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Observation Of Bimodality In Nanocrystalline Cobalt - Ferri - Chromites

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Abstract. In this communication we present detail analysis of particle size distribution curves, differential size distribution and cumulative undersize distribution, recorded for nano particles of spinel ferrite system, CoCrxFe2-xO4 (x = 0.0, 1.1 and 2.0), synthesized by chemical co-precipitation technique. It is found that the distribution is bimodal as well as not mono disperse. Observed bimodality has been explained in the light of Ostwald ripening. Various parameters have been determined and the role of Cr3+ - substitution in governing signature of distribution patterns has been discussed.

Keywords: Nanoparticles, Particle Size Distribution, Bimodality.

PACS: 81.07.Bc

INTRODUCTION

Particle size growth may be monitored during operations such as granulation or crystallization. For determining the particle size of powders, requirement of mixing is common since materials with similar and narrower distributions are less prone to segregation [1].

Particle size distribution data can be presented in tabular format i.e. numerically or graphically. In graphical form, data are presented in differential and cumulative distribution curves. Both the forms are interrelated i.e. if one differentiates the cumulative distribution curve, the differential distribution is obtained. On the other hand, if one integrated the differential distribution curve, the cumulative distribution is obtained [2]. The differential distribution shows the relative amount at each particle size. From the different size distribution, measures of central tendency such as the modal and mean diameters are determined. The diameter at the peak of the differential distribution is the modal diameter while the mean diameter is the average diameter.

The corresponding cumulative distribution curve demonstrates the relative amount at or below a particular size. The median diameter is another measure of central tendency. It is the diameter at the 50th percentile, designed d50. Quartile diameters include d25, d50 and d75. There are several measures of absolute width one can derive given the cumulative distribution. One common measure is the span, d90 -- d10. A dimensionless measure of width is the relative span defined as span/d50. Other relative measures of width include percentile ratios such as d90/d10 and d75/d25.

EXPERIMENTAL DETAILS

Nanoparticles of spinel ferrite system of general chemical formula, CoCrxFe2-xO4, with selected compositions, x = 0.0, 1.1 and 2.0, were prepared by the co-precipitation route using the corresponding metal sulphates and sodium hydroxide as reported previously [3]. Laser particle size analyzer (model: Helos-BF, make: Sympatec, Germany) has been used to study particle size distribution patterns, by dispersing 100 mg of nanocrystalline ferrite powder in de-ionized water followed by ultrasonication.

RESULTS AND DISCUSSION

Typical particle size distribution patterns, differential size distribution and cumulative undersize distribution, for x = 0.0 and 1.1 and 2.0 compositions of spinel ferrite system, CoCrxFe2-xO4, are shown in
Figure 1. The distribution is bimodal (double peaked) as well as not mono disperse (all one size).

Earlier, a bimodal size distribution was observed for the as prepared sample and the sample annealed at 300 °C with an average particle sizes of (~ 2 nm and ~ x = 2.0, (~ 4 nm and ~ 8 nm) respectively, for the two samples of nickel ferrite synthesized using the sol-gel process [4].

On the other hand, the existence of a broad (bimodal) distribution in the crystallite size has also been reported for the high energy mechanically milled NiFe$_2$O$_4$, MgFe$_2$O$_4$, Fe$_3$O$_4$ nano particles and other ultrafine mechanically alloyed materials [5]. The origin of the bimodality lies in the growth process by which the particles are formed. In a chemical growth process such as co-precipitation which is used here, growth occurs by initial nucleation and growth via a ‘seed and grow’ mechanism, followed by Ostwald ripening. For smaller particle systems, where the growth has been restricted, some original seeds remain in the colloid. For the larger particle systems a greater percentage of the seeds have been observed in the ripening process leading to a more uniform particle size distribution [6].

Ostwald ripening is the phenomena in which smaller particles in solution dissolve and deposit on larger particles in order to reach a more thermodynamically stable state wherein the surface to area ratio is minimized. Ostwald ripening occurs because molecules on the surface of particles are more energetically unstable than those within. Therefore, the unstable surface molecules often go into solution shrinking the particle over time and increasing the number of free molecules in solution. When the solution is super saturated with the molecules of the shrinking particles those free molecules will redeposit on the large particles. Thus, small particles decrease in size until they disappear and the large particles grow even larger. The shrinking and growing of particles will result in a larger mean diameter of a particle size distribution.

A careful examination of Figure 1 shows that for x = 0.0 composition two well separated peaks are observed. The peak on the left hand side is with less intensity and asymmetric one i.e. the curve tails to the left more than to the right, that means the skew is negative. The peak on the right hand side with more intensity having symmetric differential distribution i.e. has zero skew. The skew is positive if curve tails to the right more than to the left. The reference point for tailing is with respect to the modal diameter. On increasing Cr$^{3+}$ - substitution (x) in the system, CoCr$_x$Fe$_{2-x}$O$_4$, for x = 1.1 composition (CoCr$_{1.1}$Fe$_{0.9}$O$_4$) both the peaks get merged and also have same intensity. On the other hand, for cobalt chromite (x = 2.0), once again two well resolved peaks are observed. The left hand side peak is with more intensity and asymmetric in nature while the peak on the right hand side is with less intensity but symmetric one.

Regarding the role of Cr$^{3+}$ - substitution (x) for Fe$^{3+}$ (2 - x) in the system, CoCr$_x$Fe$_{2-x}$O$_4$, it is found that when Fe : Cr ratio is found ~ 1 : 1 (x = 1.1) mono dispersivity (single peak) is observed, as one deviates from this ratio, bimodality (x = 0.0 and 2.0) is clearly seen. It leads to conclude that Fe : Cr ratio plays very important role in governing particle size distribution in the system. Furthermore, on increasing Cr$^{3+}$ - concentration broadening of peak corresponds to small size particles (LHS peak) decreases and intensity...
increases. On the other hand, intensity as well as broadening of peak corresponding to large size particles decreases. Above observations suggest that on increasing Cr$^{3+}$ content size distribution in small size particles becomes narrow and population increases while distribution of particle size and population both decrease for large size particles. The overall effect is reduction in particle size on Cr$^{3+}$ substitution as supported by X-ray powder diffraction patterns and transmission electron micrographs analysis [3].

There are several measures of width. One measure of width is FWHM, the full width at half maximum. It is obtained by drawing a horizontal line at 50% of the maximum and taking the difference between the two places it intersects the distribution. HWHM, the half width at half maximum, is another measure of width. It is defined as FWHM/2. A relative fractional measure of width is obtained by dividing HWHM by the measure of central tendency from which it was derived, the modal diameter (HWHM/modal diameter).

The size of the particles shown in Figure 1 is in micrometer ($\mu$m) order. These particles were agglomerates which were found to break further and further to submicron level with more and more powerful ultrasonic de-agglomeration techniques.

The important parameters such as: modal diameter, mean/average diameter, full width half maximum (FWHM), span ($d_{10}$-$d_{90}$), relative span (span/$d_{50}$), quartile ratio ($d_{75}/d_{25}$) and median diameter ($d_{50}$), for CoCr$_2$O$_4$ ($x=2.0$) are determined and tabulated in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LHS Peak</th>
<th>RHS Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modal diameter</td>
<td>85 $\mu$m</td>
<td>300 $\mu$m</td>
</tr>
<tr>
<td>Average diameter</td>
<td>95 $\mu$m</td>
<td>350 $\mu$m</td>
</tr>
<tr>
<td>FWHM</td>
<td>177.5 $\mu$m</td>
<td>200 $\mu$m</td>
</tr>
<tr>
<td>Span</td>
<td>246.5 $\mu$m</td>
<td>–</td>
</tr>
<tr>
<td>Relative span</td>
<td>4.93</td>
<td>–</td>
</tr>
<tr>
<td>Quartile ratio</td>
<td>8.12</td>
<td>–</td>
</tr>
<tr>
<td>Median diameter</td>
<td>55 $\mu$m</td>
<td>–</td>
</tr>
<tr>
<td>Relative percent measure of width</td>
<td>104.4 %</td>
<td>–</td>
</tr>
</tbody>
</table>

$\text{d}_{10} = 4.5 \mu$m, $\text{d}_{25} = 15.4 \mu$m, $\text{d}_{50} = 55 \mu$m, $\text{d}_{75} = 125 \mu$m and $\text{d}_{90} = 250 \mu$m.

### CONCLUSIONS

1. Particle size distribution curves analysis suggests that the distribution is bimodal as well as not mono disperse and having negative skew.

2. Size of particles is of micrometer order and ultrasonic de-agglomeration is required before further analysis.

3. The reason for bimodality lies in the growth mechanism and the relative proportion of particles formed by nucleation and Ostwald ripening.

4. The substitution of Cr$^{3+}$ ions effectively controls size distribution and population of particles.

5. Various important parameters can be determined from the differential size distribution and cumulative undersize distribution curves.

### REFERENCES