

**STRUCTURAL AND MICROSTRUCTURAL CHARACTERIZATION OF NiO-8YSZ
NANOPOWDERS WITH VARYING WEIGHT PERCENTAGE OF NiO**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

**Bachelor of Technology
in
Ceramic Engineering**

By
PASHUPATI NATH MISHRA



**Department of Ceramic Engineering
National Institute of Technology
Rourkela
2011**

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Under the Guidance of
Prof Arun Chowdhury



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Rourkela

CERTIFICATE

This is to certify that this thesis entitled, “**STRUCTURAL AND MICROSTRUCTURAL CHARACTERIZATION OF NiO-8YSZ NANOPOWDERS WITH VARYING WEIGHT PERCENTAGE OF NiO**” submitted by Mr. **PASHUPATI NATH MISHRA** in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date:

Prof Arun Chowdhury
Assistant Professor
Department of Ceramic Engineering,
National Institute of Technology,
Rourkela- 769 008

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6th May, 2011

Pashupati Nath Mishra

ABSTRACT

Synthesis of NiO-8YSZ nanopowders with varying wt% of NiO, using the salts of NiCl₂·6H₂O, ZrOCl₂·8H₂O, and Y₂O₃ powder. NaOH was used for gelation and precipitation with the increase in pH. Thermal analysis (DTA, DSC) of the precursors was done, and the results were analyzed in comparative manner. Calcinations of the precursors were done at 800°C for 1hr and XRD data was analyzed comparatively. Pellets were made by uniaxial pressing and sintered at 1200°C for 2hr. XRD, SEM micrographs, density and porosity of the pellets were also analyzed in comparative manner. The c- ZrO₂ crystallite size was found greater in pure 8YSZ than in NiO-8YSZ. The bulk density jumps from 3.51 to 3.96 for the addition of NiO. The porosity gradually increases with wt% of NiO from 20 to 40 wt%. Analyzing the microstructure it reveals that, NiO addition causes the grains to be very uniform and small with the nice connectivity between pores.

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Chapter 1

GENERAL INTRODUCTION

1.1 Introduction

The high operating temperature of solid oxide fuel cells (SOFC), i.e. 900–1000 °C, leads to various material problems which have been difficult to remove in a cost-effective manner. Therefore it is required to reduce the SOFC operating temperature without any penalty for the power density achieved at high temperatures. The ionic resistance of the electrolyte has to be decreased in order to reduce the losses inside the cell.

Among various solid oxide fuel cell (SOFC) configurations, Ni–YSZ (8 mol% yttria stabilized zirconia) anode-supported thin YSZ electrolyte SOFC is attracting the most attention because it can operate at lower temperatures. It can be fabricated by traditional ceramic technique, and its anode polarization is quite low with hydrogen as fuel^[1]. In SOFC, the performance of the anode is strongly dependent on the fabrication methods and thus obtained microstructure of the cermet. Improvements to electrode performance are essential to accelerate the commercialization of SOFC technology. Since porosity in Ni–YSZ cermet is mainly formed during the final stages of the cermet preparation (reduction of NiO to metallic Ni), it is reasonable to predict that uniform porosity with controlled pore size distribution can be achieved from NiO–YSZ mixtures initially formed of nano-sized particles. Performance of the SOFC electrode crucially depends upon the length and distribution of three or triple phase boundaries (TPB: Ni–YSZ–fuel interface in the microstructure) which provide an indication of electrochemical performance.

In this paper we limited and focussed ourselves on the synthesis of NiO-8YSZ powders by the precipitation route and studied the change in structure, microstructure, thermal properties, porosity and density with the variation of wt% of NiO.

1.2 Structure and properties of zirconia

Bulk ZrO₂ is polymorphic, exhibiting cubic (c) fluorite structure (Zr atoms are coordinated to eight oxygen atoms), tetragonal (t) structure (distorted fluorite structure whose diffraction patterns can be indexed to a face centered tetragonal cell) and monoclinic (m) structure (sometimes referred to as the baddeleyite structure). The transformation from m-phase to t- or c-phase is reversible so the high temperature polymorphs do not retain on cooling back to room temperature. Pure ZrO₂ has monoclinic structure at room temperature and undergoes m→t and t→c phase transitions at 1173°C and 2370°C respectively^[3,4].

1.3 Yttria Stabilized Zirconia

It has been found that the high temperature ZrO_2 forms can be stabilized at room temperature by addition of a small amount of oxides as MgO, CaO, Y_2O_3 , CeO_2 etc ^[5,6].

1.4 Ni-8YSZ

In a Ni-YSZ anode, Ni acts as the catalyst for the oxidation of fuel and provides electronic conductivity, while YSZ mainly acts as a matrix to support the Ni network and prevent Ni from agglomeration under operating conditions. The fuel gas percolates through the pores and meets Ni and YSZ phases to form a triple-phase boundary (TPB) where the electrochemical reaction takes place. YSZ is also used to extend the Ni-YSZ-gas (fuel) triple-phase boundary (TPB) into the anode. It has been shown that the length of the TPB determines the reaction rate for electrochemical oxidation of hydrogen ^{[2], [7]}. Thus, the extension of the TPB into the anode can improve anode performance. Large TPBs can be obtained from homogeneous and contiguous structure of pores, Ni and YSZ fine grains. It has been shown that a smaller particle size of Ni-YSZ anode increases the length of TPBs and improves the electrical performance of the anode ^{[8] [9]}. Hence, nanocrystalline Ni-YSZ can offer the advantage of greater TPBs and improved anode performance.

1.5 Applications of NiO-8YSZ nanopowders

YSZ is a good conductor of O_2^- , the presence of Ni increases the electronic conductivity therefore, NiO-8YSZ is used to prepare SOFC (solid oxide fuel cell) anode. It is also used as high temperature zirconia oxygen sensors.

1.6 Outline of project report

The physical size of ZrO_2 when reduced to nano dimensions, it affects the structure and phase transformation behavior. Preliminary introduction about Ni-8YSZ, about its application and about the required properties of NiO-8YSZ and organization of project report is discussed in chapter 1. Chapter 2 provides a detailed discussion of literatures. The main objective of the present work, which is based on the literature survey, is presented towards the end of chapter 2. In chapter 3, the various synthesis and characterization techniques used in the present work are described in detail. Chapter 4 describes the synthesis and characterization of NiO-8YSZ prepared. Finally, conclusions of this project work are given in Chapter 5.

Chapter 2

LITERATURE REVIEW

2.1 Synthesis and microstructural properties of NiO-8YSZ nanopowders

NiO-8YSZ composite, synthesized via co-precipitation of hydroxides. The solubility curve shows that the $Zr(OH)_4$ starts precipitating prior to $Y(OH)_3$ and $Ni(OH)_2$ and is finished at pH 4. The particles synthesized at ≤ 12 , involved large angular NiO particles with size greater than 1 μm due to slower precipitation or agglomeration of $Ni(OH)_2$, while NiO/YSZ nanocomposite particles with primary size of less than 100 nm were obtained at pH 13. This can be attributed to rapid precipitation as well as better dispersion of the hydroxides in the aqueous solution at pH 13.^[10]

The performance of a Ni-YSZ anode-supported SOFC depends strongly upon the anode microstructure which is decided by the characteristics of nickel oxide powder. The highest SOFC performance was obtained from the cell with finest nickel oxide powder (synthesized by glycine-nitrate combustion method), while the lowest performance was with the coarsest powder purchased from a general chemical supplier.^[11]

If the NiO and YSZ particles are in nanometre scale and randomly distributed, relative sintered densities higher than 90% were obtained at sintering temperatures as low as 1200 °C. A sintering temperature 1200 °C was also recognized as the preparation temperature that provided the smallest Ni grains in the final Ni-YSZ cermet with an average Ni-particle diameter as low as 0.27 μm .^[12]

The Ni-YSZ composite anode is commonly fabricated by directly mixing NiO and YSZ powders, which are subsequently reduced by the fuel in SOFCs^[13]. The reduction of NiO to Ni results in the desirable porosity of the anode. However, some authors proposed adding pore-forming additions like graphite, starch, etc., for suitable porosity (40–60%) for the gas flow. For such a method of cermet anode preparation, consisting in mixing YSZ with NiO powder, sufficient electronic and ionic conductivity may be achieved when the concentration of Ni in the composite is above 30 vol.%^[14](above 40 wt.%).

Taking into account the fact that the performance of the anode is strongly influenced by its microstructure, which is determined by the method of preparation, two other methods- co-precipitation and impregnation were investigated. The aim of the work was to determine the

effect of the cermet preparation method on both the structural and the electrical properties of the cermet.^[15]

The one step, simple, and cost effective process for the synthesis of NiO-YSZ is the combustion synthesis process. The processed powder of NiO-YSZ was found to be nanocrystalline with crystallite sizes of 29 and 22 nm for NiO and YSZ respectively by XRD and TEM analysis. XRD analysis also shows that the precursor salts are converted to highly crystalline phases of NiO and YSZ (8 mol% Y₂O₃) without any intermediate calcination step and no undesirable phases are present. The microstructure of the sintered and reduced sample shows a well defined network of pores which is necessary for the effective functioning of the anode. The electrical conductivity measurement confirms the metallic behaviour.^[16]

Sintering with different soaking time revealed that the porosity of the specimens decreases with increasing soaking time. Ni-YSZ cermet with varying open porosities between 23 and 41% was obtained by reduction of NiO-YSZ. The electrical conductivity decreased while thermal expansion coefficient remained essentially the same with increasing porosity. SEM results confirmed the connectivity of open pores.^[17]

NiO-YSZ ceramic materials were prepared by three methods: physical mixture, a modified Pechini route, and impregnation with Ni(NO₃)₂.6H₂O respectively. NiO completely reduced at temperatures up to 1000 °C and their temperature-programmed reduction (TPR) profiles indicated that higher reduction temperature corresponds to the higher calcinations temperature. Furthermore, the composites synthesized through impregnation presented nickel oxide species more easily reducible than those prepared by the two other methods. SEM and X-ray photoelectron spectroscopy (XPS) evidenced a larger nickel oxide coating on yttria-stabilized zirconia for the composite synthesized through the impregnation method.^[18]

For the preparation of Ni-YSZ with 30 wt% of NiO, two different routes, co-precipitation (CP) and combustion (CB) were adopted, and calcinations at 600, 800 and 1000 °C.. The CB cermets presented good catalytic activity and stability at 900 °C in steam of methane, showing high resistance to coke deposition and to sintering of metallic particles.^[19]

To increase performance and durability of Ni-YSZ electrode, the Pechini process for the synthesis of NiO-YSZ powder was investigated. The anode made from NiO/YSZ composite

powder, which has a high homogeneity and plenty of contact sites between Ni and YSZ, has an excellent tolerance against thermal and redox cycling. The functional NiO/YSZ composite powder will reduce the degradation of anodes and enhance the long-term stability (stability against redox reaction) at elevated temperatures. ^[20]

Ni/YSZ cermets were prepared with varying the Ni Concentration between 7.23 and 64.99 wt%. Bulk samples were prepared using these nickel coated YSZ powders by uniaxial pressing followed by sintering in the temperature range 1200–1350 °C with a soaking time of 2–6 h. Samples prepared, shows metallic conductivity at a Ni concentration as low as 27.04 wt%. A detailed microstructural investigation of the samples is also reported. ^[21]

NiO-YSZ powders fabricated by advanced mechanical method in dry process gave better homogeneous mixing of NiO and YSZ particles, where submicron NiO particles were covered with finer YSZ particles. After sintering and reduction of NiO to Ni, it showed the porous structure in which Ni and YSZ grains of less than several hundred nano-meter as well as micron-size pores were uniformly dispersed. The cermet anode achieved high electrical performance at low temperature operation (<800 °C).

It was led by larger electrochemical area successfully obtained by the excellent structure of the anode. ^[22]

Ni–YSZ cermet anodes for solid oxide fuel cells (SOFCs) were fabricated at various sintering temperatures by spray pyrolysis (SP) technique. NiO particles covered with fine YSZ (Y₂O₃ stabilized ZrO₂) particles were used as the composite particles, and the initial ratio of Ni and YSZ was set at 75:25 (mol %). As a result, the cermet anode sintered at 1350 °C showed the morphology in which fine YSZ grains were uniformly dispersed on the surface of Ni grain network. The anode fabricated at 1350 °C showed the highest electrical performance. ^[23]

The main microstructure change was the agglomeration and coarsening of metallic Ni. The YSZ coating layer on the NiO surface using the coating precipitation method efficiently prevented the sintering and agglomeration of Ni. ^[24]

2.2 Summary of Literature

Summary of the literature survey are:

1. Sintering in the temperature range of 1200°C gives the best desirable properties.
2. For rapid precipitation and better dispersion of each hydroxides in the solution, pH>13 must be fulfilled.
3. The results showed that the microstructure of nickel oxide powder has significant effect on the performance of a Ni–YSZ anode-supported SOFC. Fine nickel oxide microstructure leads to fine and connected anode microstructure and results in low SOFC resistance (including ohmic resistance, interfacial resistance of overall resistance) and high output performance.
4. Cermet materials containing $\text{ZrO}_2 + 8\text{mol}\% \text{Y}_2\text{O}_3$ (8YSZ) and Ni particles, were prepared using two methods: co-precipitation and impregnation. Both proposed preparation methods provide suitable anode materials for SOFCs. XRD analysis revealed that the materials were composed from well crystallized phases of 8YSZ and Ni. Their porosity was ca. 50%. The proposed preparation methods make it possible to obtain sufficient open porosity without adding any pore-forming additions.
5. In a Ni–YSZ anode, the electrochemical reaction takes place at the triple-phase boundary (TPB) and the electrons liberated by the reaction are transported by the metallic Ni phase to the external circuit. Therefore, the anode should have a microstructure with uniform and continuous distribution of the Ni phase with better Ni-Ni contact for enhanced conduction.
6. The conductivity of Ni–YSZ specimens decreased with increasing porosity of the specimen. The decrease in electrical conductivity with increasing porosity was correlated to the open microstructure. The stability of the cermet for long time use for the SOFC applications was exhibited by the constant conductivity value of the cermet heated at 1000 °C up to 100 h. However, the thermal expansion coefficient of the Ni–YSZ composite was independent of the porosity. The morphology of the Ni–YSZ specimens confirms the presence of pores having average diameter of 1–2 mm forming interconnected open channels in the specimen containing well sintered Ni and YSZ grains.

7. The Ni/YSZ cermet material was prepared with 30 wt% of NiO by two different routes, co-precipitation (CP) and combustion (CB), and calcination at 600, 800 and 1000°C. The mean crystallite size of NiO is smaller for CB samples (20–33 nm), showing the higher Ni dispersion of these systems. The CB samples have also a more homogeneous particle size distribution, mainly at high calcination temperatures. The cermets showed high activity and stability in steam reforming of methane at 900°C. It showed high resistance to coke deposition and sintering of the metallic particles.
8. A YSZ layer coated on the NiO surface was prepared by the coating precipitation method. NiO/YSZ composite powder was well crystallized at 600 °C. The continuous network of YSZ was formed in the sintered Ni/YSZ cermet and efficiently prevented the sintering and agglomeration of Ni particles (YSZ covers the Ni). It also contributed to the improvement of electrical conductivity. The electrical conductivity of the Ni/YSZ cermet reached about 900 S/cm between 600 and 800 °C. So it proved to be suitable anode material for intermediate-temperature SOFC.

2.3 Objective of the present studies

Few works have been done in the area of - change in structure, microstructure, thermal properties, porosity and density with the variation of wt% of NiO. In this paper we limited and focussed ourselves on the synthesis of NiO-8YSZ powders only, and studied the change in structure, microstructure, thermal properties, porosity and density with the variation of wt% of NiO.

- (1) Synthesis of NiO-8YSZ nanopowders with varying wt% of Ni, using the salts of Ni, Zr, and Y₂O₃ powder. Using NaOH for gelation and precipitation.
- (2) Thermal analysis (DTA, DSC) of the precursors thus formed up to 1000°C. And analyzing the results in comparative manner.
- (3) Calcinations of the precursors thus formed at 800°C for 1hr and study the XRD for comparative - structural analysis, crystallite sizes of the phases, vol % NiO.
- (4) Making pellets of the powders and sintering at 1200°C for 2hr, taking SEM micrographs, measuring density and analyzing the results in comparative manner.

Chapter 3

EXPERIMENTAL WORK

3.1 Introduction

Sol-gel and precipitation technique is one of the important techniques for synthesizing nanosize ceramic materials. In this work, nano size pure 8YSZ and NiO-8YSZ with varying percentage of NiO has been prepared through gelation and precipitation techniques. Several different characterization techniques have been used to study the properties of nano ZrO₂ powders. In this chapter, the synthesis and characterization techniques are described in detail.

3.2 Synthesis of pure 8YSZ

Nanosize zirconia powders were prepared through gelation and precipitation technique by using NaOH. An aqueous solution of ZrOCl₂.8H₂O using 30ml water was prepared from high purity salt. Similarly Y₂O₃ was dissolved in few amount of water. The Zr-salt solution is highly acidic with a pH of ~ 0.3. On the other hand the NaOH solution has a highly basic pH of ~ 14. This solution (NaOH) is added drop wise to the Zr-salt solution so that gel formation will take place at a particular pH followed by precipitation at higher pH. The reaction mechanisms for all these cases can be expressed as follows.

3.2.1 Experimental setup

For the preparation of 10g batch of 8YSZ, 22.5574g of ZrOCl₂.8H₂O and 1.3g of Y₂O₃ was taken. ZrOCl₂.H₂O was dissolved in 30ml of water and Y₂O₃ was dissolved using water and drop wise addition of HNO₃ up to clear solution with the aid of heating. After they were mixed together in a beaker and drop wise addition of NaOH (5M) was done using burette.

3.3 Synthesis of NiO-8YSZ nanopowders

For the synthesis of NiO-8YSZ, NiCl₂.6H₂O was taken as NiO source, Y₂O₃ powder for Y₂O₃, ZrOCl₂.8H₂O for ZrO₂ was used. The salts and Y₂O₃ were mixed together. The reaction takes place by formation of gel followed by precipitation with the addition of NaOH.

3.3.1 Experimental setup

(a)NiO-20 wt%

For the preparation of 10g batch of NiO-8YSZ with 10 wt% of NiO, 6.373g of NiCl₂.6H₂O, 18.046 of ZrOCl₂.8H₂O and 1.10g of Y₂O₃ were taken. ZrOCl₂.8H₂O was dissolved in 30ml of water, NiCl₂.6H₂O in 10ml and Y₂O₃ was dissolved using water and drop wise addition of conc.HNO₃ up to clear solution with the aid of heating. After they were mixed together in a beaker and drop wise addition of NaOH (5M) was done using burette.

(b)NiO-30 wt%

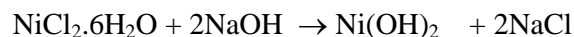
For the preparation of 10g batch of NiO-8YSZ with 30% of NiO, 9.559g of NiCl₂.6H₂O, 15.709g of ZrOCl₂.8H₂O and 0.962g of Y₂O₃ were taken. ZrOCl₂.8H₂O was dissolved in 30ml of water and Y₂O₃ was dissolved using water and drop wise addition of conc.HNO₃ up to clear solution with the aid of heating. After they were mixed together in a beaker and drop wise addition of NaOH (5M) was done using burette.

(c)NiO-40 wt%

For the preparation of 10g batch of NiO-8YSZ with 40% of NiO, 12.746g of NiCl₂.6H₂O, 13.534g of ZrOCl₂.8H₂O and 0.825g of Y₂O₃ were taken. ZrOCl₂.8H₂O was dissolved in 30ml of water and Y₂O₃ was dissolved using water and drop wise addition of conc.HNO₃ up to clear solution with the aid of heating. After they were mixed together in a beaker and drop wise addition of NaOH (5M) was done using burette.

3.4 Hydrolysis by NaOH

The evolution of nano size zirconia powders is studied as a function of reaction with Zr-salt solution by both NaOH. The process involves a controlled hydrolysis of Zr⁺⁴ cations to ZrO(OH)₂ and Zr(OH)₄ (with increase in pH).



The reaction occurred slowly and there was a regular increase of average viscosity of the solution. It has been observed that gel formation was formed at low pH of nearly 5-6 for NaOH. After the gel formation, the precursor solution was increases to high pH of 13 so that complete precipitation will take place for all these three cases by adding more amounts of hydrolyzing agents. The high pH precursor was thoroughly washed with distilled water in order to remove the water soluble reaction products completely. The products were dried in oven at 80 °C for 24 hrs. The dried powders were grounded (pulverized) in a mortar pestle to form fine powders of as-prepared NiO-8YSZ or 8YSZ. The fine powders obtained after drying were heat treated at selected temperatures of 800 °C for 1 hour to study the formation and thermal stability of ZrO₂ polymorph and NiO structure.

3.5 General characterization

3.5.1 Thermal

Thermal decomposition of $\text{ZrO}(\text{OH})_2$ gel to an amorphous ZrO_2 powder followed by its reconstructive nucleation of t- ZrO_2 nanoparticles were studied using thermogravimetric and differential scanning calorimetric (TG-DSC) by heating the sample at $10\text{ }^\circ\text{C}/\text{min}$ in argon in a thermal analyzer (Model STA 4096, NETZSCH, Germany)

3.5.2 X-ray diffraction

Phase analysis was studied using the room temperature powder X-ray diffraction (Model: PW 1830 Diffractometer, Phillips, Netherland) with filtered 0.154056 nm $\text{Cu K}\alpha$ radiation. Samples are scanned in a continuous mode from $20^\circ - 80^\circ$ with a scanning rate of $0.04\text{ (degree) / 1 (sec)}$.

3.5.3 Scanning Electron Microscope

Microstructural features were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan). For preparation of SEM sample, the pellets placed in acetone in an ultra sonication bath (20 kHz , 500 W) for half an hour. These pellets after sonication were used for microscopy.

3.5.4 Particle size measurement

Size of the particles is usually obtained with the help of scanning electron microscopy (SEM). The size corresponds to the mean value of the crystalline domain size of the particles is determined from the X-ray line broadening using Debye-Scherrer formula with correction factor as given below,

$$D_x = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{Where } \beta = \sqrt{\beta_{\text{sample}}^2 - \beta_{\text{standard}}^2}$$

Where D_x is average crystalline size, λ is the X-ray wavelength used, β the angular line width of half maximum intensity and θ the Bragg's angle in degree.

3.5.5 Density and apparent porosity

Density and apparent porosity were measured by using vacuum assisted soaking of pellets in kerosene medium for about 2hr. The dry weight, suspended weight, and soaked

weight were taken to calculate bulk density and apparent porosity using the following formula.

Bulk density of the material is given by the relation,

$$\text{Bulk Density} = \frac{D}{W-S} \times \text{density of liquid medium}$$

Liquid medium in our case is kerosene with density of 0.78–0.81 g/cm³.

Where, D, W, S stands for dry weight, soaked weight and suspended weight respectively of the sample.

Apparent porosity is the percentage relationship between the volume of the pore space and the total volume of a material. *Evacuation method* was used to measure it.

$$\text{Apparent Porosity} = \frac{W-D}{W-S} \times 100(\%)$$

Chapter 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter describes the thermal, structure, microstructure, porosity and density analysis of NiO-8YSZ nanopowders prepared through precipitation by hydrolysis technique using NaOH.

4.2 Thermal behavior of as-prepared 8YSZ and NiO-8YSZ nanopowders

Fig. 4.1 (a) and (b) show the Thermal Gravimetric (TG) – Differential Scanning Calorimetric (DSC) curves of as-prepared 8YSZ and 40 wt % NiO- 8YSZ nanopowders prepared through precipitation route using NaOH respectively.

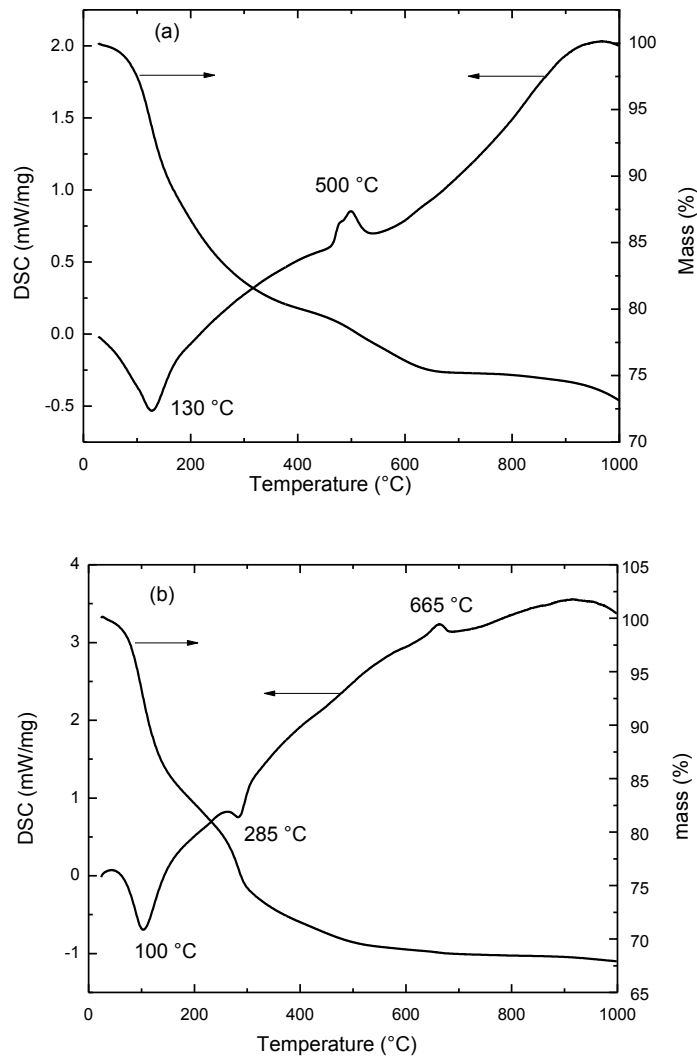


Fig. 4.1 (a) and (b): TG-DSC of as-prepared 8YSZ and 40 wt % NiO-8YSZ nanopowders prepared through precipitation route using NaOH.

4.2.1 Remarks

The TG curve shows two stages of major weight loss. One stage ranges from room temperature to 400 °C. In the DSC plot there are an endothermic peak at 130 °C for 8 YSZ and two endothermic peaks at 100 °C and 285 °C for 40 wt % NiO-8YSZ samples. The endothermic peaks are associated with the loss of absorbed and or adsorbed water. The exothermic peak at 500 °C (for 8YSZ sample) and 665 °C (for 40 wt % NiO-8YSZ sample) is probably due to crystallization of cubic zirconia (c-ZrO₂) by the important weight loss of ~ 5 %. The TG curve shows that major weight losses (about 25% 0-30 % weight loss) were associated with both endothermic and exothermic effects. It was confirmed from the thermal results that with addition of 40 wt % NiO, the crystallization temperature shifts from 500 °C to higher temperature of around 665 °C.

4.3 Structural properties of NiO-8YSZ nanopowders

The presence of various phases, crystallite size, and lattice parameter as well as cell volume were determined from the X-ray diffraction pattern. Fig. 4.2 (a) shows the X-ray diffraction pattern of the dried as-prepared 8YSZ powders after calcination at 800 °C for 1h.

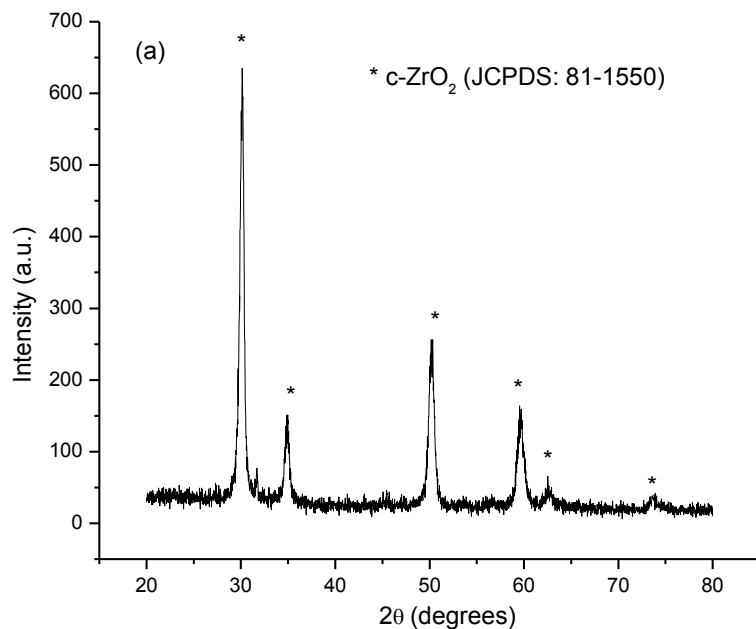


Fig. 4.2 (a) XRD pattern of 8YSZ nanopowders calcined at 800 °C.

Fig. 4.2 (b) shows the X-ray diffraction pattern of the dried as-prepared 20 wt % NiO-8YSZ powders after calcination at 800 °C for 1h.

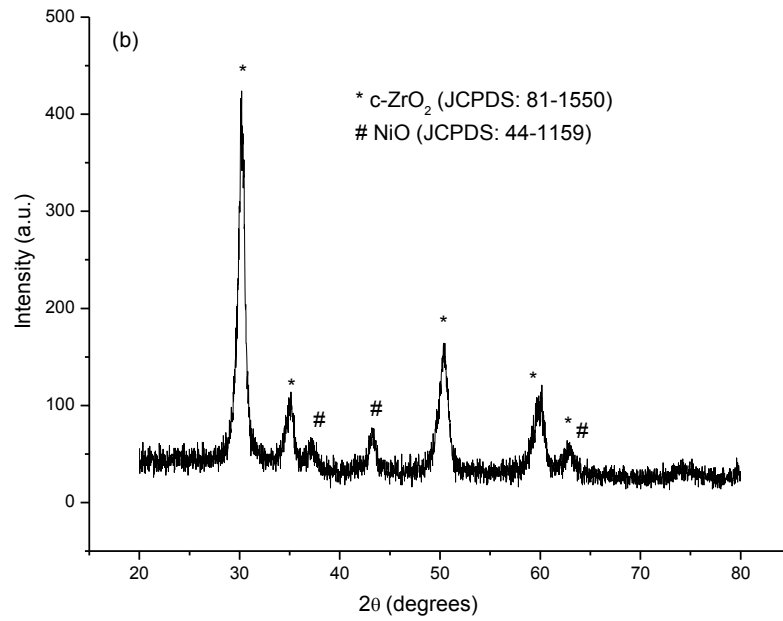


Fig. 4.2 (b) XRD pattern of 20 wt % NiO-8YSZ nanopowders calcined at 800 °C.

Fig. 4.2 (c) shows the X-ray diffraction pattern of the dried as-prepared 20 wt % NiO-8YSZ powders after calcination at 800 °C for 1h.

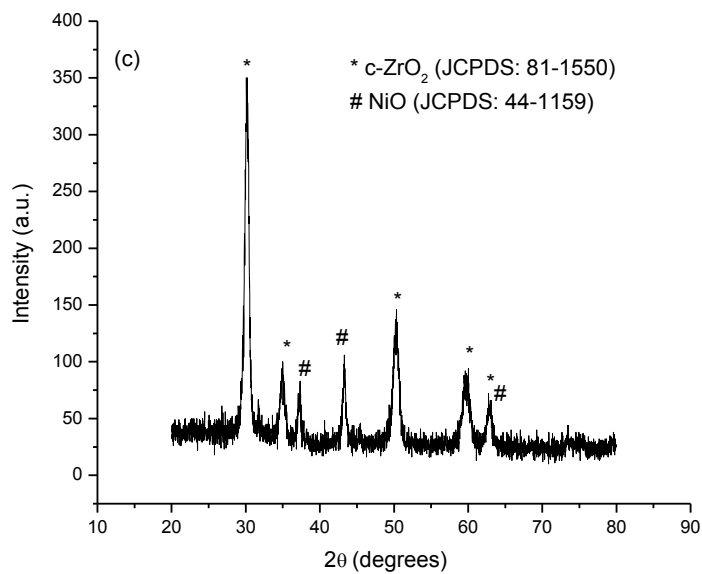


Fig. 4.2 (c) XRD pattern of 30 wt % NiO-8YSZ nanopowders calcined at 800 °C.

Fig. 4.2 (d) shows the X-ray diffraction pattern of the dried as-prepared 40 wt % NiO-8YSZ powders after calcination at 800 °C for 1h.

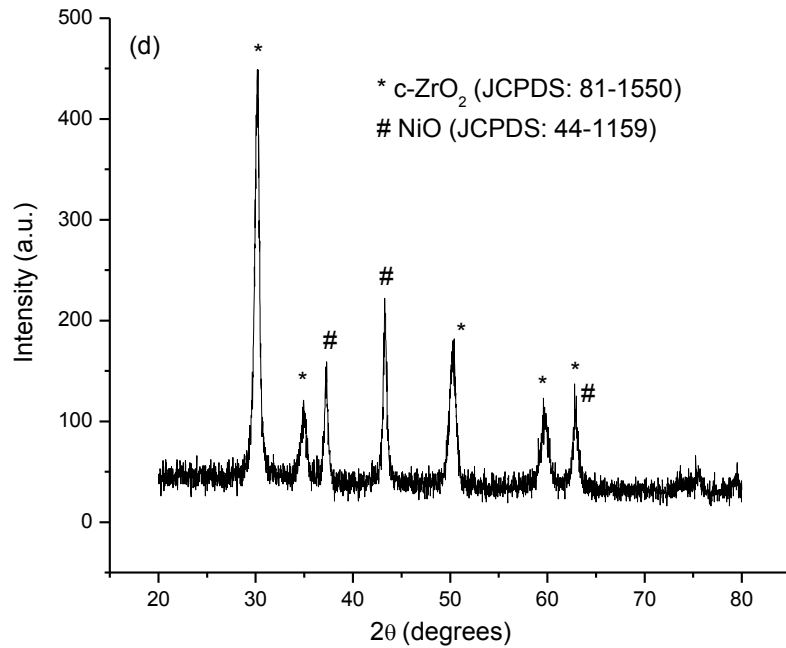


Fig. 4.2 (d) XRD pattern of 40 wt % NiO-8YSZ nanopowders calcined at 800 °C.

4.3.1(a)Remarks

All the peaks are assigned to either c- ZrO₂ or NiO phase as confirmed from the JCPDS files as mentioned in the figures. With increase in wt % of NiO, the peak intensity at 43.5° increases. The crystallite size, lattice parameter and cell volume of 8YSZ and NiO-8YSZ powder samples calcined at 800 °C are given in Table 4.1. The crystallite size of c-ZrO₂ for 8YSZ sample was found to be around 18 nm. With addition of NiO, the crystallite size decreases to 14-16 nm. However, the crystallite size of NiO was larger as compared to c-ZrO₂ for 30-40 wt % NiO addition samples.

Table 4.1: Crystallite size, lattice parameter and cell volume of 8YSZ and NiO-8YSZ samples.

Sample	Crystallite size of c-ZrO ₂ (nm)	Crystallite size of NiO (nm)	Lattice parameter and cell volume of c-ZrO ₂	Volume % of NiO phase
8YSZ	18	-	5.14/135.62	
20 wt% NiO-8YSZ	13	11	5.12/133.96	11.92
30 wt% NiO-8YSZ	14	22	5.13/134.64	25.85
40 wt% NiO-8YSZ	16	23	5.12/134.28	29.26

Fig. 4.3 (a) shows the X-ray diffraction pattern of the sintered (at 1200 °C for 2h) 8YSZ pellets.

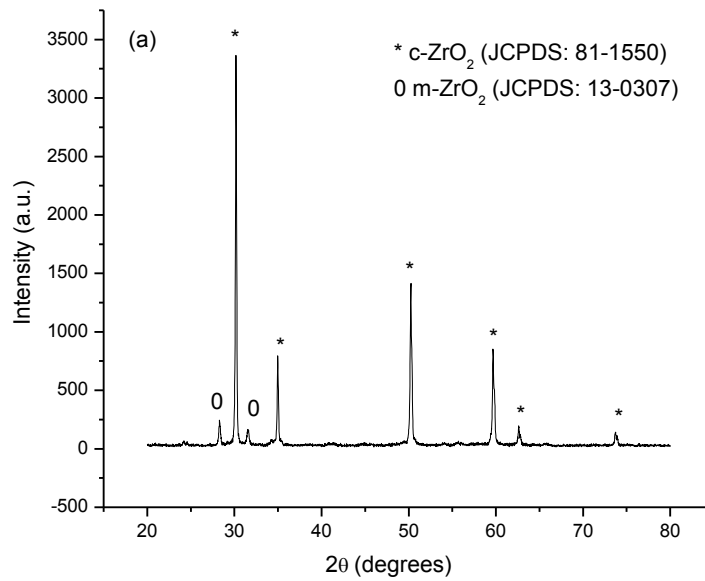


Fig. 4.3 (a) XRD pattern of 8YSZ sintered pellets.

Fig. 4.3 (b) shows the X-ray diffraction pattern of the sintered (at 1200 °C for 2h) 20 wt % NiO- 8YSZ pellets.

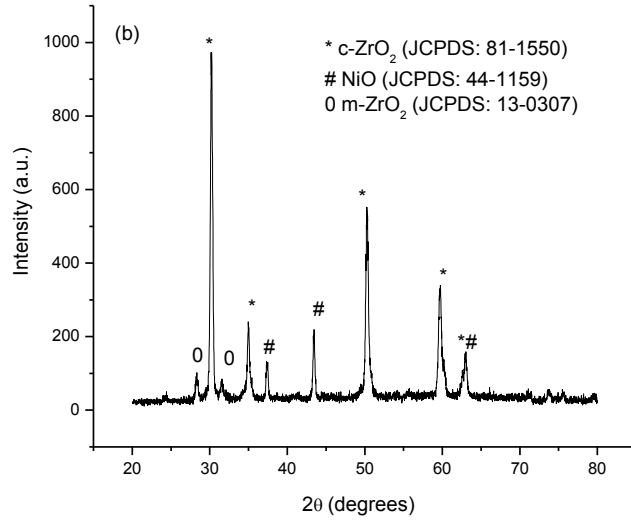


Fig. 4.3 (b) XRD pattern of 20 wt % NiO-8YSZ sintered pellets.

Fig. 4.3 (c) shows the X-ray diffraction pattern of the sintered (at 1200 °C for 2h) 30 wt % NiO- 8YSZ pellets.

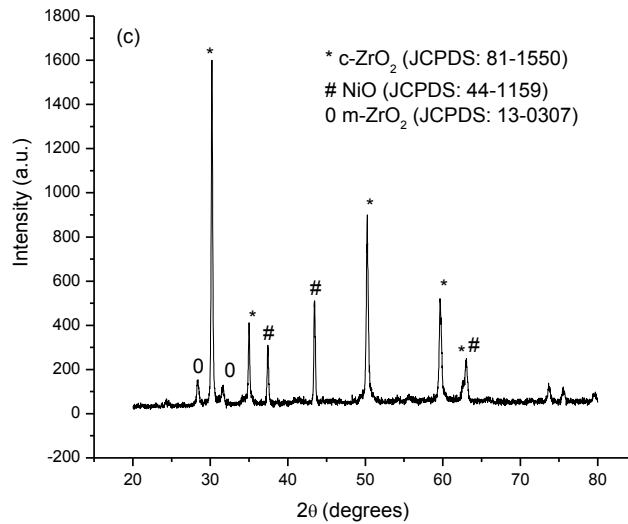


Fig. 4.3 (c) XRD pattern of 30 wt % NiO-8YSZ sintered pellets.

Fig. 4.3 (d) shows the X-ray diffraction pattern of the sintered (at 1200 °C for 2h) 30 wt % NiO- 8YSZ pellets.

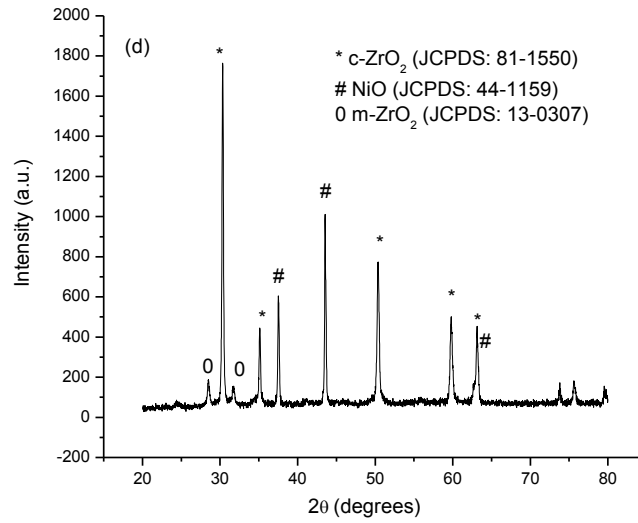


Fig. 4.3 (d) XRD pattern of 40 wt % NiO-8YSZ sintered pellets.

4.3.1(b) Remarks

All the peaks are assigned to either c- ZrO₂, m-ZrO₂ or NiO phase as confirmed from the JCPDS files as mentioned in the figures. With increase in wt % of NiO, the peak intensity at 43.5 ° increases. The crystallite size, lattice parameter and cell volume of 8YSZ and NiO-8YSZ sintered samples are given in Table 4.2. The crystallite size of c-ZrO₂ for 8YSZ sample was found to be around 56 nm. With addition of NiO, the crystallite size decreases to 25-40 nm. However, the crystallite size of NiO was larger as compared to c-ZrO₂ for 30-40 wt % NiO addition samples.

Table 4.2: Crystallite size, lattice parameter and cell volume of 8YSZ and NiO-8YSZ samples.

Sample	Crystallite size of c-ZrO ₂ (nm)	Crystallite size of NiO (nm)	Volume % of NiO phase
8YSZ	56	-	
20 wt% NiO-8YSZ	25	31	20.23
30 wt% NiO-8YSZ	42	38	29.85
40 wt% NiO-8YSZ	39	46	32.05

4.4 Microstructural properties of NiO-8YSZ nanopowders

Scanning electron microscopy (SEM) gives the information about the size, shape and agglomeration behavior of NiO-8YSZ pellets. Fig. 4.4 (a), (b) (c) and (d) show the microstructural SEM secondary and backscattered images of 20 wt % NiO, 30 wt % NiO and 40 wt % NiO (SE and BSE images) sintered pellets, respectively. The particle size is nearly spherical and agglomerate in nature.

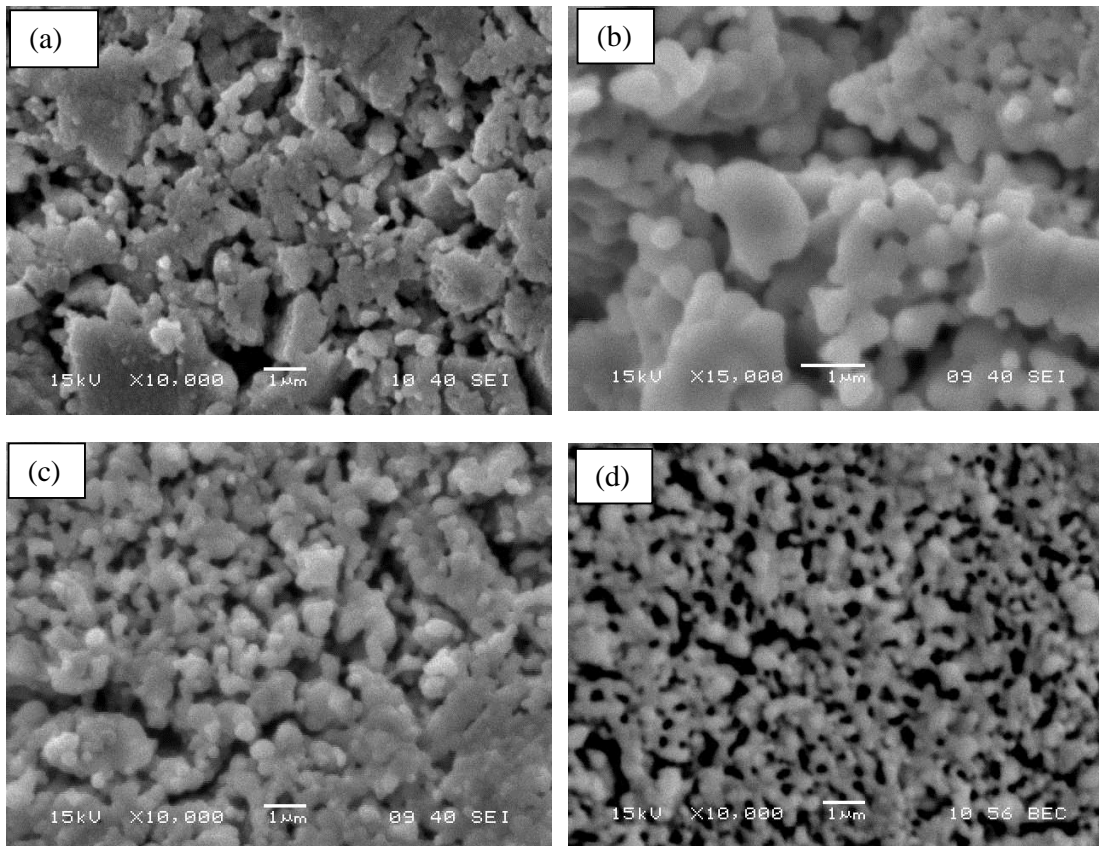


Fig. 4.4 SEM images of (a) 20 wt % NiO-8YSZ, (b) 30 wt % NiO-8YSZ and (c) and d) 40 wt % NiO-8YSZ sintered pellets.

4.4.3 Remarks

Analyzing the microstructure it reveals that, NiO addition causes the grains to be very uniform and small with the nice connectivity between pores.

4.5 Density and porosity of NiO-8YSZ pellets

Apparent porosity and bulk density of NiO-8YSZ pellets are given in Table 4.3.

Table 4.3: Apparent porosity and bulk density of 8YSZ and NiO-8YSZ samples.

Sample	Dry wt (g)	Soaked wt (g)	Suspended wt (g)	AP	BD
8YSZ	.53	.5728	.4551	33.9	3.51
20 wt % NiO-8YSZ	.594	.6292	.5132	30.3	3.99
30 wt % NiO-8YSZ	.6315	.6730	.5486	33.36	3.95
40 wt % NiO-8YSZ	.631	.6740	.5497	34.594	3.96

4.5.3 Remarks

There is jump in BD (Bulk Density) from 3.51 to 3.99 with the addition of NiO. And the porosity gradually increases with wt% of NiO from 20 to 40 wt%.

Chapter 5

CONCLUSIONS

The present work deals with the synthesis, structure and microstructure and study of NiO-8YSZ. NiO-8YSZ powders were synthesized through gelation and precipitation techniques by using a strong hydrolyzing (NaOH) agent. The significant findings of this work are:

1. Mass% at 200°C for 40wt% NiO-8YSZ is 83% whereas for 0wt% is 87%, i.e. mass loss is more for 40% NiO as compared to pure 8YSZ.
2. With increase in weight percentage of NiO, the powder showed more intense peaks for NiO at around 43°, the vol% as calculated from XRD peaks increase from 11 vol% to 29 vol % for the powders and from 20 vol% to 32 vol% for the sintered pellets.
3. Pellets showed minute amount of monoclinic ZrO₂ along with major c-ZrO₂.
4. The c- ZrO₂ crystallite size is greater in pure 8YSZ than in NiO-8YSZ. In case of NiO-8YSZ it increases with the increase in NiO content.
5. The bulk density jumps from 3.51 to 3.96 where as apparent porosity gradually increases with wt% of NiO from 20 to 40 wt%.
6. Analyzing the microstructure it reveals that, NiO addition causes the grains to be very uniform and small with the nice connectivity between pores.

Future prospects

For the use for SOFC anode there should be triplephase boundary (TPB) more the TPB more will be the rate of reaction. As the present work shows the bulk density as well as porosity is optimum for 40wt% NiO-8YSZ. This confirms that, NiO addition causes the grains to be very uniform and small with the nice connectivity between pores. Hence with increase in NiO content the TPB concentration increases.

If we further sinter the NiO-8YSZ in the reducing environment the TPB will be further increased due to reduction of NiO to Ni. Further work in this area involves sintering in reducing environment along with the relation between % of NiO to the strength of the material and optimization.

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