Synthesis and Thermal Properties of Ni-Alloy/Al_2O_3 Cermets for Interconnector Materials in Solid Oxide Fuel Cells

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ABSTRACT

Ni-alloy/Al_2O_3 cermets are considered for interconnector materials of solid oxide fuel cells. In this study the sintering behaviour of cermets and their thermal expansion in dependence upon the Al_2O_3 content were investigated. Sintering in vacuum at 1340°C gave samples with a relative density up to 95.5%. Thermal expansion coefficients were calculated from expansion curves of various cermet compositions. Cermets with high metallic content showed only small deviations from coefficients calculated from the rule of mixtures, whereas cermets with higher Al_2O_3 contents showed significantly lowered thermal expansion coefficients ranging from 10 x 10^{-6}/K down to 8.3 x 10^{-6}/K for pure Al_2O_3.

1. INTRODUCTION

Solid oxide fuel cells (SOFCs) directly convert chemical into electrical energy without losses of thermal heat or mechanical energy /1/. Their electrochemical active part consists of a dense electrolyte, separating the porous anode and cathode. These three components form one single cell. The cells are connected in series by interconnectors. The interconnector plates also separate the air and the fuel gas compartments. Besides high temperature corrosion resistance at operating temperatures up to 950°C matching of the thermal expansion coefficients (TEC) of the components is one of the main requirements. Nickel-superalloys are known for their excellent corrosion resistance but possess TECs too high for the use as interconnectors in combination with the other materials actually used in SOFCs. Because ceramics normally possess lower TECs than metals a combination of an electrical conducting nickel-based alloy and alumina seems promising /2/.

2. EXPERIMENTAL

Spherical Ni80Cr20 powder with particle sizes of 5-22 µm (VALCO 3001, Valco GmbH) and α-Al_2O_3 with an average particle size of 0.22 µm (TM-DAR, Taimei Chemicals Co.) were used as starting powders. This Al_2O_3 powder shows a high sintering activity. Different compositions of Al_2O_3 and Ni80Cr20 were mixed with 0.5 weight% polyvinyl acetate (Vinnapas B5, Wacker) as binder and acetone. After drying, specimens were uniaxially pressed applying pressures between 100 and 1500 MPa. Afterwards the specimens were sintered in vacuum for 5 h at temperatures between 1250 and 1340°C. The binder was removed during the same heat treatment.

For dilatometry a high-temperature push-rod dilatometer was used (DIL 402 E, Netsch) calibrated with a sapphire single crystal and a rod of Ni80Cr20 alloy. Thermal expansion curves were recorded on specimens of 28 x 5 x 5 mm with mechanically polished faces between room temperature and 1100°C in flowing Ar/4% H_2 atmosphere. The gas tightness was measured using a two-chamber apparatus in which the two gas volumes were separated by the sample. After evacuation, one volume was filled with helium at a pressure of 200 mbar, on the other side the increase of pressure after 120 s was measured. Relative densities were determined geometrically.

3. RESULTS and DISCUSSION

Relative densities up to 95.5 % of the theoretical density were attained after sintering at 1340°C for samples of 50 vol% Al_2O_3. The dependence of the relative density as a function of sintering temperature is shown in Figure 1. While the density increases

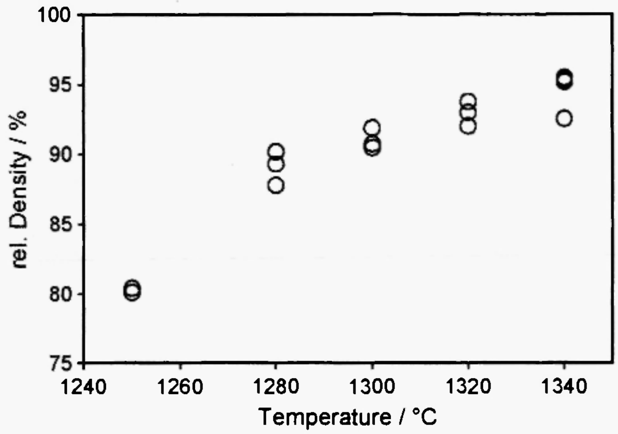

Fig. 1: Relative densities of samples with 50 vol% Al_2O_3 and 50 vol% Ni80Cr20 after sintering in dependence upon the sintering temperature. The pressure of uniaxial pressing was 450 MPa. Sintering was performed in vacuum.

significantly with raising temperature, partial melting of the Ni-alloy prevents the application of higher sintering temperatures. The dependence upon the pressure of uniaxial pressing is presented in Figure 2. With increasing pressure the relative green densities rise up to 75 % for a composition of 50 vol% Al_2O_3. This also effects the density after sintering up to a pressure of 500 MPa. Higher pressures do not improve the density any more.

Although the densities of the cermets are relatively high, the gas tightness for their use as interconnectors might not be sufficient. Measurements of the gas tightness by the leakage of helium showed a strong reduction of leakage with increasing geometrical densities as expected. However, even samples with 95.5% relative density at a composition of 50 vol% Al_2O_3 and 50 vol% Ni80Cr20 still showed a leakage of 8×10^{-9} mol / s cm^2, as shown in Figure 3.

High Ni80Cr20 contents raise the relative density

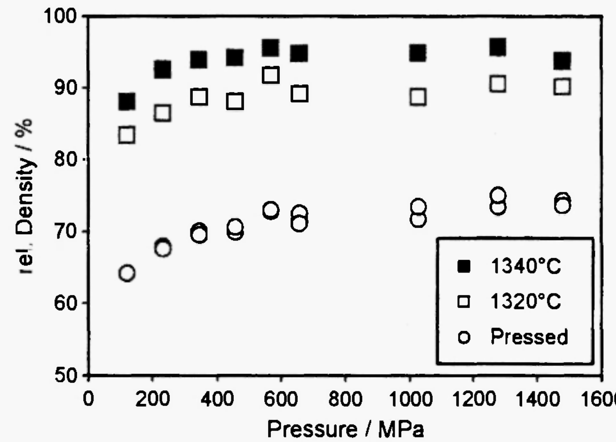

Fig. 2: Relative densities of samples of 50 vol% Al_2O_3 and 50 vol% Ni80Cr20 in dependence upon the pressure of uniaxial pressing. Values are given for pressed specimens and for the same specimens after sintering at 1320°C and 1340°C in vacuum.

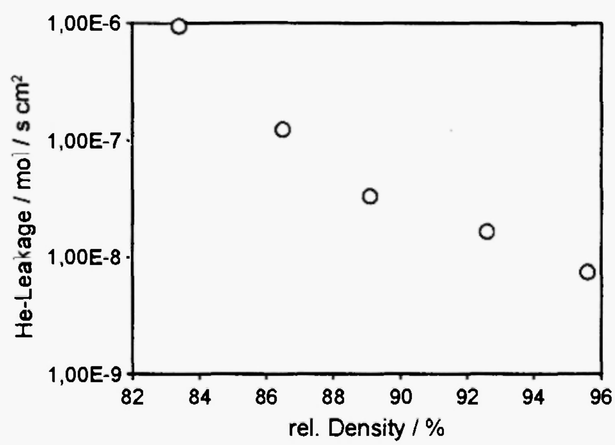

Fig. 3: Helium leakage as a function of the geometrical density for samples of 50 vol% Al_2O_3 and 50 vol% Ni80Cr20. Specimens with differences in the relative density of about 2 % were taken for the measurements. The used pressure difference was 200 mbar.

after uniaxial pressing with 450 MPa significantly due to the ductility of the metal. While a sample of pure Al_2O_3 shows a relative density of less than 60 %, Ni80Cr20 is densified to 75 %. However, figure 4 shows that the positive influence of higher green densities on the sintered density (Fig. 2) is

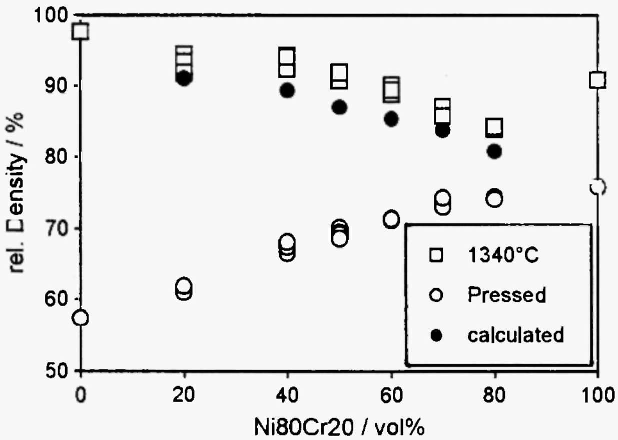

Fig. 4: Relative densities of Ni80Cr20- Al_2O_3 cermets in dependence upon the Ni80Cr20 content. For uniaxial pressing 450 MPa were applied. Specimens were sintered at 1340°C. The calculated values were attained using the rule of mixtures for the shrinkage (assuming the shrinkage of Ni80Cr20 inclusions as 0 %) and the pressed densities.

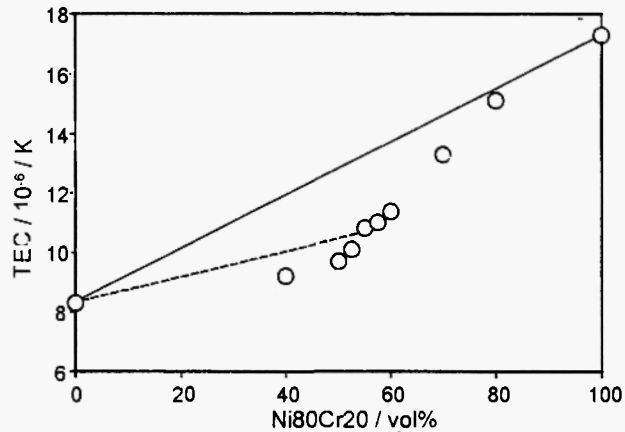

Fig. 5: Linear TEC data between 30 and 1000°C ($\alpha_{30\text{-}1000°C}$) for various compositions in the system Al_2O_3-Ni80Cr20. Specimens were pressed with 380 MPa and sintered at 1340°C. For comparison, the calculated α-values are inserted, following the rule of mixtures (—) and the formula given by Tummala and Friedberg /7/ (---).

overcompensated by the negative influence of the increasing amount of the Ni80Cr20. The nickel alloy behaves as a rigid inclusion for the alumina as described in /3/. The calculated values in Figure 4 were attained using the pressed densities and the rule of mixtures for the shrinkage. The linear shrinkage of the pure alumina was 17.1%, the shrinkage of the Ni80Cr20 inclusions was assumed as 0%. Scherer /4/ suggested the rule of mixture for volume fractions of the inclusions of less than 10%. However, it seems that even at high Ni80Cr20 contents the shrinkage of the alumina determines the densification.

With increasing content of the Ni-alloy the TEC increases as shown in Figure 5. The TECs are lower than calculated values following the rule of mixtures. The deviations are even higher than predicted by the well-known theoretical approaches of Kerner /5/ or Turner /6/. Only the theoretically derived formula for elastic spheres dispersed in a matrix continuum reported by Tummala and Friedberg /7/ gives a reasonable agreement in the Al_2O_3-rich part of Figure 5.

4. CONCLUSIONS

Cermets of Ni80Cr20 and alumina might be suitable interconnector materials in SOFCs. Their advantage is the adjustable thermal expansion coefficient to other SOFC materials. Even if alternative materials for new SOFC concepts are used it seems easy to adapt the interconnector to the modified conditions. Nevertheless some problems are still unsolved: On the one hand the dependence of the density upon the sintering temperature of the examined cermets was shown to be strong. On the other hand Ni-alloys possess low melting temperatures. Therefore the range of the sintering temperature to realise high density without melting of the metal is very small. To achieve higher gastightness than 8×10^{-6} mol / s cm^2 the application of other processing methods than pressureless sintering might be necessary.

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