000 h. It is, therefore, summarized that the FCC-TiB filled ECAs have better oxidation resistance.

Both the Cu filled and FCC-TiB filled ECAs were simultaneously aged at 130 °C for 200 h. Figure 7 shows the relationship between the bulk resistivity and ageing time for both ECAs. As can be seen, both keep a resistivity of about 0.1 Ω·cm from the onset of ageing within 60 h, but the resistivity of the Cu filled ECAs rises rapidly after ageing for 60 h. On the other hand, the bulk resistivity of FCC-TiB filled ECAs still remains unchanged. This also shows that FCC-TiB filled ECAs have good oxidation resistance. Figure 8 presents XRD patterns for both the FCC-TiB filled and Cu filled ECAs after ageing at 130 °C for 200 h. Some diffraction peaks appearing in scanning line for the Cu filled ECAs can be recognized as the diffraction peaks resulting from Cu_2O (see Fig. 8(b)). This indicates that the Cu particles are oxidized. In contrast, the diffraction peaks for the FCC-TiB filled ECAs before and after ageing show no change (see Fig. 8(a)), indicating that the FCC-TiB particles keep stable during ageing. The reason for the FCC-TiB ECAs having good bulk resistivity can be attributed to the better oxidation resistance and better stability of the FCC-TiB particles. It is well known that ECAs filled with FCC-TiB ceramic powders have longer service life compared with that filled with normal metal powder.

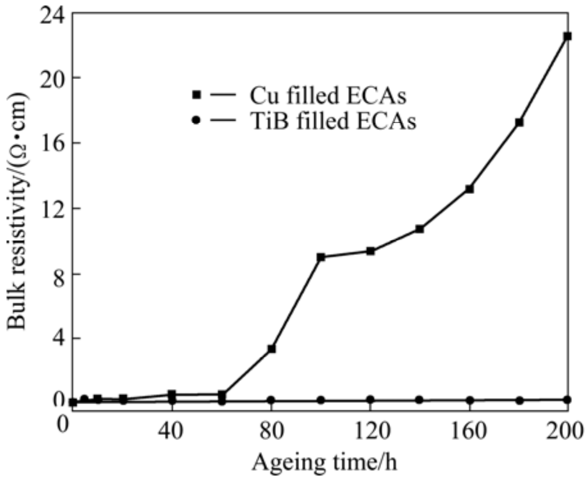

Fig. 7 Variation of bulk electrical resistivity with ageing time for both FCC-TiB filled and Cu filled ECAs aged at 130 °C for 200 h

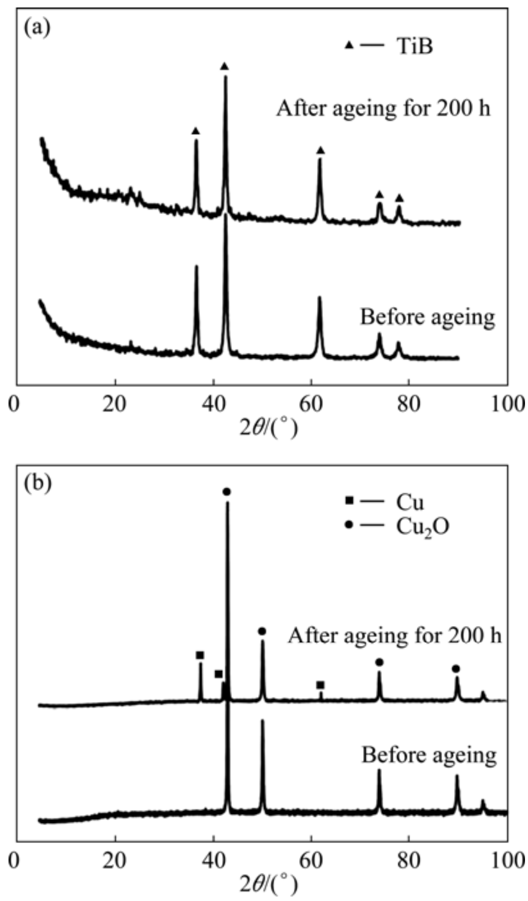

Fig. 8 XRD patterns of FCC-TiB (a) and Cu (b) filled ECAs before and after aging at 130 °C for 200 h

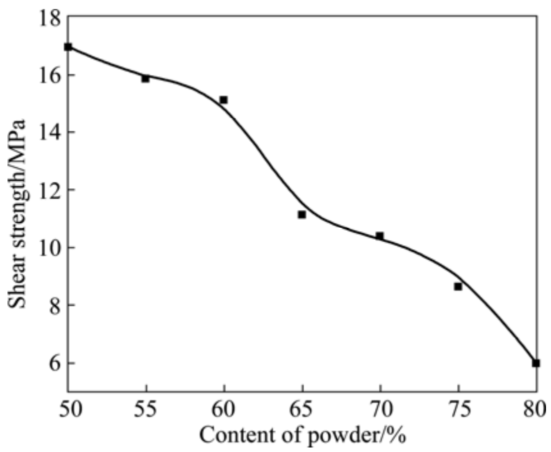

Fig. 9 Relationship between shear strength and content of FCC-TiB powders

3.4 Shear strength of FCC-TiB filled ECAs

Figure 9 shows the relationship between the shear strength and content of FCC-TiB powders for the FCC-TiB filled ECAs aged at 150 °C for 1 h. It can be seen that the shear strength drops with the content of FCC-TiB powders, but the shear strength is greater than 15 MPa if the content of conductive powders does not exceed 60%, and is lower than 10 MPa if the content exceeds 70%. The shear strength is 12.26 MPa at the content of 70% TiB powder. It is well shown that the content of the FCC-TiB powders has a bad effect on shear strength, and it cannot exceed 70% if we want to obtain the reliable mechanical property. This means that electro-conductibility must be sacrificed accordingly.

4 Conclusions

FCC-TiB powders were used as filler to make ceramic ECAs. The bulk electrical resistivity decreases with increasing the FCC-TiB content of ECAs. A minimum electrical resistivity of 0.1 Ω·cm is obtained at content of 75% FCC-TiB powders. The FCC-TiB filled

ECAs also show the percolation behavior that usually occurs for the metal-filled ECAs. The oxidation resistance of the FCC-TiB filled ECAs is better than that of Cu filled ECAs. The FCC-TiB can be taken as an available candidate to be used as filler for making ceramic ECAs. The content of the FCC-TiB powders has a bad effect on shear strength. The shear strength is 12.26 MPa at the content of 70% TiB powders. The mechanical properties are not desirable although its conductive property is perfect.

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面心立方 TiB 陶瓷粉末填充型导电胶

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摘　要：将纯钛渗硼方法合成的面心立方 TiB 导电陶瓷粉末作为填料，制作了树脂基陶瓷导电胶。研究了陶瓷导电胶的电性能。导电胶的体电阻率随着面心立方 TiB 粉末含量的变化而变化。面心立方 TiB 陶瓷粉末填充型导电胶表现出与金属填充型导电胶相同的逾渗行为，渗流阈值出现在面心立方 TiB 陶瓷粉末含量为 60%时。当面心立方 TiB 含量为 75%时获得了最小体电阻率，0.1 Ω·cm。为检验力学性能的可靠性，进行拉伸试验，测量不同 TiB 粉末含量导电胶的剪切强度，发现剪切强度随着面心立方 TiB 粉末含量的增加而降低，当 TiB 粉末含量为 70%时，剪切强度约为 12.26 MPa。制备了铜粉添加型导电胶用作对比，评估了 2 种导电胶的抗氧化性能。结果表明，陶瓷导电胶具有优异的抗氧化性能和良好的稳定性。

关键词：陶瓷粉末；面心立方；TiB；导电胶；体电阻率；氧化；剪切强度

(Edited by Xiang-qun LI)