INVESTIGATION OF NOVEL ALLOY TiC-Ni-Ni$_3$Al FOR SOLID OXIDE FUEL CELL INTERCONNECT APPLICATIONS

(Preliminary Evaluation of TiC-Ni-Ni$_3$Al for DECISION POINT)

Topical Report

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ABSTRACT

Solid oxide fuel cell interconnect materials must meet stringent requirements. Such interconnects must operate at temperatures approaching 800°C while resisting oxidation and reduction, which can occur from the anode and cathode materials and the operating environment. They also must retain their electrical conductivity under these conditions and possess compatible coefficients of thermal expansion as the anode and cathode. Results are presented in this report for fuel cell interconnect candidate materials currently under investigation based upon nano-size titanium carbide (TiC) powders. The TiC is liquid phase sintered with either nickel (Ni) or nickel-aluminide (Ni_3Al) in varying concentrations. The oxidation resistance of the submicron grain TiC-metal materials is presented as a function weight change versus time at 700^oC and 800°C for varying content of metal/intermetallic in the system. Electrical conductivity at 800°C as a function of time is also presented for TiC-Ni to demonstrate the vitality of these materials for interconnect applications. TGA studies showed that the weight gain was 0.8 mg/cm^2 for TiC(30)-Ni(30wt.%) after 100 hours in wet air at 800^oC and the weight gain was calculated to be 0.5205 mg/cm^2 for TiC(30)- Ni(10 wt.%) after 100 hours at 700^oC and 100 hours at 800^oC. At room temperature the electrical conductivity was measured to be 2444 1/[ohm.cm] for TiC-Ni compositions. The electrical conductivities at 800^oC in air was recorded to be 19 1/[ohm.cm] after 125 hours. Two identical samples were supplied to PNNL (Dr. Jeff Stevenson) for ASR testing during the pre-decision period and currently they are being tested there.

Fabrication, oxidation resistance and electrical conductivity studies indicate that TiC-Ni-Ni_3Al ternary appears to be a very important system for the development of interconnect composition for solid oxide fuel cells.

EXECUTIVE SUMMARY

The material requirements for the interconnect are the most strict among the components of SOFCs, anode, cathode, electrolyte, and interconnect. Successful development of capable and affordable interconnect is vital to the commercialization of SOFC operating at temperatures lower than 1000°C. Therefore, the new materials or composites that are competent of meeting the exacting requirements of interconnect component needed to be developed.

Doped chromites do not satisfy many of the requirements for SOFC applications. They are difficult to sinter at temperatures less than 1750°C and in oxidizing conditions [1]. Sr-doped $LaCrO_3$ is the state of the art interconnect material for SOFC operating at temperatures ~1000°C because of its relatively high electronic conductivity and its stability under the operating conditions. However, its major disadvantages include reduction in electrical conductivity at low oxygen pressures [2] and difficulty of processing under conditions suitable for other cell components. The latter is the most critical since both the Y-stabilized ZrO_2 (YSZ) electrolyte and the Sr-doped $LaMnO_3$ (LSM) cathode sinter at relatively lower temperatures in air. The production of intermediate temperature SOFC require sintering of the cell components under the same conditions, it is therefore essential to develop a material that can be fabricated at lower temperatures and at low cost.

The present investigator's research results on $(La,Ca)(Cr,Co)O_3$ have shown that lanthanum chromite could be sintered at temperatures below 1400°C in air [3]. This was accomplished by Ca and Co substitutions on both A and B-sites of the lanthanum chromite lattice, respectively. However, $LaCrO_3$ based interconnects suffer from their extreme sensitivity to oxygen partial pressure, low electronic conductivity and high fabrication cost. Because of these issues, metallic interconnects have been investigated for the development of interconnects for SOFC operating at temperatures lower than 1000°C.

Chromia formed on the surface of chromium-based metallic alloys are intrinsically too volatile to be viable as interconnects for SOFCs operating at about 800°C [4]. Some intermediate phases occurring between iron-based interconnect and cathode significantly increase the contact resistance [4].

Our initial results in the $TiC-Ni-Ni_3Al$ system are showing that these materials are more suitable to solid oxide fuel cell interconnect applications than metallic alloys do. Because they are stable in reducing and oxidizing conditions at high temperatures, they have 100 % electronic conductivity in 10^6 S/cm range and their thermal expansion coefficient can easily be matched to that of other SOFC components. In addition to these properties, they can be fabricated at comparable cost using every processing methods which can be

applied to metals and ceramics (metallurgical processing such as melting, casting etc. or powder metallurgy methods, including CVD thin film methods) [5,6,7].

The proposed work will include the investigation of compositions within the ternary TiC-Ni-Ni$_3$Al system where exact thermal expansion match with other cell components is expected. The chosen compositions will be subjected to solid oxide fuel cell simulated gaseous environments and to extensive thermogravimetric and electrical conductivity studies under reducing and oxidizing conditions. Long term evaluations of the selected materials in fuel cell environment will be performed at PNNL. The investigations will result in development of a superior interconnect materials for SOFC. A summary of the properties of TiC, Ni and SOFC components is given in Table I [8,9,10,11,12,13,14,15,16].

Table I. Properties of TiC, Ni and SOFC Materials

Properties	TiC	Ni	Y-PSZ	LSM	LSC
Density, g/cm3	4.92	8.9			
Melting Point, oC	3065	1454			
Thermal Conductivity, W/mK	17.2	80			
Thermal Expansion Coeff. (1/^{o}C x 10^{-6})	7.4	13.3	10.30	12.4	11.10
Electrical Conductivity (ohm.m)$^{-1}$ x 10^6	1	11.8		low	very low

By investigating the alloy system based on TiC-Ni-Ni$_3$Al to develop a superior interconnect component for SOFCs will increase the competitive advantage of SECA Industrial Teams and the commercialization of the SOFC.

EXPERIMENTAL METHOD, RESULTS AND DISCUSSIONS

I. Oxidation Resistance Studies:

TiC prepared using the patented process [8,13] from 29.5wt%C-containing carbon coated precursor was mixed with 30wt% Ni and 30wt% Ni$_3$Al. PVP was used as a binder for the consolidation of these powders under approximately 8 tons uniaxial compression. Note that a measurement error resulted in some pellets being produced with 25wt% Ni and

25wt% Ni_3Al, which were processed and tested in the same manner as the correct 30wt% samples. The pressed pellets were sintered at 1500°C for two hours in flowing Ar with heating and cooling rates of 4°C/min. Pellets were cut and placed on an Al_2O_3 plate and heated to 800°C in flowing wet air for 100 hours; separate experiments were run for the 25wt% samples and the 30wt% samples. Comparison of pre- and post-test weight indicated a weight gain on all samples, though the 25wt% samples exhibited a much higher weight gain than the 30wt% samples. This indicates either a transition point in the behavior as a result of the composition or an irregularity between the two separate heating experiments. Further experiments are required to determine which is the case. The heated samples were cut and polished to examine the surfaces for oxidation. SEM and EDX of the heated samples were performed. The 25wt% samples, in addition to the higher weight gains shown in Table I had a thicker reaction layer on the surfaces. The reaction layers are shown in Figures 1 and 2 for the 30wt% samples and Figures 3 and 4 for the 25wt% samples. EDX spectra for each sample's surface layer are included with the micrographs. Comparing these spectra to the untested spectra shows that the low angle peak of Ti (as identified by the EDX software) in the tested samples was not present in the untested samples. The position of this peak corresponds, however, to oxygen as well, though whether the oxide is from reaction with Ni, Al, or Ti (as possible) is indeterminate as yet. Note that the presence of Al and Si peaks in samples which should not have them (none have Si and the Ni samples have no Al) is due to signal from the sample holder and/or to the polishing of the samples (SiC and Al_2O_3 media were used).

The 100 hour oxidation in wet air of the 30wt% Ni- and 30wt% Ni_3Al-containing samples was completed. Measured weight gains were minimal compared to 25wt% samples, with all results shown in Table I.

In the tested samples, there was notable closed and open porosity, though these areas were not imaged in the included micrographs. This porosity indicates that an in-depth investigation of the densification of these materials with the current proportions must be performed to develop fully-dense parts.

The weight gain of TiC-30Ni and TiC-30Ni_3Al samples was measured after 100 hours in wet air at 800°C. The weight gains were 0.24% and 0.77%, or 0.008 and 0.018 mg/mm^2, respectively. The oxide layer was imaged in the SEM. Precise composition of the oxide layer is indeterminate at present. It is believed that the oxide layer will be in the form of TiO_2 or NiO and in both situations they must be acting as a protective layer for oxidation.
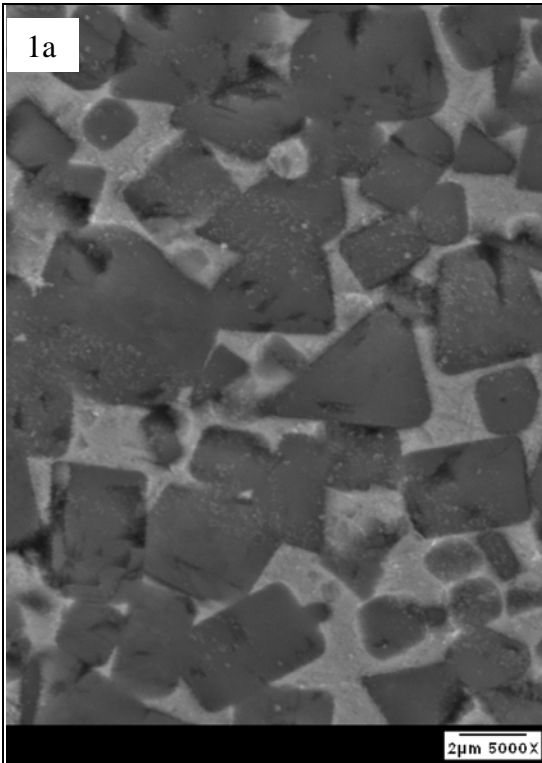
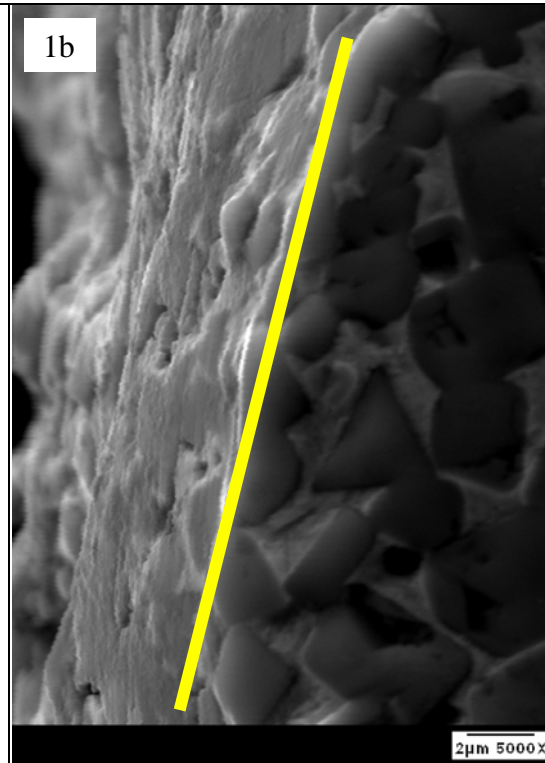Figure 1a. TiC-30Ni internal (polished) microstructure after oxidation

Figure 1b. TiC-30Ni oxidized and polished surfaces. Right of the line is the polished internal surface, left of line is oxidized surface. Grains (and open pores) are visible within the oxidized layer
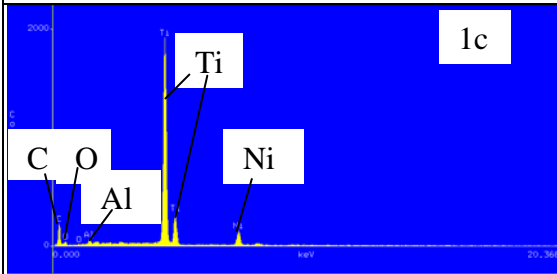
Figure 1c. EDX spectrum from TiC-30Ni sample surface after oxidation. Comparing this data with the untested spectrum shows that an oxygen (O) peak has appeared (left near the carbon (C) peak). Spectrum shows both Ti and Ni, though the latter appears similar to untested TiC grain spectrum. This might indicate that the surface layer is a titanium oxide and not a nickel oxide. Al peak is either from the sample holder or from the polishing media.
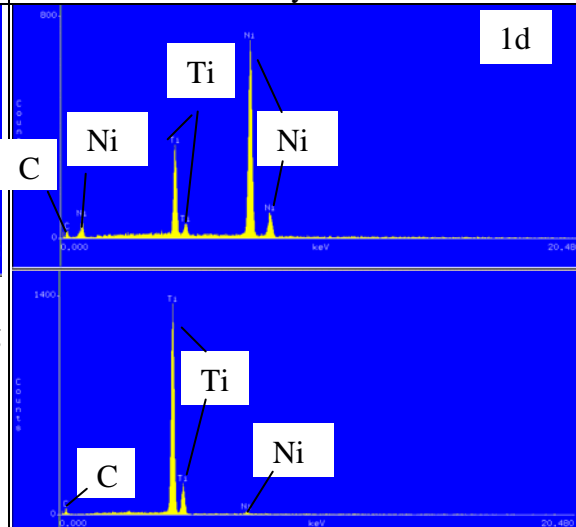
Figure 1d. EDX spectra from untested sample. Top spectrum is from Ni region, bottom spectrum from TiC grain.
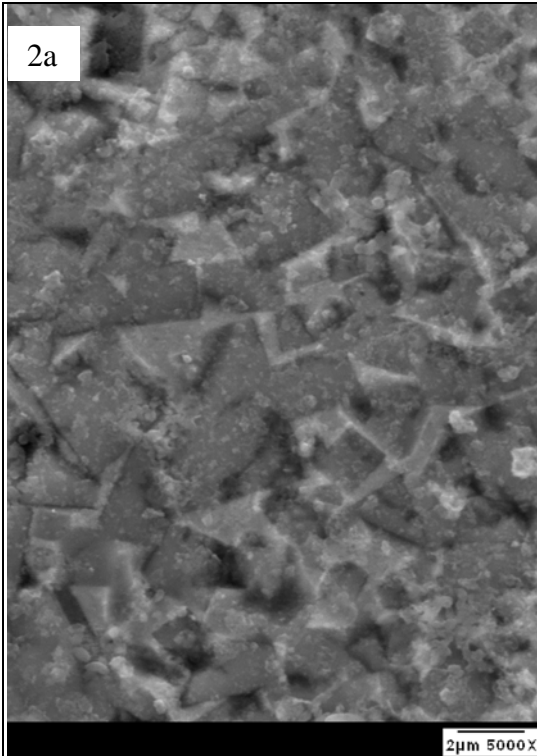
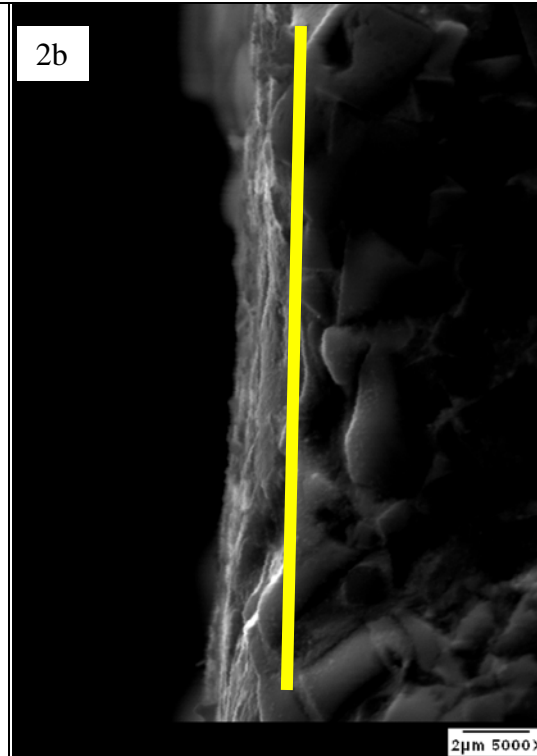Figure 2a. TiC-30Ni₃Al internal (polished) microstructure after oxidation

Figure 2b. TiC-30Ni₃Al oxidized and polished surfaces. Right of the line is the polished internal surface, left of line is oxidized surface. Grains (and open pores) are visible within the oxidized layer.
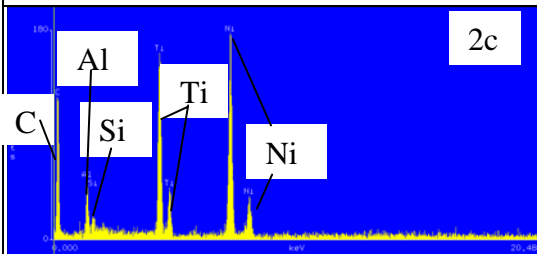

Figure 2c. EDX spectrum from TiC-30Ni₃Al sample surface after oxidation. Unlike the 30Ni sample, no oxygen (O) peak is apparent, indicating perhaps that the content is too low relative to the detected elements. The Al peak is expected, but of greater intensity than for the untested sample. This increased intensity, along with the detected Si peak, likely is due to the polishing media. As SiC was used, this might also explain the higher C peak intensity.
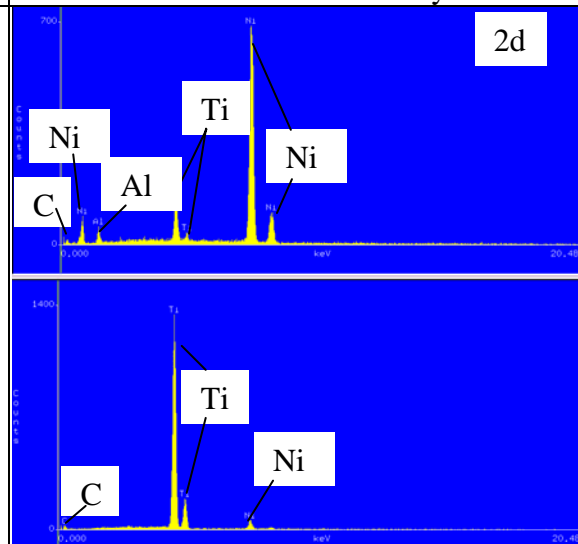

Figure 2d. EDX spectra from untested sample. Top spectrum is from Ni₃Al region, bottom spectrum from TiC grain.
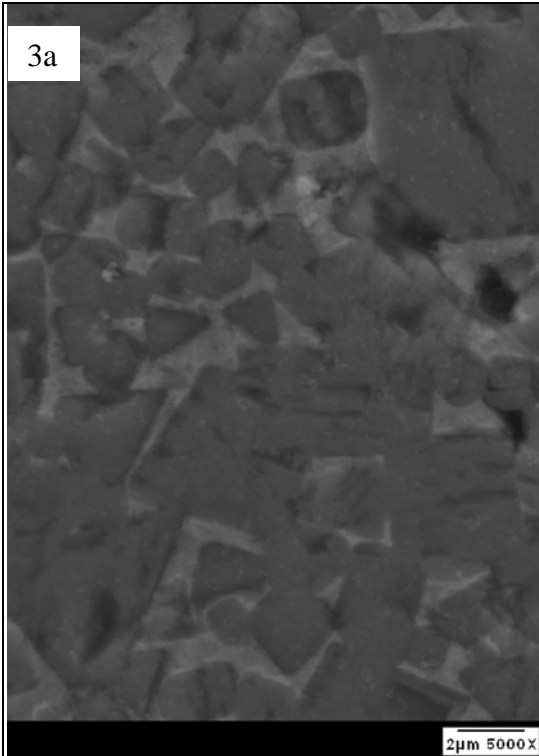
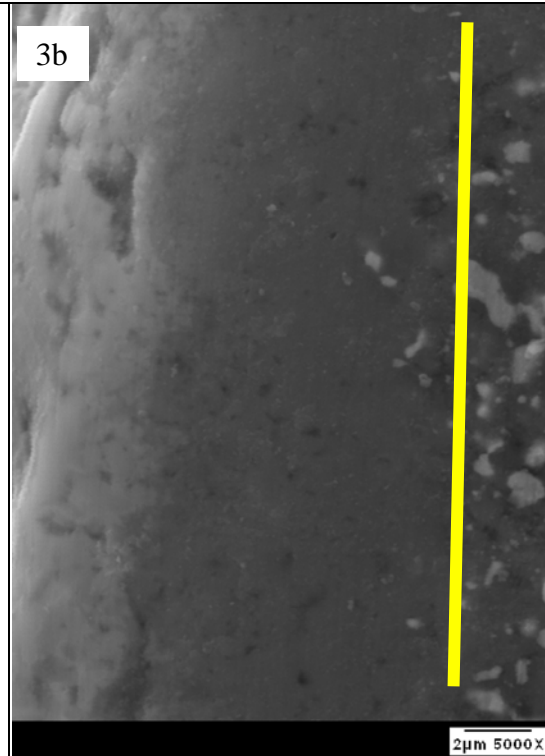Figure 3a. TiC-25Ni internal (polished) microstructure after oxidation

Figure 3b. TiC-25Ni oxidized and polished surfaces. Right of the line is the polished internal surface, left of line is oxidized surface. This layer is much thicker than that of the 30wt% Ni sample (Fig. 1b) after subjection to the same conditions.
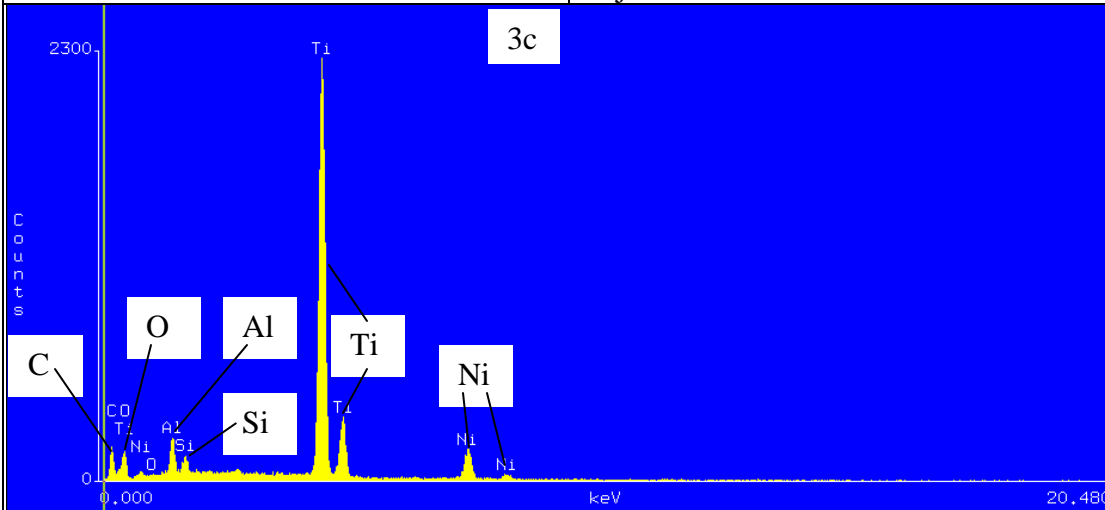

Figure 3c. EDX spectrum from TiC-25Ni sample surface after oxidation. Ti is the primary element present, with slight Ni detected. Again, the polishing media give rise to peaks from Al and Si. There is a more notable peak for O, at low keV. This might indicate that oxides of Ti are prevalent.
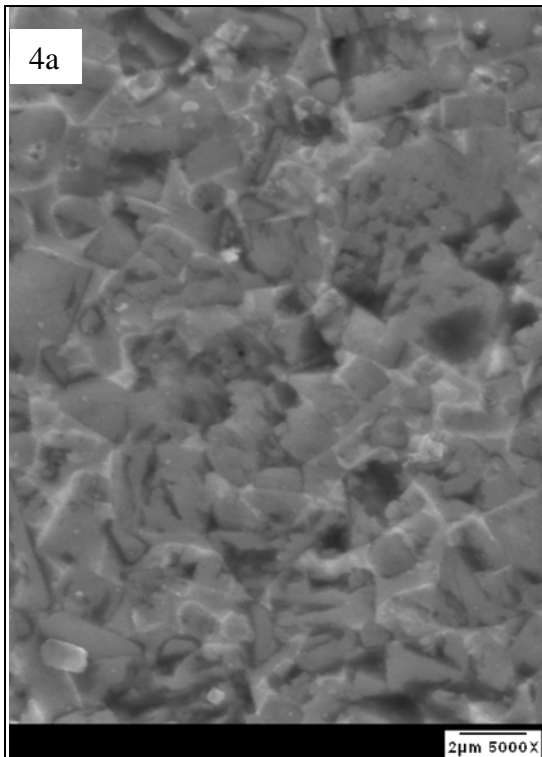
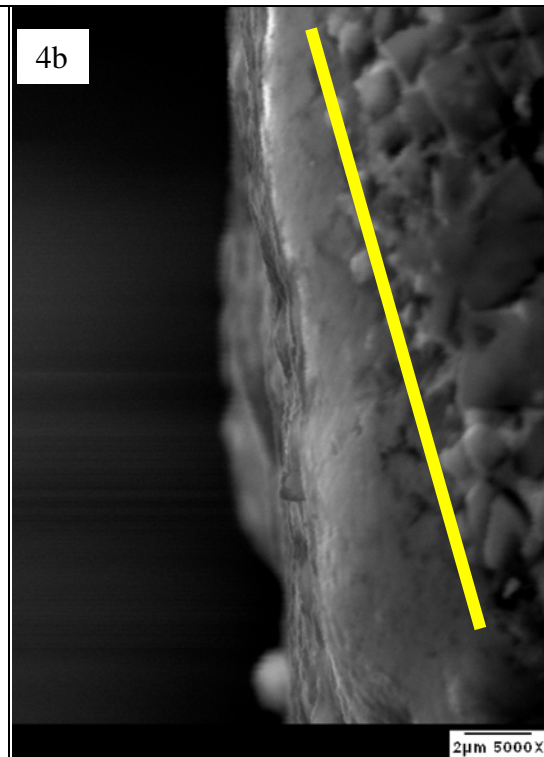Figure 4a. TiC-25Ni$_3$Al internal (polished) microstructure after oxidation

Figure 4b. TiC-25Ni$_3$Al oxidized and polished surfaces. Right of the line is the polished internal surface, left of line is oxidized surface. The oxide layer is approximately 1-2μm thick.
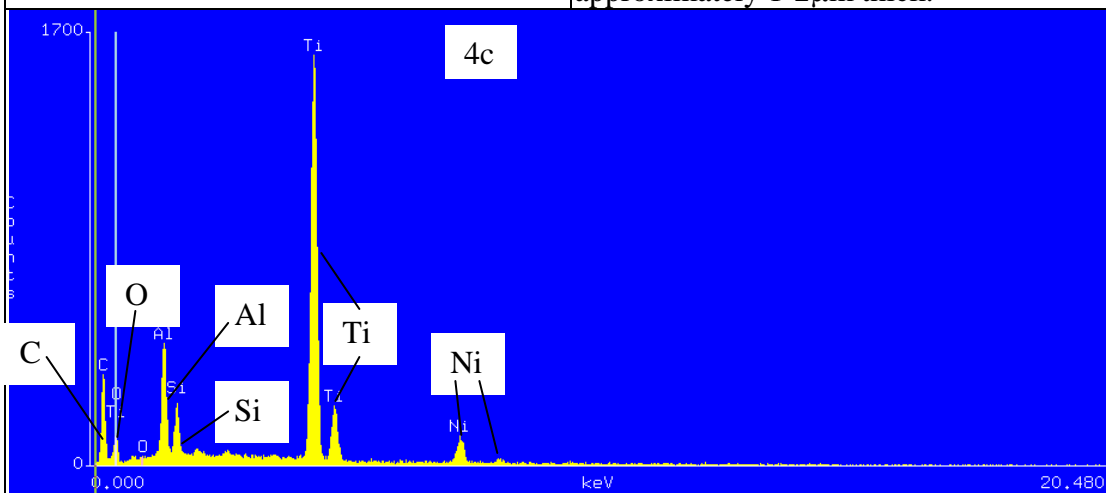

Figure 4c. EDX spectrum from TiC-25Ni$_3$Al sample surface after oxidation. Detected elements are similar to the 25Ni sample, save that the Al peak is of greater intensity, which correlates to the presence of Al in the intermetallic and not just from the polishing media. This indicates that for this sample, the oxide may be both Al and Ti oxides.
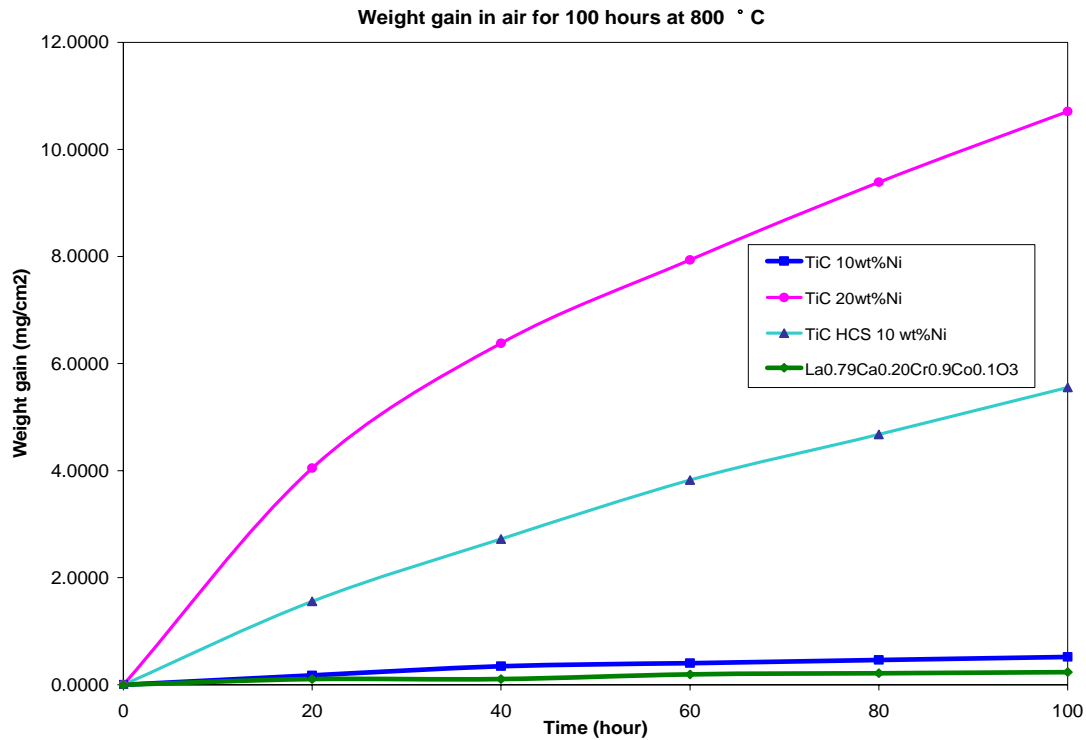
Table I. Weight gain of TiC-Ni and TiC-Ni3Al samples after 100 hours at 800°C in flowing wet air.

Sample composition	Weight gain (%)	Weight gain (mg/mm^2)
TiC-30wt% Ni	0.24	0.008
TiC-30wt% Ni$_3$Al	0.77	0.018
TiC-25wt% Ni	2.2	0.06
TiC-25wt% Ni$_3$Al	4.8	0.13

Table II. Weight gain in air for 100 hours at 800˚C (Results for La$_{0.79}$Ca$_{0.20}$Cr$_{0.9}$Co$_{0.1}$O$_3$ included for comparison).

	Materials	Weight gain after 20hr (mg/cm^2)	Weight gain after 40hr (mg/cm^2)	Weight gain after 60hr (mg/cm^2)	Weight gain after 80hr (mg/cm^2)	Weight gain after 100hr (mg/cm^2)
1	TiC 30C 10wt%Ni	0.1735	0.3470	0.4048	0.4627	0.5205
2	TiC 34C 20wt%Ni	4.0452	6.3790	7.9349	9.3870	10.7090
3	TiC HCS 10wt%Ni	1.5583	2.7199	3.8248	4.6748	5.5530
4	La$_{0.79}$Ca$_{0.20}$Cr$_{0.9}$Co$_{0.1}$O$_3$	0.1067	0.1067	0.1921	0.2135	0.2348

Figure 5. Weight gain in air for 100 hours at 800˚C for various compositions.

Weight gain in air for 100 hours at 800 ˚C

II. Electrical Conductivity:

The sample was cut into a bar of dimension 0.237x0.359x1.179 cm^3. Four-wire conductivity measurements were performed using a Linear Research Inc LR-700 AC Resistance Bridge operating at a frequency of 16 Hz. The sample was heated from room temperature (23˚C) to 800˚C at a speed of 5 to 7˚C per minute using a Carbolite Model CTF 17/75/300 Tube Furnace. An S-type thermocouple was placed close to the sample. The resistivity of a sample (TiC-Ni 30wt.%) at room temperature, 100˚C, 200˚C and 300˚C was read until the reading was stable about 2 hours after the expected temperatures were reached. As temperature increased higher than 300˚C, the resistivity of sample significantly increased and reached a maximum at 700˚C, the electrical conductivity of 6.78E-4 was recorded, and after that the electrical conductivity of the sample linearly started to increase. When the temperature was set to 800˚C, the electrical conductivity values were measured in the range of 0.168 to 19.17 1/ohm.cm. Electrical conductivity at 800˚C in air as a function of time did not show any significant change as the formation of oxides on the surface completed (See Figure 6 and 7).
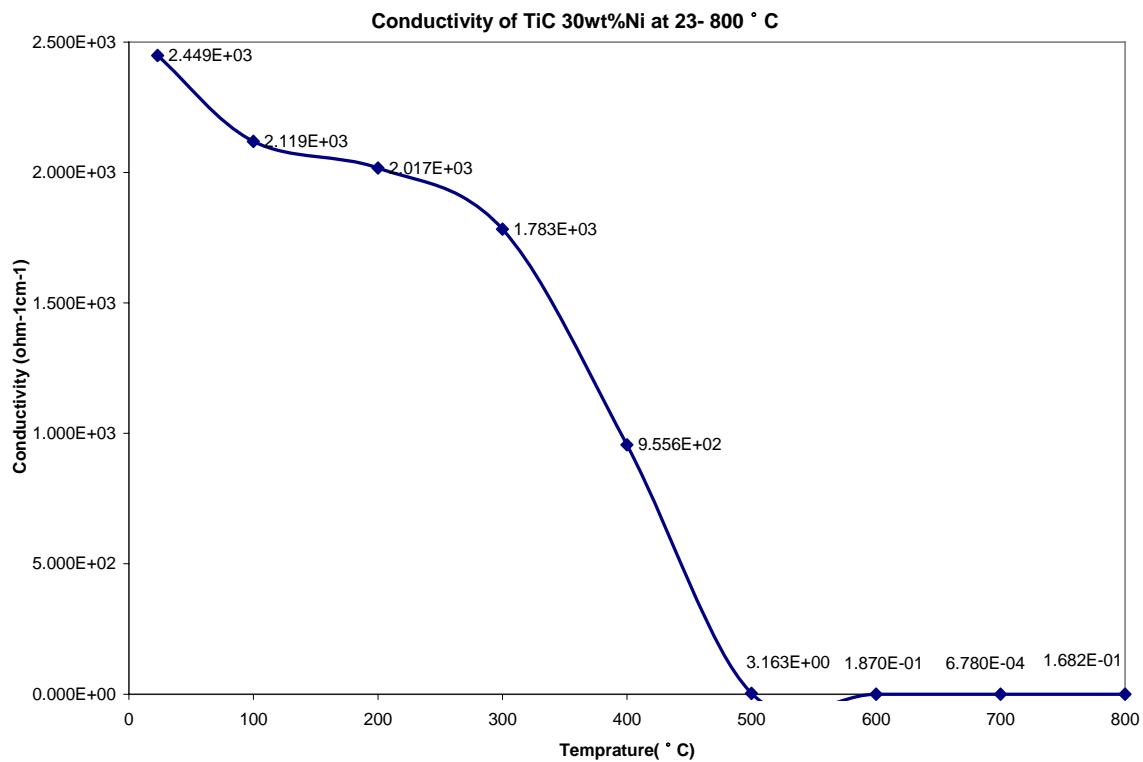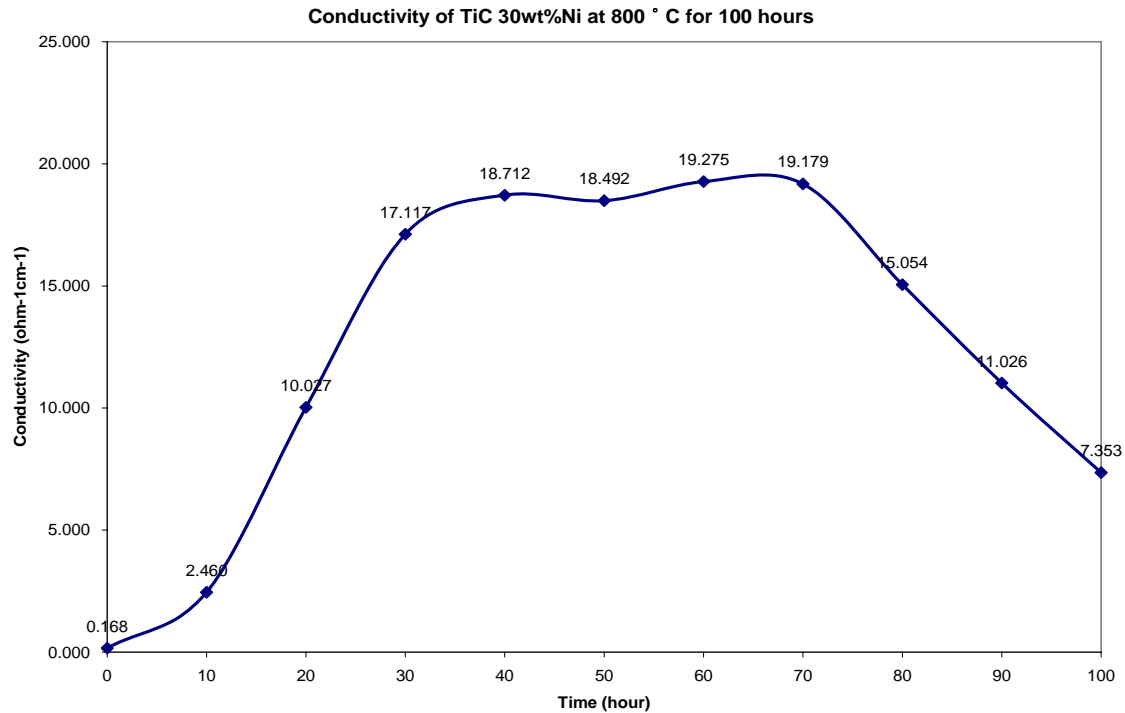
Figure 6. Conductivity of TiC-Ni 30wt.% at 23-800˚C

Figure 7. Conductivity of TiC-Ni 30wt.% at 800˚C for 100 hours

Conductivity of TiC 30wt%Ni at 800 ˚ C for 100 hours

The drastic increase of the resistivity at 700˚C is thought to be due to the forming of the oxidation layer on the surface of the sample and the reading was a combination of the resistivity of the oxidation layer (which becomes a protective layer after the completion and oxidation stops just like in the case of Cr_2O_3 in stainless steel) and the sample (TiC-Ni). According to the electrical conductivity during that period, TiO_2 is believed to be the major oxidation product because the electrical conductivity of TiO_2 is reported to be below 10^{-7}ohm^{-1}cm^{-1} at 700˚C[17] and that of NiO is between 10^{-4} and 1 ohm^{-1}cm^{-1}[18]. The increase of the electrical conductivity at 800˚C may be due to the additional formation of oxides of Ni, because the conductivity of TiO_2 is around 5×10^{-7}ohm^{-1}cm^{-1} at 800˚C[17] and that of NiO is between 10^{-3} and 1 ohm^{-1}cm^{-1} [18].

CONCLUSIONS

•TiC-Ni-Ni₃Al materials are more suitable to SOFC interconnect applications than metallic alloys
•No Cr evaporation problems
•They have 100 % electronic conductivity in 2449 1/ohm.cm in reducing conditions
•They have electrical conductivity of 20-30 1/ohm.cm in oxidizing condition due to formation of oxides of Ti or Ni on the surface which acts as protective layer in oxidation which stops the further oxidation of the samples.
•CTE match is expected to be compatible with other cell components or it can be easily tailored.
•They are stable in reducing and oxidizing conditions at 800ᴼC, no degradation.

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