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NANO-ENGINEERED THERMOELECTRIC COATING

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1. Abstract

A nano-engineering approach has been developed for the synthesis of the thermoelectric composite materials. A possible way for enhancing ZT is to incorporate thermoelectric materials, e.g. Skutterudite, into the nano-sized pores of three-dimensional periodic arrays. The present study reports the development of a method for making a Nano-Engineered Thermoelectric (NETE) coating on silica particles. The coated particles are assembled into three-dimension array of opals to form NETE composite. The process consists of coating silica particles with gold and then with thermoelectric material. Gold coating has the advantage that post-coating assembly provides a continuous network of Skutterudite-filled gaps between gold interconnects. The second coating was carried out by chemical co-precipitation of Co and Sb precursors from a solid solution onto the surfaces of the gold-coated particles under controlled conditions. Through further heat-treatments (calcination, reduction and alloying), a Skutterudite layer has been formed in high purity. Both the gold- and gold/Skutterudite-coated particles retain the morphology of the original silica particles. In this paper, the processing conditions and materials characterizations are reported and discussed

2. Introduction

Thermoelectric (TE) materials are of major interest for both heat pump and electrical generator applications. The figure of merit ZT determines the achievable efficiencies of such devices. This dimensionless quantity is defined as $ZT = TS^2\sigma/\kappa$, where T is the absolute temperature, S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity (which is composed of electronic and lattice components). The unavailability of thermoelectrics with ZT much larger than unity presently limits to the applicability of thermoelectrics for both heat pumps and electrical generation. In order to obtain the high ZT that is required for high efficiency devices, materials with high S, high σ, and low κ are being sought.

One approach being pursued for increasing ZT is through introducing nanoscale structures. Mahan [1-3] and Rowe [4] have predicted that κ will be suppressed in nanoparticle arrays due to increased phonon scattering. Nano-engineered materials with grain sizes below 100 nm have a very high interface to volume ratio - e.g., about 50% of the atoms are at the interface for 30-40 nm diameter grains. Such a high density of interfacial material is expected to increase phonon scattering - thereby decreasing the lattice thermal conductivity. Worlock [5] reported that a large κ decrease was obtained for NaCl by the incorporation of a very small concentration of colloidal silver particles. While the presence of enhanced photon scattering at interfaces will decrease thermal conductivity, electronic carrier scattering at these interfaces may also decrease electrical conductivity. Hence, the overall goal is to obtain an enhancement of σ/κ.

G.M. Chow et al. (eds.), Nanostructured Films and Coatings, 149–156.

The synthesis of Nano-Engineered Thermoelectrics (NETE) with properly tailored structures for increasing ZT provides the motivation for the present research.

As an alternative to the surface scattering approach, atomic-scale phonon scattering centers can be introduced to increase ZT with increasing σ/κ. For example, non-stoichiometric TE compositions can be made by doping, either by partially substituting an element on lattice sites or by filling interstitial atoms into oversized cages within the lattice. In order to reach the required composition and distribution of a dopant, nano-engineered materials are advantageous - since a large volume of disordered intergranular phase can facilitate doping. Lattice defects, vacancies or interstitial atoms, are important determinants for both electrical and thermal conductivity. A large fraction of lattice defects may greatly decrease the lattice thermal conductivity, while increasing the concentration electrical carriers for both n- and p-type TE materials [6,7].

Among a number of promising materials, the most interesting is a large family of Skutterudites having a general formula $R_xM_4X_{12}$ (X = Sb, As, or P; M = Co, Fe, Ru, or Os; R is a rare earth, and x = 0-1) [7]. This structure belongs to a cubic space group Im3. Its unit cell contains 8 MX_3 groups and 2 oversized atomic cages, which can be filled by interstitial atoms R (which are called "rattler" atoms). There is major opportunity for optimizing the thermoelectric properties of these Skutterudites. For example, doping Skutterudites with suitable elements, by either substituting M or X or filling R into the cages, can significantly increase electrical conductivity, and/or decrease its thermal conductivity, thus enhancing ZT.

A new concept for enhancing ZT is to incorporate TE materials, e.g. a Skutterudite, into the nano-sized pores of three-dimensional periodic arrays to form a NETE composite. Either zeolites or self-assembled silica opal might be suitable for this purpose. The NETE composite is expected to have intergranular TE phase between particles, resulting in a network of nano-sized TE junctions. This could drastically decrease the thermal conductivity while perhaps limiting the negative effect on the electrical conductivity. Also, enhancement in the Seebeck coefficient is possible for a suitably designed NETE.

Since it is generally difficult to fill nano-sized pores with a complex material of defined composition, such as Skutterudite $CoSb_3$, an alternative approach is to coat the desired material on the individual particles before assembling them. After assembly of the coated particles, the particle surfaces form the interparticle interfaces. The present work is focused on the development of such a process. As the first step in this direction, we will describe the synthesis of Skutterudite on monodispersed gold-coated SiO_2 particles. The strategy of first coating the SiO_2 particles with gold (prior to formation of the Skutterudite layer and particle assembly) has the advantage that post-coating assembly provides a continuous network of Skutterudite-filled gaps between gold interconnects. For suitably thin Skutterudite gaps, ballistic electron transport across these gaps might be possible – leading to a cooling effect that is the solid-state analogue of thermoionic cooling.

We recently developed a novel chemical route for the synthesis of NETE powders of $CoSb_3$ Skutterudite [8,9]. The present study is to establish the technical feasibility of applying this low-temperature chemical alloying route for making a NETE coatings on silica particles.

3. Solution Chemistry

Computer-aided thermodynamic modeling was applied for choosing the synthesis conditions used for particle coating including both dissolution and precipitation processes. For this purpose we used the computer software and database for multi-component aqueous systems similar to that we developed for chemical equilibrium calculations [10,11]. In this section, some typical calculation results are discussed in order to illustrate the utility of this approach.

The present process for coating particles with cobalt-antimony compounds is based on our previous development of a synthetic route to bulk powders of the same materials [8,9]. In this paper, we present some typical calculated chemical equilibrium results for a system of H^+-Co^{2+}-Sb^{3+}-Cl^--$C_2O_4^{2-}$-NH_3 [9].

When dissolved in water, an antimony salt usually decomposes into a basic precipitate in the following two steps:

$$SbCl_3(s) \rightarrow Sb^{3+} + 3\ Cl^- \tag{1}$$

$$Sb^{3+} + Cl^- + H_2O = SbOCl(s) + 2\ H^+. \tag{2}$$

The reaction described in Eqn. 2 can be avoided only if the acid concentration is sufficiently high. Complete dissolution of $SbCl_3$ in 3 M HCl can be expected for a stock solution having the atomic ratio of $CoSb_3$ (containing 0.75 M Sb^{3+} and 0.25 M Co^{2+}). Moreover, the solubility of $SbCl_3$ in HCl solution is increased by the formation of soluble complexes of $SbCl_n$ (n = 1-6). Also, $CoCl_2$ is very soluble in water.

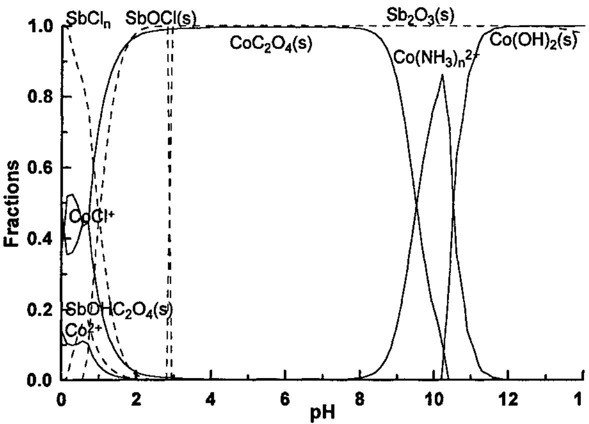

Fig. 1. Respective distributions of $Co^{2+}$and Sb^{3+} species in the presence of ammonia and oxalate vs. pH

According to the calculation results plotted in Fig. 1, complete co-precipitation of Sb_2O_3 and CoC_2O_4 with Sb/Co = 3 is expected at pH = 3-8, which is mainly limited by the solubility of CoC_2O_4. The presence of ammonia results in the formation of soluble complexes of $Co(NH_3)_n^{2+}$ (n = 1-6) at pH > 8. Neither the addition of ammonia or oxalate would affect the precipitation of Sb_2O_3 in the same pH region - although the precipitation of SbOCl and $SbOHC_2O_4$ could take place in more acidic region at pH <3 and < 2, respectively. When Ni was used for partial substitution of Co to form a final product of $Co_{1-x}Ni_xSb_3$, the dissolution and precipitation of nickel species are similar to those of cobalt species. The solution chemistry of such a system including Ni^{2+} will be presented elsewhere.

4. Experimental

4.1 SOLUTION PREPARATION

The p.a. grade chemicals and de-ionized water were used for preparation of the stock solutions.

The solution of 0.25 M Co and 0.75 M Sb was prepared by dissolving $CoCl_2$ and $SbCl_3$ in 3 M HCl in order to avoid the precipitation of SbOCl. The alternative solutions including $NiCl_2$ were also prepared in the same way, but in this case the molar ratio was Sb/(Co+Ni) = 3.

The solutions of 0.2 M $H_2C_2O_4$ and 1 M NH_3 were prepared by dissolving the respective chemicals in water. The precise concentrations of metals were analyzed by atomic absorption spectroscopy (AAS), while that of $H_2C_2O_4$ was titrimetrically determined.

4.2 MATERIALS PROCESSING

Figure 2 presents a conceptual scheme for the overall process for generating a double-layer coating on the silica particles. The experiments were carried out using the following:

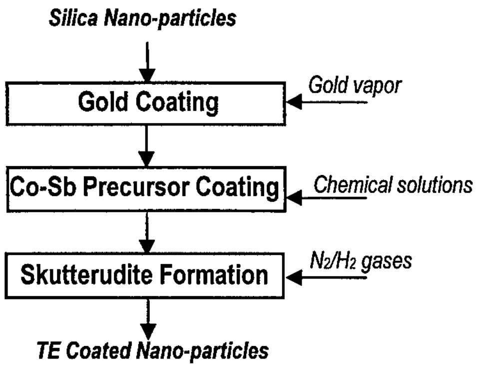

Fig. 2. A conceptual process scheme of double-layer coatin

Gold coating: The uniform-sized silica sphere particles (300 nm) were coated by sputtering gold until the white color of silica disappeared. In order to obtain full coverage of the SiO_2 sphere surface, the particles were processed through several repetitions of shaking and sputtering procedure:

Co-Sb precursor coating: About 8mg of the Au-coated particles were dispersed in 100 ml of $NH_4C_2O_4$ solution under ultrasonic vibration for 5-10 minutes. Then 80 ml of Co(-Ni)-Sb solution was slowly added to the suspension, drop by drop, while maintaining pH = 5-7 (2-3 when including Ni) by regularly adding ammonia solution. After 2-5 hours of reaction equilibration, the precursor-coated particles were filtered, washed several times with water, and then dried at 100°C for more than 3 hours.

Skutterudite formation: The SiO_2 particles coated with the Co-Sb precursor was calcined in flowing nitrogen gas at 300-400°C for 1-2 hour, then heated in a flowing hydrogen gas at 450-550°C for 2-3 hour, and then cooled to room temperature.

The samples obtained at different processing steps were characterized by several techniques: Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersed X-ray Analysis (EDX), Thermogravimetric Analysis (TGA), and X-ray Diffraction (XRD).

5. Results and Discussions

5.1 GOLD COATING

The initial white color of the silica particles eventually changed to golden brown during the sputtering of gold onto the SiO_2 particles. As shown by the SEM photograph for Au-coated silica particles (Fig. 3), most of the gold coated particles have the spherical shape of the original SiO_2. However, a few smaller particles are also present in the sample, and are identified by EDX to be clusters of pure gold. TEM micrographs indicate that the SiO_2 spheres are coated with a layer of gold, as shown in Fig. 4. However, the thickness of the gold layer on different SiO_2 spheres varies over a relatively large range (10-60 nm).

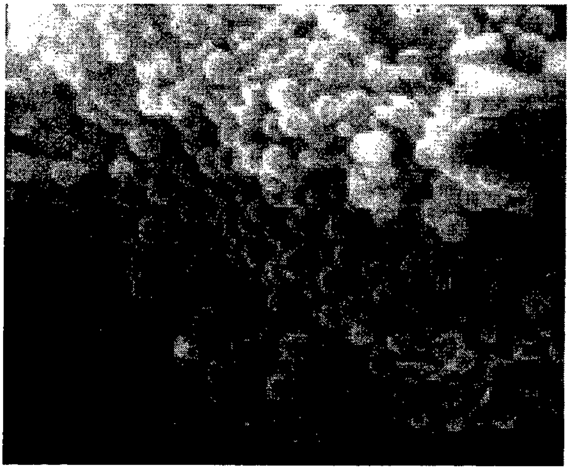

Fig. 3 SEM micrograph of Au-coated particles (bar = 1 μ)

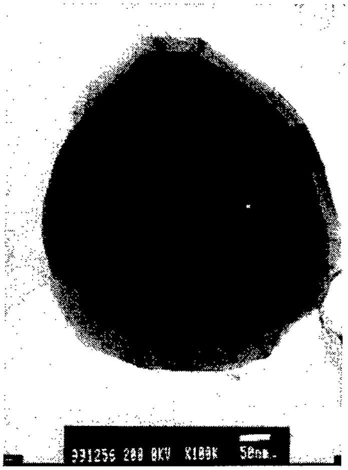

Fig. 4. TEM of gold-coated particle

5.2 PRECURSOR COATING

The stock solution of a mixture of $CoCl_2$ and $SbCl_3$ in HCl was purple in color. After precipitation and filtration, the solution obtained at pH = 5-7 was colorless. Chemical analysis of those filtrate liqours indicated that more than 99% of Sb and Co was precipitated. The color of the coated particles changed to pink, lighter than that of the pure CoC_2O_4 precipitate, while the pure Sb_2O_3 precipitate was white. Similar to the pattern for the co-precipitated powders [8,9], the XRD pattern of the coated silica particles indicates very low crystallinity, as shown in Fig. 5. The crystalline XRD peaks of the as-coated particles correspond to Sb_2O_3, while the CoC_2O_4 and any other possible deposited material appear to be amorphous. The low crystallinity of the as-coated layer is one of main characteristics for metastability, which is preferred for obtaining relatively high reactivity in the further treatments of the precursor-coated layer. Interestingly, a SEM image (Fig. 6) indicates the formation of a novel morphology. The coating layer links the SiO_2 particles into long wire-like bead arrays (Fig. 6), which are up to 10 μm long [9].

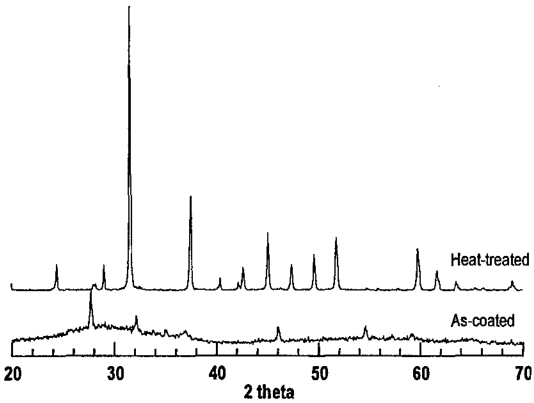

Fig. 5. XRD patterns of Co-Sb coated particles before and after thermal treatments

Fig. 6. SEM micrograph of precursor-coated silica particles (bar = 10 μm)

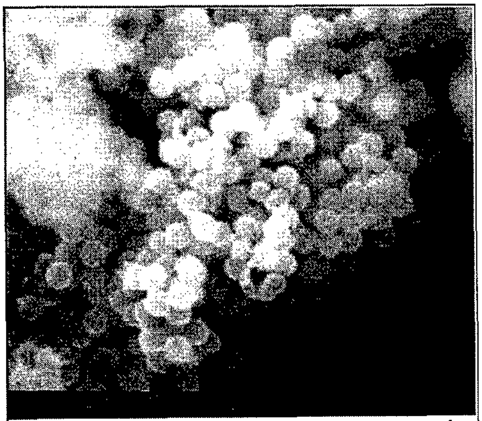

Fig. 7. SEM micrograph of $CoSb_3$/Au coated particles (bar = 1 μm)

5.3 SKUTTERUDITE FORMATION

After the thermochemical treatments first in nitrogen and then hydrogen, the coated SiO_2 particles became dark gray in color. As indicated by the XRD pattern in Fig. 5, the crystalline phase in the heat-treated sample is the desired phase of the $CoSb_3$ Skutterudite, with very little detectable impurity (< 3%). There is no indication in the XRD of either crystalline or amorphous forms of silica. Figure 7 shows a SEM photograph of the $CoSb_3$/Au coated silica particles. This micrograph shows that, after the heat treatments, the doubly-coated particles have regained their spherical shape and uniform size, thus resembling the original or Au-coated silica particles. The assembly of the NETE coated particles into particle arrays and the TE properties of the assembled sphere arrays will be presented in future work.

6. Conclusions

A chemical alloying route has been demonstrated for NETE coating on silica particles. The conclusions for this route are:

1) The chemical route for the synthesis of bulk powders of Skutterudite compounds can be directly utilized for NETE coating, without significant modification of synthesis conditions;
2) The primary coating of gold on the particles by sputtering is simple to accomplish, although there is significant polydispersity in the thickness of the gold layer on different particles.
3) Both the gold- and gold/Skutterudite-coated particles retain the morphology of the original silica particles. However, we find that the SiO_2 particles assemble into chains that are internally linked by the coating that is precursor to the Skutterudite.
4) The NETE layer of Skutterudite structure has the same or higher purity than Skutterudite powders produced by the same technique.

7. Acknowledgments

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