Influence of Mo Addition on Dielectric Properties of AlN Ceramic Matrix Composites

Yan ZHANG, Zhimin YANG, Huina MA and Jun DU
Institute of Advanced Electronic Material, General Research Institute for Non-ferrous Metals, Beijing 100088, P. R. China
E-mail:zhy126111@163.com

Abstract. AlN-Mo composite ceramics were prepared by spark plasma sintering (SPS) with CaF₂ as sintering aids. Effect of Mo addition on the thermal conductivity and dielectric properties of the composite ceramics had been studied. The results show that the room temperature thermal conductivity increases with increasing the content of Mo, and the value begins to decrease slightly when the Mo concentration exceeds 20 vol. %. Analyses indicate that the key factors to dielectric properties are the metal phase concentration and the microstructure of Mo particles. 1 vol. % Ni has been added into the composite ceramics to change the distribution of the Mo phase. The elongated shape particles which link with each other have a tendency to acquire rounded forms which are thermodynamically more stable. Consequently, the dielectric constant and loss of the composite ceramics could be adjusted and the material becomes an electrical conductor in the case of Mo volume fraction of more than 23%. Furthermore, the dielectric properties could be improved to a large extent by transforming the microstructure of the metal particles when the concentration of Mo is fixed.

1. Introduction
Microwave lossy materials are widely used in vacuum electronic devices to suppress unwanted electromagnetic modes, prevent self-oscillation, enhance the bandwidth of resonant cavities, and provide matched electromagnetic terminations [1]. Electromagnetically lossy ceramic materials based on BeO matrix have traditionally been the best choice of materials due to their high thermal conductivity. However, its field of application with BeO-containing materials is restricted because of health issues. Aluminum Nitride ceramics attract growing interests for applications which need high thermal conductivity, good electrical properties, low density value and a low thermal expansion coefficient. According to the microstructure and composition of the sintered ceramics, it presents a good thermal stability at temperatures higher than 2673 K, whereas thermal conductivity of polycrystalline AlN varies between 80 and 200 Wm⁻¹K⁻¹[2-4]. New AlN-based materials are developed as the lossy materials instead of traditional material BeO. The way of improving microwave absorbing property of the AlN-based composites could be the addition of a metallic phase with higher electronic and thermal properties [5-6]. Molybdenum was chosen due to its sufficiently high melting point (2883 K), high thermal conductivity (138 Wm⁻¹K⁻¹), good electrical properties and close to AlN thermal expansion coefficient (~7x10⁻⁶ K⁻¹ between 300 and 1200 K, against ~6.5x10⁻⁶ K⁻¹ for pure AlN in the same range of temperature) [7-9].

In the present study, for the first time, composites of AlN and Mo were sintered by spark plasma sintering to evaluate the density of the composites. The objective of this work was to study the
influence of molybdenum addition on the dielectric properties of AlN-Mo composites in order to investigate the thermal conductivity, the percolation threshold, and to explore the factors which were vital to dielectric properties.

2. Experimental procedure
Commercially available AlN, Mo and CaF$_2$ were used as the starting powders. The average particle sizes of AlN and Mo were 0.1~1 μm and 1~10 μm, respectively. The combined powders were prepared by wet ball milling in alcohol for 24 h with zirconium dioxide balls. After drying at 80°C, the mixtures were blended by dry milling for a period of 12 h. Each of the resulted powders was put into a graphite die with a pressure of 20 MP in vacuum for 5 min to produce a ceramic disk. A thin BN film was deposited on the inner wall of the mould in order to avoid any interaction between the powder and graphite. The sintering temperature employed for SPS varied from 1500°C to 1700°C.

The crystalline phases were characterized by X-ray diffraction (XD-2) with Cu Kα radiation. The microstructure was analyzed by BRIGHT A100 digital microscope. DRP-4W thermal conductivity equipment and Agilent 4284A were employed to test the thermal conductivity and dielectric properties, respectively.

3. Results and discussion
3.1. Thermal Conductivity
The values of room temperature thermal conductivity of AlN-Mo composites, as a function of Mo concentration, are presented in figure 1. It is obvious that the thermal conductivity variation has been due mainly to the variation in volume fraction of metal phase. It could be seen that the value for pure AlN reaches 89 Wm$^{-1}$K$^{-1}$. The relatively low value is mainly attributed to two causes: the presence of oxygen impurities within the AlN lattice and on the AlN grain surface [10-11], besides, the low compact structure because of the nature of AlN. Its value decreases when a little portion Mo had been added in and increases to about 105 Wm$^{-1}$K$^{-1}$ with increasing the content of Mo to 20 vol. %. However, the value begins to decrease slightly to about 101 Wm$^{-1}$K$^{-1}$ for a composite containing 23 vol. % Mo. Because of the ductile nature of AlN, the addition of Mo is supposed to improve the sintering performance as well as the thermal conductivity. Presence of Mo played an important role to develop a perfect contact with the matrix and to reduce the thermal contact resistance at the interface. Due to the addition of CaF$_2$, densification was further increased. Therefore, the values of room temperature thermal conductivity increase rapidly. However, high proportion of Mo reduces the value because of its lower thermal conductivity compared with AlN.

![Figure 1](image-url)

**Figure 1.** Room temperature thermal conductivity of composites as a function of Mo volume fraction
3.2. Microstructure Characterization

Earlier studies prove that when two surfaces having different work functions are in contact, a charge transfer takes place in such a manner that the surface having higher value of work function is enriched in electrons. This transfer of charge at the interface between metallic particle and the ceramic matrix is responsible for the formation of a space charge layer at the particle surface [12-13]. The dielectric properties of the system depend upon the electronic concentration in the space charge layer, the thickness of the space charge layer and the distance between the two particles. Analyses indicate that the key factors to dielectric properties are the metal phase concentration and the microstructure of Mo particles. According to the results, the efforts to increase the Mo concentration and to control the microstructure are essential.

![Figure 2](image)

**Figure 2.** The microstructure of AlN-Mo composite ceramics with different ratio of Ni (a) Without Ni (b) 1% Ni by volume (c) 2% Ni by volume

Figure 2(a) shows the typical microstructure of the sintered AlN-Mo sample containing 20 vol.% Mo (AM20). The black areas are AlN, and the white phases with clear contrast are of Mo. The structure is relatively homogeneous, showing metal particles quite uniformly distributing in the AlN matrix. The metal particles which contact with each other present slim strip shape. The sample becomes a conductor without any dielectric property. Figure 2 (b) and (c) illustrates the structures of AM20 doped with 1 vol.% Ni and 2 vol.% Ni, respectively. Three samples were prepared under same processing with a pressure of 20 MPa and the temperature of 1500°C. Compared to figure 2(a), the angular slim structure of initial Mo powder particles is not preserved in the sintered structure. The particles have a tendency to acquire rounded forms which are thermodynamically more stable and the particle size is increased wherever a contact is established. With the increasing content of Ni, the size of metal particles becomes larger. Presence of Ni makes for forming liquid phase which improves sintering process. It is obvious that a little liquid phase leads to rounded metal particles to keep from contacting with each other during the sintering processes. This phenomenon makes for increasing the Mo concentration and controlling the microstructure of metal phase which are key factors for dielectric properties.

Figure 3 shows the X-ray diffraction analysis of the AM20 doped with 1 vol.% Ni after sintering at 1500°C for 5 min. It can be seen that no trace of Ni phase was found in the sintered specimens. Mo2C are newly formed phases, and are resulted from the reaction of Mo with graphite although 1.5mm cemented layer has been removed to void carbide for each side. It can be concluded that Mo solid solution with Ni has been formed during sintering process owing to high temperature and the magnetic properties won’t be influenced.
3.3. Dielectric Properties

Figure 4(a) and (b) give the variation of the dielectric constant and loss as a function of Mo volume fraction at 1MHz, respectively. The results show that the values of dielectric constant and loss increase with increasing the volume fraction of Mo in the composite to 23%. The dielectric constant $\varepsilon_r$ reaches 73.3 and loss $\tan\delta$ reaches 0.26 when the Mo content is 23%. When the distance between metal phase particles in the solid material is decreased due to an increase in the metal phase concentration, the free electron population in the region between the two particles is increased. This insulator to conductor transformation can be attributed to a percolation phenomenon due to the presence of metal particles in the ceramic matrix. The metal particles are in contact with each other for a volume fraction bigger than 23%. Critical concentration corresponding to AlN-Mo composites can be viewed as 23% by volume. It can be seen in figure 4, both the dielectric constant and loss increase rapidly before the volume fraction of Mo reaching 20%, the values don’t show an remarkably improvement when molybdenum concentration in the AlN matrix is increased from 20% to 23%.

![Figure 3. XRD analysis of AM20 doped with 1% Ni](image)

![Figure 4. Dielectric constant and loss of composites as a function of Mo volume fraction](image)

Figure 5 show the variation of the dielectric constant and loss as a function of frequency under different sintering temperatures for AM20. The results show that dielectric constant and loss can be changed evidently by different sintering performance when the Mo concentration is fixed. The phenomenon can be the result of the changed microstructure of metal phase.
4. Conclusions
The effects of Mo addition on the thermal conductivity and dielectric properties of the composite ceramics have been studied. The value of room temperature thermal conductivity increases with the increasing content of Mo, and the value begins to decrease slightly when the Mo concentration exceeds 20 vol. %. Increasing the Mo concentration and controlling the microstructure of metal phase are key factors to increase dielectric properties, adding 1vol. % Ni into the composite ceramics plays an important role to control the properties. The dielectric properties also could be adjusted by transforming the microstructure of the metal particles when the concentration of Mo is fixed.

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