Technion – Israel Institute of Technology
Department of Materials Science & Engineering

Structure and Energy of the Equilibrated Ni-YSZ Solid-Solid Interface

Russell Berrie Nanotechnology Institute
המכון לננוטכנולוגיה ע"ש ראסל ברי

Hadar (Bratt) Nahor, Hila Meltzman and Wayne D. Kaplan
Department of Materials Science and Engineering, Technion , Haifa, Israel

Introduction

The stability of metal films on oxide surfaces is important for the performance of devices such as solid oxide fuel cells (SOFCs) and thermal barrier coatings (TBCs) [1,2,3]. Ni-YSZ serves as an anode material in SOFCs, where the three-phase boundaries (Ni/YSZ/fuel-gas) are essential for catalytic activity which controls the electrical properties.

The only data found in the literature concerning the Ni- ZrO_2 interface energy is for liquid-solid interfaces, i.e. liquid Ni in contact with solid c-ZrO_2, rather than solid-solid interfaces. Mantzouris et al. reported a liquid-solid Ni-8YSZ interface energy of 1.793 J/m^2 based on contact angle measurements at 1500˚C in Ar-4%H_2, between liquid Ni and polycrystalline 8YSZ [4]. Nikolopoulos et al. suggested a semi-empirical approach by which the interface energy of a polycrystalline solid oxide in contact with liquid metals can be calculated based on the values of the surface energy of the oxides and the liquid metals [5]. According to this approach the calculated value of the interface energy between polycrystalline cubic 5%-CaO-ZrO_2 and liquid Ni at T_m of Ni is 1.624 J/m^2. Furthermore, Nikolopoulos et al. suggested a linear temperature function of the interface energy between polycrystalline ZrO_2 and liquid Ni, according to which, the interface energy at the T_m of Ni is 1.668 J/m^2 [6].

The orientation relationship (OR) observed in the literature was $Ni[1\bar{1}0](111) \parallel YSZ[1\bar{1}0](111)$ [7].

In this work, agglomeration of a thin Ni film ("solid state dewetting") on YSZ substrates was carried out to form equilibrated Ni-YSZ interfaces. The shape of the Ni crystals was determined and the interfacial structure was investigated using high resolution scanning and transmission electron microscopy (HRSEM, HRTEM). The solid-solid interfacial energy was determined using Winterbottom analysis.

Experimental Methods

Dewetting Experiments

YSZ substrates (99.99%) with a surface parallel to (111) and to (001) were provided by MaTeck Material Technology & Crystal GMBH. The polished substrates were ultrasonically cleaned in acetone and ethanol. A ~150 nm thick Ni film was deposited on the substrates by e-beam evaporation. After deposition, solid-state dewetting was conducted at 1350˚C (0.94 T_m of Ni) in Ar+H_2 99.9999%, at $P(O_2)=10^{-20}$ atm for 6 hr.

Characterization

High resolution scanning electron microscopy (HRSEM; Ultra Plus: Zeiss) was used to examine the morphology and the relative orientation of the equilibrated Ni particles.

Transmission electron microscopy (TEM) and aberration-corrected high resolution transmission electron microscopy (HRTEM) were used to characterize the Ni free surface, to determine the interface plane, and the OR between the Ni particles and the YSZ substrate.

A dual beam focused ion beam (FIB) equipped with a nano-manipulator was used for preparation of TEM specimens from the center of particles with a known morphology and orientation using the "lift out" technique [8,9].

Results and Discussion

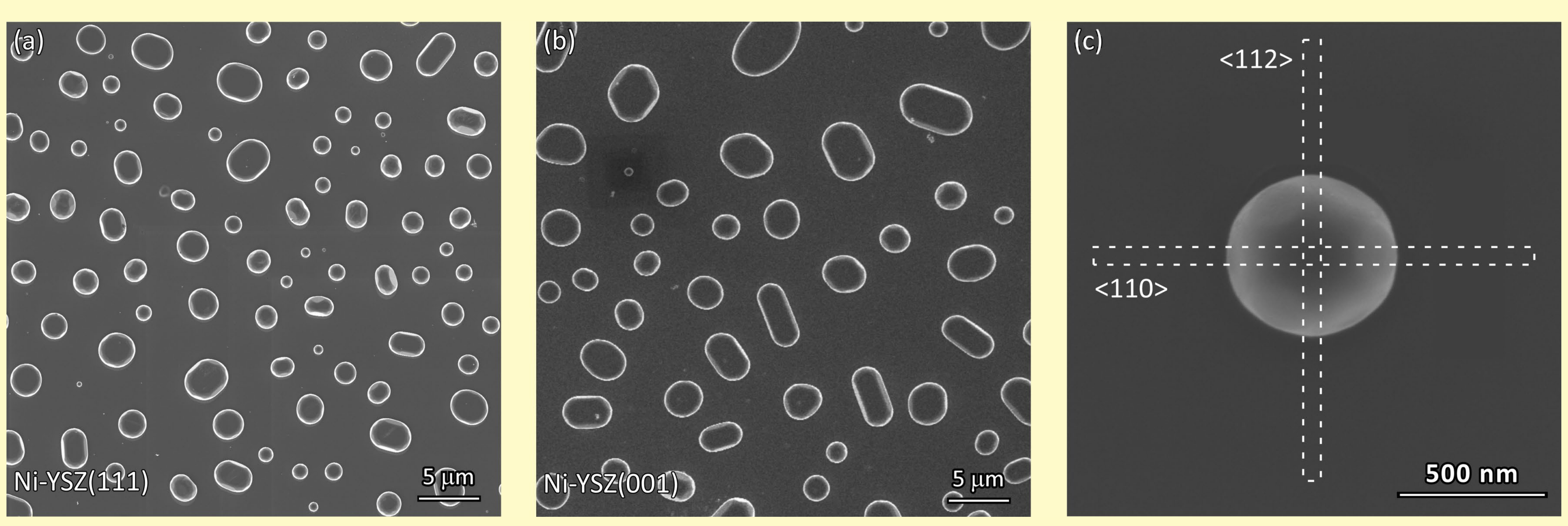

Figure 1: (a,b) Secondary electron HRSEM micrograph of Ni particles on (111) and on (001) YSZ substrates. Most of the particles are oriented with the (111) plane parallel to the substrate surface. It seems that the dewetted Ni particles are distributed in a more sparse way on the (001) than on the (111) YSZ substrate. It is clear that not all the particles reached equilibrium. Only equilibrated particles were investigated. (c) HRSEM micrograph of an equilibrated single-crystal Ni particle on the (111) substrate, oriented with the (111) plane parallel to the substrate surface. The dashed rectangles indicate the locations and directions of FIB sectioning.

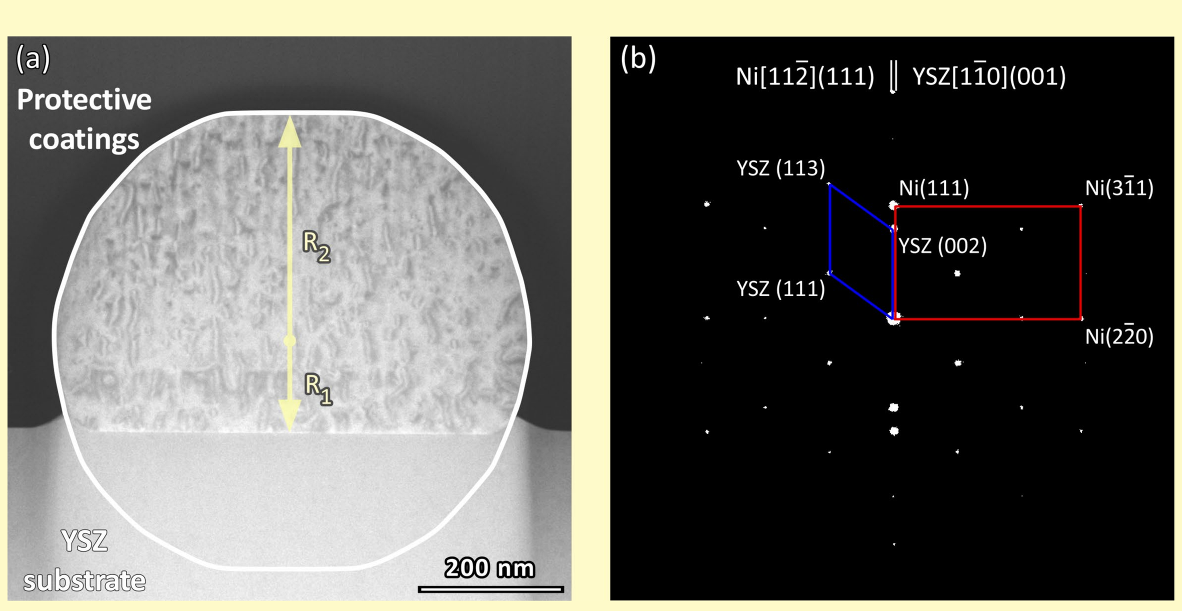

Figure 2: (a) HAADF STEM micrograph of an equilibrated Ni particle on (001) YSZ substrate, along the <112> projection of Ni. The Wulff shape (white line) is indicated. (b) SAD pattern of the equilibrated particle in contact with the YSZ substrate, demonstrating the low index OR which exist at equilibrium: $Ni[11\bar{2}](111) \parallel YSZ[1\bar{1}0](001)$.

The solid-solid interfacial energy was determined using Winterbottom analysis. The absolute surface energies taken from the literature were: $\gamma_{YSZ(111)}=1.232$ J/m^2 [10]; $\gamma_{Ni(111)}=2.05$ J/m^2 [11].

For $Ni[1\bar{1}0](111) \parallel YSZ[1\bar{1}0](111)$: $R_1/R_2 \approx 0.27 \rightarrow \gamma_{Ni\text{-}YSZ(111)(0^\circ)} = \mathbf{1.8 \pm 0.1}$ $\mathbf{J/m^2}$ [12]

For $Ni[\bar{1}10](111) \parallel YSZ[1\bar{1}0](111)$: $R_1/R_2 \approx 0.40 \rightarrow \gamma_{Ni\text{-}YSZ(111)(180^\circ)} = \mathbf{2.1 \pm 0.1}$ $\mathbf{J/m^2}$ [12]

For $Ni[11\bar{2}](111) \parallel YSZ[1\bar{1}0](001)$: $R_1/R_2 \approx 0.40 \rightarrow \gamma_{Ni\text{-}YSZ(001)} = \mathbf{2.1 \pm 0.1}$ $\mathbf{J/m^2}$

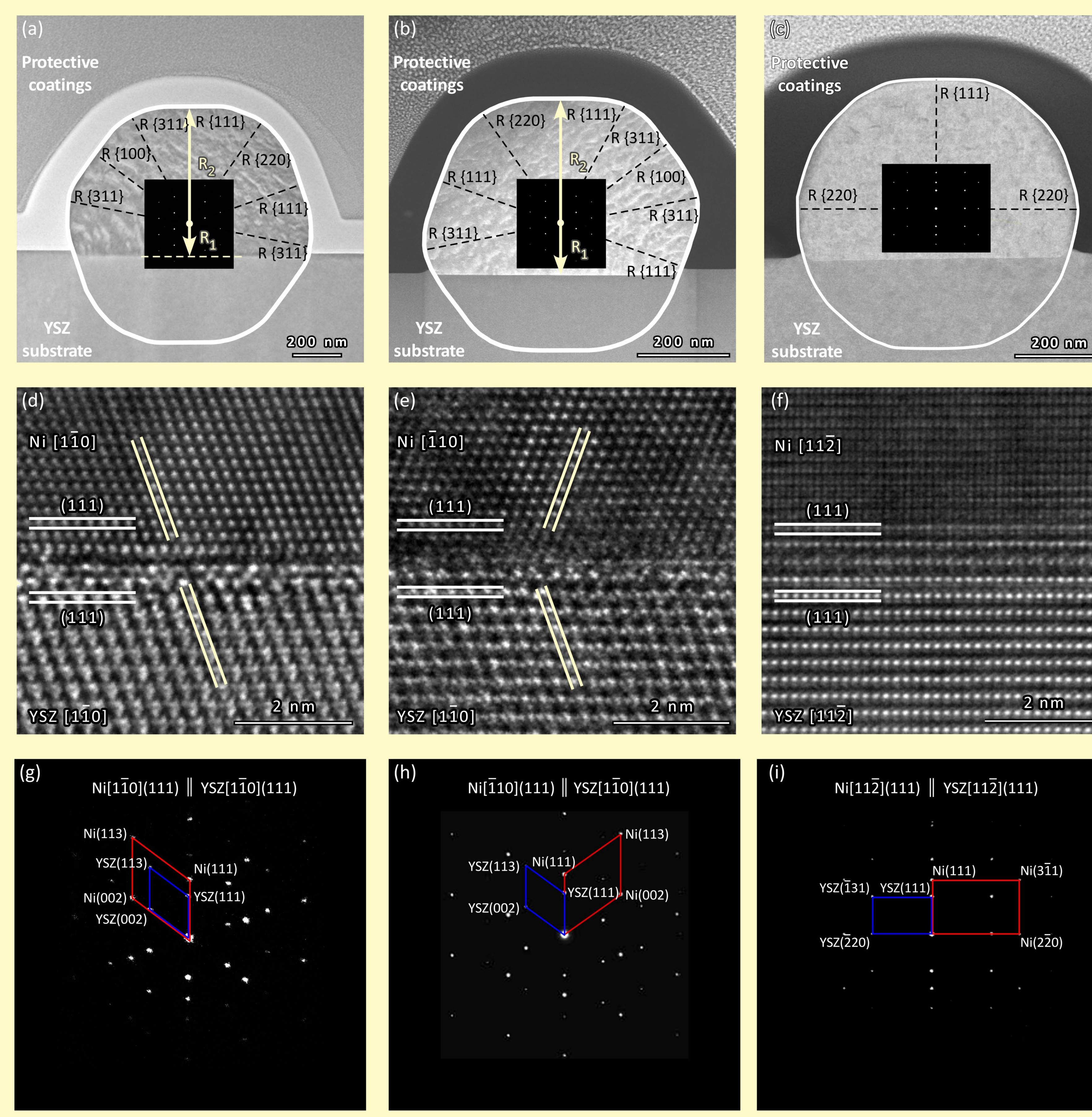

Figure 3: (a,b,c) Bright field TEM micrograph (a) and HAADF STEM micrographs (b,c) of an equilibrated Ni particle on (111) YSZ substrate, along the <110> projection (a,b) and the <112> projection of Ni (c). The insets present SAD patterns of the Ni particle. The Wulff shape (white line), and distances from the Wulff point to the {hkl} facets (dotted lines, marked as R {hkl}) are indicated. (d,e,f) HRTEM micrographs acquired from the interface region of the particles in (a,b) and (c). (g,h,i) SAD patterns of the equilibrated particles in contact with the YSZ substrate, demonstrating the low index ORs which exist at equilibrium [12]: $Ni[1\bar{1}0](111) \parallel YSZ[1\bar{1}0](111)$ (0˚) and $Ni[\bar{1}10](111) \parallel YSZ[1\bar{1}0](111)$ (180˚).
For the OR observed from the <112> projection , 180˚ rotation about the interface normal cannot be detected.

Summary and Conclusions

- The orientation relationships observed between the Ni particles and the YSZ substrates are: $Ni[1\bar{1}0](111) \parallel YSZ[1\bar{1}0](111)$, $Ni[\bar{1}10](111) \parallel YSZ[1\bar{1}0](111)$ and $Ni[11\bar{2}](111) \parallel YSZ[1\bar{1}0](001)$.
- The measured solid-solid Ni-YSZ(111) interfacial energy at equilibrium was found to be slightly different for each OR: $\gamma_{Ni\text{-}YSZ(111)(0^\circ)} = 1.8 \pm 0.1$ J/m^2 ; $\gamma_{Ni\text{-}YSZ(111)(180^\circ)} = 2.1 \pm 0.1$ J/m^2 ; $\gamma_{Ni\text{-}YSZ(001)} = 2.1 \pm 0.1$ J/m^2
- The atomistic structure and the interface chemistry must be investigated to understand the difference between the different ORs.
- The measured solid-solid Ni-YSZ interfacial energy is lower for the cube-on-cube OR on the (111) substrate than for the non cube-on-cube OR on the (001) substrate.
- As expected, the measured solid-solid Ni-YSZ interfacial energies are higher than the Ni-YSZ liquid-solid energies reported in the literature.
- The energy values measured in this work are slightly lower than the solid-solid Ni(111)-Al_2O_3(0001) interface energy measured by Meltzman et al. [13] at similar conditions: 2.16±0.07 J/m^2.

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