JOURNAL OF MATERIALS SCIENCE **38** (2003) 3073–3080

Reactive hot pressing of Al_2O_3-Ni composites

W. G. FAHRENHOLTZ
Department of Ceramic Engineering, University of Missouri-Rolla, Rolla, MO 65409, USA
E-mail: billf@umr.edu; www.umr.edu/~billf

Reactive hot pressing has been used to form Al_2O_3-Ni composites from Al and NiO. The effect of attrition milling on the precursor powder and subsequent composite formation was examined. The surface area, phase assemblage, reaction temperature, and morphology of precursor powders were characterized as a function of milling time, which ranged from 0 (unmilled) to 480 min (8 hrs). During milling, particle surface area increased from less than 1 to more than 11 m^2/g as the size of the Al and NiO particles decreased. At the same time, the temperature at which Al and NiO reacted to form Al_2O_3 and Ni decreased from more than 1000°C to around 600°C. Formation of Al_2O_3 or Ni during milling was not detected, regardless of time. Precursor milling time also affected the morphology and phase assemblage of composites produced by reactive hot pressing. Composites formed from unmilled powders contained a small amount of unreacted NiO and had a Ni ligament size greater than 10 μm. The composite forming reaction went to completion when powders milled for one hour or more were hot pressed. Based on microstructural evidence and analogy to similar reactions, it appears that the composite forming reaction proceeds by Al diffusing into and reacting with NiO. © *2003 Kluwer Academic Publishers*

1. Introduction

In the past 15 years, a variety of reaction-based processing methods have been developed for the preparation of ceramic-metal composites. The processing routes include directed metal oxidation [1], reaction bonding [2–4], and several techniques based on displacement reactions [5–9]. The strength and toughness of reactively formed materials are often far superior to properties reported for conventionally sintered cermets of the same composition. The enhanced performance is attributed to high relative density, good wetting/adhesion at the ceramic-metal interface, and the interpenetrating, two phase composite microstructure [10, 11].

As with other reaction-based forming techniques, reactive hot pressing utilizes thermodynamically favorable reactions during processing [12–14]. The advantage of reactive hot pressing over the other techniques is its wide degree of compositional flexibility. Some compositions that have been prepared by reactive hot pressing include Al_2O_3-Ni, Al_2O_3-$MoSi_2$, ZrB_2-SiC, TiB_2-SiC, $MoSi_2$-SiC, and Al_2O_3-Ni_3Al [12–16]. Research by Claussen *et al.* has shown that similar reaction-based processes can be extended to reactive pressureless sintering routes, if powder processing and compaction processes are precisely controlled [17, 18]. Zhang *et al.* have investigated the formation of several non-oxide systems and have studied diffusion paths during reaction. For the formation of ZrB_2-SiC from Zr, Si, and B_4C, they concluded that B and C diffuse from the B_4C precursor into Zr and Si particles based on the size of microstructural features in the final composite [13].

Al_2O_3-Ni composites are attractive because of the potential for high strength and toughness [19–21]. Alumina and Ni are thermodynamically compatible, refractory phases and the composites should be resistant to oxidation and corrosion at room and elevated temperatures (~1000°C) [22]. However, to date, most composite processing techniques produce only modest gains in toughness over un-reinforced Al_2O_3. In contrast, toughness gains have been much higher for Al_2O_3 reinforced with Al [23]. The strength and toughness of Al_2O_3-Ni composites prepared by several different techniques are listed in Table I and compared to reported values for an Al_2O_3-Al composite. A variety of fabrication techniques have been investigated for Al_2O_3-Ni composites including pressureless sintering [22, 24], sol-gel processing [25, 26], reduction of $NiAl_2O_4$ [27], and reactive hot pressing [16, 28, 29]. Of these, reactive hot pressing has shown the highest strength and toughness.

The purpose of this investigation was to determine the effect of attrition milling time on the formation of Al_2O_3-Ni composites by reactive hot pressing.

2. Procedure

Aluminum (−325 mesh, 99.5%, Alfa) and nickel oxide (−325 mesh, 99%, Alfa) were combined in the molar ratio from Reaction 1. Calculated weight and volume

Present address: Dr. Bill Fahrenholtz, Assistant Professor of Ceramic Engineering, 222 McNutt Hall, University of Missouri-Rolla, Rolla, MO 65409, USA.

0022–2461

TABLE I Comparison of strength and toughness of Al_2O_3-Ni composites prepared by different techniques

Processing method	Strength (MPa)	Toughness (MPa · $m^{1/2}$)	Metal content (vol%)	References
Hot pressing	N/A	7	20	19
Sol-gel processing	N/A	6.7	30	26
Sintering	200^b	2	20	22
Reduction of $NiAl_2O_4$	N/A	9	20	27
Reactive hot pressing (1995)	250^a	6	41	28
Reactive hot pressing (2000)	610^b	12.1	35	16
Al_2O_3-Al	800^b	8	Varied	23

[a] Three point bending.

[b] Four point bending.

TABLE II Moles, weight percent, and volume percent of the reactants and products predicted from the composite forming reaction

Constituent	Al	NiO	Al_2O_3	Ni
Moles	2	3	1	3
Weight percent	19.4	80.6	36.7	63.3
Volume percent	37.8	62.2	56.4	43.6

percentages of the reactants and products of Reaction 1 are given in Table II.

$$2Al + 3NiO \rightarrow Al_2O_3 + 3Ni \qquad (1)$$

Powder mixtures were attrition milled for times ranging from 0 (unmilled) to 480 min. The unmilled powders (0 min milling) were homogenized by batching into a polyethylene jar (no milling media) and shaking for five minutes. Attrition milling was carried out in a laboratory scale mill (Model 01, Union Process) using a 500 ml polymer-lined container, a polymer-coated spindle, and 3 mm diameter ZrO_2 milling media. Mill speed was 600 rpm. For a typical batch, the mill was charged with 50 vol% media ($\sim$1500 g of Y-stabilized ZrO_2), 40 vol% methanol (200 ml), and 5 vol% powder (25 cm^3 or 29.7 g Al and 123.5 g NiO). After milling, the powder slurry was separated from the milling media by sieving through a 35 mesh stainless steel sieve. The slurry was dried overnight in an open glass dish inside a fume hood. After drying, the powder cake was lightly crushed using a high purity alumina mortar and pestle and then passed through a 50 mesh stainless steel sieve. Powders were stored in airtight containers.

Powder mixtures were analyzed as a function of milling time to determine surface area, phases present, reaction temperature, and morphology. Surface area was measured by N_2 gas adsorption using a 5 point BET isotherm [30]. Phases were determined using X-ray diffraction analysis (XRD, Pad-V, Scintag, Cu K_α source). The temperature at which Reaction 1 initiated was determined using differential thermal analysis (DTA) using a 10°C/min heating rate in a flowing argon atmosphere. Powder morphology was characterized using scanning electron microscopy (SEM, S-4700, Hitachi) and chemical analysis was performed using energy dispersive spectroscopy (EDS, Phoenix System, EDAX).

Powders that were milled for 0 hrs (unmilled), 60 min, and 480 min were hot pressed to form Al_2O_3-Ni composite billets. Hot pressing was conducted in an argon atmosphere using BN coated graphite dies according to a previously published procedure [16]. Powders were heated from room temperature to 1400°C with no applied load. Once the process temperature was reached, a load of 3000 kg was applied resulting in a pressure of 26 MPa. The sample was held at 1400°C for 30 min and then it was cooled under load at a rate of approximately 20°C/min. Composite billets were sectioned and polished cross sections were examined in SEM/EDS for characterization of microstructure and chemical composition. A small piece of each billet was ground and examined by XRD.

3. Results and discussion

The surface area, reaction temperature, and morphology of the precursor powders changed as a function of attrition milling time, but the phases present (by XRD) did not change. Surface area and reaction temperature data are summarized in Table III. The powder surface area increased from less than 1 m^2/g for the unmilled Al and NiO mixture to 11 m^2/g for powder milled for 480 min. Differential thermal analysis of unmilled powders found an endothermic peak corresponding to Al melting at 660°C and an exothermic peak at 1050°C corresponding to the composite-forming reaction (confirmed by XRD analysis that is not shown). As the powder surface area increased, the temperature at which the composite-forming reaction initiated decreased. After 60 min of milling, a small exothermic peak was detected by DTA at around 610°C, well below the melting temperature of Al, in addition to the other two peaks. As milling time increased, the size of the 610°C exotherm increased and the size of the other exotherm decreased and shifted to slightly lower temperatures (Table III). After milling for 480 min, the higher temperature exotherm and the 660°C endotherm had disappeared leaving only the 610°C exotherm. For powders milled for 480 min, the composite-forming reaction initiated at 610°C prior to Al melting resulting in a solid-state displacement reaction, in contrast to liquid-solid displacement reactions for shorter milling times. Logically, the solid-solid reaction should be preferable for composite formation since the absence of liquid phase would limit the possibility of phase segregation facilitated by the formation of a liquid phase during the hot pressing cycle. However, examination of hot pressed composite microstructures will show that this is not the case.

TABLE III Summary of surface area and DTA data for Al-NiO powder mixtures unmilled and after milling

Milling time (min)	Surface area (m^2/g)	Endothermic peak (°C)	Exothermic peaks (°C)
Unmilled	<1	660	1025
15	3	660	1015
30	–	660	1015
60	9	660	610 (minor) 975 (major)
480	11	Not detected	610

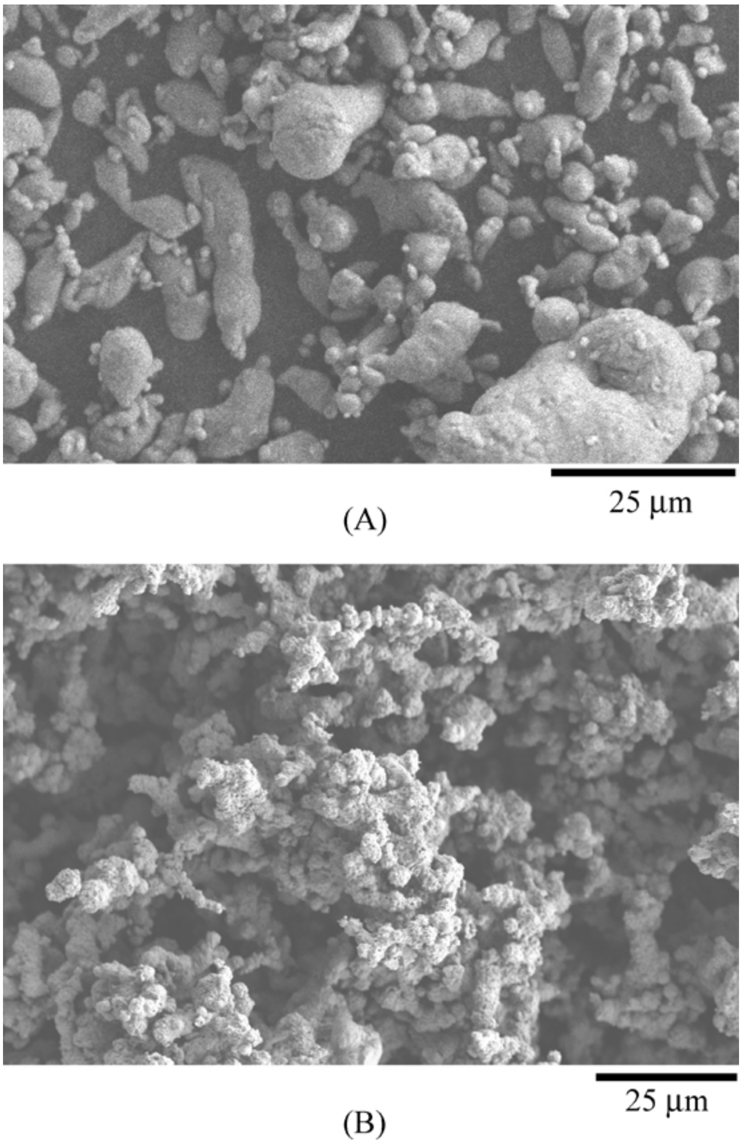


Figure 1 Morphology of as-received (A) Al and (B) NiO powders.

Particle morphology also changed dramatically during milling. Unmilled Al powders ranged in size from 2 and 50 μm (Fig. 1A). Most Al particles were between 20 and 40 μm in diameter and they had smooth, rounded surfaces. Unmilled NiO powders were agglomerates with angular surface features and appeared to be made up of many small crystallites (Fig. 1B). The size of the individual crystallites was around 1 μm, but the agglomerates were 25 μm in diameter or larger. The morphology of both powders changed significantly during attrition milling. After just 15 min of milling, the shearing forces in the attrition mill flattened the aluminum particles into disks, 5 to 10 μm thick and 10 to 20 μm wide (Fig. 2A). The NiO particles were broken down into smaller chains of NiO crystallites up to 5 μm long (Fig. 2B). After milling for 60 min (Fig. 3), the area of the Al disks continued to increase as the thickness of the disks decreased. The NiO agglomerates appeared to have been broken down into individual primary crystallites. Higher magnification observations (not shown) found that a small fraction ($\sim$10%) of the NiO crystallites were embedded in the Al flakes, which were up to 5 μm thick and 25 μm wide. Examination of powders milled for two and four hours revealed that milling times longer than 60 min did not result in further reduction of the NiO particle size. During this time, the Al flakes continued to get thinner and began to fracture into smaller pieces. Powder morphology after 480 min of milling is shown in Fig. 4. At this stage, the aluminum particles were thin, small platelets, 5 to 10 μm wide and around 1 μm thick. Strangely, all of the NiO crystallites were either embedded into or attached to the surface of the aluminum platelets. This intimate mixing combined with the small particle size are, presumably, the reasons that the reaction temperature declined so steeply.

Despite the large increase in particle surface area and the accompanying changes in morphology, the powders did not react significantly during milling according to X-ray diffraction analysis. This is in sharp contrast to reports of significant oxidation of aluminum during attrition milling for reaction bonding of Al_2O_3 [3]. As shown in Fig. 5, X-ray diffraction detected only Al and NiO in samples milled up to 480 min. Certainly, any aluminum surface produced during milling will be coated with a thin oxide layer, but the volume fraction of Al_2O_3 was not large enough for detection by XRD analysis. The change that can be seen

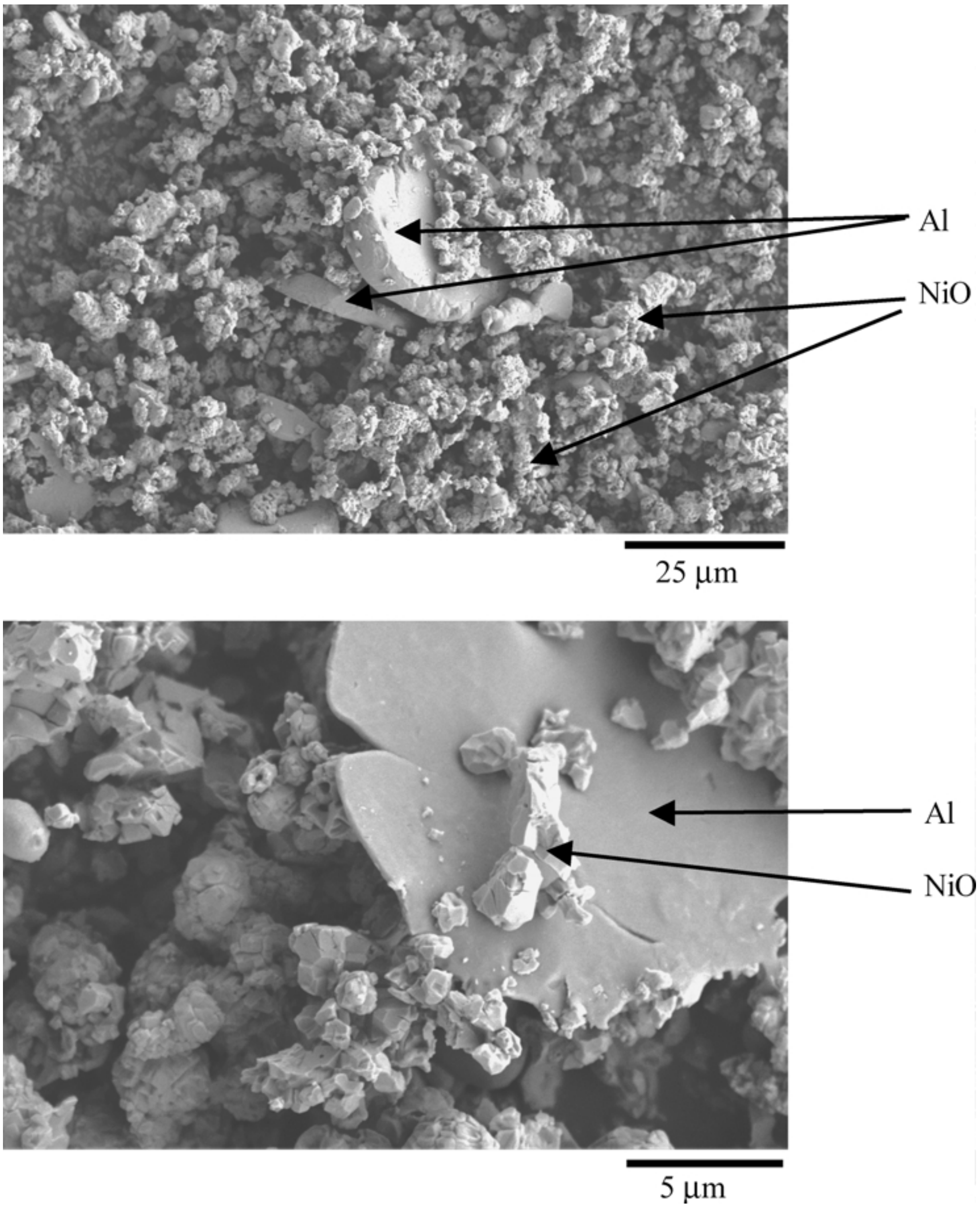


Figure 2 A mixture of Al and NiO particles that was attrition milled for 15 min.

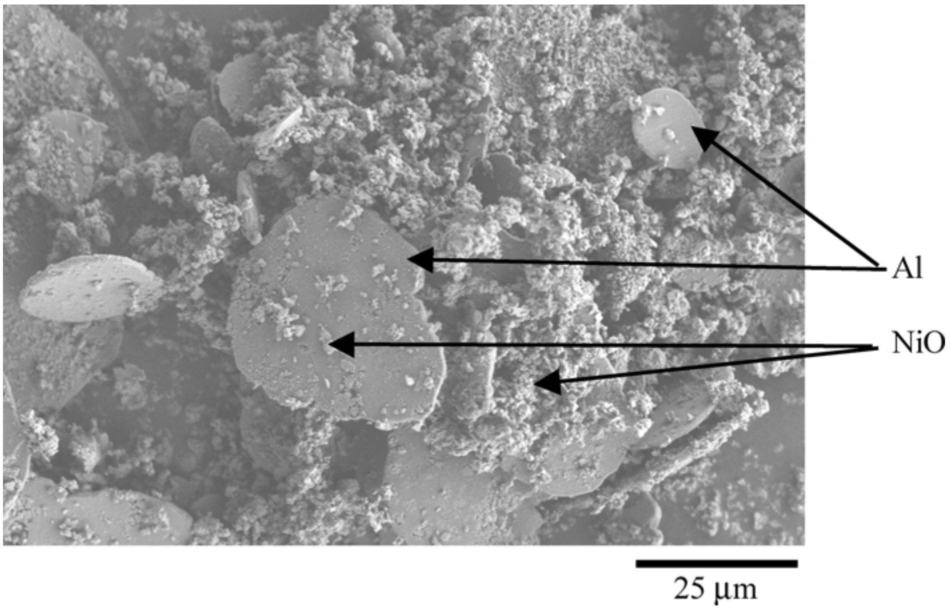


Figure 3 A mixture of Al and NiO particles that was attrition milled for 60 min.

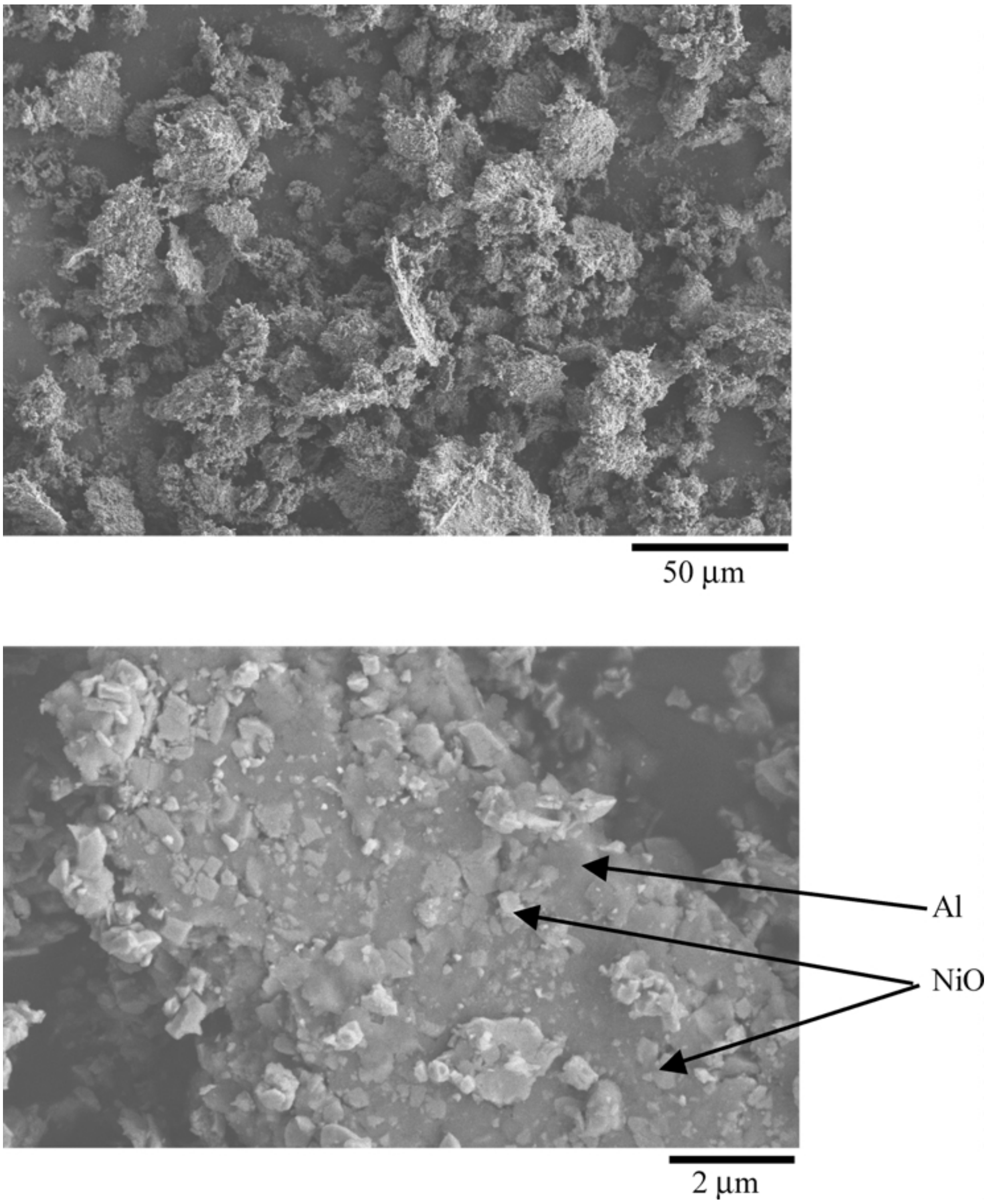


Figure 4 NiO crystallites embedded in an Al flake produced by attrition milling a mixture Al and NiO powders for 480 min.

by XRD is the broadening of the peaks associated with Al and NiO. The peak broadening is attributed to particle size reduction and an increase in strain induced by milling.

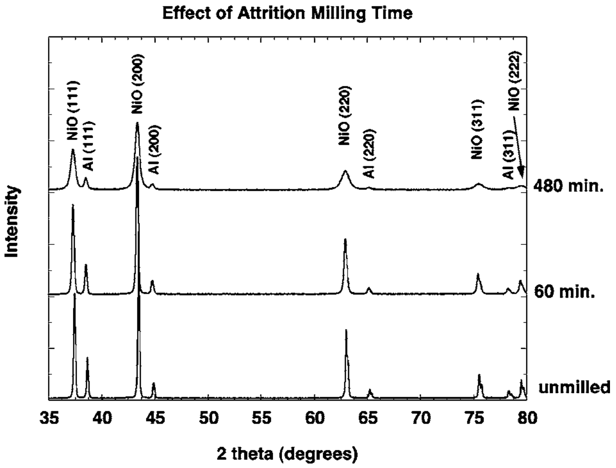
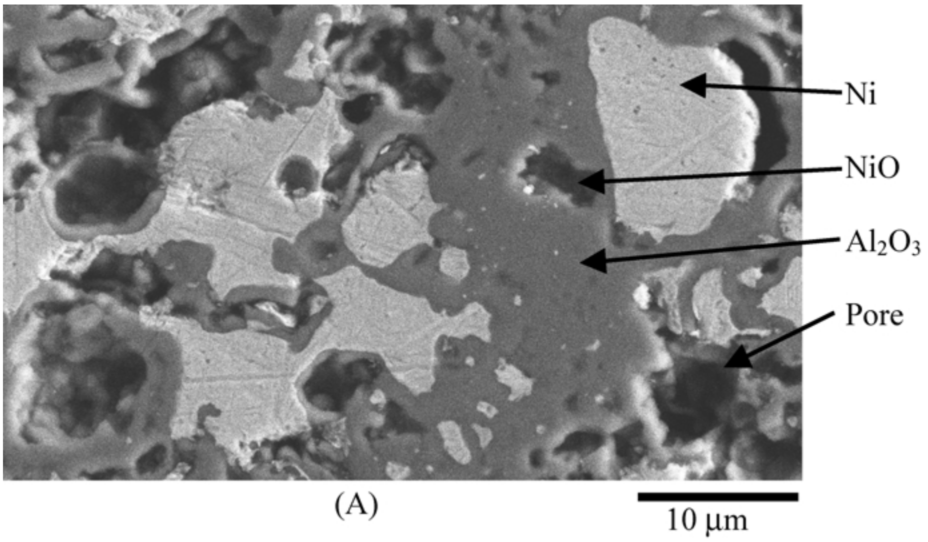


Figure 5 X-ray diffraction analysis of Al and NiO powder mixtures attrition milled for 0, 60, and 480 min.

Milling had a significant effect on the density and microstructure of composites produced by subsequent reactive hot pressing. Hot pressing of unmilled powder resulted in a composite that had open porosity. Characterization of microstructure by SEM and chemical analysis by EDS indicated that a small amount (<5 vol%) of residual NiO was present, Fig. 6A, although only Al_2O_3 and Ni were detected by XRD (Fig. 7). Despite the presence of some unreacted NiO, no Al was apparent in the SEM micrographs, the EDS analysis, or the XRD analysis. A small excess of aluminum could easily be dissolved into the Ni phase without altering the appearance of the SEM images. No impurity phases were detected in the composites by XRD or observed in SEM/EDS. In addition, the molten Al present during hot pressing of the unmilled powder did not appear to interact with the graphite; the billet did not stick to the die nor were any additional phases (e.g., Al_4C_3) observed by SEM, EDS, or XRD. The density of the hot pressed composite was 3.8 g/cm^3, approximately 70% relative density, which is consistent with the observation (Fig. 6A) of porosity in the sample. Based on the microstructure of the composite produced from unmilled powder, comparisons to the work of Zhang [13], and the mechanism observed for the reaction of Al and mullite [31], it appears that the composite forming reaction in this system proceeds by diffusion of Al into NiO leading to the composite forming reaction. A study to confirm this proposed reaction path is underway.

Increasing the milling time to 60 min resulted in a composite that was fully reacted as probed by XRD (Fig. 7) and SEM/EDS (Fig. 6B). The relative density of composites produced from powders milled for 60 min was above 95% (5.5 g/cm^3). The scale of the microstructure in this composite was much finer (Fig. 6B) than the composite produced from unmilled powder (Fig. 6A). The width of the Ni inclusions was around 5 μm for the composite formed from powder milled for one hour, compared to over 10 μm for the composite produced from the unmilled powder. A previous study of composites produced from powder that was attrition milled for 60 min found that the resulting composites had high strength (610 MPa) and toughness (12 MPa $\cdot$ m$^{1/2}$) [16].

Milling the precursor powder for 480 min produced additional changes in composite density and microstructure. Relative density was above 98% (5.7 g/cm^3). The small fraction of apparent porosity visible in Fig. 6C is attributed to surface damage during polishing since density measurements gave no indication of a significant amount of open or closed porosity in hot pressed billets. The average size of the Ni inclusions in a composite produced from powders milled for 480 min was around 2 μm, but the distribution of Al_2O_3 varied within the composite. Some areas (Fig. 6C) had uniformly distributed Al_2O_3, but others (Fig. 6D) contained almost no Al_2O_3. Analysis by SEM/EDS and XRD (Fig. 7) indicated that the composite forming reaction had gone to completion. The uneven distribution of Al_2O_3 may have been caused by the formation of localized “hot spots” during the hot pressing cycle that led to phase segregation during reaction. Segregation of precursors prior to reaction is unlikely since the NiO particles are actually embedded in the Al flakes during the 480 min milling cycle, as observed by SEM (Fig. 4). Segregation of the precursor powders during hot pressing is also unlikely because the reaction proceeds in the solid state prior to the formation of a liquid phase that might facilitate particle rearrangement and/or dewetting of molten aluminum.



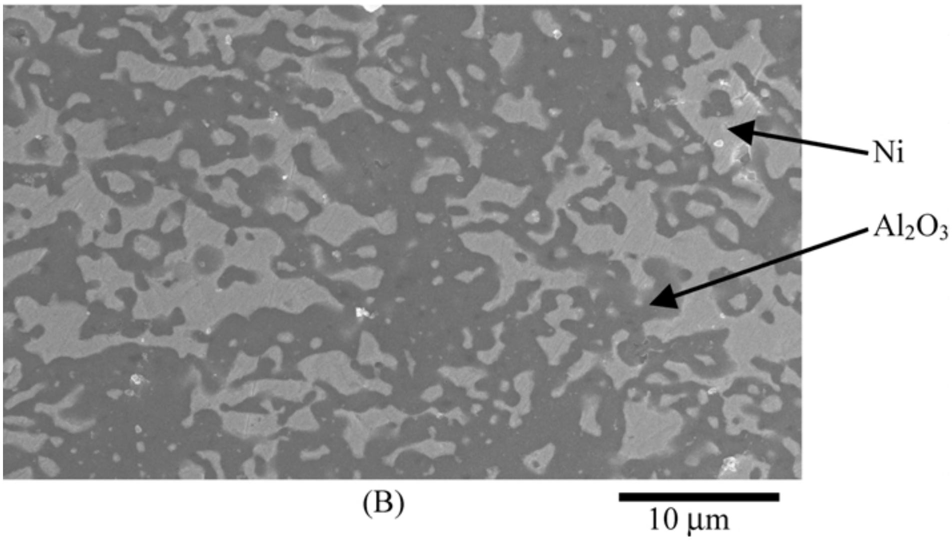


Figure 6 Microstructure of Al_2O_3-Ni composites produced by reactive hot pressing of Al and NiO powders that were attrition milled for (A) 0, (B) 60, and (C and D) 480 min. (*Continued*)

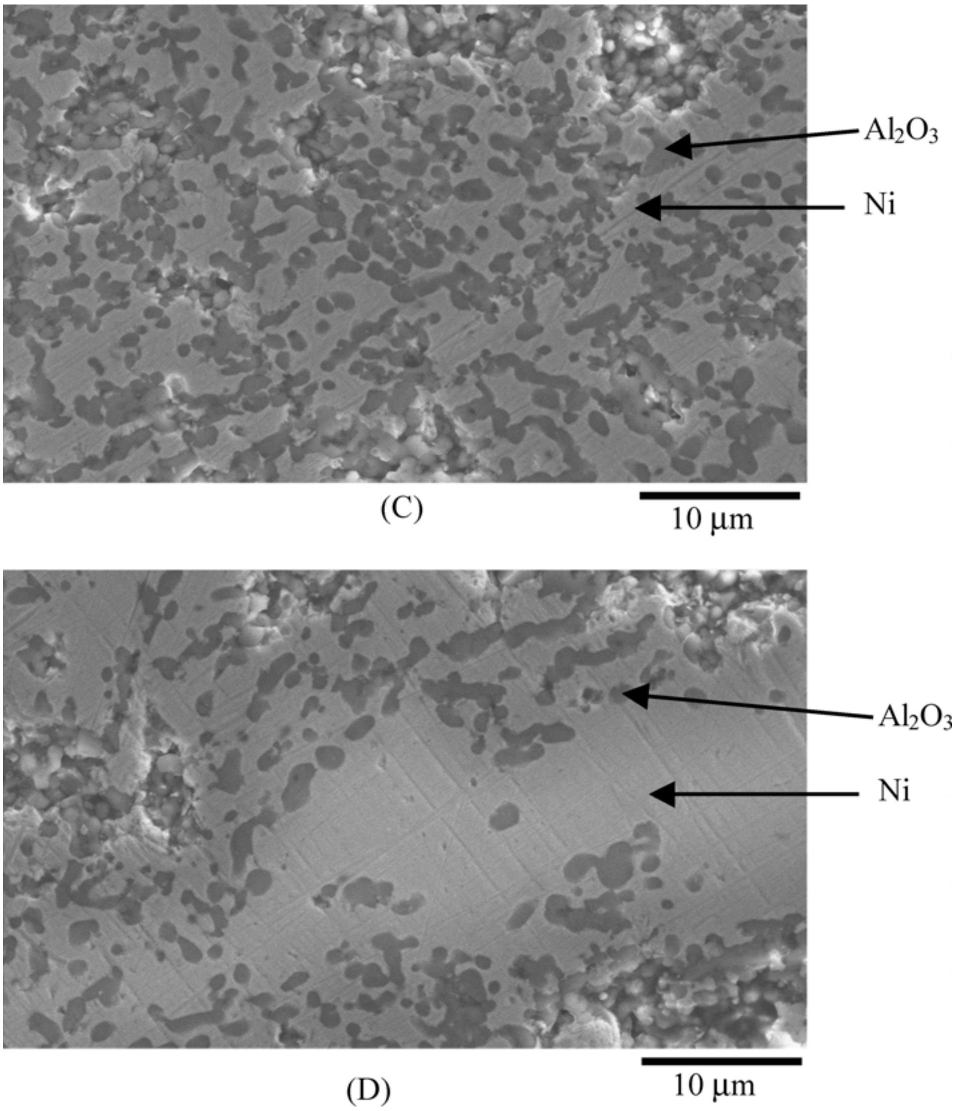


Figure 6 (*Continued*).

The most likely mechanism for phase segregation is formation of local hot spots during hot pressing due to the highly exothermic nature of the reaction [16], which can result in ignition of a self-propagating exothermic reaction during the hot pressing cycle. For powders milled for times ranging from 0 to 60 min, the heat generated by the composite forming reaction was mitigated using a slow (1°C/min) heating rate during the hot pressing cycle. This may be insufficient to suppress local exothermic heating in the finely divided powder mixtures.

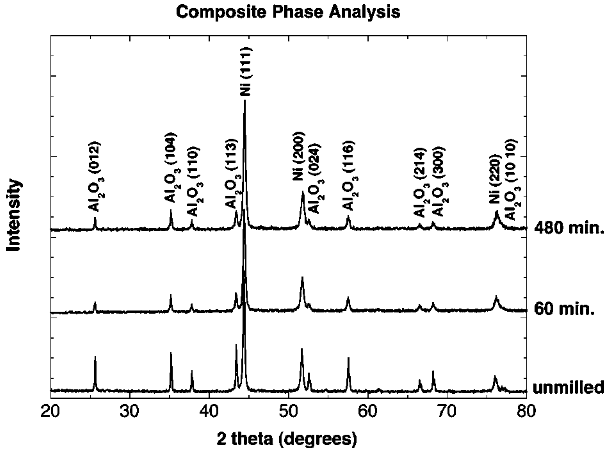


Figure 7 X-ray diffraction analysis of composites produced by hot pressing at 1400°C for 30 min. The precursor powder mixtures (Al and NiO) were attrition milled for 0, 60, or 480 min prior to hot pressing.

4. Summary and conclusions

This paper reports on the effect of attrition milling time on precursor powder morphology and on the microstructure and density of Al_2O_3-Ni composites produced by reactive hot pressing of Al and NiO. Powder surface area increased as milling time increased. This was accompanied by a substantial decrease in the temperature at which the composite forming reaction initiated. As milling proceeded, the size and shape of the precursor particles changed significantly. However, no reaction was detected during milling by XRD analysis. When milled powders were hot pressed, the powder morphology and mixing affected the density and microstructure of the resulting composites. Reaction of unmilled powders produced a porous composite with some unreacted NiO. Milling for 60 min produced a dense composite with a fine, interpenetrating microstructure. Milling for 480 min resulted in some segregation of Ni in the reacted composite. Analysis of the developing composite microstructure indicates that Reaction 1 proceeds by Al diffusing into NiO and then reacting to form Al_2O_3 and Ni.

Based on examination of the microstructure and composition of the composites, a precursor milling time of 60 min seems to be an acceptable compromise for total processing time, composite density, completion of the composite forming reaction, and resulting microstructure. Shorter milling times result in incomplete reaction and porous composites. Longer milling times result in non-uniform composite microstructures. It may be possible to produce a more uniform Al_2O_3-Ni composite from powder milled for 480 min by modifying the hot pressing schedule (e.g., slower heating rate or use of isothermal holds). A future study of the mechanical behavior of composites prepared from powders milled for different times will be used to set the final process conditions.

Acknowledgments

The author wishes to thank Laura Brennecka and Daniel Ragland for technical assistance with this project. Support for this project was provided by Caterpillar, Inc. The SEM/EDS used in this work was purchased on Grant DMR 9704288 from the National Science Foundation. The assistance of SEM operator Clarissa Vierrether is also acknowledged.

References

1. M. S. NEWKIRK, A. W. URQUART and H. R. ZWICKER, *J. Mater. Res.* **1** (1986) 81.
2. S. HOLZ, S. WU, S. SCHEPPOKAT and N. CLAUSSEN, *J. Amer. Ceram. Soc.* **77** (1994) 2509.
3. S. P. GAUS, P. M. SHEEDY, H. S. CARAM, H. M. CHAN and M. P. HARMER, *ibid.* **82** (1999) 909.
4. F. L. RILEY, *Mater. Sci. Forum* **47** (1989) 70.
5. S. SCHICKER, D. E. GARCIA, J. BRUHN, R. JANSSEN and N. CLAUSSEN, *Acta Mat.* **46** (1998) 2485.
6. N. CLAUSSEN, D. E. GARCIA and R. JASSEN, *J. Mater. Res.* **11** (1996) 2884.
7. M. C. BRESLIN, J. RINGNALDA, J. SEEGER, A. L. MARASCO, G. S. DAEHN and H. L. FRASER, *Cer. Eng. and Sci. Proc.* **15** (1995) 104.
8. R. E. LOEHMAN, K. G. EWSUK and A. P. TOMSIA, *J. Amer. Ceram. Soc.* **79** (1996) 27.
9. K. A. ROGERS, P. KUMAR, R. CITAK and K. H. SANDHAGE, *ibid.* **82** (1999) 757.
10. D. R. CLARKE, *ibid.* **75** (1992) 739.
11. F. F. LANGE, B. VELAMAKANNI and A. G. EVANS, *ibid.* **73** (1990) 388.
12. C. H. HENAGER, J. L. BRIMHALL and J. P. HIRTH, in "Structural Intermetallics," edited by R. Darolia, J. J. Lweandowski, C. T. Liu, D. Miracle, and P. L. Martin (TMS, Pittsburgh, 1993) p. 799.
13. G.-J. ZHANG, Z.-Y. DENG, N. KONDO, J.-F. YANG and T. OHJI, *J. Amer. Ceram. Soc.* **83** (2000) 2330.
14. W. G. FAHRENHOLTZ, R. E. LOEHMAN and K. G. EWSUK, *ibid.* **85** (2002) 258.
15. G. J. ZHANG, Z. Z. JIN and X. M. YUE, *J. Mater. Sci.* **32** (1997) 2093.
16. W. G. FAHRENHOLTZ, D. T. ELLERBY and R. E. LOEHMAN, *J. Amer. Ceram. Soc.* **83** (2000) 1279.
17. S. SCHICKER, D. E. GARCIA, J. BRUHN, R. JANSSEN and N. CLAUSSEN, *Acta Mater.* **46** (1998) 2485.
18. N. CLAUSSEN, D. E. GARCIA and R. JANSSEN, *J. Mater. Res.* **11** (1996) 2884.
19. X. SUN and J. YOEMANS, *J. Amer. Ceram. Soc.* **79** (1996) 2705.
20. *Idem.*, *ibid.* **79** (1996) 562.
21. W. H. TUAN and R. J. BROOK, *J. Eur. Ceram. Soc.* **6** (1990) 31.
22. *Idem.*, *ibid.* **10** (1992) 95.
23. H. PRIELIPP, M. KNECHTEL, N. CLAUSSEN, S. STREIFFER, H. MUELLENJANS, M. RUHLE and J. ROEDEL, *Mater. Sci. Eng.* A **197** (1995) 19.
24. W. H. TUAN, M. C. LIN and H. H. WU, *Ceram. Intl.* **21** (1995) 221.
25. E. D. RODEGHIERO, O. K. TSE, J. CHISAKE and E. P. GIANNELIS, *Mater. Sci. and Eng.* A **195** (1995) 151.
26. E. BREVAL, Z. DENG, S. SHIOU and C. G. PANTANO, *J. Mater. Sci.* **27** (1992) 1464.
27. E. ÜSTÜNDAG, P. RET, R. SUBRAMANIAN, R. DIECKMANN and S. L. SASS, *Mater. Sci. Eng.* A **195** (1995) 39.
28. S. A. JONES, J. M. BURLITCH, E. ÜSTÜNDAG, J. YOO and A. T. ZEHNDER, in "Ceramic Matrix Composites—Advanced High-Temperature Materials," Vol. 365, edited by R. A. Lowden, M. K. Ferber, J. R. Hellmann, K. K. Chawla and S. G. DiPietro (Materials Research Society, Pittsburgh, PA, 1995) p. 53.
29. W. G. FAHRENHOLTZ, K. G. EWSUK, R. E. LOEHMAN and A. P. TOMSIA, *Met. Mater. Trans.* A **27A** (1996) 2122.
30. S. LOWELL and J. E. SHIELDS, "Powder Surface Area and Density" (Chapman and Hall, New York, 1984).
31. W. G. FAHRENHOLTZ, K. G. EWSUK, R. E. LOEHMAN and PING LU, *J. Amer. Ceram. Soc.* **81** (1998) 2533.

Received 4 September 2002
and accepted 6 May 2003