Sintering behaviour, microstructural characterisation and thermal expansion properties of Sn substituted ZrMo$_2$O$_8$

Jayanth R. Ramamurthy$^{a}$, Roy Johnson$^b$, Ravi Kumar$^{ab,⁎}$

$^a$ Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras (IIT Madras), Chennai 600036, India
$^b$ International Advanced Research Centre for Powder Metallurgy and New Materials, Balapur, Hyderabad 500005, India

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A B S T R A C T

The coefficient of thermal expansion (CTE) of ZrMo$_2$O$_8$ can be fine-tuned by controlling the amount of tin substitution in zirconium lattice sites. The sintering challenges associated with this material and the optimal sintering conditions were investigated in this study. Powders of tin substituted ZrMo$_2$O$_8$ were synthesised by co-precipitation technique. X-ray diffraction studies confirmed the formation of cubic SnMo$_2$O$_8$. Sintered pellets were produced from the powders and optimal sintering without decomposition of the phase was achieved at the expense of porosity. The material was found to be thermally stable up to 600 °C using thermogravimetric analysis. Dilatometric analysis of the sintered compacts shows that the CTE of the sample is in the order of $3.9 \times 10^{-6} / K$, between 25°C and 600°C.

1. Introduction

Materials that exhibit negative thermal expansion (NTE) employ supramolecular structural mechanisms such as displacive phase transitions from a distorted to a structurally stable phase, magnetostrictive transitions, librations and rigid unit modes (RUM) [1]. These mechanisms supersede the thermal expansion that occurs due to lengthening of interatomic bond lengths when heated. Materials belonging to zirconium tungstate (ZrW$_2$O$_8$) family, zirconium vanadate family (ZrV$_2$O$_7$), scandium tungstate family (Sc$_2$(WO$_4$)$_3$) and aluminium phosphates (AlPO$_4$) exhibit NTE based on RUM mechanism [2–4]. Zr$_2$W$_4$O$_{12}$ family has AM$_2$O$_8$ type cubic structure (where A = Zr, Hf and M = W, Mo) consisting of AO$_6$ octahedra and MO$_4$ tetrahedra connected by corner-sharing oxygen atoms [5]. The transverse vibrations of the corner-sharing atoms can lead to tilting of the polyhedra causing the exhibition of NTE by RUMs [6]. ZrW$_2$O$_8$ has been well studied in the past owing to the exhibition of positive thermal expansion (PTE). This anomalous behaviour was attributed to the relatively smaller cell volume and increased stiffness of the SnO$_6$ octahedra. The ordering of MoO$_4$ tetrahedra also significantly affects the thermal expansion properties of SnMo$_2$O$_8$ [14]. In 1988, Buiten described a way to produce stable cubic SnMo$_2$O$_8$ for the first time by leading SnCl$_4$ in oxygen atmosphere over a fluidised bed of MoO$_3$ [15]. Previous studies have shown that controlling the coefficient of thermal expansion (CTE) of ZrW$_2$O$_8$ and ZrMo$_2$O$_8$ by doping are not very effective [16–19]. Tal lentire et al., reported a wide range of solubility of Sn in ZrMo$_2$O$_8$ at the A site using co-precipitation route, thus successfully controlling the CTE by chemical substitution. The CTE in each case was found by means of change in lattice parameter using powder X-ray diffraction (XRD). It was shown that the CTE could be controlled by zirconium substitution and at compositions close to equimolar ratios of Sn and Zr, the CTE was very close to zero [14].

The present work continues on the idea that isotropically expanding material with very low CTE can be achieved in a single phase by substituting A site in negatively expanding ZrMo$_2$O$_8$ with positively expanding species such as Sn in equimolar ratios with emphasis on the sintering aspects of this material. The usage of this material in near-net shaped component form requires bulk manufacturing and that requires a comprehensive understanding of sintering mechanisms followed by microstructural evolution which have not been addressed in the literature. The current work seeks to understand the challenges in the sintering of this material in bulk form and deduce optimal sintering conditions. A composition containing equal molar ratios of Sn and Zr was chosen and was used to prepare sintered compacts. Detailed
microstructural characterisation was carried out and the sintering behaviour was analysed. The CTE of the sintered samples were determined by dilatometry to understand the influence of any additional phases and thus achieve a more realistic estimate.

2. Materials and methods

2.1. Synthesis of \( \text{Sn}_x\text{Zr}_1-x\text{Mo}_2\text{O}_8 \) powders

Sn substituted ZrMo\(_2\)O\(_8\) were prepared using wet chemical route employing coprecipitation process \([14]\). 5.261 g of SnCl\(_4\)5H\(_2\)O and 4.830 g of ZrOCl\(_2\)·8H\(_2\)O (Sigma-Aldrich Chemicals, India) were dissolved in a beaker containing water. 10.687 g of (NH\(_4\))\(_2\)Mo\(_2\)O\(_4\)·4H\(_2\)O (Johnson Matthey Chemicals, India) was dissolved separately in another beaker of water to form a clear solution. The two solutions were then mixed dropwise by adding through dropping funnel and stirred using a magnetic stirrer continuously for 12 h. The resulting solution was dried in an oven at 50 °C in ambient atmosphere for 12 h to evaporate the water content. The dried powders were pulsed in mortar and pestle and were heat-treated at a furnace at 400 °C, 500 °C, 590 °C and 700 °C and held for 30 min at each of these temperatures in ambient atmosphere. The expected stoichiometry of the heat-treated powder was Sn\(_0.5\)Zr\(_0.5\)Mo\(_2\)O\(_8\).

2.2. Sintering

The heat-treated powders of the samples were compacted using a hydraulic press at a pressure of 350 MPa, using polyvinyl alcohol (PVA) as a binder, to form pellets. The pellets were then sintered at three different temperatures viz., 400 °C, 500 °C and 600 °C for three different soaking periods viz., 4, 8 and 12 h each in ambient atmosphere at a heating rate of 2 °C/minute.

2.3. Physical and spectrochemical characterisation

2.3.1. Density measurements

The densities of the pellets were measured using water displacement method employing Archimedes principle. The dry weight of the sample was measured using a digital balance. After taking the dry weight, the sample was submerged in water for two hours at 50 °C. The submerged weight of the sample was then taken while being suspended in water using a steel wire setup. Care was taken to ensure no bubbles were present on the sample or on the walls of the beaker. The sample was then taken out of the beaker and wiped clean using a tissue to remove the water adhering to the surface. The weight of the soaked sample was then taken. These weights were used to calculate the bulk density of the pellets.

2.3.2. Induction coupled plasma optical emission spectrometry (ICP-OES)

ICP-OES (Thermo Fischer ICAP6500 DUO view) was carried out for the powder samples heat-treated at 590 °C to obtain the chemical composition data. The experiment was restricted only to the 590 °C heat-treated powders as it displayed higher amount of the desired cubic phase (discussed later in results). A small amount of the sample was weighed to find the mass and was then dissolved in this digestion mixture. This solution was converted to an aerosol and was sprayed into argon plasma. The elements present in the solution was atomised or ionised at very high temperature of about 6500 K. This temperature results in the electronic excitation of atoms and ions leading to the emission of light. Echelle optics was used to split the spectrum of the emission lines. The intensity of the emitted radiation from the excited ions and atoms were used to determine the concentrations of the elements.

2.4. Structural characterisation

2.4.1. X-ray diffraction

The X-ray diffraction (XRD) of heat-treated powders and the sintered samples were carried out using Bruker Discover D8 diffractometer (USA). A collimated beam of Cu K\(_\alpha\) radiation with a wavelength of 0.154 nm was used to irradiate the sample. The data was collected over a range of 10° to 60° (2\(\theta\)) with a step size of 0.15° and scan rate of 2 s/step. The accelerating voltage used was 30 kV and the current was set at 25 mA. The sintered samples were well polished to achieve a flat surface prior so that any effects of surface irregularities can be prevented. Phase analysis was carried out with the diffraction data using X’pert high score plus software and International Center for Diffraction Data (ICDD) database. The diffractograms were subjected to background correction and removal of K\(_{\alpha\,2}\) peaks before analysis.

2.4.2. Scanning electron microscopy (SEM)

Microstructural analysis was carried out using Hitachi S4800 scanning electron microscope (Japan). The pellets were well polished prior to SEM, using SiC abrasive papers of fine grit sizes from 1500 to 5000. Gold sputter coating of approximately 5 nm thickness was carried out on the samples before imaging to prevent charging effects. All the images were taken in high vacuum at a voltage of 5 kV in secondary electron (SE) mode. Energy dispersive X-ray spectroscopic (EDS) data was also collected using Si(Li) – Liquid N\(_2\) cooling type X-ray detector (Horiba, Japan) for sintered samples. The EDS data was collected for qualitative chemical analysis over an area to find out the elements present. Point EDS was also carried at to identify the secondary phases formed.

2.5. Thermal characterisation

2.5.1. Thermogravimetry

Thermogravimetry (TGA) and differential scanning calorimetry (DSC) was done using Netsch STA 409 (Germany). The sintered samples showing the best results based on microstructure and density were alone investigated using TGA and DSC to observe their thermal stability. The tests were carried out in an inert atmosphere of argon with a flow rate of 50 ml/min. Approximately 5 mg of the sample was taken in a small cylindrical alumina crucible and was placed on the platinum holder. The temperature range that was chosen for investigation was 25 °C to 700 °C, and the heating was carried out at a rate of 5 °C/min.

2.5.2. Dilatometry

Dilatometry was executed using a vertical push-rod type dilatometer, SETSYS Evolution TMA (France). Thermal expansion studies of the sintered samples were carried out using fused alumina as the pushrod. Spacers made of 99% pure alumina were placed between the sample and the pushrod to prevent any undesirable interaction. Baselines were run before testing the sample to account for equipment contribution during measurements. These baseline values were subtracted from the measurement values of the sample. The dimensional changes of the samples were measured over the range 30 °C to 600 °C at a constant heating rate of 5 °C/min. The experiment was carried out in an inert atmosphere of argon. The samples were made into small bars of dimensions 4 × 4 × 8 mm. The tests were performed only for the samples showing the best results based on microstructure and density. SnMo\(_2\)O\(_8\) samples without any Zr addition were prepared through the same route and were also subjected to dilatometry for the purpose of comparison.

3. Results

3.1. Density measurements

The density of the pellets sintered in various conditions was
measured by water displacement method and are shown as a function of sintering time and temperature in Fig. 1. With increase in sintering time, the densities of the samples sintered at 400 °C remains almost constant at 2.8 g/cm³ even as the sintering time is increased from 4 to 8 h. At a sintering temperature of 500 °C, the density increases marginally by 0.35% when the sintering time is increased from 4 to 8 h. However, when the time is increased to 12 h, the density is increased to 3.54 g/cm³. Samples sintered at 600 °C for 4 and 8 h have higher densities (3.09 g/cm³ and 3.4 g/cm³ respectively) than the ones sintered at 400 °C and 500 °C. On further increase in the sintering time, the density drops to 2.94 g/cm³.

3.2. ICP-OES

Table 1 shows the results of compositional analysis of the powder obtained using ICP-OES. The weight percentage of Zr is greater than twice of Sn. Molybdenum’s weight percentage is 50%. The standard deviation is within the acceptable levels of 1%. It is seen that Sn/Zr ratio equals 0.47.

3.3. Phase analysis

X-ray diffractograms of the powder samples heat-treated at different temperatures of 400 °C, 500 °C, 590 °C and 700 °C are presented in Fig. 2. The formation of the cubic $\beta$-ZrMo$_2$O$_8$ is confirmed by the appearance of peaks at 24°, 22° and 27.5° of 2θ (marked by ♦) [13,20]. There are no distinct reference diffractograms of cubic ZrMo$_2$O$_8$ available in the ICDD database to the best of the authors’ knowledge. The presence of peaks at 23.46°, 30.89° and 50.42° correspond to the peaks of trigonal $\alpha$-ZrMo$_2$O$_8$ and is marked by * (ICDD: 98-007-1870). The presence of other peaks in the diffractogram indicates the existence of secondary phases such as $\alpha$-ZrMo$_2$O$_8$ and MoO$_3$. Peaks corresponding to MoO$_3$ are identified in diffractogram and are marked with the # symbol. MoO$_3$ peaks were referenced using ICDD: 98-007-8649.

The monoclinic $\beta$-ZrMo$_2$O$_8$ was referenced using ICDD: 98-007-8649. The X-ray diffractograms of the sintered samples are shown in Fig. 3. The diffractogram of the samples sintered at 400 °C for 4 h, 500 °C for 8 h and 600 °C for 12 h are alone presented in the figure in order to clearly distinguish the appearance/disappearance of the cubic peak. The peak positions are unchanged from the diffractograms of the heat-treated samples. The cubic $\gamma$-ZrMo$_2$O$_8$ phase is retained along with the trigonal phase and MoO$_3$. The intensities of the cubic phase have significantly increased compared to the heat-treated samples. It is noticed that the relative intensity of the cubic peaks in comparison with that of MoO$_3$ is maximum for the samples sintered at 500 °C for 8 h. Further heating to 600 °C increases the relative fraction of MoO$_3$ in evidenced by the relative increase in intensities. As the temperature is raised to 500 °C and 590 °C there is no additional phase evolution. From the relative intensities of the peaks, it is seen that highest volume fraction of the cubic phase is obtained for the powders heat-treated at 590 °C and therefore it is chosen for further compaction and sintering studies.

When the powder is subjected to 700 °C, peaks corresponding to $\gamma$ cubic phase significantly lose intensity. In contrast, MoO$_3$ peaks gain intensity and appear as the major phase. In addition to the trigonal $\alpha$ phase, the monoclinic phase of $\beta$ - ZrMo$_2$O$_8$ also appears in the sample. The monoclinic phase is marked b. The monoclinic $\beta$ - ZrMo$_2$O$_8$ was referenced using ICDD: 98-007-8649.

Table 1

Table 1 presents the results of compositional analysis obtained through ICP-OES.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weight percentages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>5.36 ± 0.23</td>
</tr>
<tr>
<td>Zr</td>
<td>11.52 ± 0.02</td>
</tr>
<tr>
<td>Mo</td>
<td>50.62 ± 0.04</td>
</tr>
</tbody>
</table>

Fig. 1. Density variations of the sintered pellets as a function of sintering time and temperature. The standard deviation is presented in the form of error bars.

Fig. 2. X-ray diffractograms of the powder samples subject to heat treatment at different temperatures (400 °C, 500 °C, 590 °C and 700 °C).

Fig. 3. X-ray diffractograms of the sintered samples. Only selected cases are presented here.
comparison with the cubic ZrMo$_2$O$_8$.

3.4. Microstructural evolution

Fig. 4 illustrates the microstructural changes in the samples as a function of sintering temperature. Fig. 4a, b and c correspond to the micrographs of samples sintered at 400 °C for 4, 8 and 12 h respectively. At 400 °C, it is noticed that there is visible porosity in the material even after 12 h of holding time. Fig. 4d, e and f correspond to micrographs of samples sintered at 500 °C and Fig. 4g, h and i correspond to 600 °C sintered samples. It is seen that at 600 °C, large grains with rod-like morphology were formed throughout the sample irrespective of the holding time. Based on the morphology and spot EDS analysis (Fig. 5) it is evident that these are crystals of MoO$_3$. At a sintering temperature of 500 °C with 8 h holding time (Fig. 4e), it can be seen that fusion of grains had taken place indicated by the formation of necks at particle boundaries. The average particle size based on image analysis of the micrograph is approximately 200 nm. However, when the holding time was increased to 12 h, it is observed that bulk MoO$_3$ crystals are formed in the material. Thus it is seen that increasing temperature above 500 °C to 600 °C results in decomposition and formation of MoO$_3$ whereas, decreasing temperature to 400 °C ensures incomplete sintering. At 500 °C, a compromise is reached between attaining complete densification and avoiding decomposition. Fig. 6 shows the area EDS data of the sample sintered at 500 °C for 8 h collected over the entire area. The EDS analysis illustrates the presence of primary elements viz., Zr, Sn, Mo and O.

Fig. 4. Scanning electron micrographs of samples sintered as a function of time and temperature.

Fig. 5. Spot energy dispersive X-ray spectroscopic (EDS) analysis of a MoO$_3$ crystal. The point of measurement is marked by the cross on the left.
3.5. Thermogravimetric analysis

The figure (Fig. 7) shows the DSC and TGA curves of the sample up to 700 °C. There is an initial loss of weight at 100 °C due to moisture. Beyond 100 °C, the sample does not undergo any mass loss indicating that it is quite stable up to 600 °C. However, by analysing the weights of the sample after heat-treatment it is seen that beyond 600 °C the sample starts to sublime and loses mass rapidly. The DSC curve shows a small endothermic peak at 100 °C of 0.05 mW/mg. This peak occurs simultaneously with the mass loss at the same temperature. The DSC curve gradually increases with a small slope along with temperature. It is observed that there are no other exothermic or endothermic peaks in the temperature range up to 600 °C. This indicates that the sample exhibits phase stability and does not undergo any transformation in the mentioned temperature range.

3.6. Dilatometric measurements

The sample conventionally sintered at 500 °C for 8 h was chosen for dilatometry as it showed best microstructural and density results. The change in the dimension of Sn substituted ZrMo2O8 and SnMo2O8 in response to temperature is shown in Fig. 8. The change in dimension is represented as the ratio of the difference in dimension after change in temperature to the original dimension before the increase in temperature. The Sn substituted ZrMo2O8 sample undergoes minor variations in displacement in the measured temperature range with a small negative slope till 100 °C and positive slope till 500 °C. The sample exhibits an average CTE of $1 \times 10^{-6}$/°C between the range 30 °C and 500 °C. Beyond 550 °C, the curve drops indicating that the material is undergoing NTE. In the case of SnMo2O8, the curve shows a small negative slope till 100 °C and then continues with a positively till the end of measurement with a small discontinuity in the slope at 500 °C. The average CTE exhibited by the SnMo2O8 sample is $6.5 \times 10^{-6}$/°C between the range 30 °C and 500 °C. The sample shows strong PTE throughout temperature range and even after 550 °C.

4. Discussion

4.1. Sintering behaviour

The heat-treatment and sintering results show that the material offers only a small window in which the heating parameters should be chosen. From Fig. 2 it is seen that at temperatures of 400 °C and below the fraction of cubic phase formed is very low. However, when the temperature is increased to 700 °C monoclinic phase transition starts to occur along with the formation and growth of MoO3. Thus the heat-treatment temperature should be chosen within the range such that cubic phase formation is promoted without decomposition of the material.

A similar scenario occurs while determining the sintering parameters for this material. The schematic in Fig. 9 lucidly illustrates the densification and sintering behaviour in the material in the case of pressureless conventional sintering. Increasing the sintering time at 400 °C does not improve the density, clearly indicating that higher temperatures are required to increase the diffusion between particles. At 600 °C the density of the sintered sample is significantly improved.
but is accompanied with formation of MoO₃. The formation of MoO₃ could be due to decomposition of the material in the presence of oxygen atmosphere at high temperatures. MoO₃ was also seen to be present in the bulk of the material indicating that this is not just a surface phenomenon. With increased holding time at 600 °C, the noticed drop in density is attributed to mass loss due to sublimation. At 500 °C, porosity is still seen in the material, but sintering appears to be more efficient than in 400 °C sintered sample. As the holding time is increased to 8 h, the densification of the sample is visibly improved (Fig. 4e) with well sintered grains. It was also seen that at this condition there was a slight improvement in density of 0.35% compared to the 400 °C sintered samples without decomposition. At 12 h, decomposition of material is triggered again shown by the presence of MoO₃ crystals on the surface. Thus it is observed that the ideal sintering conditions fall near a temperature of 500 °C with a holding time of 8 h.

The decomposition of ZrMo₂O₈ during heat-treatment has been recorded earlier in literature. Previous investigations of preparation of ZrMo₂O₈ have also reported the presence of MoO₃ as secondary phase [20,21]. Samant et al., while producing trigonal ZrMo₂O₈ by solid state synthesis overcame this problem by heating at temperatures high enough to cause the vapourisation of MoO₃ [22]. In comparison, ZrW₂O₈ can be easily produced employing solid-state synthesis route by heating powders of Zr₂O₂ and WO₃ to 1105 °C and rapidly quenching it to room temperature [23,24].

The sintering in the material occurs by solid state diffusion and therefore is governed by the slowest diffusing species among them. The self-diffusion coefficients of Zr, Sn and Mo were taken from literature and were found to be of the order 10⁻²², 10⁻³ and 10⁻¹³ cm²/s respectively.[16,25–27]. It is seen that among the elements present in the material, zirconium is the slowest diffusing species and it is diffusion could be the rate limiting step for the sintering process in this material.

4.2. Thermal expansion characteristics

Pure γ-ZrMo₂O₈ phase expands negatively with a CTE of −5 × 10⁻⁶/°C [28]. The trigonal and monoclinic phase of ZrMo₂O₈ exhibit positive thermal expansion in the measured temperature range of 30 °C to 500 °C. MoO₃ has an orthorhombic structure with a high CTE of 50 × 10⁻⁶/°C. Therefore the presence of minor amounts of MoO₃ can increase the overall CTE. Also, it is speculated that increased exposure to high temperature for prolonged periods could lead to the removal of Sn from the lattice positions of ZrMo₂O₈ which leads to the exhibition of prominent NTE behaviour by the sample above 550 °C.

Tallentire et al., reported CTE values of 5 × 10⁻⁷/°C for Sn₀.₅Zr₀.₅Mo₂O₈ and −6 × 10⁻⁸/°C for Sn₀.₄Zr₀.₄Mo₂O₈ based on lattice parameter calculations [14]. The observed CTE by dilatometry was higher than these values by almost an order or magnitude. This is attributed to the presence of secondary phases which contribute to PTE. Composites with ZrW₂O₈ fillers in Cu matrix also exhibit tunable expansion and at 40 vol% of fillers the CTE exhibited was 0.8 × 10⁻⁶/°C [29].

The higher CTE associated with conventional sintered samples can be reasoned by speculating that the fractions of SnMo₂O₈ and ZrMo₂O₈ formed are not equal even though the right amount of initial chemicals was added to attain Sn/Zr ratio of unity. The presence of ambient atmosphere during heat treatment allows the formation of MoO₃ thus affecting the chemistry and could lead to the presence of Sn and Zr in oxide form in minor quantities. This situation could be aggravated during sintering as the decomposition reaction continues on exposure to increased heat. Reduction of initial Sn addition in the sample can lead to decreased CTE.

5. Conclusions

Metastable β-cubic phase was produced by coprecipitation route. Synthesis of the material is found to be very sensitive to the processing route employed, heat-treatment and sintering parameters. Optimisation of heat-treatment and sintering conditions were carried out in order to maximise the formation of the cubic phase by achieving a compromise between the formation of secondary phases and reduced density. Thermal expansion behaviour of the bulk material was studied by using dilatometry and was compared with the values found using lattice parameter calculations reported in the literature. The effect of secondary phases on CTE was found to be significant. The CTE of Sn substituted ZrMo₂O₈ was 1 × 10⁻⁶/°C which was almost an order of magnitude higher than values reported earlier. The increased SnMo₂O₈ is attributed to the presence of MoO₃ phase fraction in the samples.

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References

C. Wilson, J.S.O. Evans, Systematic and controllable negative, zero, and positive thermal expansion in cubic Zr$_{1-x}$Sn$_x$Mo$_2$O$_8$, J. Am. Chem. Soc. 135 (2013) 12849–12856.


