

SYNTHESIS OF NANOCRYSTALLINE NICKEL OXIDE POWDERS VIA GLYCINE-NITRATE COMBUSTION

J. C. Toniolo*, R. Bonadiman, L. L. Oliveira, J. M. Hohemberger, C. P. Bergmann

*Department of Materials Engineering, Federal University of Rio Grande do Sul, ,
90035190 Porto Alegre, RS, Brazil*

ABSTRACT

NiO is a candidate material for a variety of potential applications, for example, active optical filters, antiferromagnetic layers, coloring agents for enamel, pigments, catalysts, cathode materials for alkaline batteries and temperature sensors. Nanocrystalline nickel oxide powders have been synthesized by the combustion technique using glycine as a fuel and nitrate as an oxidizer. The precursor solution was heated to evaporate water, yielding a viscous liquid. It ignited and underwent self-sustaining combustion, producing an ash composed of the oxide product. The as-synthesized particles have been characterized by X-ray diffraction (XRD), and scanning electron microscopy (SEM). Nanocrystalline nickel oxide was possible to be obtained from fuel-lean ratios. The smallest crystallite size was obtained under fuel-lean (0.09) formulation. The size of the NiO nanoparticles varied from 4 to 18 nm.

KEYWORDS: Ceramics; Nanoparticle chemical synthesis; X-ray diffraction; Thermodynamic properties.

RESUMO

O NiO é um material candidato para uma variedade de aplicações: filtros óticos ativos, camadas antiferromagnéticas, agentes corantes para vidrados, pigmentos, catalisadores, cátodos como materiais para baterias alcalinas e sensores de temperatura. Pós de óxido de níquel nanocristalino foram sintetizados pela técnica de combustão, usando glicina como combustível e nitrato como oxidante. A solução precursora foi aquecida até evaporar a água, gerando um líquido viscoso. Ela sofre ignição e combustão auto-sustentada, produzindo uma cinza a qual é composta de um óxido como produto. As partículas como-sintetizadas foram caracterizadas pela difração de raios X (DRX), e microscopia eletrônica de varredura (MEV). O óxido de níquel nanocristalino foi obtido de reações deficientes em combustível. O menor tamanho de cristalito foi obtido com a formulação deficiente em combustível (0.09). Os tamanhos de nanopartículas de NiO variaram de 4 a 18 nm.

* To whom correspondence should be addressed.
E-mail: jtoniolo@zipmail.com.br (J.C. Toniolo).

INTRODUCTION

Nanoscale oxide particles are gaining increasing technical importance for classic areas of application such as catalysts, passive electronic components, and ceramic materials¹. NiO nanoparticles are desirable for many applications in the manufacture of ceramic, magnetic, electrochromic and heterogeneous catalytic materials.

The technique of combustion synthesis is an inexpensive method to produce oxides and mixtures of submicrometric or nanometric powders. This method consists of heating an aqueous solution made of inorganic salts, usually nitrates which act as an oxidant agent and an organic combustible, which can be also a complexant agent of the metallic ions. Firstly, it is necessary to ensure the homogeneity of the system with the complete dissolution of the components. After that, the solution is heated until its ignition, giving rise to a fast exothermic reaction that leads to oxides formation. The complexant/combustible agent plays a fundamental function preventing the precipitation of the individual precursors prior the ignition.

In this article, we described experiments employed to synthesize NiO powders by different fuel-to-oxidant molar ratios using glycine as complexant/combustible agent and nitrate as an oxidizer. The produced powder was characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) Enthalpies and adiabatic flame temperatures can be calculated for the different formulations.

EXPERIMENTAL

Nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Vetec Química, Brazil) and glycine (Synth, Brazil) with 97% and 98.5% purities respectively (vendor specification) were used as the starting material. These salts were dissolved in 80 mL of water in the appropriate amount to obtain the desired molar proportion.

The ignition of the solution containing a complexant/combustible agent and the precursor salts was carried out in an electrical oven at 400°C. A 500ml stainless steel recipient was used to perform the ignition process. A portion of the solution was reserved to TGA/DTA analysis. The general flowchart for the process is shown in Fig. 1.

Before the combustion, small portions of each mixture were separated for thermal gravimetric (TG) and differential thermal analyses (DTA) according to the Boersma method². A STA Harrop 736 thermal analyzer was used. Platinum crucibles containing 34±4mg of material were used; they were heated up to 800°C at a rate of 10K/min and 50 mL/min air gas flow. XSEM micrographs were recorded with a Jeol (model JSM-5800) instrument after coating the samples with gold.

All the samples were analyzed with a Philips (model X'Pert MPD) diffractometer, equipped with a graphite monochromator and a rotative anode of copper operating a 40 kV

and 40 mA. All measurements were made using Cu K α radiation; the scanning rate was 1°/min for phase analysis and 0.4°/min for crystallite size determination.

WinFit 1.0 software was used to determine the crystallite size of the synthesized powders. The profile shape function used was a split Pearson VII function and the single line variance approach of Toth³ and Arkai and Toth⁴ was considered for the crystallite size calculation. The K α_2 contribution was removed by the Rachinger correction, and the Stokes deconvolution method was employed to remove the instrumental contribution of the experimental peaks after introducing the profile shape function of pure-line standard. A sample of nickel oxide, which was annealed at 1000 °C for 4 h, was used as standard. Very sharp and well defined peaks were obtained with this procedure. From the Pearson exponent of the profile shape function, the contribution of Gaussian and Lorentzian components could be calculated. Such contributions are assumed to be proportional to the amount of crystallite size broadening and strain broadening, respectively. Finally, Fourier analysis was used to calculate size and strain parameters.

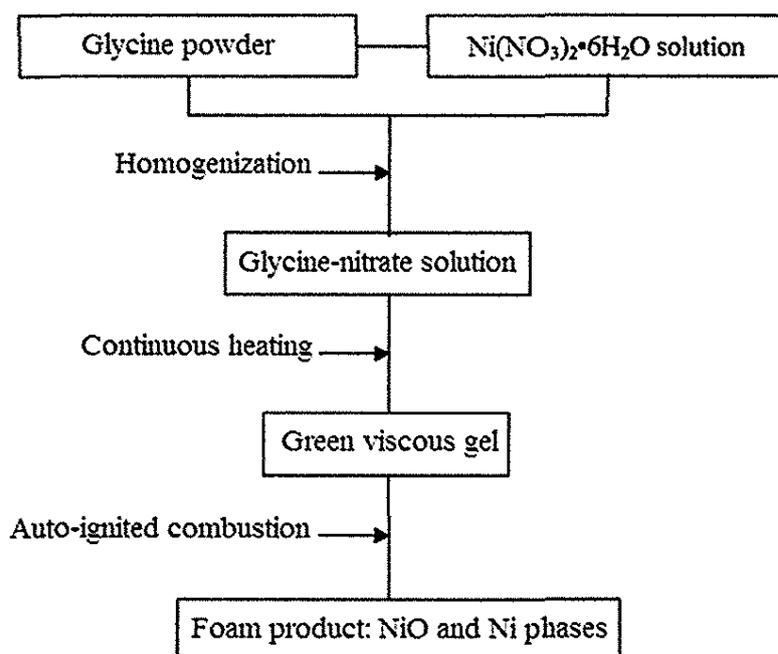


Fig. 1. Flowchart of the synthesis process.

RESULTS AND DISCUSSION

A typical DTA run of the mixture is shown in Fig. 2. This precursor solution dehydrates endothermically, with broad peak at 80-150 °C. The small exothermic peak around 215 °C is attributed to the rapid combustion wave front which burns all existing organic phases. From the TG graph it is also observed that the precursor solution exhibited a tumble loss weight up to 25 °C due to dehydration. It is also verified a second drop around 215 due to the organic matter loss. Actually, the ignition temperature does not depend on the fuel-to-oxidant ratio in accordance with evaluated experiments.

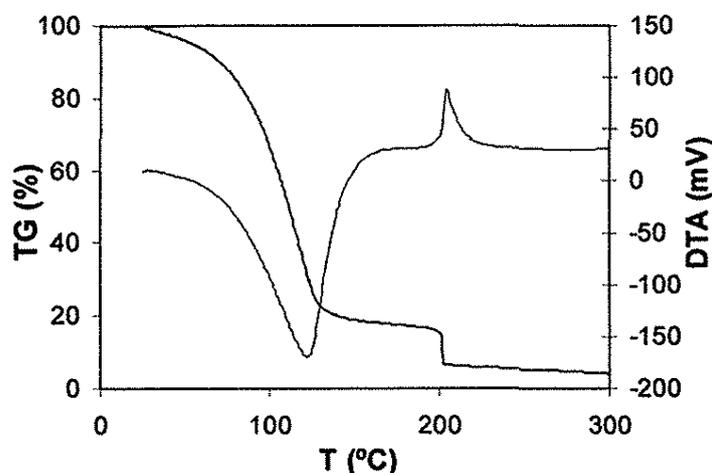


Fig. 2. Simultaneous TG-DTA curves of the precursor glycine-to-nitrate solution.

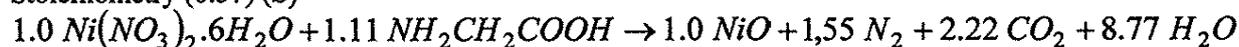
Thermodynamic considerations

The combustion of nickel nitrate-glycine mixture appears to undergo a self-propagating and non-explosive exothermic reaction.

A stoichiometric mixture of fuel and oxidant is one in which the quantity of oxidant present is theoretically correct for complete oxidation⁵. The reaction occurs in the presence of air. Any thermodynamic calculation involving flame temperature must also take into account the oxygen and nitrogen present in air.

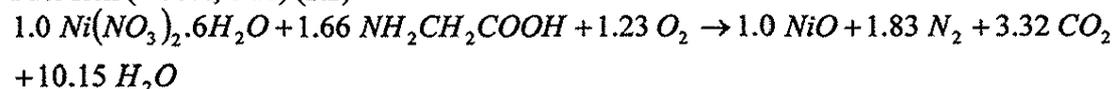
The first reaction illustrated below gives the true stoichiometric reaction. The fuel-rich reactions involve increase in glycine with respect to the stoichiometric equation. On the other hand, the fuel-lean reactions involve a decrease in the quantity of glycine. In both cases the amount of nitrate is maintained constant. All experimental combustion reactions were carried out in the presence of air.

Stoichiometry (0.37) (S)



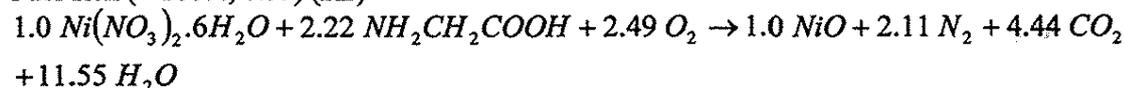
(Eq. 1)

Fuel-rich (+ 50%, 1.11) (R1)



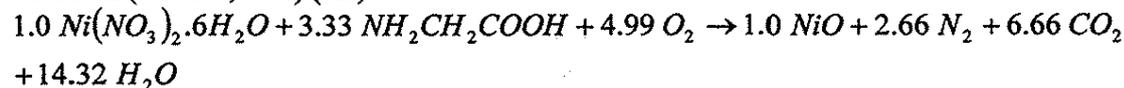
(Eq. 2)

Fuel-rich (+ 100%, 0.55) (R2)



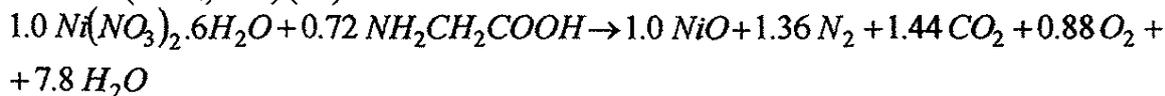
(Eq. 3)

Fuel-rich (+ 200%, 0.74) (R3)



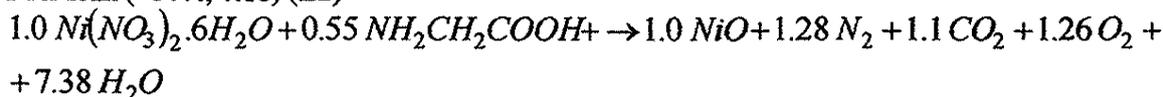
(Eq. 4)

Fuel-lean (- 25%, 0.24) (L1)



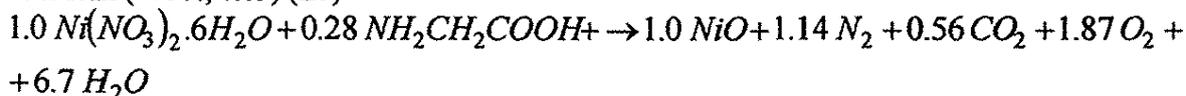
(Eq. 5)

Fuel-lean (- 50%, 0.18) (L2)



(Eq. 6)

Fuel-lean (- 75%, 0.09) (L3)



(Eq. 7)

Available thermodynamic data in literature^{6,7} for various reactants and products are presented in Table 1. It is well known that the enthalpy of combustion can be expressed as:

$$\Delta H^0 = \left(\sum n \Delta H_p^0 \right) - \left(\sum n \Delta H_r^0 \right)$$

and

$$\Delta H^0 = \int_{T_0}^T \left(\sum n C_p \right) dT, \text{ or } T = T_0 + \frac{\Delta H_r^0 - \Delta H_p^0}{C_p}$$

where n is the number of the mol, ΔH_r^0 and ΔH_p^0 are the enthalpies of formation of the reactants and products, respectively, T is the adiabatic flame temperature, T_0 is 298 K and C_p is the heat capacity of products at constant pressure. Using the thermodynamic data for various reactants and products listed in the Table 1, the enthalpy of combustion and the theoretical adiabatic flame temperatures as a function of glycine-to-nitrate molar ratio can be calculated. Nevertheless, the measured flame temperatures are typically much lower than calculated values as a result of radiative losses, incomplete combustion, and heating of air.

The adiabatic flame temperature T of the reaction is influenced by the type of fuel, fuel to oxidizer ratio, and the amount of water remaining in the precursor solution at the ignition temperature⁸. The temperature can be increased with the addition of excess oxidizer such as ammonium nitrate⁹, or by increasing the fuel/oxidizer molar ratio. Segadães et al.¹⁰ calculated theoretical adiabatic flame temperatures in the case of urea-nitrate combustion synthesis of ZnO. Purohit et al.⁵ also calculated theoretical adiabatic flame temperatures involving glycine-nitrate combustion synthesis of CeO₂.

The variation of enthalpy with the glycine-to-nitrate molar ratio could be seen in Fig. 3. As expected, they increase substantially with the amount of the fuel used during combustion.

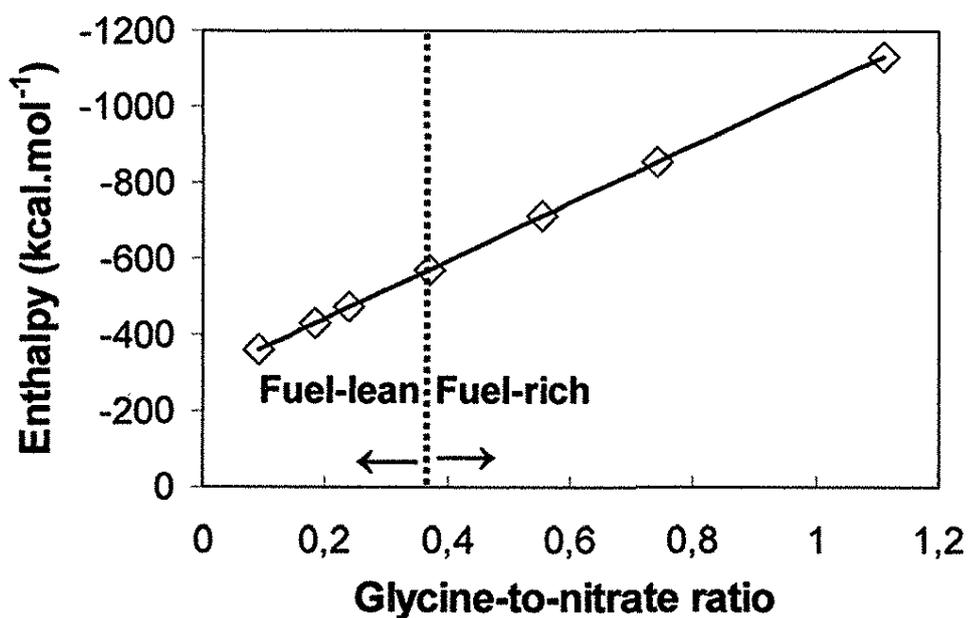


Fig. 3. Variation of enthalpy as a function of glycine-to-nitrate molar ratio.

Table 1 – Relevant thermodynamics data

Compound	ΔH_f (kcal mol ⁻¹)	C_p (Cal mol ⁻¹ K ⁻¹)
Ni(NO ₃) ₂ .6H ₂ O (c)	-113.50	-
NH ₂ CH ₂ COOH (c)	-79.71	-
NiO (c)	-58.40	11.30 + 0.00215 T
CO ₂ (g)	-94.051	10.34 + 0.00274 T
N ₂ (g)	0	6.50 + 0.0010 T
O ₂ (g)	0	5.92 + 0.00367 T
H ₂ O (g)	-57.796	7.20 + 0.0036 T
NO ₂ (g)	-33.2	-

^a (c) = Crystalline, (g) = gas. ^b T = Absolute temperature. ^c Calculated from the discrete values.

Phase formation and morphology

X-Ray Diffraction (XRD) revealed the presence of well-crystallized NiO for all glycine-to-nitrate ratios as can be noticed on Fig. 4. The Ni phase was detected only for stoichiometric and fuel-rich ratios.

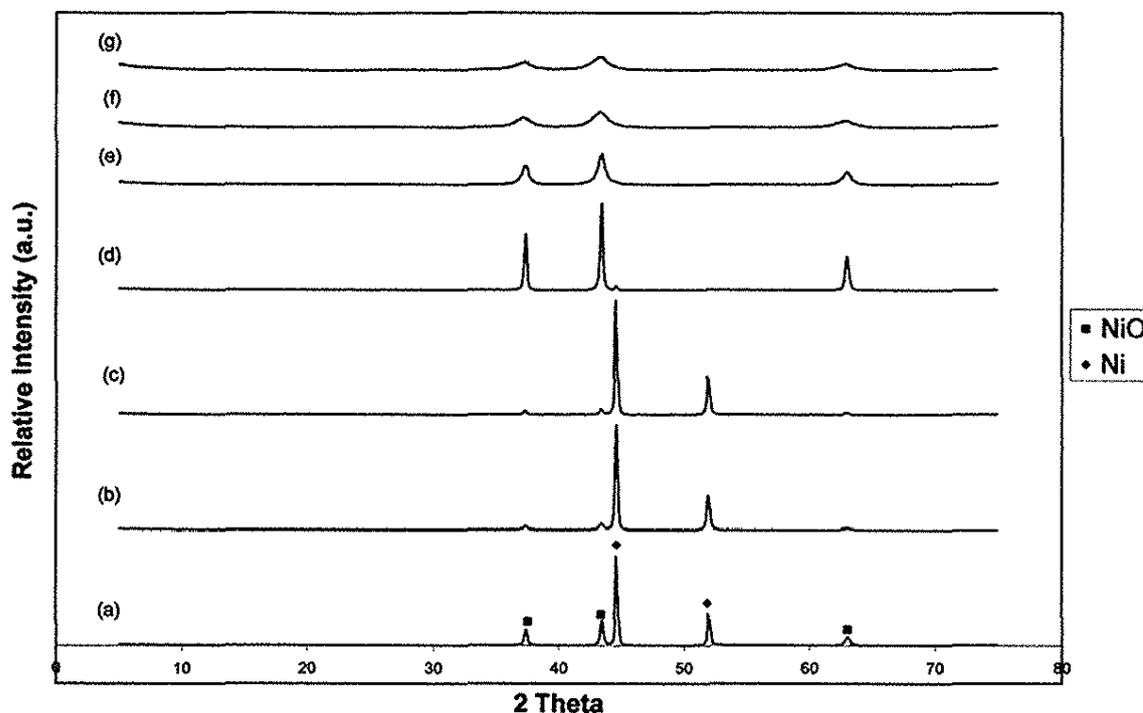


Fig. 4. X-ray diffractions of the as-synthesized powders: (a) fuel-rich (1.11), (b) fuel-rich (0.74), (c) fuel-rich (0.55) (d) stoichiometric (0.37), (e) fuel-lean (0.24) (f) fuel-lean (0.18) and (g) fuel-lean (0.09).

The NiO as single-phase was exclusively synthesized under fuel-lean ratios. It is attributed to the fact that those reactions were carried out under an oxidant condition. In the case of fuel-rich ratios, the reducing condition allowed to grow the nickel metallic phase.

The amount of fuel employed definitely plays an important, perhaps crucial role, in the determination of the properties of NiO synthesized by solution combustion synthesis.

Crystallite sizes are presented in Fig. 5. The lowest crystallite sizes were obtained under lean glycine-to-nitrate ratios. It is attributed to a decrease in flame temperature, which difficult crystal growth. In the case of stoichiometric formulation the powder synthesized was not nanometric.

There is a correlation between the increase in crystallite size as a function of fuel content in the case of glycine-nitrate combustion. Many authors have already observed this relationship^{11,12}.

The morphology of the agglomerates of the as-synthesized powders is shown in Fig. 6. The formulation fuel-lean (0.09) and fuel-rich (1.11) (a and c, respectively) exhibited foamy agglomerated particles with a wide distribution. Formation of these features is attributed to the evolution of a larger amount of gas during combustion. In the figure 6b (stoichiometric formulation) a dense structure can be seen probably due a local sinterization among particles caused by the high flame temperature.

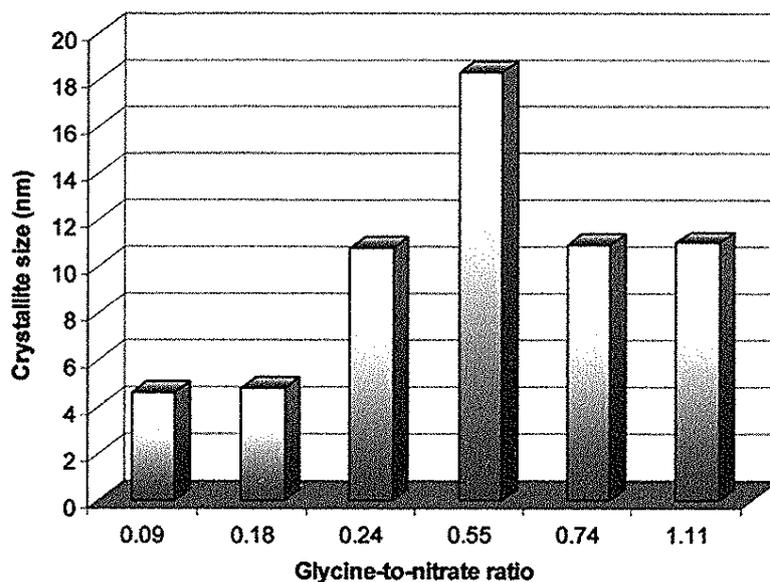


Fig. 5. Crystallite size for NiO phases under different glycine-to-nitrate ratios.

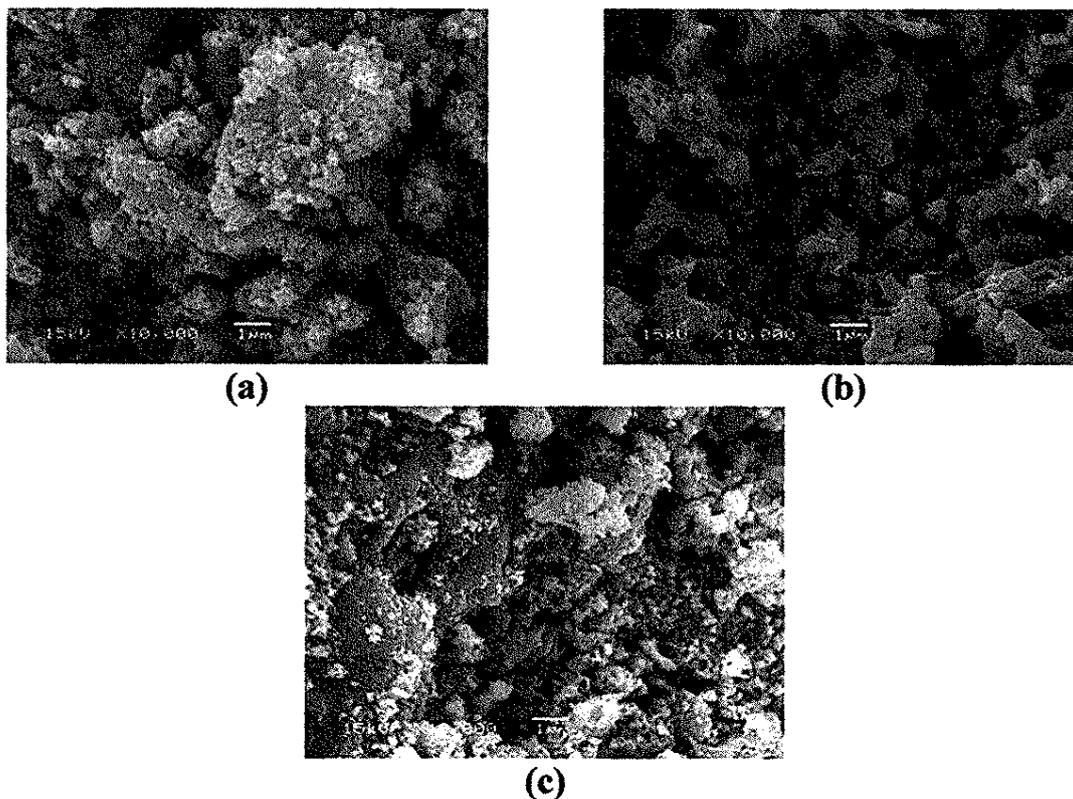


Fig. 6. SEM micrographs of nickel oxide powders prepared by (a) fuel-lean (0.09), (b) stoichiometric (0.37) and (c) fuel-rich (1.11), all at 10,000X magnification.

CONCLUSION

Glycine-nitrate combustion synthesis has a potential for producing pure nanocrystalline nickel oxide powders. Optimal crystallite size could be obtained with fuel-lean molar ratio. Thermodynamic modeling of the combustion reaction shows that when glycine-to-nitrate molar ratio increases the amount of gas produced and the adiabatic flame temperature also increase.

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