Investigation of the Melting Point Depression of Copper Nanoparticles

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Abstract. In this paper copper nanoparticles (Cu NPs) have been produced by solvothermal method. One of the objectives of the present research was to create Cu NPs using aqueous medium technology. The analysis of the produced particles was performed by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). In the course of the experiments, copper core and organic shell nanoparticles were created successfully. It has been found that the average diameter of the created Cu NPs was 50 nm. The thermal behaviour of these particles was investigated by Differential Scanning Calorimetry (DSC). The melting temperature depression of the one-pot synthesized Cu NPs was 633 °C.

1. Introduction

The melting point is one of the most important thermodynamic properties of all metal materials. The melting point characterizes the bulk materials independently on the size in the microscopic range. It is well known that the large surface-to-volume ratio in nano-sized particle (NPs) systems has significant influence on their thermodynamic properties and phase relations. NPs have high surface to volume ratio, and as a result the melting temperature will be size-dependent in the nano-range. Pawlow [1] in 1909 postulated that the melting point depression exists due to the large influence of the surface energy on the energy and structure of small particles. Allen et al. [2] have investigated the effect of reduction in size of lead, tin, indium and bismuth. Oxidation can also be significant in nano-size range, so a decrease in the melting point is measurable only in an oxide-free environment. A number of similar researches have been carried out on alumina [3], SAC (Sn3.5Ag0.5Cu) [4], gold [5][6], lead [7], indium [7][8], tin [9], bismuth [9][10]. Similarly, the melting temperature depression of Sn-based nanoalloys synthesized via various techniques has also been regarded as a promising property for applications in electronics [11]. The melting point depression of nanoparticles can vary from a few to several hundred degrees.

This size reduction naturally opens up new ways for the industry to use copper. The properties of copper nanoparticles have been investigated for the following systems, such as electronic and optical...
nano-devices [12], catalysts [13], lubricants [14], thermal conductive nanoliquids [15], antibacterial agents [16], biosensors [17], as well as solar collectors [18].

In line with modern challenges, there is a growing demand for the development of technologies that allow joining of heat-sensitive materials. The main requirements for brazing are to be reliable, low-temperature processes that allow the widespread use of heat-sensitive materials in industrial application. Nanoparticles can be the solution to such difficulties, as nano-effect, such as melting point depression, or wetting properties can open up new opportunities for technological challenges [19].

Copper is very important in brazing technologies of the steel structures in the industry. Its importance is even greater when we consider microelectronic application. Increasing cost of production of raw materials, as well as the reduction in size mainly in the electronics industry, have led researchers to set smaller targets for stable copper nanoparticles. There have been relatively few studies on the melting point depression of Cu nanoparticles. A sol-gel method was used to form a SiO$_2$ matrix composite reinforced with Cu/Cu$_x$O particles by Yeshchenko et al. [20]. They separated two melting regimes based on the temperature dependence of the surface-plasmon resonance energy and its width. The aim of the current research work is to create copper nanoparticles (Cu NPs) by solvothermal method in order to develop braze material with melting point depression. Another goal is to analyse the thermal properties and the microstructure of the obtained nanoparticles.

2. Experimental

2.1. Materials

All of the chemicals were of analytical grade and used as purchased without further purification. Copper(II)chloride hexahydrate (CuCl$_2$·6H$_2$O) salt was dissolved in distilled water. Polyethylene glycol (PEG 400) was used as the capping agent. Sodium borohydrate (NaBH$_4$) and ascorbic acid (C$_6$H$_8$O$_6$) were used as reducing agents. Sodium hydroxide (NaOH) was also used to adjust the pH and accelerate the reduction reaction in water (Table 1.).

2.2. Synthesis of copper nanoparticles

The first step of the preparation of copper nanoparticles starts with dissolving copper(II)chloride hexahydrate salt (CuCl$_2$·6H$_2$O) in distilled water to obtain a greenish solution. The solution was in a beaker under stirring constantly in a water bath at 60 °C. Dissolved polyethylene glycol 400 was added to the copper(II)-chloride solution. Sodium borohydrate (NaBH$_4$), ascorbic acid (C$_6$H$_8$O$_6$) and sodium hydroxide (NaOH) were measured and dissolved in distilled water and added to the solution dropwise. The colour of the solution changed from greenish via yellowish to black/red. This colour change confirmed that reduction reaction had been started and finished. The mixture was further stirred rapidly (500 rpm) for 1 hour in closed system to complete the reaction.

| Component                      | Concentration | Others                           |
|--------------------------------|---------------|----------------------------------|
| Copper(II)-chloride hexahydrate| 2.4 g/L       |                                  |
| Polyethylene glycol (PEG 400)  | 35.6 g/L      |                                  |
| Sodium hydroxide               | 4.0 g/L       |                                  |
| Ascorbic acid                  | 3.5 g/L       |                                  |
| Sodium borohydrate             | 3.8 g/L       |                                  |
| Temperature                    |               | 60 °C                            |
| Reaction time                  |               | 1 hour                           |
| Water bath, stirring constantly, closed system |               |                                  |
2.3. Characterization

The synthesized particles were separated from the solution with an Eppendorf Centrifuge 5804 R centrifuge, using 5000 rpm. For the separation distilled water and ethanol were used. The temperature was 20 °C during the centrifugation.

The synthesized samples were studied applying Scanning Electron Microscopy (Hitachi S-4800 SEM) equipped with a BRUKER AXS type energy-dispersive X-ray spectrometer (EDS) and X-Ray Diffraction (Bruker D8 Discovery). Differential Scanning Calorimetry (Netzsch STA 449 F3 Jupiter TG-DSC) was used for the determination of the melting point of the copper nanoparticles. The tests were carried out in vacuum (10⁻⁴ mbar) to minimize the oxidation; the heating rate was 10 °C/min. The equipment measures the change of the mass of the sample continuously.

3. Results and discussion

It can be seen on the SEM micrograph that the particles obtained are connected to each other and have a diameter of 60-70 nm (Figure 1a.). The EDS analysis shows that the significant part of the connected particles is Cu (Figure 1b) which means that the synthesis method is pure.

![SEM micrograph (a) and EDS spectrum (b) of the copper-containing samples](image_url)

Figure 1. SEM micrograph (a) and EDS spectrum (b) of the copper-containing samples

It can be observed in the larger magnification image (Figure 2.) that these particles are stuck together due to the PEG 400 addition to the system. The nanoparticle core and the PEG organic shell surrounding the particle are clearly visible in Figure 2b featuring SEM image obtained using transmission electron (TE) detector. It proves that an inorganic core/organic shell structure was obtained. The PEG layer is also responsible for separating the particles, i.e. preventing their aggregation. PEG 400 is a low-molecular-weight grade of polyethylene glycol which is strongly hydrophilic. PEG 400 changes the available surface energy of the particles so that the surface tension decreases. The Kelvin barrier moves, allowing more particles to avoid the aggregation process and as a result lowering the mean particle size.
Using STEM mode, the real particle size of the copper particles can be estimated being of 50 nm in average (Figure 3). It means that the particles, which can be seen in the Figure 1, do not agglomerate but they are generally connected by PEG.

The phase identification was performed by X-ray diffraction (Figure 4) which shows that some of the produced particles are pure copper, however a significant amount of Cu$_x$O was also formed. A large amount of Cu NPs has an X-ray amorphous structure based on the amorphous halo in the beginning of the diffractogram (Figure 4).
In the current research work, the melting point of the copper-containing particles has been measured by Differential Scanning Calorimetry (DSC). The results showed (Figure 5.) that the endothermic peak at 473 °C is followed by an exothermic peak, from which one can deduce a melting and a crystallization. This may mean that the pure copper nanoparticles melted at 447 °C and then crystallized after the fusion of the particles again with a peak temperature of 563 °C. After the melting process of Cu particles an intensive oxidation starts, which proceeds up to 803 °C.

The melting point measured is in agreement with experiment of Yeshchenko et al. [20]. The difference between the data reported and the current measurement is that the authors used SiO₂ matrix to determine the melting point of the Cu NPs. Here, the Cu NPs were separated only by the organic shell, for which the boiling point is less than 250 °C. The volume melting point of 440 °C determined
in [20] is equivalent to the melting point measured for 50 nm diameter particles. Fig. 5 shows an endothermic peak at 820 °C. Observing the TG line a mass loss step of 8 wt.% was detected under this endothermic process. Heinemann et al. [21] dealt with stability of various copper oxides. It was found that the reduction of Cu₂O to pure copper occurred at a pressure of 10⁻⁴ torr and at around 820 °C.

Based on the literature and the data obtained in the current research, it can be concluded that the pure copper nanoparticles produced have melted at 450 °C in the DSC and then recrystallized as they collapsed. Further increase in temperature leads to decomposition of Cu₂O started at 785 °C and indicated by high endothermic peak in Figure 5. The Cu NPs formed during the decomposition of Cu₂O were oxidized again during the further temperature increase according to TG measurement. Due to oxygen reduction the pressure changed in the chamber; the oxidation can start again after decomposition of Cu₂O.

4. Conclusions
In this paper, copper nanoparticles were successfully synthesized by a chemical reduction method in water. The main conclusions, which can be drawn are as follows:

1. The size of the Cu NPs obtained was around 50 nm. Due to the small size and high surface area NPs easily oxidized.
2. Based on SEM results, it can be stated that a metal core and an organic shell structure has been created. This type of structure is beneficial for determination of the melting point of metal NPs since they are separated from each other.
3. The reduction of the melting point due to the nano-size range was detected using differential scanning calorimetry method (DSC).
4. The copper nanoparticles melted at 450 °C, which means that the depression of the melting point of bulk copper was equal to 633 °C.

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References

[1] Pawlow P 1909 Ober die Abhängigkeit des Schmelzpunktes von der Oberflächenenergie eines festen Körpers (Zusat.) Zeitschrift für Phys. Chemie 65U
[2] Allen G L, Bayles R A, Gile W W and Jesser W A 1986 Small particle melting of pure metals Thin Solid Films 144 297–308
[3] Joshi N, Mathur N, Mane T and Sundaram D 2018 Size effect on melting temperatures of alumina nanocrystals: Molecular dynamics simulations and thermodynamic modeling Comput. Mater. Sci. 145 140–53
[4] Kim H J, Jang S P, Lee J-H and Park Y-J 2016 Transformation of SAC (Sn3.0Ag0.5Cu) nanoparticles into bulk material during melting process with large melting-point depression Micro Nano Lett. 11 840–3
[5] Sambles J R 1971 An electron microscope study of evaporating gold particles: the Kelvin equation for liquid gold and the lowering of the melting point of solid gold particles Proc. R.
Buffat P and Borel J-P 1976 Size effect on the melting temperature of gold particles Phys. Rev. A 13 2287–98

Coombes C J 1972 The melting of small particles of lead and indium J. Phys. F Met. Phys. 2 441–9

Zhang M, Efremov M Y, Schiettekatte F, Olson E A, Kwan A T, Lai S L, Wisleder T, Greene J E and Allen L H 2000 Size-dependent melting point depression of nanostructures: Nanocalorimetric measurements Phys. Rev. B 62 10548–57

Frongia F, Pilloni M, Scano A, Ardu A, Cannas C, Musinu A, Borzone G, Delsante S, Novakovic R and Ennas G 2015 Synthesis and melting behaviour of Bi, Sn and Sn–Bi nanostuctured alloy J. Alloys Compd. 623 7–14

Kellermann G and Craievich A F 2002 Structure and melting of Bi nanocrystals embedded in a B2O3–Na2O glass Phys. Rev. B 65 134204

Jiang H, Moon K and Wong C P 2013 Recent advances of nanolead-free solder material for low processing temperature interconnect applications Microelectron. Reliab. 53 1968–78

Wang Y H, Peng S J, Lu J D, Wang R W, Mao Y L and Cheng Y G 2008 Optical properties of Cu and Ag nanoparticles synthesized in glass by ion implantation Vacuum 83 408–11

Judai K, Numao S, Nishijo J and Nishi N 2011 In situ preparation and catalytic activation of copper nanoparticles from acetylide molecules J. Mol. Catal. A Chem. 347 28–33

Zhang B-S, Xu B-S, Xu Y, Gao F, Shi P-J and Wu Y-X 2011 Cu nanoparticles effect on the tribological properties of hydrosilicate powders as lubricant additive for steel–steel contacts Tribol. Int. 44 878–86

Bönnemann H, Botha S S, Bladergroen B and Linkov V M 2005 Monodisperse copper- and silver-nanocolloids suitable for heat-conductive fluids Appl. Organomet. Chem. 19 768–73

Stelzig S H, Menneking C, Hoffmann M S, Eisele K, Barcikowski S, Klapper M and Müllen K 2011 Compatibilization of laser generated antibacterial Ag- and Cu-nanoparticles for perfluorinated implant materials Eur. Polym. J. 47 662–7

Lu L-M, Zhang X-B, Shen G-L and Yu R-Q 2012 Seed-mediated synthesis of copper nanoparticles on carbon nanotubes and their application in nonenzymatic glucose biosensors Anal. Chim. Acta 715 99–104

Musa A ., Akomolafe T and Carter M . 1998 Production of cuprous oxide, a solar cell material, by thermal oxidation and a study of its physical and electrical properties Sol. Energy Mater. Sol. Cells 51 305–16

Janczack-Rusch J, Kaptay G and Jeurgens L P H 2014 Interfacial Design for Joining Technologies: An Historical Perspective J. Mater. Eng. Perform. 23 1608–13

Yeshchenko O A, Dmitruk I M, Alexeenko A A and Dmytruk A M 2007 Size-dependent melting of spherical copper nanoparticles embedded in a silica matrix Phys. Rev. B 75 085434

Heinemann M, Eifert B and Heiliger C 2013 Band structure and phase stability of the copper oxides Cu2O, CuO, and Cu4O3 Phys. Rev. B 87 115111