Influence of Processing on the Microstructure and Properties of Ni-Al_2O_3 Nanocomposites

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Introduction

- Ceramic nanocomposites consist of a ceramic matrix reinforced with sub-micron metal or ceramic particles.
- Nanocomposites are known for their improved mechanical properties such as fracture strength and wear resistance, in comparison to the properties of monolithic ceramics [1-3].
- Control of the nanocomposite microstructure is extremely important, since it determines the final bulk properties [4].
- The microstructure strongly depends on two main parameters: the processing conditions and additives/impurities.

Goals

- Detailed investigation of the microstructure during each stage of the nanocomposite process, with emphasis on the infiltration stage, by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM).

Experimental

Processing

- Ball-milling (12 hours) of high purity alumina powder doped with Mg nitrate to provide MgO as a solute in the sintered alumina.
- Pressure filtration at 9.8 MPa.
- Drying at room temperature for 12 hours.
- Cold Isostatic Pressing (CIP) at 207 MPa.
- Drying at 60°C for 12 hours.
- Firing at 1100°C for 2 hours.
- Infiltration with a 70 wt.% nickel nitrate water-based solution .
- Drying at 110°C in air.
- Reduction at 650°C in forming gas.
- Sintering in He in a graphite furnace at 1400°C for 4 hours.

Specimen Preparation

- **Drilling** the reduced specimen to create a **3mm diameter cylinder.**
- **Cutting** 500μm thick discs.
- **Infiltration with a low viscosity epoxy**.
- **Vacuum** for 12 hours.
- **Heating** at 150°C for 3 hours for **curing**.
- **Mechanical thinning** to 80-100μm.
- **Dimpling** with 1μm diamond paste.
- **Ar ion milling** to form an electron-transparent specimen.

Characterization Methods

- HAADF STEM
- TEM
- STEM EDS

Results & Discussion

Infiltration & Reduction – Pre Sintering

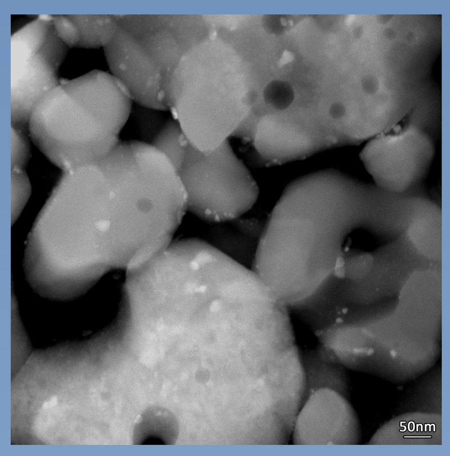


Fig. 1: HAADF STEM micrograph of an infiltrated specimen with ~1wt.% Ni.

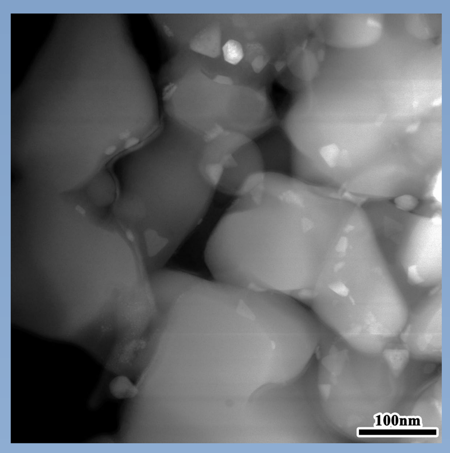


Fig. 2: HAADF STEM micrograph of specimen after two infiltration stages (2.5wt% Ni).

The Ni particle size after the 1st reduction at 650°C was measured via TEM and was found to be 19±23 nm. After and additional infiltration/reduction process the Ni particle size was 24±9nm. While there was no significant increase in particle size, there was a decrease in the standard deviation.

A sessile drop experiments of the nitrate solution on a Ni coated sapphire substrate showed dissolution of the Ni, indicating that the second infiltration process dissolved the Ni particles formed in the first infiltration stage.

Fracture

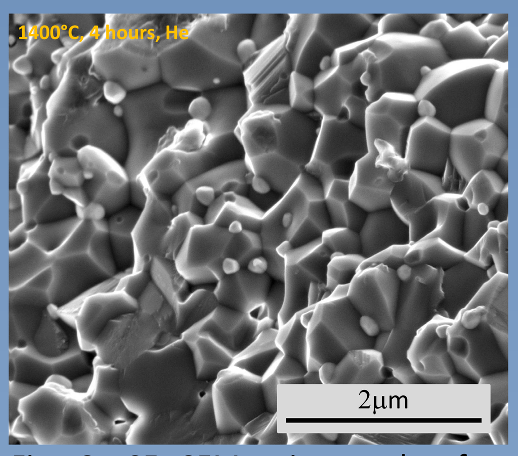


Fig. 3: SE SEM micrograph of a fractured specimen sintered at 1400°C in He for 4 hours

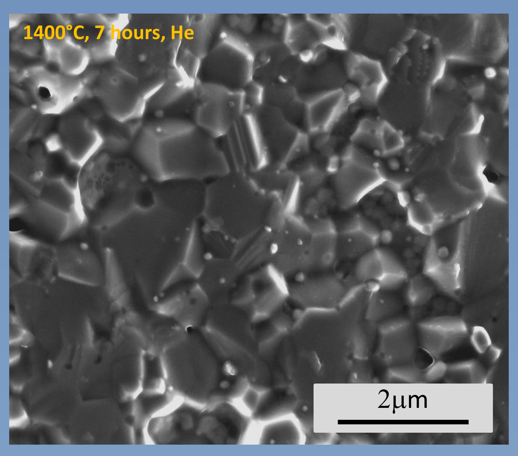


Fig. 4: SE SEM micrograph of a fractured specimen sintered at 1400°C in He for 7 hours

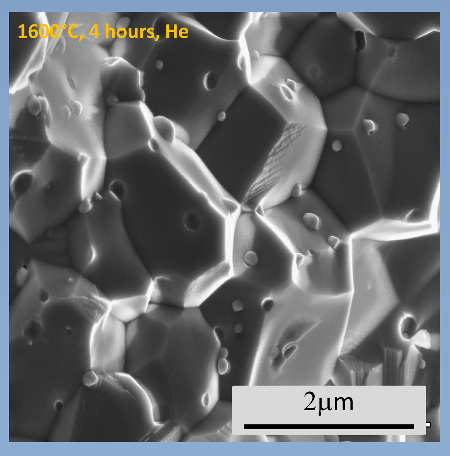


Fig. 5: Fracture SE SEM image of specimen sintered at 1600°C in He for 4 hours

Grain growth of the alumina occurs only when increasing the sintering temperature to 1600°C (~1micron), but increasing the sintering time the alumina grain size remains at 850nm but has a larger distribution (800nm vs. 350nm).
A mixed fracture mode is seen in the specimens sintered at 1400°C while the specimen sintered at 1600°C shows only inter-granular fracture.

Ni Particles Location& Size

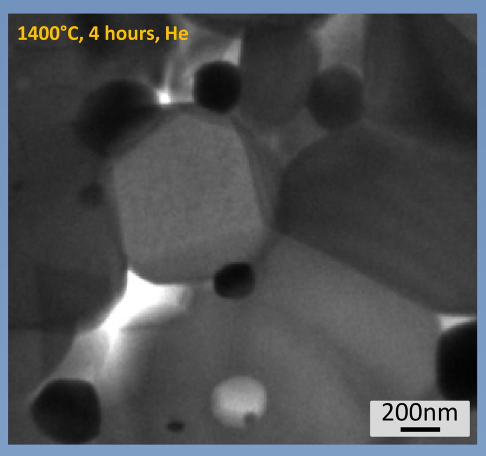


Fig. 6: BF TEM micrograph. Only 3% of the Ni particles were occluded

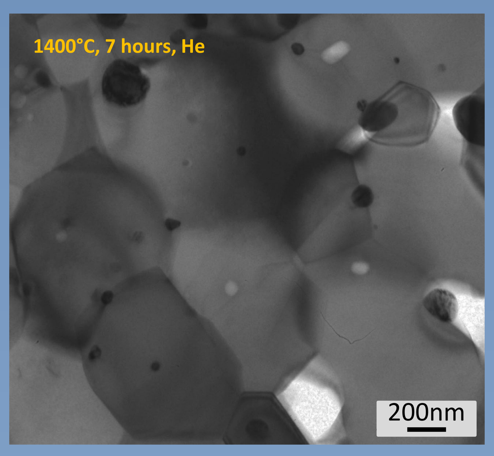


Fig. 7: BF TEM micrograph. Increasing the sintering time increases the amount of occluded Ni particles to 14%

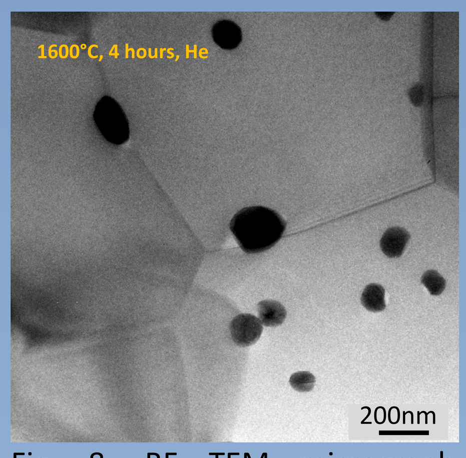


Fig. 8: BF TEM micrograph. Increasing the sintering temperature so that the Ni is liquid dramatically increases the amount of occluded Ni particles to 30%

The mean Ni particle size measured from the specimens sintered at 1400°C for 4 hours is 208±114nm, for the specimens sintered at 1400°C for 7 105±51nm and the specimens which were sintered at 1600°C had a mean particle size of 164±163nm.
An increase in the number of occluded particles is seen when the sintering time is increased to 7 hours (14%), and when the sintering temperature is increased to 1600°C (30%)

Density Measurements

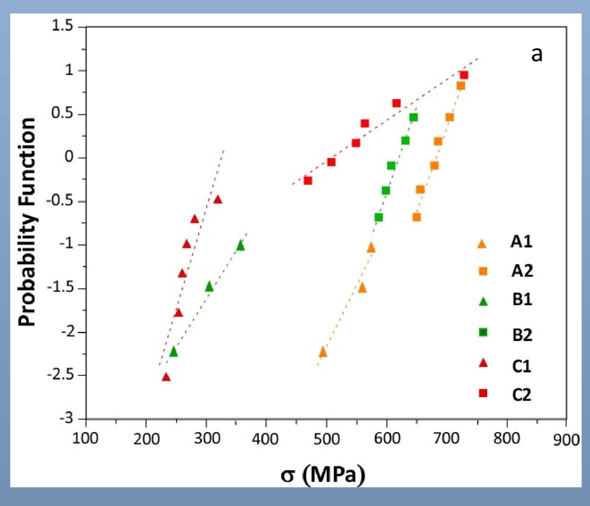
Process	Nickel Amount [wt.%]	Average Normalized Density [% of theoretical]
A (1400°C, He, 4 hours)	2.4±0.1	95±2
A - Control	0	92
B (1400°C, He, 7 hours)	2.5±0.2	95±1
B - Control	0	91
C (1600°C, He, 4 hours)	2.5 ±0.8	99±1
C - Control	0	99

Fig. 3: Density calculations done by Archimedes test shows no increase in the bulks density with an increase in sintering time. Increase in sintering temperature increases density.

3 Point Bending

Specimen/process	Average Flexural Strength [MPa]
A – 1400ºC, 4 hours, He	637±77
A Control	531±241
B – 1400ºC, 7 hours, He	420±172
B Control	N/A
C – 1600ºC, 4 hours, He	531±185
C Control	522±168

Fig. 7: Average flexural strength of both the nanocomposites and the control specimens. No difference in flexural strength between the control specimens and the nanocomposites sintered at 1600°C observed.
The highest average flexural strength measured for Ni reinforced alumina sintered at 1400ºC for 4 hours, 637±77MPa.



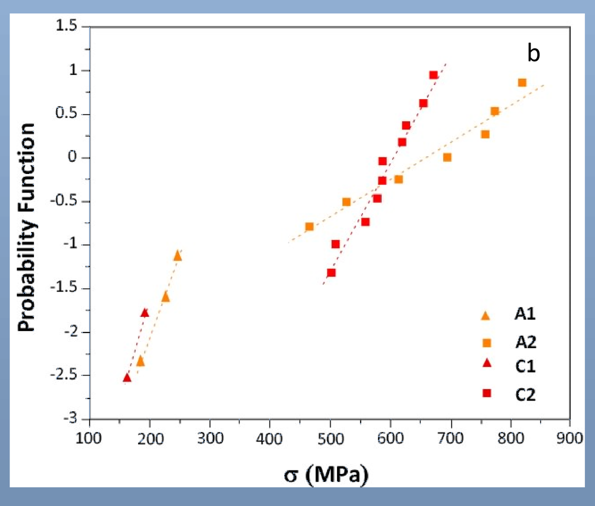


Fig 10. Weibull modulus analysis for the nanocomposites (a) and control specimens (b). The triangle and the square are two different trends that were found in each set of specimens from the same process, due to micro-cracks created in the pressure filtration stage. The highest Weibull modulus was found for specimen A with a relative density of only 95%.

Conclusions

- The particle size distribution is reduced after the second infiltration due to the dissolution of the Ni in to the nitrate solution which results in a higher effective Ni concentration in the solution and increased nucleation sites during drying.
- After sintering at 1400°C for 4 hours, a minimal amount of 3% occluded particles was detected, while after 7 hours at 1400°C the amount of occluded Ni particles reached 14%. At 1600°C the amount of occluded particles increased to 30%. Comparing these results to the results from Lieberthal et al. and Avishai et al. it can be concluded that MgO promotes occlusion of the Ni particles.
- Nanocomposites significantly improve the Weibull modulus , probably due to the decreased effective flaw size.
- Since the thermal expansion coefficient of Ni is higher than that of the alumina matrix, the particles which contribute to grain boundary reinforcement are the particles located at grain boundaries and triple junctions. Since the specimen sintered at 1600°C contains a significant amount of occluded particles relative to the specimen sintered at 1400°C, and despite it's higher density, its Weibull modulus and flexural strength are lower.

Acknowledgments

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References

[1] T. Sekino, T. Nakajima, S. Ueda and K. Niihara, "Reduction and Sintering of a Nickel-Dispersed-Alumina Composite and its Properties", *Journal of The American Ceramic Society*, **80**[5]:1139-1148, 1997.

[2] M. Lieberthal and W.D. Kaplan, "Processing and Properties of Al_2O_3 Nanocomposites Reinforced with Sub-Micron Ni and $NiAl_2O_4$", *Materials Science and Engineering A*, **302**[1]:83-91, 2001.

[3] M. Sternitzke, B. Derby and R.J. Brook, "Alumina/Silicon Carbide Nanocomposites by Hybrid Polymer/Powder Processing: Microstructures and Mechanical Properties", *Journal of The American Ceramic Society*, **81**[1]:41-48, 1998.

[4] W.D. Kaplan and A. Avishai, "Processing & Microstructural Control of Metal Reinforced Ceramic Matrix Nanocomposites, Chapter in "Ceramic-Matrix Composites: Microstructure/Property Relationship", Edited by J.M. Low, Woodhead Publishing, pp. 285-308, February 2006.