Carbon coated metallic copper nanoparticles produced by an enclosed FSP for dielectric elastomers.

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Abstract

Copper nanoparticles is a very interesting material because of their optical, catalytic, mechanical and electrical properties, which is of importance in metallurgy, catalysis and optoelectronics.[1] Wet phase [2-4] and gas phase[1,5-7] methods have been used to produce copper nanoparticles. For the case of gas phase methods, it has been reported that a highly reducing atmosphere is required to obtain metallic copper,[5] and a protection layer is needed to avoid oxidation, such as carbon/silica[2] and pure carbon encapsulation.[1,6] Now a days numerous nanoparticles are manufactured industrially by flame synthesis in the kilogram to ton scale. FSP has many advantages when compared to wet phase methods because it is a fast, dry, versatile and single step process which is suitable for industrial applications.[7]

In this study, FSP with an enclosed system (glass quartz tube) was used to investigate the formation of carbon coated metallic copper nanoparticles controlled oxidation atmosphere changing the equivalence ratio (ϕ) from 0.87 to 1.37. XRD spectra shows slightly oxidized nanoparticles at $\phi < 1.0$ and completely metallic nanoparticles at $\phi > 1$. The crystal size decreases from 40 to 4 nm while increasing ϕ, due to lower temperatures of combustion and the inhibition of coagulation and sintering of copper by the formation of carbon black (CB) on the available surface of the copper indicating the sequential formation of Cu nuclei followed by surface growth of carbon. TGA analysis was useful to determine the carbon black content, and combined with XRD crystal size, the thickness of the CB layer was calculated, which resulted in values from 1 to 6 nm while increasing ϕ. Raman spectroscopy confirmed the presence of a strong G band indicating ordered graphite structures and D band which is accredited to a size effect with growing intensity for smaller crystallite size. A minimum temperature is reached at maximum carbon yield and the SSA reached a maximum for stoichiometric combustion as reported elsewhere for a platinum embedded system. A maximum in SSA of 35 m²/g was observed for $\phi=0.91$ where segregated carbon black is produced, this indicates the formation of CB by both paths homogeneous and heterogeneous

nucleation. The segregated CB was corroborated by TEM images. For $\phi > 1$, XRD particle diameter for copper were below 10 nm and the SSA below 10 m2/g which means that the metallic copper nanoparticles are embedded in the CB with BET diameters between 200-250 nm. This is corroborated by the metallic state of the nanoparticles where the CB avoids oxidation. In order to illustrate one possible novel application of this material, the nanoparticles were admixed into a paraffin base polymer in order to increase the relative permittivity of the material. Increasing the filler content from 0 to 30 vol%, it was possible to increase the dielectric constant from 2.7 to 120 respectively..

KEYWORDS: Nanoparticles / carbon coated metallic copper / FSP / Dielectrics / homogeneous and heterogeneous nucleation

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Now a days numerous nanoparticles are manufactured industrially by flame synthesis in the kilogram to ton scale. FSP has many advantages when compared to wet phase methods because it is a fast, dry, versatile and single step process which is suitable for industrial applications.7

 In this study, FSP with an enclosed system (glass quartz tube) was used to investigate the formation of carbon coated metallic copper nanoparticles controlled oxidation atmosphere changing the equivalence ratio (φ) from 0.87 to 1.37. XRD spectra shows slightly oxidized nanoparticles at φ < 1.0 and completely metallic nanoparticles at φ > 1.

The crystal size decreases from 40 to 4 nm while increasing φ, due to lower temperatures of combustion and the inhibition of coagulation and sintering of copper by the formation of carbon black (CB) on the available surface of the copper indicating the sequential formation of Cu nuclei followed by surface growth of carbon. TGA analysis was useful to determine the carbon black content, and combined with XRD crystal size, the thickness of the CB layer was calculated, which resulted in values from 1 to 6 nm while increasing φ.

Raman spectroscopy confirmed the presence of a strong G band indicating ordered graphite structures and D band which is accredited to a size effect with growing intensity for smaller crystallite size. A minimum temperature is reached at maximum carbon yield and the SSA reached a maximum for stoichiometric combustion as reported elsewhere for a platinum embedded system. A maximum in SSA of 35 m2/g was observed for φ=0.91 where segregated carbon black is produced, this indicates the formation of CB by both paths homogeneous and heterogeneous nucleation. The segregated CB was corroborated by TEM images. For φ > 1, XRD particle diameter for copper were below 10 nm and the SSA below 10 m2/g which means that the metallic copper nanoparticles are embedded in the CB with BET diameters between 200-250 nm. This is corroborated by the metallic state of the nanoparticles where the CB avoids oxidation. In order to illustrate one possible novel application of this material, the nanoparticles were admixed into a paraffin base polymer in order to increase the relative permittivity of the material. Increasing the filler content from 0 to 30 vol%, it was possible to increase the dielectric constant from 2.7 to 120 respectively.

Fig. 1 a) Reactor and b) Schematic of an FSP enclosed unit with quartz glass.

Introduction

Dielectric elastomers (DE) are functional materials that undergo a change in size, shape or stress upon the application of an electrical stimulus. When a voltage is applied across the electrodes, the polymer shrinks in thickness and expands in area.1 DE are high performance materials which are applied in many domains: aerospace, mechanics, medicine etc.2 DE, for instance, were used as active membranes for designing micro-pumps or, more generally, to handle fluids in micro-systems. 3

There are several possibilities to raise the εr, which can be done when mixing a soft material for example a thermoplastic which has low relative permittivity, with a material with high relative permittivity as it is the case with BaTiO3.6 It has been also shown that metallic particles admixed into the polymer matrix, can increase the relative permittivity exponentially just below the percolation threshold. This term is the characteristic point before a conductive path is formed allowing a conductive path between the electrodes.

It has been shown that on metallic fillers, there is a small window where an exponential increase in the relative permittivity is observed. These values vary from 16 up to 30 vol%.6

FSP with an enclosed system (glass quartz tube) was used to investigate the formation of metallic copper nanoparticles. The advantage of using FSP when compared with other wet phase methods is that it is a single step process which is suitable for industrial applications.7

It has been reported that in order to obtain metallic copper, a highly reducing atmosphere is required.1 Furthermore in order to avoid oxidation of the nano-particles when contact with air a protection layer is needed.1

Copper nanoparticles present oxidation problems when they are exposed to ambient conditions.

Specifically, for the case of FSP, Carbon Black (CB) platinum coated nanoparticles have been produced by Ernst et al.8 The FSP setup was based on this work in order to form the CB coating and prevent oxidation of the nanoparticles.

Experimental

Copper oxide (Sigma-Aldrich, purity ≥ 98 %) was used as the metallic source and dissolved in 2-ethylhexanoic acid (EHA, Riedel-de Haën, ≥ 99%) while heated and refluxed at 130 °C for 2 hours. Xylene (Xyl, Riedel-de Haën, ≥ 99%) was added to the solution in a 2:1 ratio by volume and stirred for at least 15 minutes to ensura a homogeneous solution. The final metal precursor solution had a concentration of 0.27 M.

The unit used is described in more detail elsewhere.20 The flow rates were based according to the paper of Ernst et al.19 where N2 (Pangas, ≥ 99.995 %) is used as dispersion gas with a flow rate of 3 ln·min-1, with a pressure drop of 1.5 bar across the nozzle which will produce an ideal Cu metallic production rate of 2.6 g·h-1. A constant liquid feed rate of metal precursor (glass syringe, Hamilton, 100 ml) was maintained with a syringe pumps (M1, Lambda, VIT-FIT). From the syringe the liquid is fed into the capillary which is embrace by a holder in order to ensure a straight alignment of the capillary into the nozzle. A supporting flamelet which is in a ring around the capillary outlet were fed with oxygen at 2.4 ln·min-1 (PanGas, ≥ 99.95 %) and methane at 1.2 ln·min-1 (PanGas, ≥ 99.5 %) ignited and sustained spray combustion as used in Ernst et al.19 Sheath gas was supplied through 36 equidistant holes (0.8 mm diameter) positioned around the flamelet (14.3 mm from center). The composition of the sheath gas was controlled and following gases were mixed: O2 (PanGas, ≥ 99.95 %), N2 (PanGas, ≥ 99.995 %) while the total sheath gas flow was kept constant to 10 ln·min-1. The Equivalence ratio (φ) was varied from 0.87 to 1.37. The equivalence ratio is defined as the total number of mols of oxygen required for stoichiometric combustion over the number of mols available in the system. The calculation of the φ was done assuming only the formation of Metallic copper and not considering the oxygen coming from the copper oxide. All the other sources (Feed gases and precursor) were taken into account.

Results

The objective of changing the equivalence ratio is to control the level of oxidation of the copper and at the same time the formation of the CB layer. The φ was changed from fuel lean (0.87) to fuel rich (1.37) conditions. Figure 2 shows the XRD spectra of the collected powder at different φ. Increasing the φ reduces the state of oxidation.
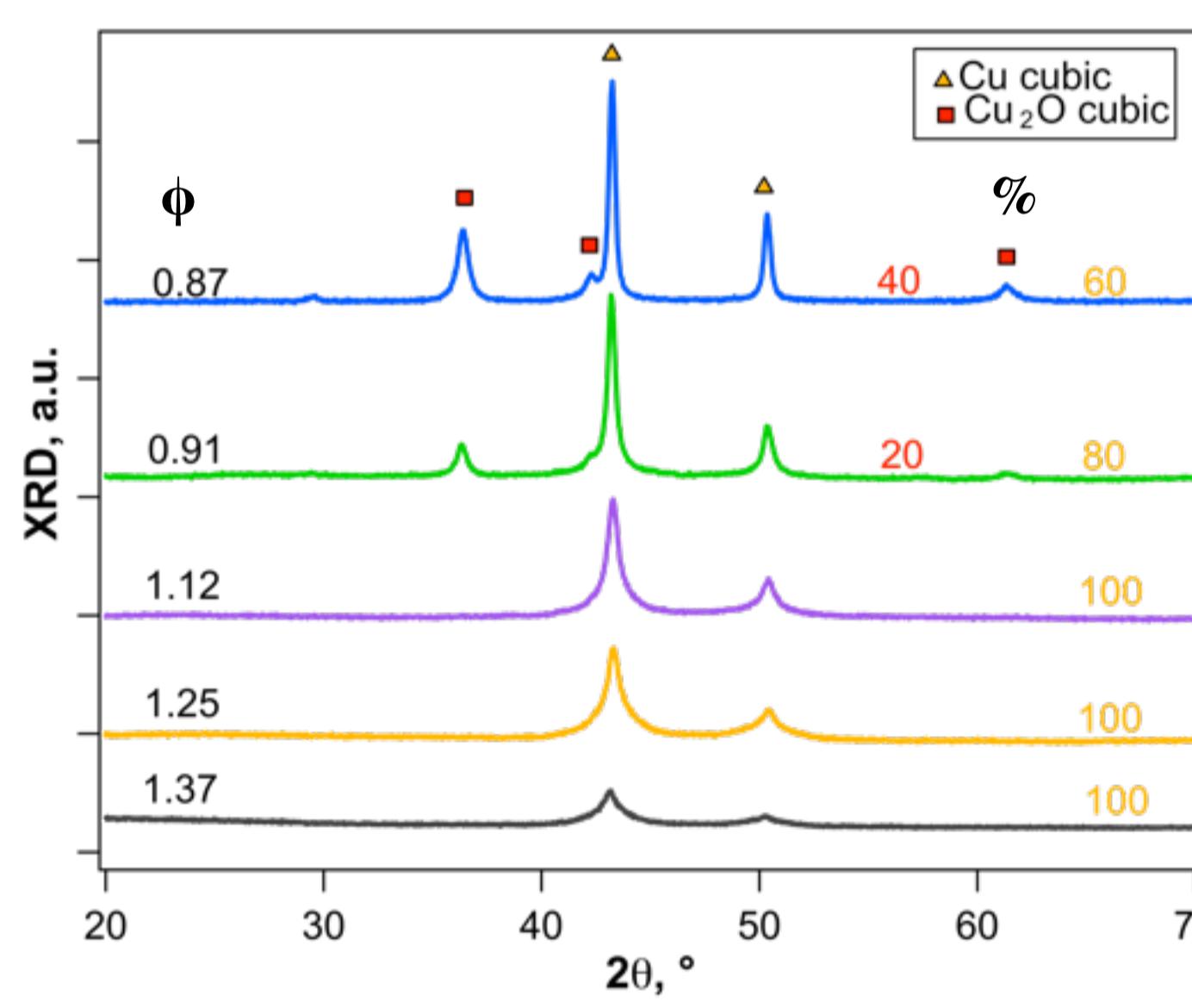
Fig. 2 XRD spectra for product nanoparticles obtained with different φ, which influence the level of oxidation of the copper. Furthermore the composition of the crystalline structure (only oxide and metallic fraction) is shown in the right hand side of the graph.

Figure 3 shows TEM images for the equivalence ratios 0.87, 0.91 and 1.12 from the top to the bottom. The copper shows a CB layer of a few nanometers thickness. The data of SSA is consistent with TEM images. For the φ of 0.87 the particles have a bigger particle size, while for φ of 0.91 there is more CB and it seems to be segregated.
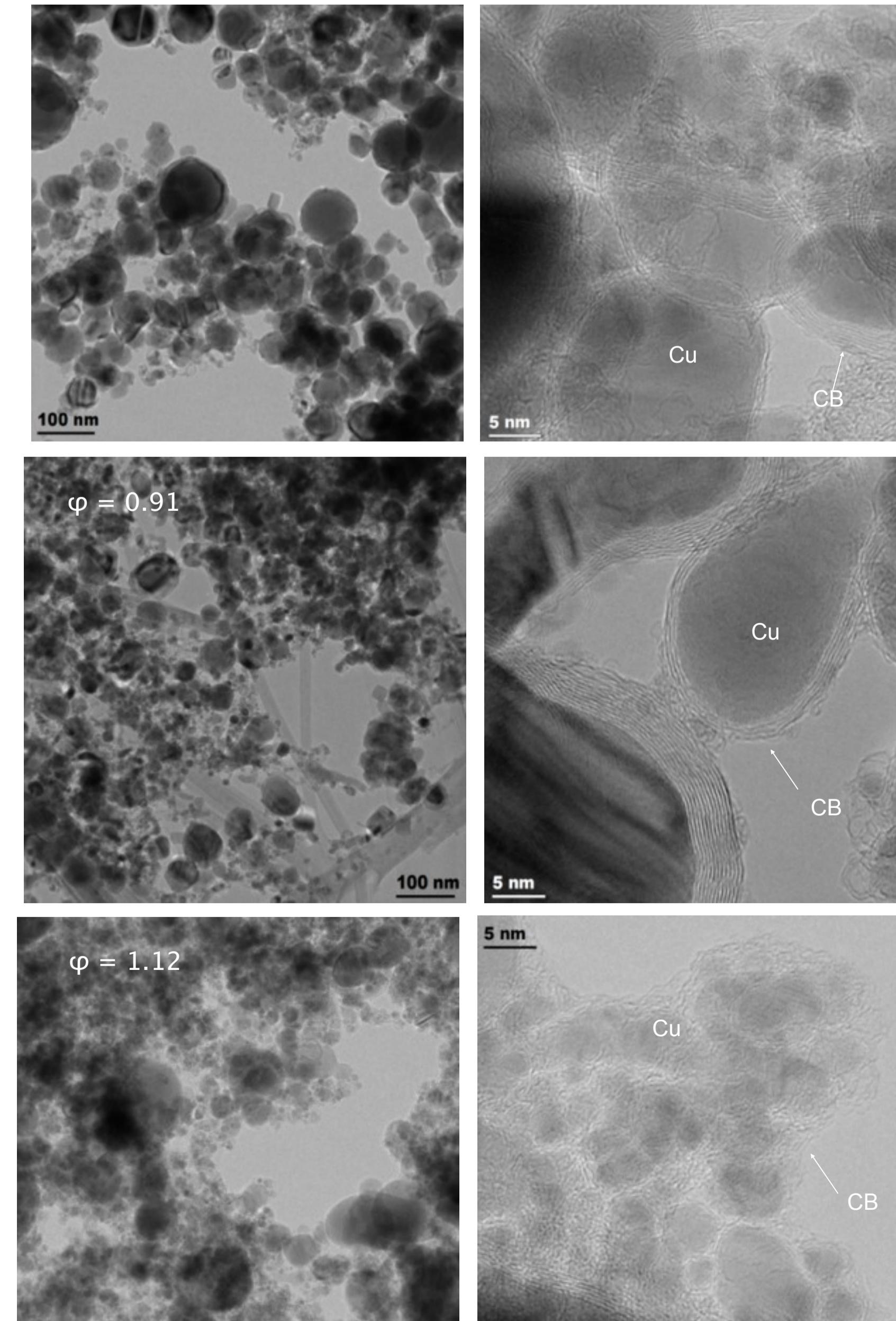
Fig. 3 TEM images of Cu nanoparticles coated with CB. From the Top to the bottom the φ increases for values of 0.87, 0.91 and 1.12 respectively.
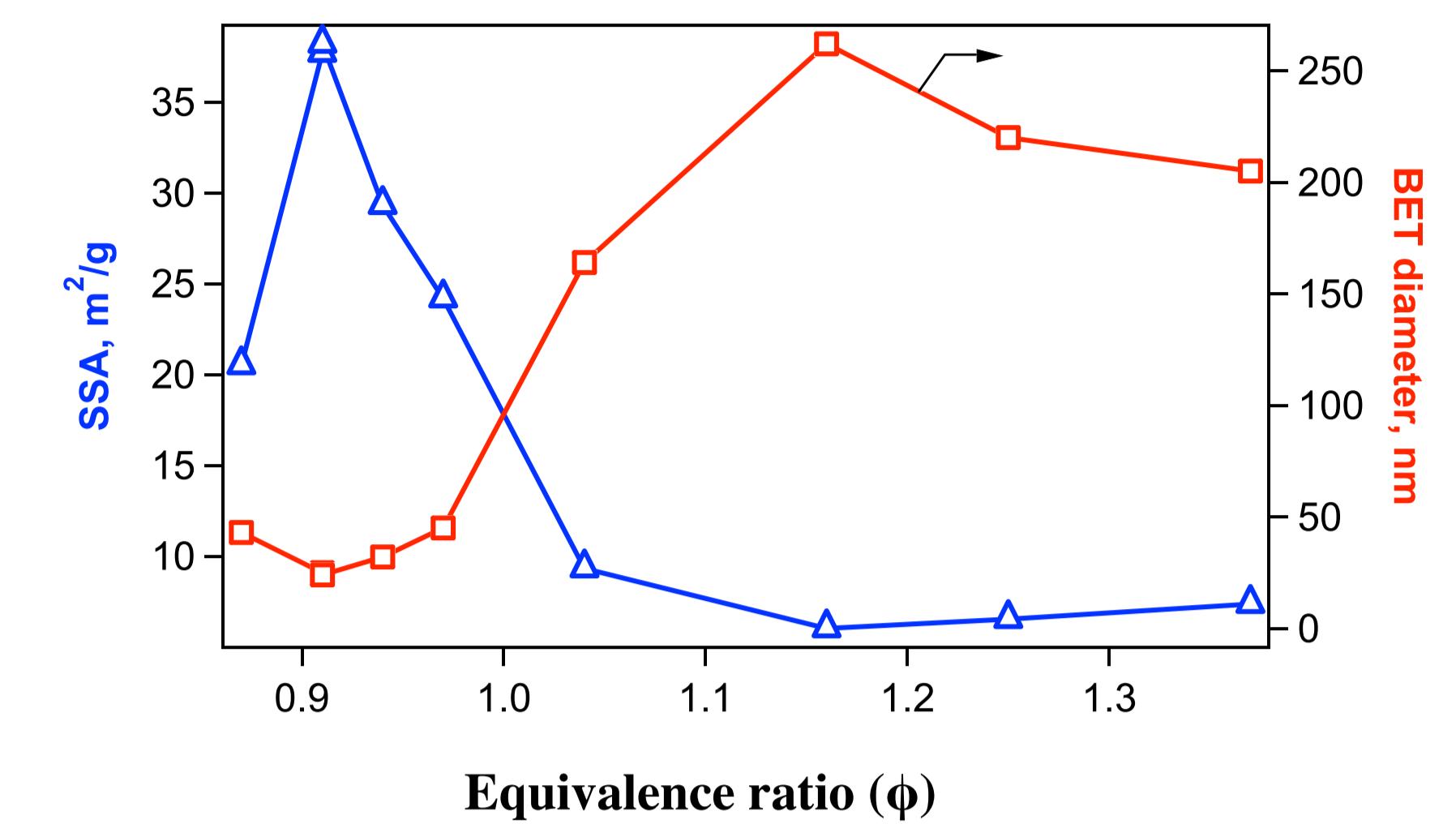
Fig. 4 SSA and equivalent BET diameter as a function of the equivalence ratio.

Figure 14 shows the SSA as a function of the φ. For the lowest value (φ =0.87) the particle size increases due to the higher temperature in the flame and the formation of less CB. For φ of 0.91 it was observed an increase in the SSA; this is correlated with the formation of CB which can be confirmed by TEM images in figure 15 and related to the high SSA which is typically for CB at values of φ below 1 as shown by Ernst el al19. When the φ increases a smaller SSA is observed, this means that bigger clusters are formed reaching a plateau for φ above 1, which is caused due to the incomplete combustion of the precursor and the high formation of CB.
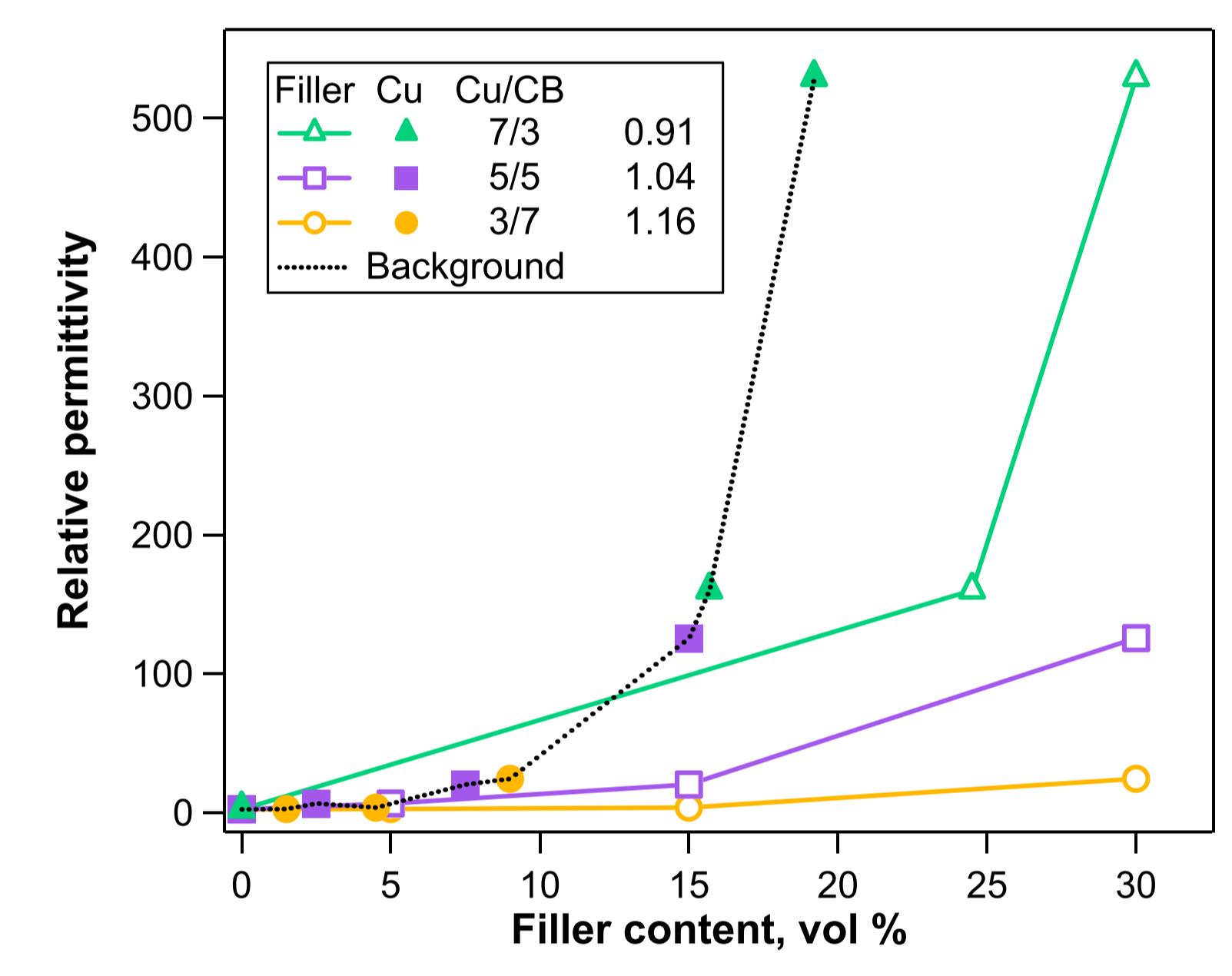
Fig. 5 Relative permittivity as a function of the total filler volume (Cu and CB, open symbols). A correlation was found for the relative permittivity as a function of the copper content (close symbols). The dotted line describes the background of such correlation. The ratio of Cu/CB is the higher for φ =0.91(Δ) middle for =1.04 (□) and the lowest for φ =1.16 (○)

It is observed that for metallic fillers, a higher relative permittivity is reached at lower filler loadings. For the case of Cu and Ni they look very similar in the increase of relative permittivity. For Ag it is slightly different, requiring higher amounts of filler. It is possible to conclude that the increase in the relative permittivity is reached at lower filler volumes for metallic composites, rather than ceramic composites as is the case of BaTiO3.

Conclusion

It was shown that it is possible to produce carbon coated nanoparticles by enclosed FSP slightly oxidized at φ < 1.0. The degree of oxidation is controlled at different when changing the φ. There is a small window for φ between 0.87 and 0.91 where segregated carbon black is produced, increasing the SSA of the product nanoparticles. The formation of CB can be controlled with the enclosed system which varies from 14 to 79 volume percent.

When the φ increases, XRD particle diameter decreases due to lower temperatures of combustion and the inhibition of collision of the copper by the formation of CB on the available surface.

It was shown that there is an increase in the relative permittivity as a function of the copper content. It has been shown that CB layer does not contribute to increase permittivity. CB content characterized by TGA and good agreement with CB layer thickness determined by TEM and

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