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Effect of external energy on atomic, crystalline and powder characteristics of antimony and bismuth powders

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Abstract. **Next to atoms and molecules the powders are the smallest state of matter available in high purities and large quantities. The effect of any external energy on the shape, morphology and structure can thus be studied with relative ease. The present investigation deals with the effect of a non-contact external energy on the powders of antimony and bismuth. The characteristics of powders treated by external energy are compared with the as received powders (control). The average particle sizes, d_{50} and d_{99}, the sizes below which 99% of the particles are present showed significant increase and decrease indicating that the energy had caused deformation and fracture as if the powders have been subjected to high energy milling.**

To be able to understand the reasons for these changes the powders are characterized by techniques such as X-ray diffraction (XRD), surface area determination (BET), thermal analytical techniques such as DTA–DTG, DSC–TGA and SDTA and scanning electron microscopy (SEM).

The treated powder samples exhibited remarkable changes in the powder characteristics at all structural levels starting from polycrystalline particles, through single crystal to atoms. The external energy had changed the lattice parameters of the unit cell which in turn changed the crystallite size and density. The lattice parameters are then used to compute the weight and effective nuclear charge of the atom which showed significant variation. It is speculated that the external energy is acting on the nucleus through some reversible weak interaction of larger cross section causing changes in the proton to neutron ratios. Thus the effect is felt by all the atoms, and hence the unit cell, single crystal grain and grain boundaries. The stresses generated in turn may have caused deformation or fracture of the weak interfaces such as the crystallite and grain boundaries.

Keywords. **Antimony; bismuth; external energy; powder.**

1. Introduction

Apart from atoms and molecules the next smallest materials available are powders. These could be single crystalline or polycrystalline, the particle size of which is in the micrometric or nano metric range (< 100 nm) (Suryanarayana 1995, 1999). Particles exhibit fine microstructures and can contain such a high density of defects (point defects, dislocations, sub (crystallite) boundaries, grain boundaries, inter phase boundaries, etc.) that the spacing between neighbouring defects in nano size powders can even approach the inter atomic distance (Gleiter 1992). As the grain size becomes smaller and smaller, a larger and larger fraction of atoms resides on the single crystal grain boundaries (at a 6 nm grain size, nearly half the atoms reside on the grain boundaries), thus the behaviour of nano sized powders is often dominated by events at the grain boundaries (Mayo 1996).

Due to the extremely small size of the grains and a large fraction of the atoms located at the grain boundaries, materials made from these powders possess properties like higher strength/hardness, enhanced diffusivity, improved ductility/toughness, reduced elastic modulus, increased specific heat, higher electrical resistivity, higher thermal expansion coefficient, lower thermal conductivity, and superior magnetic properties much improved over those exhibited by conventional grain sized (> 10 μm) polycrystalline materials (Suryanarayana 1995).

Both micro meter and nano meter sized powders are produced by methods like mechanical milling (Mohan *et al* 1999), inert gas condensation, spray conversion process,

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chemical processes (Amarchand *et al* 2000), and electro deposition (Suryanarayana 1995), etc. Often mechanical milling is used for synthesis of fine and nano sized powders in bulk quantities using simple equipment and at room temperature (Suryanarayana 1999). During this process, the metal powder particles are subjected to severe mechanical deformation from collisions with the milling tools. Consequently, plastic deformation at high strain rates ($\sim 10^3$–10^4 s^{-1}) occurs within the particles and the average grain size can be reduced to a few nanometers after extended milling (Benjamin 1976; Fecht 1996). Plastic deformation generally occurs by slip and twinning at low and moderate strain rates, while at high strain rates it occurs by the formation of shear bands, consisting of dense networks of dislocations. The plastic strain in the material increases due to increasing dislocation density in the early stages of ball milling. At a threshold dislocation density, even at moderately elevated temperatures, the material relaxes into sub grains separated by low-angle boundaries, leading to a decrease of atomic level strain. During subsequent milling the process of high deformation/sub grain formation is repeated resulting in the sub grains becoming finer and finer, and the relative orientation of the sub grains with respect to each other ultimately becoming completely random. Once the sub grains reach a critical level of refinement, further refinement becomes virtually impossible since the stresses required for dislocation movement are enormously high due to the Hall–Petch strengthening. Thus nano sized powders with a minimum grain size are produced (Suryanarayana 1999). Titanium powders of about 2 μ particle size when subjected to high energy attrition milling in an argon atmosphere after 15 h of milling yielded an average particle size of 35 nm (Dabhade *et al* 2001). Thus it is now possible to produce large quantities of ultra fine and nano powders by high energy milling.

In the present study the effect of a non contact external energy on antimony and bismuth powders was investigated. These powders were chosen as they belong to the same group in the periodic table and have low melting points. Metals of low melting point generally exhibit low bond energy and were thought to be more significantly affected by the external energy. Powders were chosen as they are the finest form of these metals readily available in high purity levels. Powders also exhibit a high surface area and thus were expected to be more receptive to the external energy.

2. Experimental

Antimony and bismuth powders (–325 mesh) of 99·5% purity were obtained from Alpha Aesar. Five sets of each powder were prepared, the first set which was untreated was designated as control while the other sets exposed to external energy referred to as treated samples. The control and the treated samples were characterized by X-ray diffraction (XRD), laser particle size analysis, surface area determination (BET), differential thermal analysis (DTA–DTG), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), simultaneous differential thermal analysis (SDTA) and scanning electron microscopy (SEM).

Average particle size and size distribution were obtained using SYMPATEC HELOS-BF laser particle size analyzer with a detection range of 0·1–875 μm (micro meters). From the particle size distribution, d_{50}, the average particle size and d_{99} (maximum particle size below which 99% of particles are present) for the control (untreated or as received powders) are taken as standard and are compared with the results obtained on four separately treated powders. Surface area determination was carried out on a SMART SORB 90 BET surface area analyser with a measuring range of 0·2–1000 m^2/g. X-ray diffraction was carried out using a powder Phillips, Holland PW 1710 XRD system. A copper anode with nickel filter was used. The wavelength of the radiation was 1·54056 Å (10^{-10} m or 10^{-8} cm). The data is obtained in the form of 2θ vs intensity chart as well as a detailed table containing $2\theta°$, d value Å, peak width $2\theta°$, peak intensity counts, relative intensity %, etc. The 'd' values are compared with standard JCPDS data base and the Miller indices h, k and l for various $2\theta°$ values are noted. The data are then analysed using PowderX software to obtain lattice parameters and unit cell volume. Differential thermal (DTA)–thermogravimetric (TGA) combined analyses were carried out from room temperature to 900°C at a heating rate of 10°C/min for antimony powders while for bismuth powders it was carried out from room temperature to 400°C at a heating rate of 5°C/min. Scanning electron microscopy of control and treated powders was carried out using a JEOL JSM-6360 instrument.

The details of the experiments and the original data obtained prior to analysis are given in link: http://www.divinelife.us/Transcendental_Science/Transcendental_Science.html.

2.1 *Method of data analysis*

The percent change in particle size of various treated powders with respect to control powders were computed using the formula

$$\text{Percent change in average particle size} = d_{50}\,(\%) = 100 \times (d_{50t} - d_{50c})/d_{50c}. \quad (1)$$

In a similar manner the change in particle size of d_{99} (%) was computed. Percent change in BET surface was calculated in a similar manner as indicated in (1).

The crystallite size was calculated using the formula

$$\text{Crystallite size} = k\lambda/b\cos\theta, \quad (2)$$