Solid state sintering behavior of zirconia- nickel composites

V.L. Arantes¹, R.B. Coutinho¹, S.S. Martins¹, S. Huang², J.Vleugels²,

¹*University of São Paulo, São Carlos School of Engineering, SP, Brazil*

²*KU Leuven, Department of Materials Engineering, Kasteelpark Arenberg,
Belgium*

e-mail: vera@sc.usp.br

Abstract: The densification kinetics of zirconia-nickel composites, containing up to 30 vol% of nickel with a medium particle size around 4 μm , was investigated. Green 3 mol% yttria stabilized zirconia (3YSZ)/Ni compacts with 56% of the theoretical density were submitted to dilatometry at constant heating rates of 5, 10 and 20°C/min. The densification kinetics of the ceramic-metal composites (cermets) were evaluated by estimation of the apparent activation energy (Q), whereas scanning electron microscopy was used to analyze the microstructure. The addition of nickel caused an increase of activation energy of densification of the composites. The densification behavior was influenced by microstructural evolution of nickel phase and percolation phenomenon. The values of activation energy for densification increased as a function of Ni content. In the initial stage, the activation energy varied from $(485 \pm 45) \text{ J.mol}^{-1}$, for pure zirconia, to $(683 \pm 28) \text{ J.mol}^{-1}$, for composites with $\text{ZrO}_2(70\% \text{vol})/\text{Ni}(30\% \text{vol})$, 70Z-30Ni. In the intermediate, these values increased from (343 ± 13) to $(480 \pm 30) \text{ J.mol}^{-1}$, for pure zirconia and 70Z-30Ni, respectively.

Keywords: sintering kinetics, densification, nickel zirconia composites, cermets.

1. Introduction

3YSZ-Ni composites present interesting properties to be applied as advanced materials owing to their great potential to be employed in different

areas such as materials for solid oxide fuel cells (SOFC) [1], thermal barriers coatings for aeronautical structures [2], cutting tools etc. [3].

Zirconia and nickel present some advantages when compared to other composites, especially, their similar values of elastic moduli and the proximity of melting temperature of nickel (1455°C) and sintering temperature of zirconia (1350-1500°C). Electrical, mechanical and thermal properties of 3YSZ and nickel-zirconia cermets have been studied in recent years. The zirconia/nickel composite properties, such as hardness, Young's modulus and creep response are strongly influenced on the composition, density and final microstructure [3-6].

3YSZ powders typically require at least 1350°C as sintering temperature in order to obtain dense compacts. The densification process of 3YSZ is facilitated by the addition of nickel oxide up to 1.0 mol% according to Song et al. [5].

The densification behavior is generally very sensitive to the initial green powder compact microstructure, possible agglomeration, pore size, particle size and homogeneity [6]. The thermal cycle affects the microstructural evolution significantly, but several studies showed that the number of pores per unit volume exert a great influence on the densification kinetics. According to Zhao and Hamer [7], an increased number of pores would enhance the densification rate at a constant mean grain size and relative density.

Literature offers a few examples of high energy ball milling to prepare Ni/YSZ powders. Wilkenhoefer et al. [8] reported on high energy milling of Ni/YSZ with Ni contents above 20 vol%, which did not achieve the percolation threshold. The percolation threshold in TZP-Ni cermets, measured by electrical conductivity and complex impedance measurements, corresponds to a nickel concentration of 34 vol% [10]. This high percolation threshold has been correlated with a partial first-neighbor ordering of the metallic inclusions inside the ceramic matrix [9].

Other authors reported that the sintering process of ZrO_2 is facilitated by the addition of nickel [10-12]. In general, these composites exhibit an improved densification process with the addition of nickel to 3YSZ, when submitted to high energy ball milling.

On the other hand, pure nickel showed a non-wetting tendency on zirconia, showing contact angles ranging from 117 to 122° [12]. Also, Nikolopoulos et al. suggested a linear decrease of the interface energy between polycrystalline ZrO_2 and liquid Ni, with temperature, according to which the interface energy at the melting temperature of Ni is 1.668 J/m^2 [13].

The wetting behavior is directly important in liquid phase sintering, whereas the interfacial energy and surface diffusivity is more relevant during solid state sintering. Nahor *et al.* investigated the Ni-YSZ [14] solid-solid interface energy by the Winterbottom analysis [15]. They determined 2 distinct values for the Ni-YSZ solid-solid interface energy: i.e., $1.8 \pm 0.1 \text{ J/m}^2$ for the $\text{Ni}[1\bar{1}0](111)||\text{YSZ}[1\bar{1}0](111)$ interface and $2.1 \pm 0.1 \text{ J/m}^2$ for the $\text{Ni}[\bar{1}10](111)\text{YSZ}[1\bar{1}1]$ interface. The authors claimed the differences between the values of interface energies could be caused by the fact that a higher orientation relationship would be the result of twinning during the dewetting phenomenon.[15]

Some models for sintering mechanisms [16] and activation energy were developed by Young and Cutler [17], Wang and Raj [18,19] and Uskoković and Exner [20]. The activation energy for densification is an important parameter to investigate the sintering kinetics related to diffusional mass transport [19-21].

Wang and Raj [18] proposed a method for the estimation of the activation energy of sintering considering constant heating rates. In this model, the sintering rate can be separated into a density dependent, temperature dependent and grain size dependent contribution.

The classic expression to calculate the apparent activation energy (Q) is given by [19]:

$$\ln \left(Tc \frac{d\rho}{dT} \right) = -\frac{Q}{RT} + \ln[f(\rho)] + \ln A - n \ln G \quad \text{Equation 1}$$

where T is the absolute temperature, c the heating rate, $\frac{d\rho}{dT}$ is the densification rate, R the gas constant, f(p) is a function of density, G the grain size, A a material parameter and n is the grain size power-law exponent. If the densification process is controlled by lattice diffusion, n=3, whereas n=4 when sintering is controlled by grain boundary diffusion.

According to Rajeswari et al. [22], the slope of the Arrhenius plot of $\ln(T.c.dp/dT)$ versus $10^4/T$ is proportional to the activation energy for sintering of ZrO₂. The slope of the isodensity lines, for distinct heating rates, determines the apparent activation energy for the whole relative density range explored.

In the present work, 3YSZ/Ni powders were subjected to dilatometry at distinct heating rates in order to determine the influence of nickel addition on the densification behavior of 3 mol % yttria stabilised zirconia.

To study the linear shrinkage behavior as a function of temperature or time at constant heating rates, a horizontal pushrod dilatometer at constant rates of 5, 10 and 20°C/min was employed. The activation energy was estimated by the Wang and Raj method.

2. Experimental Procedure

2.1. Materials and processing conditions

Spray dried high purity 3 mol% Y₂O₃-stabilised ZrO₂ (3YSZ) (grade TZ-3Y, Tosoh, Tokyo, Japan), with a specific surface area of 16±3 m²/g, crystallite size of around 50 nm) was used as starting material with the addition of 5, 10, 20, 25 or 30 vol% nickel carbonyl based metal powder (NI-110/112, Atlantic Equipment Engineers, Bergenfield, NJ, USA).

ImageJ software was used to analyze scanning electron microscopy (SEM) images of the nickel and 3YSZ starting powders, shown in figure 1. The

mean particle size of the nickel powder and 3YSZ spray dried agglomerates was measured to be 4 μm and 60 μm respectively.

Figure 1 SEM, secondary electrons (SE) images: a) Nickel and b) spray dried 3YSZ starting powder. (acceleration voltage: 5 kV)

The powders were milled in isopropyl alcohol, using high energy ball milling (Fristch, model Pulverisette 4), in zirconia jars with a ball to powder ratio of 3:1 using $\varnothing=20$ mm zirconia cylinders at 400 rpm for 12 hours. The slurry was dried and compacted using uniaxial pressing to form cylindrical pellets ($\varnothing = 6$ mm, height = 1.2 mm), which were cold isostatically pressed for 2 min at 200 MPa. The theoretical density ρ_T was calculated by the rule of mixtures, using 6.05 g/cm³ and 8.91 g/cm³ as theoretical density of 3YSZ and nickel, respectively. The relative green densities, namely geometrical one, were measured to be (56 $\pm$ 2)% of the theoretical density.

The nomenclature of the different powder mixtures directly reflects the composition. 90Z-10Ni, for example, refers to the powder mixture with 90 vol % YSZ and 10 vol % Ni.

2.2. Sintering

To evaluate the thermal behavior of the composites and the influence of the nickel content on the densification kinetics, dilatometry tests were performed at 3 different heating rates (5, 10 and 20°C/min) in a horizontal pushrod dilatometer (model DIL 402E, Netzsch, Germany), up to 1400°C, with a soaking time of 10 minutes in an argon 5.0 gas flow of 50ml/min. The dilatometer was calibrated using alumina standards. Nearly isotropic shrinkage was observed by evaluating the change in both axial and radial dimensions before and after the dilatometric experiments. The instantaneous relative density, ρ_i , was calculated using the following expression:

$$\rho_i = \left(\frac{1}{1 - \Delta L/L_0} \right)^3 * \rho_g \quad \text{Equation 2}$$

where ρ_g is the relative green density of the starting pellet, namely geometrical one, and $\Delta L/L_0$ is the linear shrinkage.

The final densities of the sintered samples were determined by the immersion technique based on the Archimedes principle [23].

Scanning Electron microscopy (Inspect F-50, FEI, The Netherlands) was used to analyze the microstructure after the thermal treatment. The detector used was the secondary electron detector and the acceleration voltage, 5 kV, in the case of powders and 10kV, for sintered samples.

3. Results and Discussion

During high energy ball milling, the nickel particles were plastically deformed, as demonstrated in figure 2.a. and ZrO₂ agglomerates were broken. The phases were homogeneously distributed after milling, as shown in Figure 2.b. for the 90Z-10Ni powder.

The mean nickel particle/agglomerate size after milling was 3.50 μm , and 0.22 μm for 3YSZ. The mean size of the spray dried 3YSZ agglomerates was 40 μm (Fig. 1.b). That means the high-energy milling method deformed the Ni particles and broke up the ZrO₂ agglomerates, resulting in a better distribution of

the powder constituents as revealed by the SEM images. High energy milling of metallic Ni and YSZ powders caused some particle refinement and deformation of the nickel phase, yielding homogeneous faceted Ni powders with a lamellar structure.

Figure 2 Secondary electron micrographs of: a) As-milled nickel powder particle and b) 90Z-10Ni powder after milling ; Zirconia and nickel are the smaller and bigger particles respectively acceleration voltage: 5kV).

Figure 3 shows the final microstructure of the 95Z-5Ni, 90Z-10Ni, 80Z-20Ni and 75Z-25Ni sintered up at 1400°C at different heating rates. Figure 3a) and 3 c) show the fracture surface of the 95Z-5Ni and 90Z-10Ni composites heated at 5°C/min. A closed porosity zirconia matrix is formed, with spheroidised dispersed dense nickel grains with a size up to about 4 µm. No Ni interdiffusion was noticed in the ZrO₂ matrix, indicating a high chemical phase stability but also low affinity and wettability in the solid state. The fracture surface reveals that the Ni grains are loosely bonded to the ZrO₂ matrix, even revealing interphase cracks in-between the Ni grains and the ZrO₂ matrix (Fig. 3a) and Ni grain pull-out (Fig. 3b). The weak bonding of the Ni grains could be due to the higher coefficient of thermal expansion of Ni ($\alpha_{Ni}=13.3 \cdot 10^{-6}$) compared to ZrO₂ ($\alpha_{ZrO_2}=10.8 \cdot 10^{-6}$), resulting in a more pronounced shrinkage of the Ni grains during cooling. The residual porosity in the ZrO₂ matrix has a rather uniform distribution with some larger dispersed pores.

Increasing Ni content to 20 and 30 vol%, as can be observed in fig. 3.e-h, the tendency of the Ni grains to densify increases. The Ni grains are dense, the ZrO₂ phase immediately around the Ni particles is also dense, whereas the ZrO₂ matrix further away from the Ni particles clearly has an open porosity. Also, the nickel grains present a microstructure typical of metals which suffer twinning.

In figure 3, corresponding to composites 70Z-30Ni, the rounded voids correspond to nickel particles and indicates the initiation of the percolation phenomenon, which results in a constrained sintering of the ZrO₂ matrix. In the same figure, one can observe the deleterious effect of detachment of the nickel grains from the matrix, indicating a very low bonding strength between Ni and ZrO₂, that occurred during the preparation of the samples for SEM.

Applying a higher heating rate of 20°C/min to the composites clearly resulted in a higher residual porosity of the ZrO₂ matrix, as illustrated by the comparison between figures 3.b,d,f and h with Fig 3.a,c,e and g. The microstructures presented in Fig 3 confirm the presence of residual porosity, mainly located in the 3YSZ matrix. The observed residual porosity in the ZrO₂ increases with increasing Ni content.

In general, 3YSZ particles remained nanometric for all compositions and grain growth was limited due to the fact that the ZrO₂ matrix still had open porosity, inhibiting grain boundary migration. Partial percolation of the nickel phase occurred for compositions with addition of 25 vol% Ni and the quality of the adhesion of the Ni particles to the ZrO₂ matrix was poor.

Figure 3 SEM, SE mode images of : (a) 95Z-5Ni sintered at 5°C/min; (b) 95Z-5Ni sintered at 20°C/min; (c) 90Z-10Ni sintered at 5°C/min and (d) 90Z-10Ni at 20°C/min; (e) 80Z-20Ni sintered at 5°C/min; (f) 80Z-20Ni sintered at 20°C/min; (g) 70Z-30Ni sintered at 5°C/min; (h) 70Z-30Ni sintered at 20°C/min. (acceleration voltage: 10kV))

Sintering

The densification behavior of composites depends on factors such as the relative grain sizes of the powder of the phases, which defines the area of contact between metal, ceramic, and metal/ceramic particles, and therefore, percolation during densification. Other crucial factors are the diffusion of the atomic species and the quality of interfacial bonding, i.e. grain boundary formation.

Figure 4 presents the linear shrinkage results as a function of temperature for pure 3YSZ and the 95Z-5Ni, 90Z-10Ni, 85Z-15Ni and 70Z-30Ni composites heated at 5°C/min up to 1450°C. According to the results, the compacts expand up to 1000°C. Shrinkage starts at 1121°C for pure 3YSZ (onset temperature of densification- T_{onset}) and continues with further increase of temperature. The discontinuities above 1420°C correspond to the nickel phase melting.

It is worthy to observe that the lower the heating rate, the higher the linear shrinkage and densification. The influence of the composition on the shrinkage was lowest at a heating rate of 5°C/min.

Figure 4 a) Linear shrinkage as a function of temperature for composites with different Ni content at a heating rate of 5°C/min.

Table 1 summarizes the onset sintering temperatures (T_{onset}) and temperatures corresponding to the maximum shrinkage rate (T_{max}) for distinct compositions. The onset sintering temperature and maximum shrinkage rate temperatures increase with increasing Ni content. The same behavior was observed with the increase of heating rate, that is even more pronounced for higher amounts of Ni.

Table 1 Sintering onset, T_{onset} , and maximum shrinkage rate, T_{max} , temperatures for different heating rates and composites.

Composition	Heating rate					
	5°C/min		10°C/min		20°C/min	
	$T_{\text{onset}}^{\circ\text{C}}$	$T_{\text{max}}^{\circ\text{C}}$	$T_{\text{onset}}^{\circ\text{C}}$	$T_{\text{max}}^{\circ\text{C}}$	$T_{\text{onset}}^{\circ\text{C}}$	$T_{\text{max}}^{\circ\text{C}}$
100Z	1121	1228	1125	1237.4	1150	1265
95Z-5Ni	1130	1237	1135	1241.4	1153	1265
90Z-10Ni	1130	1239	1140	1251.1	1154	1266
85Z-15Ni	1131	1240	1144	1259.9	1161	1278
80Z-20Ni	1145	1247	1164	1281.3	1158	1276

75Z-25Ni	1155	1262	1167	1280.8	1161	1276
70Z-30Ni	1152	1243	1168	1286.7	1160	1271

In order to understand the densification process and its effect on the final microstructure, it is essential to know the sintering mechanisms. Herle *et al.* observed that small additions of NiO reduced the solid state sintering temperature, however no sintering mechanism was reported [24]. Higher additions of NiO (0.5-1 mol%) did not significantly affect the densification behavior of 8YSZ according to Song et al [5]. It is worthy to note NiO reduction occurs at 900-1000°C.

Similar results were found by Restivo et al. [25], who added metallic Cu and Ni to a 8 mol% yttria stabilized zirconia by means of high energy milling. They observed that the addition of higher amounts of metallic nickel resulted in higher initial sintering temperatures, what became more evident at higher heating rates.

Figure 5 presents the linear shrinkage rate results as a function of temperature for zirconia-nickel cermets. The determination of the temperature at which the maximum linear retraction (shrinkage rate) occurs is important to determine the initial sintering stage. According to Lange [26], for 8 mol % Y₂O₃ stabilized ZrO₂ and pure alumina, the initially touching particles sinter up to form a metastable network and the sintering kinetics are dominated by densifying mechanisms at temperatures below the maximum linear retraction rate. Above this temperature, further shrinkage would be controlled by slower bulk diffusivity. All of the investigated materials presented a similar shrinkage behavior, but the addition of nickel and/or an increased heating rate caused an increase of the maximum shrinkage rate temperature (T_{max}).

Figure 5 Shrinkage rate of 3YSZ/Ni cermets as a function of temperature at heating rates of 5, 10 and 20°C/min for a) pure zirconia; b) 95Z-5Ni; c) 90Z-10Ni; d) 85Z-15Ni; e) 80Z-20Ni; f) 70Z-30Ni.

The instantaneous relative density curves were calculated according to equation 2 for all materials. Figure 6 shows the relative density versus

temperature for pure 3YSZ and composites with increasing addition of nickel, sintered at different heating rates.

No significant variation was observed up to 1100°C for all materials, since the green density of the different compositions was almost constant. Above 1150°C, the relative density increased almost linearly with temperature. A higher heating rate promoted lower levels of densification, especially above 1300°C.

Figure 6 Relative density versus temperature for a) pure zirconia; b) 95Z-5Ni; c)90Z-10Ni; d) 85Z-15Ni; e) 80Z-20Ni; f) 70Z-30Ni.

Figure 7 shows the densification behavior as a function of temperature for pure zirconia and composites. The addition of nickel did not change the

densification profile when compared with pure 3YSZ. In general, the densification rate decreased with increasing heating rate, and the curves shifted to higher temperatures. Also, the maximum densification rate decreased with the addition of nickel, which implies Ni addition slows down the densification of the ZrO_2 phase.

According to Rajeswari et al. [22], the features of the densification curve are related to the activation energy of yttria-stabilized zirconia and grain boundary diffusion is the dominant mechanism in the early and intermediate stages of sintering.

In the composites selected for this work, the initial matrix /inclusion particle radius ratio was approximately 0.15, which should present an onset of sintering between 16 and 18 vol % of nickel, according to Bouvard and Lange [27]. In that work, ceramic particles were considered to be rigid inclusions, which is not the case in this work. In this work, the metal Ni particles are the inclusions and their particle size is substantially larger than that of the ZrO_2 matrix, which explains the difference between our results and Bouvard's ones.

Figure 7 Densification curves as a function of temperature for a) pure zirconia; b) 95Z-5Ni; c) 90Z-10Ni; d) 85Z-15Ni; e) 80Z-20Ni; f) 70Z-30Ni, sintered at different heating rates.

Figure 8 shows the densification rate as a function of density for all compositions. Decreasing the heating rates shifts the curves to higher densification rates and relative densities.

Although there are many studies about the effect of ceramic particles, considered to be rigid, on the densification of metal matrix composites, only few dealt with the solid state densification of ceramic matrix composites. Besler et al. [28], employed the discrete element method to simulate sintering of alumina-nickel composites. They considered equally-sized and homogeneously distributed spherical particles. They observed that both the densification rate and density decreased with increasing alumina content up to 20 vol%. For percolating phase composites and alumina-rich composites, the average coordination number of metal grains (Ni-Ni) did not change considerably and, in the case of alumina-rich composites, the sintering is dominated by the alumina phase and the addition of nickel had no significant effect on the sintering of the composites.

In this work, there was a considerable difference between the ceramic and metal particle size, which was responsible for the decrease in the densification rate of the ceramic rich composites and compositions around the percolation threshold.

Figure 8 Densification rate versus relative density for compositions a) pure zirconia; b) 95Z-5Ni; c) 90Z-10Ni; d) 85Z-15Ni; e) 80Z-20Ni; f) 70Z-30Ni, sintered at different heating rates.

Arrhenius plots for pure PSZ and zirconia/nickel composites, determined for distinct relative densities, are shown in figure 9. For four different values of relative density in the intermediate-stage of sintering ($65\% \leq \rho \leq 80\%$), the

activation energies have been estimated from the slopes of these curves. Table 2 shows the activation energies for densification determined by the Wang-Raj method for the early ($57\% \leq p \leq 60\%$) and intermediate ($65\% \leq p \leq 80\%$) stage of sintering.

Most of the reported activation energies for densification of 3% mol Y_2O_3 -stabilized ZrO_2 by grain boundary diffusion (GBD) are between 309-373 kJ/mol [29,30] and 460-616 kJ/mol [31,32] for lattice diffusion and superimposed diffusion mechanisms. The activation energy determined by the Wang and Raj method for the intermediate stage, 342.97 ± 12.78 kJ/mol, is close to the one reported by Yeh and Sacks, 307 ± 10 kJ/mol [33] and Rajeswari, 350 kJ/mol [34].

Figure 9 Arrhenius plot $\ln((dp/dT).c.T)$ versus $(10^4/T)$, obtained by the Wang and Raj method, for a) pure zirconia; b) 95Z-5Ni; c) 90Z-10Ni; d) 85Z-15Ni; e) 80Z-20Ni; f) 70Z-30Ni, sintered at different heating rates.

Table 2 Activation energies determined by the Wang-Raj method

Material	Activation Energy (kJ.mol⁻¹)	
	57% ≤ ρ ≤ 60%	65% ≤ ρ ≤ 80%
100Z	408±45	343±13
95Z-5Ni	492±57	370.40±11
90Z-10Ni	531±48	402.44±15
85Z-15Ni	582±66	420.08±19
80Z-20Ni	604±18	436.09±15
75Z-25Ni	658±19	452.93±15
70Z-30Ni	683±28	480±30

The addition of nickel caused an increase in the activation energy for the whole relative density range, and the activation energy increased with increasing Ni content up to 30 vol%. This means the Ni addition is actually slowing down the densification and more energy is required to reach the same level of densification for these composites, despite the high energy milling step that in some cases was claimed to reduce the sintering temperature [35]. The same effect was observed by Rabin and Heaps [36], in their investigation of alumina-nickel composites. According to Ashby et al. [37], metallic nickel sintering is inhibited in the presence of small ceramic particles, as in the case of reinforced cermets.

In the YSZ/Ni composites, the first sintering stage was influenced by the morphology of the nickel faceted particles. One can also observe a higher activation energy in the initial stage of sintering. Besides volume and relative particles size, the Ni particle morphology should be considered. During the sintering process, the nickel particles changed morphology and spheroidized (compare Fig. 2.a and 10.d). The conventional assumption that densification is proportional to the inverse of the radius of curvature does not apply to faceted boundaries, as proposed by Choi and Kang (38). The densification and grain growth are drastically reduced for faceted boundaries phases, which implies that in the initial sintering stage, densification of zirconia was the sintering rate-limiting one.

Also, the addition of large multi-faceted nickel powders to homogeneous smaller zirconia matrix particles decreased the number of zirconia-zirconia contacts, as well as the mean distance between the zirconia grains.

Probably, in the intermediate stage, twinning of nickel particles occurred, which corroborates Nahor hypothesis about wetting of zirconia by nickel [14]. The twinning was accomplished by spheroidization and densification of the metal phase grains. After densification of the Ni phase grains, constrained sintering, a common phenomenon which takes place in some composites with compounds exhibiting dissimilar densification rates, occurred [36]. The constraint caused by the spheroidised Ni particles substantially influenced the densification of the ZrO_2 matrix. The dense Ni grains inhibited the densification of the ZrO_2 matrix in-between the Ni grains. The constrained sintering was dominant in the intermediate and final stages of sintering.

Conclusions

The addition of micrometer sized nickel particles to a nanometric yttria-stabilized ZrO_2 matrix increased the onset temperature of sintering and the maximum shrinkage rate temperature of 3YSZ-Ni composites. Both temperatures

increased with increasing Ni content and increased heating rate, resulting is a reduced density with increased Ni content and heating rate.

The final microstructure of the solid state sintered (1400°C) composites was composed of spheroidized Ni particles in an open porosity ZrO₂ matrix. Due to the constraint sintering of the ZrO₂ matrix, the residual porosity of the composites increased with increasing Ni content.

Using the Wang and Raj method, the activation energy of sintering for the 3YSZ-Ni composites was measured to increase from 408 (pure 3YSZ) to 658 (30 vol % Ni) kJ/mol in the first stage of sintering ($57\% \leq p \leq 60\%$), whereas the activation energy for the intermediate stage ($65\% \leq p \leq 80\%$) increased from 343 to 453 kJ/mol, showing the sintering inhibiting effect of the addition of large Ni particles.

Acknowledgments

The authors thank the Brazilian federal government agency (CNPq (process 236288/2013-0), the support offered by the department of Materials Engineering (MTM) of KU Leuven and prof. Rollo from SMM/São Carlos School of Engineering.

References

- [1] S.T. Aruna, M. Muthuraman, K.C. Patil, Synthesis and properties of Ni-YSZ cermet: anode material for solid oxide fuel cells, *Solid State Ionics*, 1998, 111(1–2), p45-51.
- [2] A.M. Rodríguez, A.B. León, A.D. Rodríguez, S.L. Esteban, J.S. Moya, M.J. Melendo, High-temperature mechanical properties of zirconia/nickel composites, *Journal of the European Ceramic Society*, 2003, 23, p2849-2856.
- [3] I. Hussainova, M. Antonov, N. Voltsihhin, Assessment of zirconia doped hardmetals as tribomaterials, *Wear*, 2011, 271, p1909-1915.
- [4] M. Takemura, T. Hyakubu, A. Yoshitake, M. Tamura, M. Niino, and A. Kumakawa, in *Functionally Gradient Materials*, Ceramic Transactions, edited by J.B. Holt, M. Koizumi, T. Hirai, and Z.A. Munir, (Proc. 2nd Int. Symp. Funct. Grad. Mater., San Francisco, CA, 1993), Vol. 34, pp. 271–278.

- [5] X.C. Song, J. Lu, T.S. Zhang, J. Ma, Sintering behavior and mechanisms of NiO-doped 8 mol% yttria stabilized zirconia, *Journal of the European Ceramic Society*, 2011, 31, p2621–2627.
- [6] D. Lance, F. Valdivieso, P. Goeuriot, Correlation between densification rate and microstructural evolution for pure alpha alumina, *Journal of the European Ceramic Society*, 2004, 24, p2749-2761.
- [7] J. Zhao, M.P. Harmer, Effect of Pore Distribution on Microstructure Development: III, Model Experiments, *Journal American Ceramic Society*, 1982, 75, p830-843.
- [8] R. Wilkenhoener, P. Vassen, H.P. Buchkremer, D. Stover, Mechanically alloyed Ni/8YSZ powder mixtures: preparation, powder characterization and sintering behavior, *Journal of Mater. Science*, 1999, 34, p257–265.
- [9] C. Pecharromán, L.S. Esteban, J.F. Bartolomé, J.S. Moya, Evidence of Nearest-Neighbor Ordering in Wet-Processed Zirconia–Nickel Composites, *Journal American Ceramic Society*, 2001, 84, p2439–41.
- [10] E.L. Honorato, M. Dessoliers, I.P. Shapiro, X. Wang, P. Xiao, Improvements to the sintering of yttria-stabilized zirconia by the addition of Ni, *Ceramics International*, 2012, 38, p6777–6782.
- [11] A. J. Flegler, T.E. Burye, Q. Yang, J.D. Nicholas, Cubic yttria stabilized zirconia sintering additive impacts: a comparative study, *Ceramic International*, 2014, 40, p16323.
- [12] C.S. Kanetkar, A.S. Kacar, and D.M. Stefanescu, The wetting characteristics and surface tension of some Ni-based alloys on yttria, hafnia, alumina and zirconia substrates, *Metallurgical Transactions*, 1988, 19A, p1833–1839.
- [13] P. Nikolopoulos, G. Ondracek, D. Sotiropoulou, Wettability and interfacial energies between zirconia ceramic and liquid metals, *Ceramic International*, 1989, 15, p201.
- [14] H. Nahor, H. Meltzman, W.D. Kaplan, Ni–YSZ solid–solid interfacial energy, *Journal Mater Sci*, 2014, 49, p3943–3950.
- [15] W.L. Winterbottom, Equilibrium shape of a small particle in contact with a foreign substrate. *Acta Metall*, 1967, 15, p303.
- [16] R.L. Coble, Sintering crystalline solids I intermediate and final state diffusion models, *Journal Appl. Phys.*, 1961, 32, p787–792.
- [17] W.S. Young, I.B. Cutler, Initial Sintering with Constant Rates of Heating, *Journal American Ceramic Society*, 1970, 53, p659–663.
- [18] J. Wang, R. Raj, Estimate of the Activation Energies for Boundary Diffusion from Rate Controlled Sintering of Pure Alumina, and Alumina Doped with Zirconia or Titania, *Journal American Ceramic Society*, 1990, 73, p1172–1175.
- [19] J. Wang, R. Raj, Activation Energy for the Sintering of Two-Phase Alumina/Zirconia Ceramics, *Journal American Ceramic Society*, 1991, 74, p1959–1963.
- [20] D. Uskoković, H.E. Exner, The Kinetics of Contact Formation During Sintering by Diffusion Mechanisms. In: Sōmiya S., Moriyoshi Y. (eds) *Sintering Key Papers*. Springer, Dordrecht, 1990.
- [21] J.D. Hansen, R.P. Rusin, M.H. Teng, D.L. Johnson, D.L.; Combined Stage Sintering Model, *Journal American Ceramic Society*, 1992, 75, p1129–1135.

- [22] K. Rajeswari, S. Padhi, A.R.S. Reddy, R. Johnson, D. Das, Studies on sintering kinetics and correlation with the sinterability of 8Y zirconia ceramics based on the dilatometric shrinkage curves, *Ceramic International*, 2013, 39, p4985–4990.
- [23] ASTM, Standard Test Methods for Apparent Porosity , Water Absorption , Apparent Specific Gravity , and Bulk Density of Burned Refractory Brick and Shapes by Boiling Water, *Astm*, 2015, C20-00, p1–3.
- [24] J.V. Herle, R. Vasquez, Conductivity of Mn and Ni-doped stabilized zirconia electrolyte, *Journal of the European Ceramic Society*, 2004, 24, p1177-1180.
- [25] T.A.G. Restivo, S.R.H. Mello-Castanho, Nickel-Zirconia cermet processing by mechanical alloying for solid oxide fuel cell anodes, *Journal Power Sources*. 185, 2008, 1262–1266.
- [26] F.F.Lange,; Powder Processing Science and Technology for Increased Reliability, *Journal Am. Ceram. Soc.*, 72, 1989, p 3-15.
- [27] D.Bouvard, , F. F. Lange, *Acta Metall. Mater.*, 1991, 39, p3083-3090.
- [28] R. Besler,; M. R. Silva; M. Dosta; S. Heinrich; R.Janssen,; Discrete element simulation of metal ceramic composite materials with varying metal content, *Journal of the European Ceramic Society*, 2016, 36 , 2245-2253.
- [29] F.R. Chien, A.H. Heuer, Lattice diffusion kinetics in Y_2O_3 -stabilized cubic ZrO_2 single crystals: A dislocation loop annealing study, *Philos. Mag. A*. 73, 1996, p681–697.
- [30] M. Mazaheri, A. Simchi, M. Dourandish, F. Golestani-Fard, Master sintering curves of a nanoscale 3Y-TZP powder compacts, *Ceram. Int.*, 35, 2009, pp. 547-554
- [31] R. Caruso, N.Mamana, E.Benavidez, Densification kinetics of ZrO_2 -based ceramics usinga master sintering curve, *J.Alloy.Compnd*. 495(2010) 570–573.
- [32] T.-S. Yeh, M.D. Sacks, Effect of Particle Size Distribution on the Sintering of Alumina, *J. Am. Ceram. Soc.* 71, 1988, C-484-C-487.
- [33] M.A.Taylor, M.Kilo,G.Borchardt, S.Weber, H.Scherrer, 96Zr diffusion in polycrystalline Scandia stabilized zirconia, *J.Eur.Ceram.Soc.*,2005, 25(9), p1591–1595.
- [34] H.J. Cho, G.M. Choi, Effect of milling methods on performance of Ni-Y2O3-stabilized ZrO_2 anode for solid oxide fuel cell, *J. Power Sources*, 2008, 176 96–101.
- [35] H.Rabin; R.J. Heaps; Powder Processing of Ni-Al₂O₃ FGM; *Ceramic Transactions, Functionally Gradient Materials*, 1993, 34, P173.
- [36] M.F.Ashby; S. Bahk; J.Bevk,; D.Turnbull,; The influence of a dispersion of particles on the sintering of metal powders and wires, *Progress in Materials Science*, 1980, p251–34.
- [37] S.Y. Choi; S.J.L. Kang; Sintering kinetics by structural transition at grain boundaries in barium titanate, *Acta materialia*, 2004, 52, p 2937–2943
- [38] D.J. Green; O.Guillon; J. Rodel,; Constrained sintering: A delicate balance of scales, *Journal of the European Ceramic Society*, 2008, 28, p451–1466.