The transition from microparticles to nanoparticles can lead to a number of changes in its properties. The objective of this work is to analyze the thermal, tribological properties of yttria stabilized zirconia nanoparticles. Nanosized yttria stabilized zirconia particles were prepared by milling the yttria stabilized zirconia (10 µm) in a planetary ball mill equipped with vials using tungsten carbide balls. After 40 hours milled the yttria stabilized zirconia nanoparticles of sizes ranging from 70-90 nm were obtained. The phase composition and morphologies of the as-synthesized particles were characterized by energy dispersive X-ray analysis, scanning electron microscope, transmission electron microscope, thermogravimetric analysis and differential scanning calorimeter, and the images of the same were obtained. From TG-DSC analysis it was confirmed that, the yttria stabilized zirconia nanoparticles were heat stable under different thermal conditions which is due to the addition of yttria to pure zirconia. Due to this property of yttria stabilized zirconia nanoparticles, it can be widely used in high transfer application such as lubricant additives. The heat transfer properties of automotive engine lubricants were determined by utilization of measured thermal conductivity, viscosity index, density, flash point, fire point and pour point revealed that lubricants with additive constituents have a significant effect on the resultant heat transfer characteristics of the lubricants.

Key words: sliding friction, hardness, thermal effects, solid lubricant, surface analysis, lubricant additives

Introduction

Nanotechnology can be regarded as one of the most important frontier fields in the 21st century. Nanotechnology is the study of manipulating matter on an atomic and molecular scale. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to investigating whether we can directly control matter on the atomic scale. Nanotechnology entails the application of fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, microfabrication, etc.

Nanotechnology is capable of creating many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials, and energy production.
The high surface to volume ratio of nanoparticles has improved the material performance compared to the bulk materials. The unique phenomenon that occurs in nanoparticles allows their properties (electrical, optical, chemical, mechanical, magnetic, etc.) can be selectively controlled by engineering the size, morphology, and composition of the particles. New materials are being discovered or produced and astonishing claims are being made concerning their properties, behaviours and applications.

Nanofluids are suspensions of nanoparticles in base fluids, a new challenge for thermal science provided by nanotechnology. It is formulated to satisfy a variety of requirements imposed by the engine system and the type of vehicular operation. Inherent in these requirement is the complex function which ultimately satisfy the heat transfer properties. As the temperature increases with the engine cylinder can lead to loss of fluid film lubrication, lubricant degradation within the piston rings, increase in oil sump temperature, all of which ultimately degrade the overall performance capabilities of the engine lubricant. As a result, an investigation was initiated to define the heat transfer characteristics of lubricants incorporated with nanoparticles to meet the performance requirements of the engine system [1].

Material selection

Yttria stabilized zirconia (YSZ) is the material which is considered in this study. Zirconia is an extremely refractory material. It offers chemical and corrosion inertness to temperatures well above the melting point of alumina. It is electrically conductive above 600 °C and is used in oxygen sensor cells and as the susceptor (heater) in high temperature induction furnaces [2-4].

Several different oxides are added to zirconia to stabilize the tetragonal and/or cubic phases: yttrium oxide, (Y₂O₃), magnesium oxide (MgO), calcium oxide (CaO), and cerium(III) oxide (Ce₂O₃) [5].

Zirconia is often more useful in its phase stabilized state. Pure zirconia when heated goes through disruptive phase changes. By adding small percentages of yttria, these phase changes are eliminated, and the material has better thermal, mechanical, and electrical properties. Pure zirconia exists in three crystal phases at different temperatures. At very high temperatures (>2370 °C) the material has cubic structure, at intermediate temperatures (1170 to 2370 °C) it has tetragonal structure, and at low temperatures (below 1170 °C) the material transforms to the monoclinic structure. In some cases, the tetragonal phase can also be metastable. If the zirconia is in metastable tetragonal phase at different stress condition, cracks will be initiated because of the volume expansion. The volume expansion is attributed to the transition of zirconia from tetragonal to cubic structure [6-9].

Key properties of YSZ are high strength and hardness, high fracture toughness, good oxygen ion conductor, good frictional and wear characteristics, high coefficient of thermal expansion, high modulus elasticity, high toughness, excellent chemical resistance, and has high melting point than aluminum oxide.

Experimental procedure

The YSZ nanoparticles were synthesized using ball mill. A ball mill is a type of grinder used to grind materials into extremely fine powder for use in lubricants, paints, pyrotechnics, and ceramics. The material to be ground and the grinding media were placed in a stationary vial. Tungsten carbide balls were used as the as the grinding media. The inner walls of the vial is also
coated with a layer of tungsten carbide because of its high hardness, wear resistance, and impact strength. Milling was done at the rate of 300 rpm under normal atmospheric conditions. The mode of operation is through a variable frequency drive whose frequency is 50 HZ. The material and the media are then agitated by a shaft with arms, which are rotating at high speed. This causes the media to exert both shearing and impact forces on the material resulting in optimum size reduction and dispersion. An internal cascading effect reduces the material to a fine powder [10-17].

The KD2 pro apparatus is a handheld device used to measure the thermal conductivity of lubricants. It consists of a handheld controller and sensors that is to be inserted into the lubricants. The single-needle sensors measure thermal conductivity and resistivity; while the dual needle sensor measures volumetric specific heat capacity and diffusivity. The KD2 pro is a battery operated device.

The viscosity index of the lubricants were determined by the ASTM standard D-445. Initially a fixed volume of lubricant is filled in the capillary tube. The time is measured for a fixed volume of lubricants to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer. Two such determinations are needed from which to calculate a kinematic viscosity result that is the average of two acceptable determined values.

The density of the lubricants were determined by the ASTM standard D-4052. A small volume of 0.7 mL of lubricants is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the lubricants.

The flash point and fire point of the lubricants were determined by Cleveland open cup tester ASTM standard D-92. A 70 mL of lubricants is filled into a test cup. The temperature of the lubricants is increased rapidly at first and then at a slower constant rate as the flash point is approached. At specific intervals a test flame is passed across the cup. The flash point is the lowest liquid temperature at which application of the test flame causes the vapours of the lubricants to ignite. To determine the fire point, the test is continued until the application of the test flame causes the lubricants to ignite and sustain burning for a minimum of 5 seconds. The pour point of the lubricants are determined by ASTM standard D-97. After preliminary heating of the lubricants, the lubricants is cooled at a specified rate and examined at intervals of 3 °C for flow characteristics. The lowest temperature at which movement of the lubricants is observed is recorded as the pour point.

Results and discussion

Energy dispersive X-rays analysis

Energy dispersive X-ray analysis (EDXA) is an analytical technique used predominantly for the elemental analysis or the chemical characterization of a specimen. Being a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in this particular case. By moving the electron beam across the material an image of each element in the sample is acquired.

Figure 1, and tab. 1, illustrate the composition of YSZ nanoparticle produced after 40 hours of ball milling in the atmospheric medium. From EDXA results, it is observed that 94.55
percentage in weight of zirconium oxide, 5.45 percentage in weight of yttrium are found in the milled nano YSZ particles. The chemical composition of YSZ remains the same after milling. From EDXA report it is also clear that the YSZ nanoparticle is free from impurities [3].

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight [%]</th>
<th>Atom [%]</th>
<th>Compound [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>24.03</td>
<td>6.41</td>
<td>–</td>
</tr>
<tr>
<td>Y</td>
<td>5.45</td>
<td>4.87</td>
<td>5.45</td>
</tr>
<tr>
<td>Zr</td>
<td>70.52</td>
<td>33.72</td>
<td>94.55</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Scanning electron microscope

The fig. 2 shows the scanning electron microscope (SEM) micrographs of the 40 hrs milled YSZ nanoparticles. After milling YSZ powder, it is observed to be nanomaterial. It is visible from the SEM micrographs that the powder particle sizes are in the range of 70-90 nm. The large particles seen are not necessarily large particles; they are the agglomerates that formed as the small particles, stick at the vial wall of the planetary ball mill during synthesis [4, 12].

Transmission electron microscope

Figure 3 shows the transmission electron microscope (TEM) micrographs of the 40 hours milled YSZ nanoparticles. The TEM micrograph shows the YSZ nanoparticle sizes are around 70 nm. It was also observed that the powder particle sizes are spherical in shape, which is visible due to the high image resolution of TEM than scanning electron microscope

4TG-DSC analysis of YSZ nanoparticles

The thermogravimetric analysis is used to determine the weight of the material with respect to the function of temperature. Figure 4 shows the thermo-
gravimetric (TGA) graph of the 40 hours milled YSZ nanoparticles. The results of TGA illustrates, the sharp decrease in the differential TGA curve below 150 °C. This is due to the desorption of water. Above 150 °C, there is minute weight loss equals to 6% is noted. Since there is no degradation of material this proves that there is no isomeric transformation from 150-1000 °C. The addition of yttria to pure zirconia replaces some of the Zr$^{4+}$ ions in the zirconia lattice with Y$^{3+}$ ions. This produces oxygen vacancies, as three O$^{2-}$-ions.

It also permits YSZ to conduct O$^{2-}$ ions, provided there is sufficient vacancy site mobility, a property that increases with temperature. This ability to conduct makes YSZ nanoparticles well suited to operate at high enough temperatures. From this study it is clear that thermal stability is high in yttria stabilized zirconia, therefore the material can be a good lubricating additive.

**Thermal properties of lubricants with and without YSZ nanoparticles**

Table 2 illustrates the thermal characterization of lubricants incorporated with and without YSZ nanoparticles. From the results it was observed that the viscosity index, thermal conductivity, density, flash point, fire point of the nanolubricants have higher performance than the lubricants without nanoparticles. This is due to the effects of YSZ nanoparticles. The properties of YSZ nanoparticles such as good oxygen ion conductor, thermal stability etc. improves the thermal properties of lubricants and also allows the lubricants to withstand even at high temperatures. It is therefore revealed that, the lubricants incorporated with YSZ nanoparticles have a significant effect on the heat transfer characteristics of the lubricants and meet the performance requirements of the engine system.

**Conclusions**

Nanotechnology is a broad interdisciplinary area of research development and industrial activity. A detailed work has been done on thermal characteriza-

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Lubricant</th>
<th>YSZ lubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vis at 40 °C cSt</td>
<td>174.21</td>
<td>176.23</td>
</tr>
<tr>
<td>Vis at 100 °C cSt</td>
<td>15.88</td>
<td>16.23</td>
</tr>
<tr>
<td>Viscosity index</td>
<td>93</td>
<td>95</td>
</tr>
<tr>
<td>Thermal conductivity [Wm$^{-1}$K$^{-1}$]</td>
<td>0.143</td>
<td>0.147</td>
</tr>
<tr>
<td>Density at 15 °C</td>
<td>0.8994</td>
<td>0.9013</td>
</tr>
<tr>
<td>Flash point, COC, °C</td>
<td>256</td>
<td>260</td>
</tr>
<tr>
<td>Fire point, COC, °C</td>
<td>264</td>
<td>270</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>0</td>
<td>+3</td>
</tr>
</tbody>
</table>
tion of YSZ nanolubricants. The YSZ were milled for 40 hrs, and following conclusion were arrived.

From EDXA report it is observed that the percent of each element in YSZ nanoparticles were found to be zirconium oxide (94.55%) and yttrium (5.45%). The SEM image of YSZ nanoparticles indicates that the milled particles are nano size range and also agglomerated. The agglomerated nanoparticle size varies from 70 nm to 90 nm. From TEM image it was observed that the milled particles were spherical in shape and indicates the particle sizes were around 70 nm.

The TGA indicates the changes in weight in relation to function of temperature. From the TGA it is clear that, residue 94.32% is obtained under thermal conditions up to 1000 °C. This study illustrates the material is heat stable under different thermal conditions, since there is no degradation of material. From the DSC it is clear that there is options of exotherm and endotherm. DSC traces shows there is no isomeric transform up to 1000 °C, since there is no degradation of material.

The heat transfer properties of nanolubricants shows higher performance which are revealed from the measurements of the viscosity, viscosity index, density, thermal conductivity, flash point, fire point and pour point which showed the improvement of 2% with the incorporation of YSZ nanoparticles in the lubricants.

**Acronyms**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>YSZ</td>
<td>yttria stabilized zirconia</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimeter</td>
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<tr>
<td>EDXA</td>
<td>energy dispersive X-ray analysis</td>
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</table>

**Acknowledgments**

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**References**