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Preparation of silver powder through glycerol process

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Abstract. High purity fine silver powder with uniform particle morphology was prepared through glycerol process. The process involves reduction of silver nitrate by glycerol under atmospheric conditions at a temperature below 175°C. Glycerol, in this process, acts as a solvent as well as a reducing agent. The powders prepared through this process were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and chemical analysis. The powders were well crystalline and contained oxygen, carbon and hydrogen as impurities. Overall purity was better than 99·9%. The yield of silver powder was better than 99%.

Keywords. Silver powder; glycerol process.

1. Introduction

Silver powder finds extensive applications in electronic industry, particularly in the field for making conducting inks and paste for thin/thick films. Conductive silver paste forms the basis for producing electronic components such as hybrid microcircuits and the internal electrodes of multi-layer ceramic capacitors (Larry *et al* 1980). For such applications, silver powder of specific morphology is desired. The powders should be composed of crystalline non-agglomerated micron/submicron particles with narrow size distribution.

Till date, silver powder has been prepared through various processes ranging from chemical, physical (atomization and milling), and electrochemical to thermal decomposition. Every process produces powders with characteristic morphology and purity that ultimately govern its functional properties. Among the various preparative methods used, chemical processes offer distinct advantage over the others in terms of powder morphology as well as efficient scale-up for mass production. There have been a number of reports that describe the synthesis of silver powder through chemical processes. These include reduction of silver salts by $NaBH_4$, HCHO/NaOH/Na_2CO_3 (Duff *et al* 1993; Burst *et al* 1994; Rao 1994; Isabel and Luis 1999; Bonet *et al* 2000; Chou and Ren 2000). The reduction of silver chloride by glucose has also been reported (Brauser 1965).

The polyol process has been successfully employed for preparation of metal powders belonging to groups VII and IB (Fievet *et al* 1989). In this process, a suitable solid inorganic/organic salt of metal is suspended in a liquid polyol, the suspension is stirred and heated to a given temperature. The reduction of metallic salt by polyol quantitatively yields metal powder in a finely dispersed form. The control of particle morphology is facilitated by the kinetic control of the nucleation and growth steps. Definite separation between the nucleation and growth stages is a prerequisite for the formation of mono-sized particle (Fievet *et al* 1989). One of the measures to separate growth from nucleation may be the addition of seed particles where seed crystals act as nuclei and homogeneous nucleation is thus replaced by heterogeneous nucleation.

The preparation of metal powders through polyol process has largely been focused on the use of ethylene glycol or di-ethelene glycol or their mixtures as reducing agent and solvent. The limitation of ethylene glycol as reducing agent, in some cases is being compensated by the use of additional reducing agent in the form of polyvinylpyrrolidone (PVP) (Silvert *et al* 1997). Recently, Sinha and Sharma (2002) described a process for preparation of copper powder using glycerol. Glycerol has higher boiling point (290°C) as compared with that of ethylene glycol (197·3°C) and hence it facilitates a higher reaction temperature. Though silver powder has been prepared through polyol route using ethylene glycol and PVP as reducing agents, the use of glycerol to prepare silver powder has not been studied. In the present investigation, silver powder has been prepared starting from silver nitrate using glycerol as solvent and reducing agent.

2. Experimental

Silver nitrate (AR grade, E-Merck India Ltd) was used as starting material for the preparation of silver powder. A predetermined amount of starting salt was suspended in glycerol (AR grade). The molar ratio (R) between silver nitrate and glycerol was varied from 0·01–0·1. No protective agent in the form of PVP or seed particle (nucleating

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agent) was used. The suspension was heated, while stirring, on a laboratory hot plate. The reaction temperature was measured using a thermometer submerged into the solution through a glass port. The silver nitrate salt started to dissolve with increase in temperature. After about one hour of incubation time, silver powder started to precipitate.

After the precipitation, the suspension of silver powder obtained was naturally cooled to room temperature and then diluted with ethanol. The metal particles were recovered from the mother solution by repeated centrifugation followed by washing with ethanol. The powder obtained was dried under vacuum at 80°C for 1 h.

The phase analysis of the dried powder was carried out by X-ray diffraction (Philips Diffractometer, Model PW1710) using CuK_a radiation at a scanning rate of 0·05°/s. The powder morphology was studied by scanning electron microscope (FEI, Quanta 200).

The estimation of oxygen and hydrogen in silver powders was carried out through inert gas fusion technique. The carbon contents of the powders were measured using a carbon analyser employing thermal conductivity detection technique.

3. Results and discussion

Though the solubility of silver nitrate in glycerol at room temperature is low, it increased with temperature leading to a blackish solution. Complete dissolution of the silver nitrate took place before reduction by glycerol into metallic silver. The dissolution of silver nitrate completed at a temperature of 70°C. The blackish colour of the solution may be attributed to the nucleation of colloidal silver particles which during heating grows to form well crystalline silver powder. The precipitation of silver from the solution started at 140°C and went to completion at 175°C. This was followed by vigorous boiling of the solution at the same temperature. The silver powder precipitated out in the form of soft sponge type mass that floated at the top of the solution.

The total incubation period for the precipitation of silver powder from the solution was less than an hour, which is

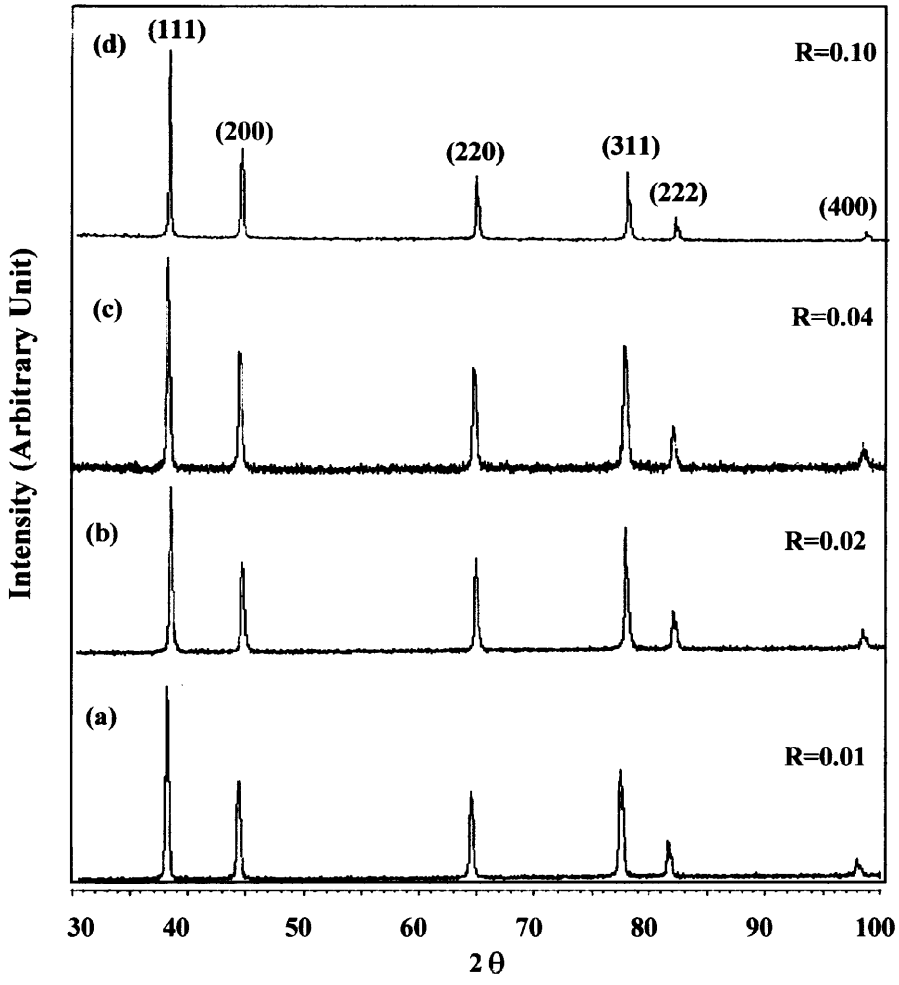

Figure 1. (a)–(d) XRD patterns of silver powders prepared through glycerol process.

much less than other polyol processes where ethylene glycol and PVP are used as reducing agents (Silvert *et al* 1997). The lower value incubation period indicates the greater reducing potential of glycerol for preparation of silver powder. This is of significant importance from the commercial point of view, as a faster process would ultimately result in greater productivity.

The XRD patterns of the silver powders prepared through glycerol route are shown in figures 1a–d. The patterns reveal the diffraction peaks corresponding to *fcc* silver phase. However, the patterns of all the powders produced through glycerol route exhibited a split in the peaks corresponding to the reflections (220), (311) and (222), respectively. Because of this splitting of XRD reflections, the estimation of crystallite size of the powders from X-ray line broadening was not attempted. To confirm the presence of split, slow scans were performed for all the samples. The typical XRD pattern taken at slow scan between $2q$ 63·5 and 65·5° on the silver powder (R = 0·01) is shown in figure 2. The pattern exhibits a split in the diffraction peak that may correspond to (220) reflection of cubic phase (1·444 Å) and (110) reflection of hexagonal phase (1·44 Å). The first two strongest reflections of hexagonal allotrope of silver are 1·44 Å (110) and 1·24 Å (201) (ICDD No. 04-0783 and 41-1402). These reflections are very close to (220) and (311) reflections of cubic allotrope of silver having the inter planar spacing of 1·445 and 1·231 Å, respectively. The listing of strongest reflections of cubic and hexagonal silver is given in table 1. The peak position and the inter planar spacing of different X-ray reflections of the silver powder produced through this process are given in table 2. The intensities of different reflections of XRD pattern suggest that the powder is composed of majority cubic phase along with minor hexagonal phase. Sterling and Gallant (1973) first reported the presence of hexagonal allotrope in silver powder prepared by reduction of silver nitrate by starch. However, no report is available in literature on

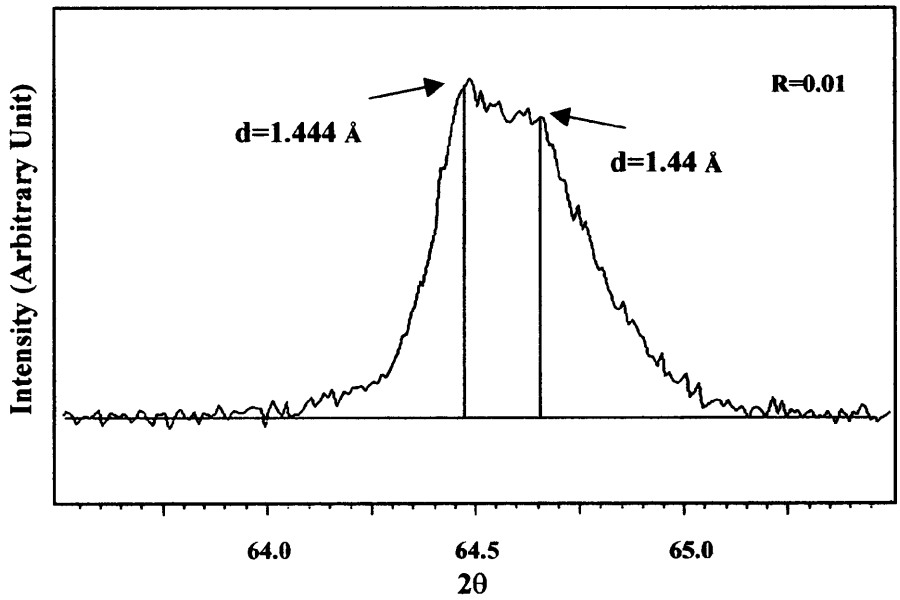

Figure 2. XRD pattern of silver powder prepared through glycerol process taken at slow scan.

Table 1. X-ray reflection of two allotropes of silver.

Ag (cubic) ICDD No. 04-0783			Ag (hexagonal) ICDD No. 41-1402		
d (Å)	Intensity	(*hkl*)	*d* (Å)	Intensity	(*hkl*)
2·359	100	111	1·44	100	110
2·044	40	200	1·24	100	201
1·445	25	220	1·17	90	203
1·231	26	311	2·00	80	103
1·1796	12	222	2·50	60	004
1·022	4	400	1·00	20	00 10

the presence of hexagonal allotrope in the silver powder prepared through polyol route using ethylene glycol as reducing agent.

The SEM photomicrographs of the silver powders produced through this route are shown in figures 3 and 4.

Table 2. XRD pattern of silver powder prepared through glycerol route (R = 0·04).

d (Å)	Intensity
2·353	100
2·039	43
1·443	28
1·439	16
1·23	29
1·228	16
1·179	9
1·175	4
1·021	3

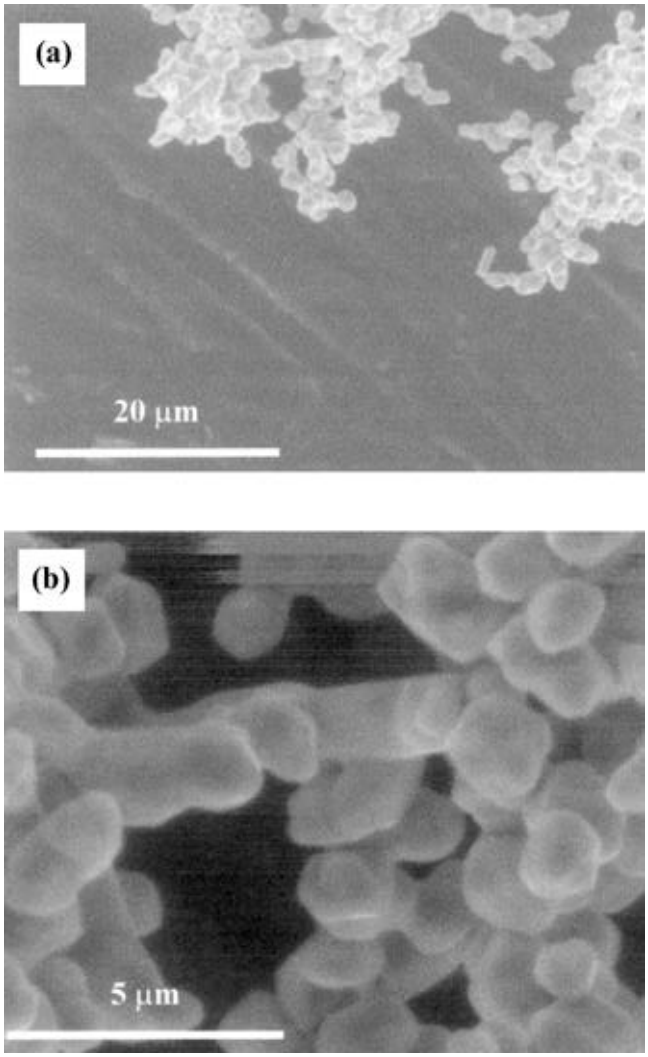

Figure 3. (a)–(b) SEM photomicrographs of silver powders produced through glycerol process using R = 0·01.

Figures 3a and b show photomicrographs of the powder prepared using R = 0·01. The micrographs reveal that the powder is made up of particles of narrow size distribution having an average particle size of 1·5 μm. Figures 4a and b show photomicrographs of the silver powder prepared through glycerol route using a molar ratio (R) of 0·02. The powder is spheroidal having narrow size distribution. The average particle size of the powder is 2·24 μm.

The typical chemical analysis of silver powder produced through this route is given in table 3. It can be seen that the total level of impurities associated with the powder is less than 0·1 wt%.

The above results suggest that powders produced through this route exhibit a very high purity and a good crystallinity. The particles have a regular and polyhedric shape i.e.

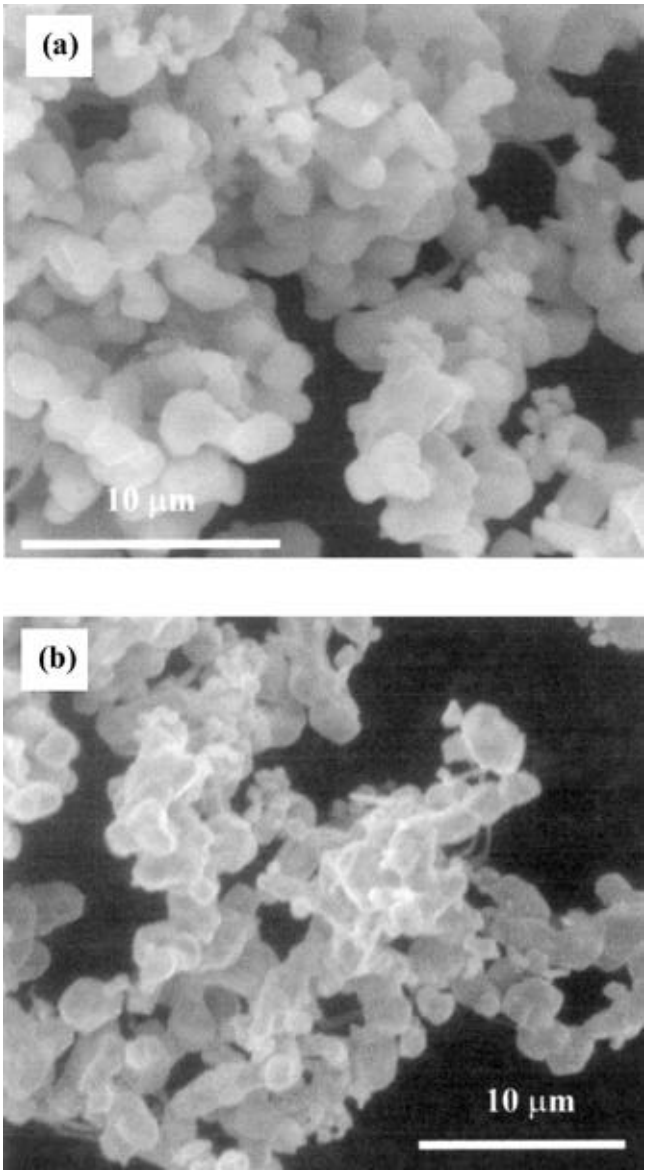

Figure 4. (a)–(b) SEM photomicrographs of silver powders produced through glycerol process using R = 0·02.

Table 3. Typical chemical analysis of silver powder produced through glycerol process.

Element	Carbon	Oxygen	Hydrogen
Wt%	< 0·040	< 0·035	< 90 ppm

their growth is isotropic. One of the basic advantages of this process is the quantitative precipitation of silver particles from the solution leading to a process yield > 99%.

The average particle size of the powder produced through this route can be controlled through the molar ratio of metal salt and glycerol (*R*). Working under similar experimental conditions, silver powders were prepared using increasing molar ratio of $AgNO_3$ and glycerol. Increasing the value of *R* from 0·01 to 0·1 causes an increase in the particle size of the powder from 1·5 to 11 μm.

4. Conclusions

A simple energy efficient process has been described for preparation of silver powder starting from silver nitrate as a precursor for silver. It essentially consists of dissolving the silver precursor in glycerol followed by reduction and precipitation from the solution. The process yields well-crystallized silver powder having purity > 99·9%. The particles have a regular and polyhedral shape that seems to indicate an isotropic growth of the particles. The average particle size of the powder has been found to depend on the ratio of silver nitrate and glycerol. The XRD analysis of the powder indicates the presence of hexagonal allotrope of silver as minor phase.

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