



## Short communication

## Nickel-Zirconia cermet processing by mechanical alloying for solid oxide fuel cell anodes

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## ABSTRACT

This paper describes the development of a process based on high energy milling (or mechanical alloying—MA) of metallic Ni and YSZ at 40 vol% Ni composition for the preparation of solid oxide fuel cell anode material. The cermet powder is consolidated using the surface activated sintering (SAS) method. The cermet pellets possess microstructural characteristics that can potentially lead to higher electrocatalytic activity and fuel reforming capability. In addition to the development of a new processing method for this purpose, a further differential of this work is the addition of Cu in partial substitution of Ni as a means to prevent the formation of carbon on its surface and, hence, the anode's degradation during service. The prepared powder samples are well dispersed and structured at the nanometric level, showing thin lamellar constituents. Suitable sintered pellets can be obtained from the powders with the required porosity and microstructure. The higher the energy delivered by MA the lower the initial sintering temperature. Activation energies are determined by stepwise isothermal dilatometry (SID) for Ni-YSZ and Ni/Cu-YSZ pellets, involving a 2-step sintering process. The Cu additive promotes sintering and leads to a refined microstructure.

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## 1. Introduction

The solid oxide fuel cell anodes developed to date have shown some limitations with regard to the use of different fuels and commercial applications. It is a well known fact that, besides the high activity for H<sub>2</sub>-bearing fuel oxidation, the major challenge is to design fuel types derived from organic sources such as hydrocarbons and alcohols. In view of Brazil's energy matrix, there is much interest in ethanol and biogas fuels. However, these fuels reportedly cause anode catalyst poisoning by surface carbon deposition. Notwithstanding these technical questions, this paper reports on the development of a method to obtain cermet anode materials for SOFC based on mechanical alloying (MA) of metallic Ni and YSZ powders. A suitable cermet processing method is one of the most relevant factors to overcome the cost and lifetime-related limitations of SOFC cells.

The co-milling MA process of the constituent powders can produce the following effects [1]: (i) refinement of the material's structure, thereby increasing the 3-phase boundary site number, and (ii) increase of the powder's sinterability through the exposure of active surfaces during MA and sintering heat cycle. The surface

activated sintering (SAS) method, which derives from the latter effect, is used to consolidate the material. The resulting cermets are expected to display microstructural characteristics that improve the electrocatalytic activity and the fuel reforming capability. The addition of Cu by partial replacement of Ni is also investigated as a means to mitigate carbon deposition on the Ni catalyst.

## 2. Materials and methods

The 40 vol% Ni(Cu)-YSZ cermet was prepared from 8 mol% yttria stabilized zirconia (8YSZ Tosoh Co., BET 13.2 m<sup>2</sup> g<sup>-1</sup>) and metallic Ni (99.6 mass% purity) with an average grain size of 29.3 μm. The purity of the Cu powder exceeded 99.9 mass% and it had an average particle size of 3 μm. The main samples were prepared by high energy milling in a shaker mill (SPEX 8000) at a rotation speed of 10 and 19 Hz for 1–16-h periods. Ultra-high molecular weight (UHMW) polyethylene and PTFE vials were used in a milling medium of 5 mm diameter tetragonal zirconia YTZ spheres. The powder-to-sphere mass ratio was 1:10. For purposes of comparison, two samples – 40 vol% Ni-YSZ and 55 vol% NiO-YSZ – were prepared by mixing and homogenizing the raw powders in alcohol slurries, and the former is referred to as homogenized cermet. The resulting powders were characterized by physical and chemical methods, and then subjected to uniaxial pressing at 100 MPa to produce pellets. Sintering was performed in a tubular furnace and a vertical TMA/dilatometer (Setaram Labsys TMA), applying

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a heating rate of  $10^{\circ}\text{C min}^{-1}$  up to  $1250\text{--}1300^{\circ}\text{C}$  and a 1-h dwell time, under air, argon and hydrogen atmospheres. The sintering kinetics was evaluated by stepwise isothermal dilatometry (SID) in the dilatometer under argon, with several 15-min isotherms programmed at  $50^{\circ}\text{C}$  intervals during heating. The data was treated with the normalized volumetric shrinkage equations [2–4]:

$$\frac{dY}{dt} = nK(T)Y(1-Y) \left[ \frac{(1-Y)}{Y} \right]^{1/n} \quad (1)$$

where:  $Y = (L_0^3 - L_t^3)/(L_0^3 - L_f^3)$ ,  $L_i$  is the sample length (0,  $t$ , and  $f$  refer to initial, at time  $t$  and final times),  $K$  is a temperature function and  $n$  is a constant.

### 3. Results and discussion

The X-ray powder diffraction patterns of the 40 vol% Ni-YSZ samples after milling displayed broadening of the peaks, which increased with longer MA times and energy increases (Fig. 1(a)). Peak broadening is expected to reflect the high defect density caused by MA allied with particle and crystallite refinement, tending to an amorphous state. Due to the high impact the powder underwent during the process, it may have become contaminated. Milling in UHMW vials produced carbon pickup of 1.5 and 2.5 mass% after 2 and 8 h of MA processing at 19 Hz, respectively. The PTFE vials reduced this contamination to 0.7 mass% of carbon. Even so, an evaluation of the diffractograms in Fig. 1 reveals a shift in the Ni peaks, since C can become dissolved in the Ni lattice even at a low

concentration. A previous study reported that  $\text{Ni}_3\text{C}$  compound can be formed after 8 h of MA at 19 Hz [1]. Fig. 1(a) compares diffractograms of Ni and YSZ raw materials and the sample compositions 40 vol% Ni-YSZ and 40%(Cu-Ni)-YSZ, in which half the volume of Ni was replaced by Cu. The addition of Cu caused a further shift of the Ni peaks. Because Cu peaks are located at slightly different  $2\theta$  degrees than Ni peaks, they can overlap at a broadened peak, thereby forming an alloy. Moreover, there was more carbon available for dissolution in Ni, since Ni was partially replaced by Cu, which repels carbon.

A scanning electron microscopy (SEM) analysis of 4-h MA powder samples revealed a typical lamellar morphology composed of alternating thin white and gray lines, which tended to become refined as the MA processing time increased (Fig. 2). After 8 h of processing, the lamellar structure was hardly visible. Fig. 3 shows transmission electron microscope (TEM) images indicating that the powder's ultimate particle size was in the nanometric range. The cermet was structured primarily as an embedded aggregation of elongated YSZ and Ni particles, with some spots containing nanoparticles of less than 5 nm.

The energy transferred to the materials by MA allowed for lower initial sintering temperatures, as indicated by the dilatometric experiments, and the behavior was independent of the type of atmosphere. Fig. 4 shows sintering curves for samples processed by MA for different lengths of time under air. Pure YSZ and NiO-YSZ samples are included, showing initial sintering temperatures of around  $950^{\circ}\text{C}$ . However, the MA cermets initially displayed expansion caused by metal oxidation. It was found that

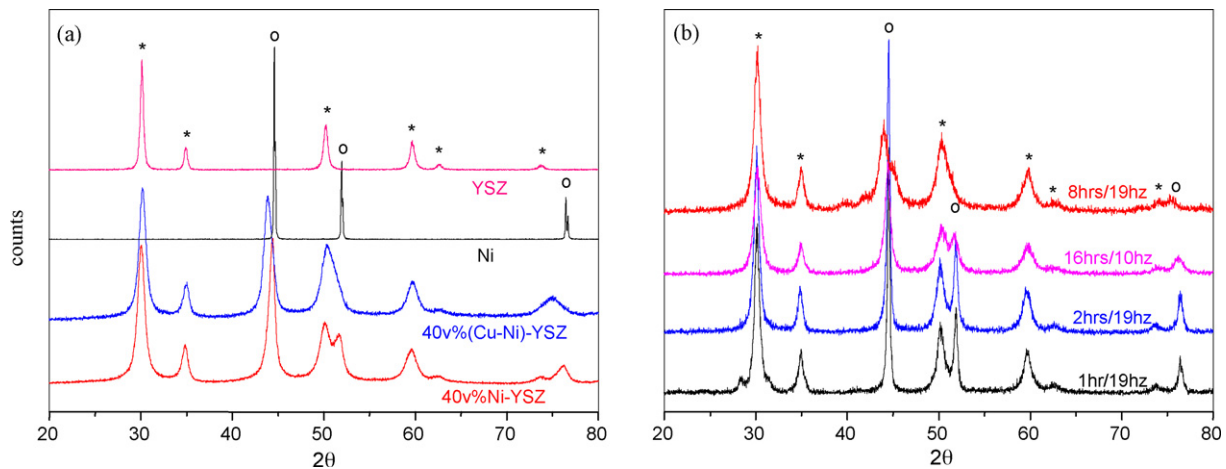


Fig. 1. X-ray diffraction profiles: (a) 40 vol% Ni-YSZ and 40 vol%(Cu-Ni)-YSZ processed by MA for 2 h; (b) 40 vol% Ni-YSZ powders processed by MA for different periods; (\*) YSZ and (°) Ni.

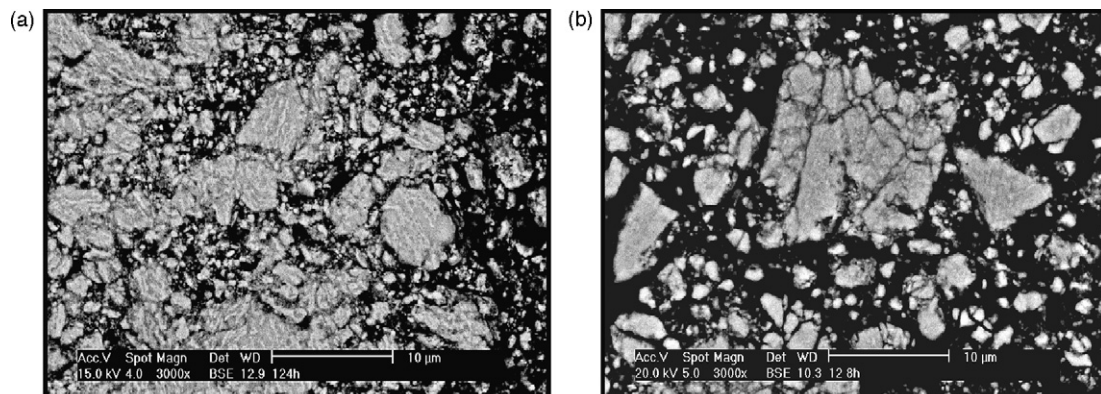


Fig. 2. SEM-BSE images of 40 vol% Ni-YSZ powders milled for 4 h (a) and 8 h (b).

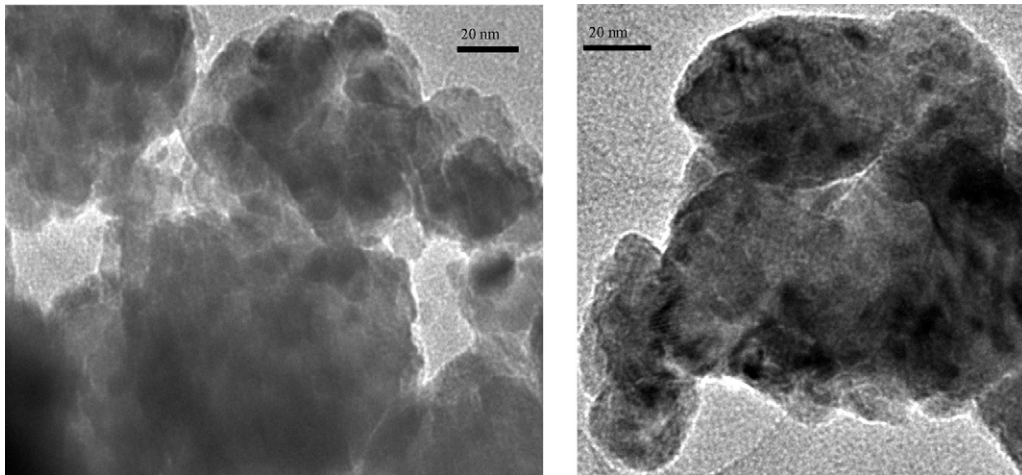


Fig. 3. TEM images of Ni-YSZ powders processed for 2 h by MA.

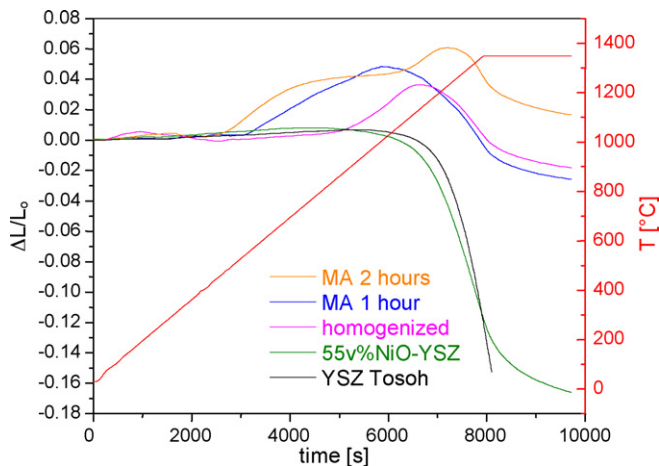


Fig. 4. Dilatometric curves of 40 vol% Ni-YSZ, NiO-YSZ and YSZ cermets measured in air.

the retraction onset temperature of these samples diminished as the MA processing time increased. For a simple homogenized sample, the onset temperature was about 1120 °C, while MA samples milled for 1 and 2 h showed onset temperatures of 990 and 860 °C, respectively. This behavior demonstrates the ability of MA processing to enhance sintering at lower temperatures by

refining particles and promoting dispersion. It should be noted that the NiO-YSZ ceramic densified extensively upon the porous material required for anode application.

Further dilatometric analyses were conducted under argon and hydrogen atmospheres, as indicated in Fig. 5(a), which no longer shows oxidation-related expansion. The general behavior was similar, i.e., the longer the milling time and hence, the delivered energy, the lower the initial sintering temperature, with the process tending to occur in two steps. Fig. 5(b) shows a detailed curve for a sample processed for 8 h by MA, indicating the shrinkage rate. The plot indicated that the initial sintering temperature occurred at 195 °C in an argon atmosphere. Raising the temperatures accelerated the densification rates, allowing liquid phase sintering to take place. In each case, total densification was inhibited compared to the YSZ and NiO-YSZ samples. The literature [5] reports that metallic Ni sintering is inhibited in the presence of thin ceramic particles, as in the case of reinforced cermets. In contrast, very thin and highly deformed Ni particles are reported to bring on sintering at temperatures below 200 °C [6,7]. The balance between these effects may explain the actual behavior during the sintering process. Our X-ray diffraction analysis of sintered pellets identified ZrC (JCPDS 35–0784) and CuZrO<sub>3</sub> (JCPDS 43–0953) compounds, as well as Ni and YSZ (Fig. 6).

Fig. 7 shows Arrhenius plots obtained by SID for pressed Ni-YSZ and Cu/Ni-YSZ pellets of MA powders milled for 8 and 2 h, respectively. The activation energy for sintering was greatly reduced for

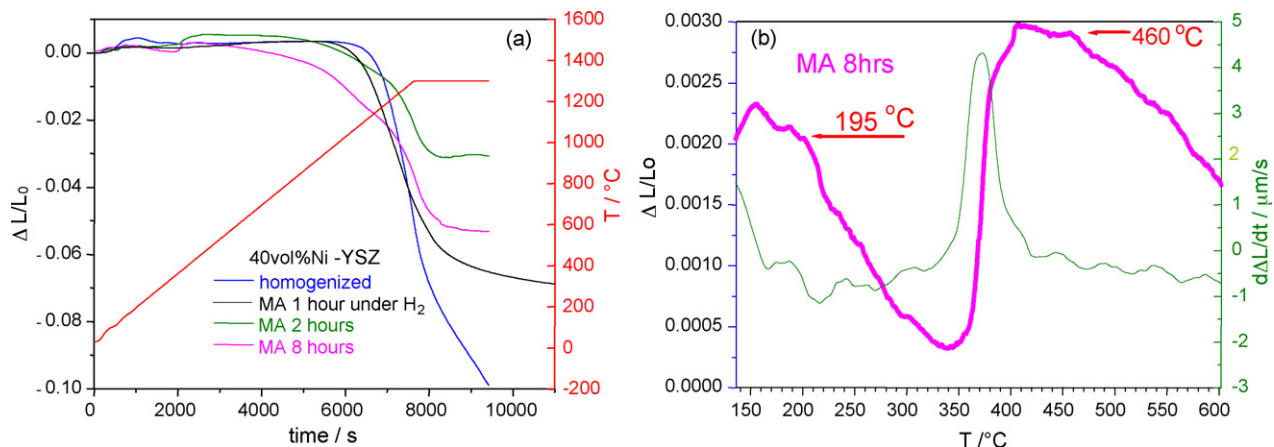
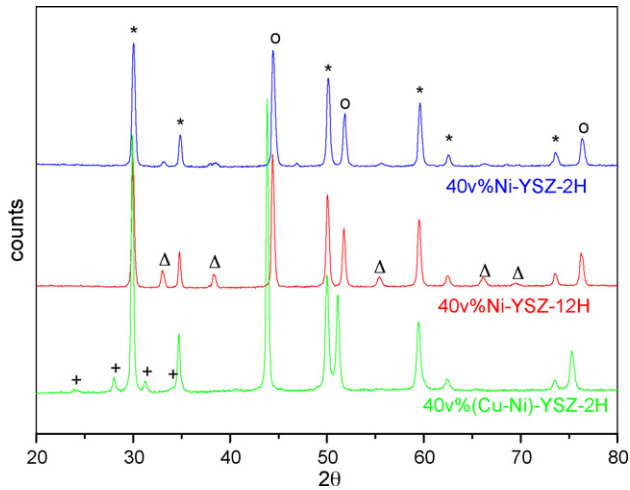


Fig. 5. Dilatometric curves (a) under argon (H<sub>2</sub>); (b) detail of 8 h MA curve showing the shrinkage rate profile  $d\Delta L/dt$ , temperature scale.



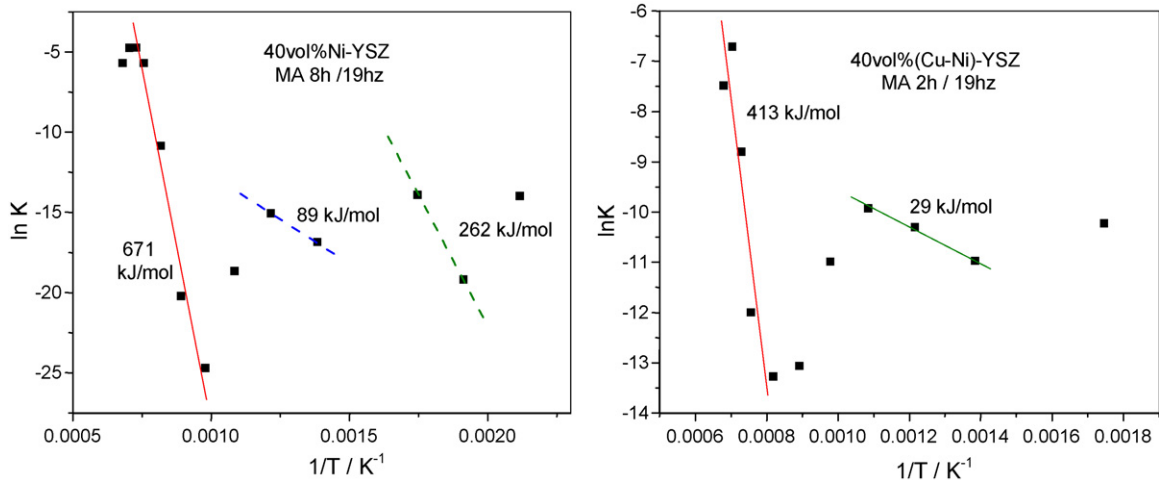
**Fig. 6.** X-ray diffractograms for sintered samples: (\*) YSZ, (°) Ni, (+) CuZrO<sub>3</sub>, and (Δ) ZrC.

Cu-containing material, suggesting the process was favored. The two distinct activation energy values and slopes revealed by our SID analysis provided new evidence to support the assumption of a 2-step sintering process, since the metallic constituents began to sinter at low temperatures while the process was controlled by zirconia starting at around 750 °C. The latter finding indicates a substantial reduction of the normal YSZ sintering temperature (950 °C, Fig. 4). The final pellet densities for all the materials fell

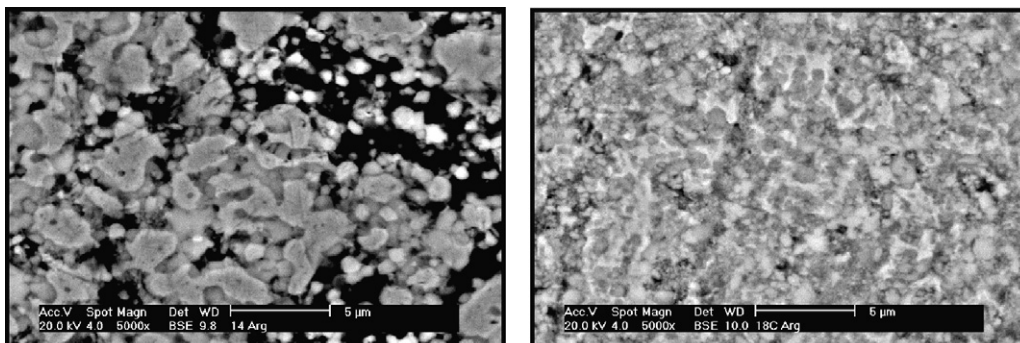
within a range of 65–75% TD (theoretical density), which satisfies the required range for SOFC anodes with well distributed porosity and phases. It should be noted the highest density (75% TD) was attained by the Cu-doped Ni-YSZ cermet.

Fig. 8 shows SEM backscattered images of microstructures of pellets sintered at 1300 °C/1 h. The Ni-rich (dark-gray) and YSZ-rich (white-gray) phases were both continuous and beneficial for electron and ion percolation. The microstructure of the Cu-containing material was clearly finer and of higher density, thus allowing for lower sintering temperatures. The phase boundary morphology indicated that the liquid phase sintering phenomenon took place owing to the lower melting point of Cu and the formation of eutectic Ni-C due to carbon pickup.

The literature offers very few examples of MA processing to prepare powders for SOFC anodes. One research group [8–10] studied the mechanical alloying of Ni/YSZ and Cu/YSZ powders followed by 900 °C annealing, aiming to develop cathode materials for high-temperature electrolysis of water vapor. Unlike the present work, their X-ray profiles did not change with longer milling times, nor did the particle size decrease under dry milling conditions. This fact suggests that the MA process examined in the present study was far more energetic, since it was able even to cause amorphization of the powder. Wilkenhoener et al. [11] reported the nonhomogenization of MA Ni/YSZ with a Ni content exceeding 20 vol%, which did not reach the percolation threshold for SOFC anodes. The high energy milling preparation method was investigated using NiO and YSZ as starting powders [12]. In this case, actual anode cermet pellets, i.e., containing metallic Ni, were obtained after 4 h of reduction under hydrogen.



**Fig. 7.** Arrhenius plots based on SID data for the study of sintering kinetics.



**Fig. 8.** SEM micrographs of sintered pellets: Ni-YSZ (left) and Cu/Ni-YSZ (right).

Well homogenized and finely microstructured powders and sintered pellets are successfully obtained by the present MA method with high energy transfer rates from vibratory mills. The sintering kinetics were determined for the first time, suggesting mechanisms in which both the ceramic and the metallic constituents control sintering in different steps, each one having its own network of particles. Cu-containing Ni/YSZ material can be sintered to the desired theoretical density at temperatures up to 1200 °C, presenting a much finer microstructure, and this finding is the most significant contribution. The newly developed method dispenses with pore-forming additives and reduces number of processes, directly yielding the metallic cermet.

#### 4. Conclusions

High energy milling (MA) of metallic Ni and YSZ powders leads to particle refinement and high deformation of metallic constituents, yielding homogeneous powders with a lamellar structure, which tends to be refined by longer processing times. The pellets obtained from such powders can be sintered at lower temperatures than simple homogenized pellets, while the total densification is lower. Conventional sintering studies as well as sintering kinetics by SID demonstrated that densification occurs in a 2-step process: Ni(Cu) sintering at low temperature (195 °C), followed by YSZ sintering starting from 750 °C. The addition of copper reduces the activation energy for sintering and leads to a refined microstructure. Preparation of Ni(Cu)-YSZ cermets by MA and SAS appears to be a promising route for the production of SOFC anodes with good properties and performance.

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