CRADA FINAL REPORT

FOR
CRADA NO. ORNL 99-0557

GRAIN REFINEMENT IN TiC-Ni_3Al COMPOSITES

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ABSTRACT

The Cooperative Research and Development Agreement (CRADA) was to develop composites of TiC-Ni_3Al with refined grain microstructures for application in diesel engine fuel injection devices. Grain refinement is important for improved wear resistance and high strength for the applications of interest. Attrition milling effectively reduces the initial particle size and leads to a reduction of the final grain size. However, an increase in the oxygen content occurs concomitantly with the grinding operation and decreased densification of the compacts occurs during sintering.

STATEMENT OF THE OBJECTIVES

The purpose of this Cooperative Research and Development Agreement (CRADA) was to develop composites of TiC-Ni_3Al with refined grain microstructures for application in diesel engine fuel injection devices.

CRADA BENEFIT TO DOE

The CRADA contributed to the development of improved materials for the reduction of exhaust emissions and improved fuel consumption. in the U. S.

TECHNICAL DISCUSSION

Introduction

Previous studies have shown that the properties of the aluminide-bonded ceramics are attractive for diesel engine applications and consequently, development of these materials was started. At the present time, TiC-40 vol. % Ni_3Al composites are being developed because they have expansion characteristics very close to those for steel. Preliminary wear testing indicated that improved wear resistance could be achieved by decreasing the grain size of the TiC. Achieving fine grain size with the high binder contents is difficult because of the large inter-grain distances. In addition, it was thought that changing the TiC grain shape from a highly faceted one to a more rounded equiaxed grain would reduce localized stress at sharp corners. This, in turn, would improve abrasion resistance from any wear debris. Consequently, grain size refinement is presently being studied. One of the most obvious ways to improve grain refinement is to reduce the initial TiC particle size prior to sintering.

The purpose of this Cooperative Research and Development Agreement (CRADA) was to develop composites of TiC-Ni_3Al with refined grain microstructures for application in diesel engine fuel injection devices. ORNL has considerable experience in fabrication, characterization and testing of TiC-Ni_3Al Composites. For several years, programs have developed WC and TiC ceramics with intermetallic alloys of Ni_3Al and FeAl. These have been quite successful and at the present time samples are being considered for a structural application in diesel engine fuel injection systems. This work is currently funded by the Heavy Duty Vehicle Propulsion Materials Project. Coors Tek is a well-known manufacturer of advanced ceramics and composites. Currently, they are interested in development of high-strength, toughened materials for use in fuel injection systems of diesel engines. Improved materials are necessary in that application for the reduction of exhaust emissions and improved fuel consumption. The TiC-

Ni_3Al composites are strong candidates to meet the requirements for the particular application. However, earlier tests have shown that a small TiC grain size is necessary to meet some of the wear requirements. Under the CRADA, composites of TiC-Ni_3Al with refined grain microstructures were fabricated by milling of commercially available powders and compared to current materials.

The CRADA project consisted of five tasks as shown below:

1. Characterization of As-Received Materials
2. Particle Size Reduction of TiC
3. Characterization of Modified TiC
4. Fabricate Specimens From Modified TiC
5. Characterization of Specimens From Modified TiC

Experimental Procedure

The attritor milling was done with one of three mill media types: (a) 3 mm ZrO_2 milling media, (b) 4.9 mm WC, or (c) 1.1 mm WC. The different milling conditions are described in Table 1. In all cases, ethanol was used as the liquid vehicle. Media wear during milling contributed some contamination to each of the compositions as shown in the table. The TiC powders were dried after milling and composites were fabricated from several of the different milled powders as shown in Table 2. The Ni_3Al content for all the composites in the study was 40 vol. %. This composition was chosen because the thermal expansion of the composites is similar to that of steel. The milled TiC powders were mixed with the Ni_3Al (IC-50) by ball milling using 10-15 mm ZrO_2 milling media. In all cases, this secondary mixing was done in ethanol with 1 wt. % PEG* added as a binder.

The mixtures were dried and screened to -100 mesh. Specimens were uniaxially pressed in 25 mm diameter steel dies at ~100 MPa (15 ksi). Sintering was done in a graphite element furnace utilizing a vacuum/low pressure hot-isostatic pressure cycle (V-LPHIP). Important parameters affecting the microstructural development and densification include the densification temperature, densification time, heating rates, intermediate temperature holds, and gas pressures. Because of the number of variables to be studied, a Taguchi experimental array was formulated to assess the impact of each of the variables on the sintering process. The various sintering parameters used are shown in Table 3.

For all of the test samples, densities were determined by the Archimedes' method. X-ray analysis was performed on machined bulk surfaces of sintered dense composites. Scanning electron microscopy (SEM) was done on polished sections using back-scattered electron (BSE) imaging.

Results

Particle Size Reduction - The milling study was done on several commercial grade TiC powders to determine the effect of particle size reduction on the densification behavior and properties.

* Polyethylene glycol, Carbowax 8000, Union Carbide, New York.

Numerous milling trials were performed and the final particle sizes and oxygen contents are summarized in Table 1.

The TiC particle size reduction behavior as a function of milling time is shown in Figs.1 and 2. For the test conditions used in the experiments, the WC and ZrO_2 mill media types (with 4.9 and 3 mm diameters, respectively) had similar behavior. It would be expected WC would result in higher milling efficiency because of its higher specific density. However, the larger media size results in fewer media-media contacts and less efficient particle size reduction. Going to a smaller WC media size (1.1 mm diameter) resulted in a substantial increase in milling rate. Because the TiC powders had essentially bimodal size distributions, one of the important parameters was the D_{90} value, which is a measurement of the larger particle sizes in the distribution. The D_{90} results, in Fig. 2, show the effectiveness of the small WC media in reducing the particle sizes for the larger grains.

As indicated in Table 1, because of the very high hardness of TiC; significant mill media wear was introduced into the batch compositions. While the zirconia is expected to be non-reactive in the TiC-Ni_3Al system, the WC is believed to take part in the solution-reprecipitation of the TiC grains during liquid phase sintering and is incorporated into the microstructure. In addition to mill media wear, oxygen contents of the TiC powder are also increased with milling. This leads to other processing problems as will be discussed below. The milling results illustrate the need to use TiC-based milling media in processing to minimize batch compositional changes.

Several of the milled TiC powders were subsequently used to fabricate composites with 40 vol. % Ni_3Al (IC-50) as indicated in Table 2. Because of the small particle sizes, high surface areas, and high oxygen content of these powders, off-gassing of volatile species during high temperature sintering was anticipated. Thermal gravimetric analysis (TGA) was performed to evaluate the weight loss behavior. The samples underwent binder burnout up to 400°C in argon prior to the TGA tests. The results are shown in Fig. 3. (The instrument had an anomaly at ~1050°C to 1150°C, which also was present in the Al_2O_3 standard sample.) Significant weight losses are observed for the fine TiC milled with the small WC media. Also a comparison between the two media types indicates that for comparable milling conditions, the WC-milled materials exhibited larger weight losses. This suggests that, in addition to TiC oxidation, WC from the wear debris may also contribute to oxygen pickup in the batch composition.

Sintering Study - The summary of the densification results from the Taguchi Study are shown in Table 4. To analyze the effects of the different sintering parameters, the densities of all of the compositions for the various runs were averaged together. The level effects and the calculated percent contributions to the densification were analyzed by an ANOVA treatment of the data and the results are shown in Table 5. As indicated, the major overwhelming influence on the densification behavior was the use of vacuum. Apparently, the off-gassing of the specimens during sintering is necessary to achieve high densities and is improved by the use of vacuum. The other factors that had any significance were the sintering temperature and the use of pressurization at the sintering temperature. The sintering time and the 800°C post-sinter hold had minor effects. The 1200°C pre-sinter hold and the heating rate had no perceptible effects in the study.

Comparisons of the different parameters are shown in Figs. 4 through 10. As indicated in Fig. 4, longer sintering times improve the densification. However, it is well known that extended high

temperature exposure increase grain size because of Ostwald ripening. Thus, while densities are improved, longer hold times are not desirable for grain refinement. The same is true for the sintering temperature. As illustrated in Fig. 5, the higher sintering temperature increases density, but is not a way to keep grain size small.

Little effect of the 1200°C hold on densification is evident from Fig. 6. In fact, the no hold at 1200°C exhibited slightly higher densities. The 1200°C hold was used in previous studies to aid in degassing samples prior to densification. Previous work had shown that even at 1200°C (before the appearance of a liquid phase), solid state reactions do occur between the TiC and the Ni_3Al. These reactions may actually be non-beneficial to the sintering process. This is reinforced when only the DC-70 samples are analyzed since this sample would have the minimum of off-gassing (since no extensive TiC milling was done) and it showed significantly better densification with no 1200°C hold (95 versus 89 % T. D.).

The effect of the heating rate (Fig. 7) indicates the slower rate is better for densification. This result may also be a consequence of the off-gassing behavior which would be more efficient at the slower ramp speeds prior to the formation of the liquid phase (and the subsequent closing of the pores). In fact, for the DC-70 sample (with minimal off-gassing), no effect of the heating rate was evident. As expected, the vacuum sintering was definitely the single most important variable as indicated in Fig. 8.

The 800°C hold was examined as a variable because in conventional processing of Ni3Al alloys, the intermediate temperature anneal is employed to develop secondary phases in the microstructure and improve properties. Thus, it was desirable to determine if it would have any desirable benefits for the composites. It was believed that the hold may affect the properties, but not the density since this temperature is well below any liquidus temperature for this system. Fig. 9 shows that the 800°C hold actually had a detrimental effect on densification. A closer look at the data reveals that the hold is more of a problem when used in conjunction with the pressurization step. Fig. 11 compares the different sets of data. These results suggest that the high-pressure argon used in the pressurization step may be incorporated into the liquid phase during sintering and that during the 800°C hold and may come out of solution. The pressurization step does improve densities (Fig. 10), however, the exact parameters (time, pressure, release point, etc.) may have to be modified to minimize any detrimental effects.

Microstructure Characterization – The effect of milling conditions on the microstructure of the TiC-Ni_3Al composites is shown in Fig. 12. As expected, as the milling intensity increased (and the initial TiC particle size decreased), the final TiC grain size becomes finer. The DC-70 sample used as-received TiC and was milled only in the secondary ball-milling operation. Smaller grain sizes were observed for the attritor milled samples (DC-74, -75, -78, and –79). Very fine grain sizes were associated with the TiC milled with the 1.1 mm WC media (DC-90 and –91). Microstructure characterization at relatively low magnification showed poor wetting behavior between the Ni_3Al and the milled TiC. Fig. 13 shows that as the TiC particle size becomes smaller (and the oxygen content increased), decreased wetting occurs. This results in regions without liquid infiltration and is the reason for decreased densities.

INVENTIONS

None.

COMMERCIALIZATION POSSIBILITIES

Coors Tek is pursuing commercialization of TiC-Ni_3Al composites fabricated by the processes similar to those studied in the CRADA.

CONCLUSIONS

Grain refinement is important for improved wear resistance and high strength for the applications of interest. Attrition milling effectively reduces the initial particle size and leads to a reduction of the final grain size. However, an increase in the oxygen content occurs concomitantly with the grinding operation and decreased densification of the compacts occurs during sintering.

Table 2. TiC-Ni_3Al composites fabricated from milled TiC powders.

Sample No.	Mill Run No.	TiC Type	Mean Particle Size (μm)*	Oxygen Content (wt. %)
DC-70	None	2000	3.16±0.9	
DC-72	None	2000	3.16±0.9	
DC-74	4	Jet-Mill	0.47±0.14	2.21
DC-75	3	Jet-Mill	0.55±0.18	1.94
DC-78	5	2000	0.61±0.32	
DC-79	6	2000	0.70±0.23	
DC-87	8	1000	0.20*	3.02
DC-88	7	1000	0.77*	1.19
DC-89	9	1000	0.50*	1.19
DC-90	11	1000	0.32±0.09	3.36
DC-91	12	1000	0.18*	2.34

*Prior to ball milling step with Ni_3Al powder.

Table 3. Optimization of sintering schedule for TiC-Ni_3Al composites to achieve grain refinement. The matrix is a L_8 (2^7) orthogonal array.

Test No.	Sinter Time (min)	Sinter Tempera-ture (°C)	1200°C Hold During Heating[a]	Heating Rate (°C/min)	Sinter Atmos-phere	800°C Hold During Cooling[b]	1 MPa Pressuri-zation Step[c]
1	40	1425	Yes	10	Vacuum	No	Yes
2	40	1425	Yes	20	Argon	Yes	No
3	40	1475	No	10	Vacuum	Yes	No
4	40	1475	No	20	Argon	No	Yes
5	20	1425	No	10	Argon	No	No
6	20	1425	No	20	Vacuum	Yes	Yes
7	20	1475	Yes	10	Argon	Yes	Yes
8	20	1475	Yes	20	Vacuum	No	No

[a] 1200°C hold for 30 min. during heating
[b] 800°C hold for 30 min. during cooling
[c] Pressurization step occurs during last half of the sintering time (i.e. either 20 or 10 min.)

Table 4. Summary of densification results from sintering study.

Run. No.	DC-70	DC-72	DC-74	DC-75	DC78	DC-79	DC-81	Ave.
1	99.2	99.5	99.9	100	93.1	98.9	80.5	95.9
2	74.2	73.9	70.7	76.8	85.0	88.6	80.2	76.9
3	98.0	96.9	91.3	91.3	95.6	100	88.1	94.5
4	97.1	89.9	87.9	91.5	92.2	95.2	83.3	91.0
5	85.8	72.3	74.9	80.2	81.7	84.6	77.1	79.5
6	99.6	90.3	90.5	82.9	78.7	94.0	84.0	88.6
7	95.2	80.6	80.5	83.0	84.9	89.2	81.1	84.9
8	97.1	94.1	96.0	89.0	89.0	93.0	82.8	91.7

Table 5. Level effects and percent contributions form the different parameters.

Variable	Level Effect	Percent Contribution
Sinter Time	3.40	5
Sinter Temp	5.30	15
1200°C Hold	1.05	0
Heating Rate	1.65	0
Sinter Atmosphere	9.56	53
800°C Hold	3.31	5
Pressurization Step	4.45	10
Error		12

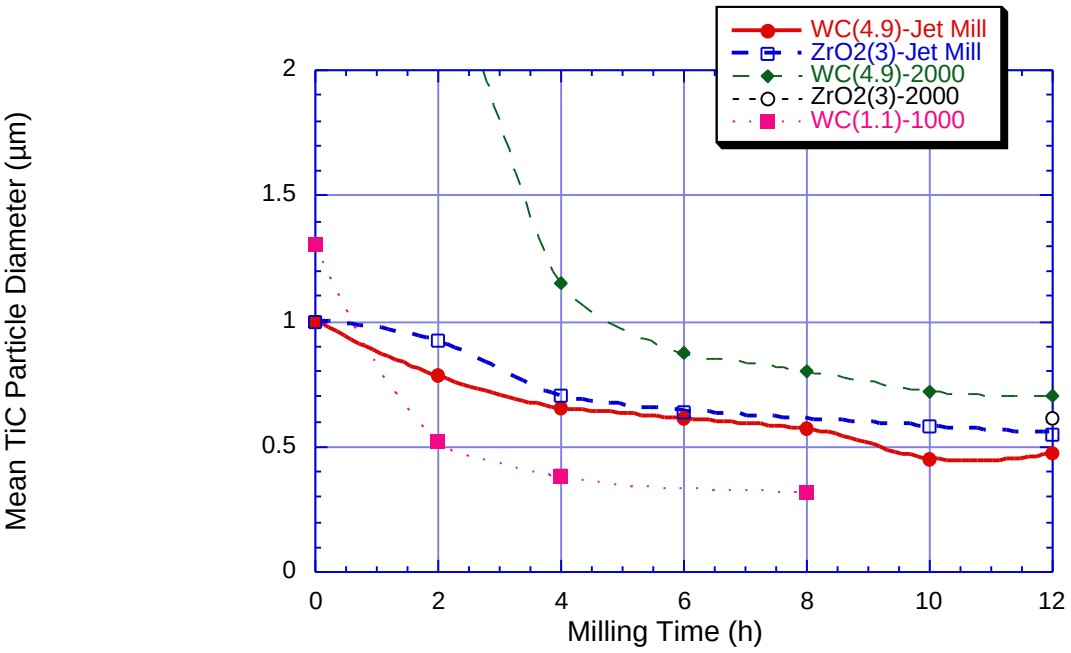

Fig. 1. Mean TiC particle size reduction during milling.

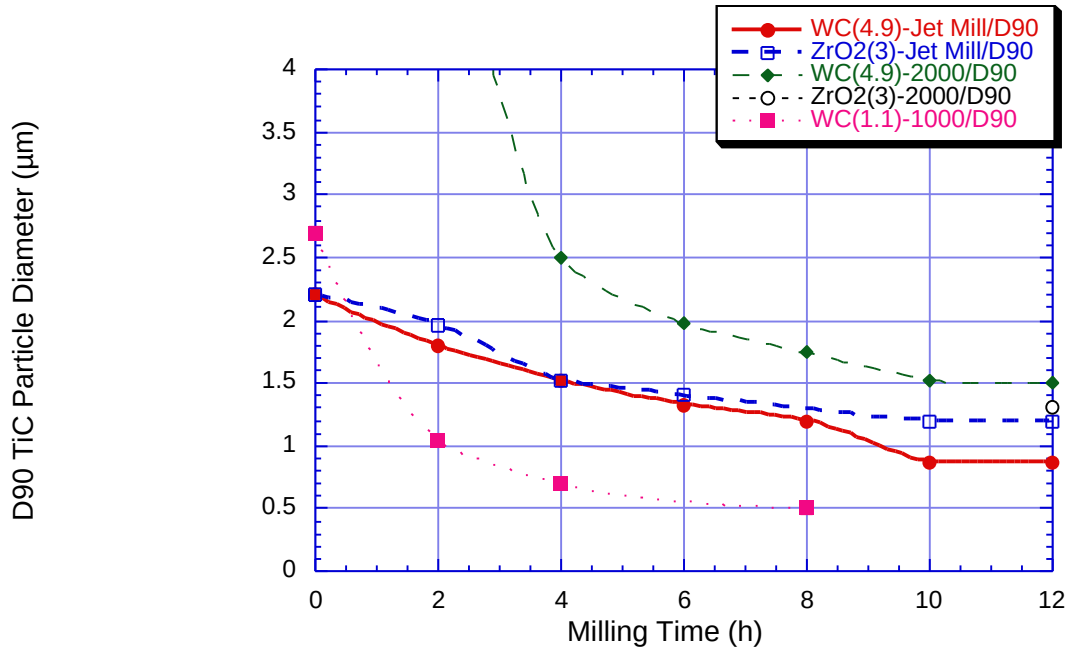

Fig. 2. D_{90} TiC particle size reduction during milling.

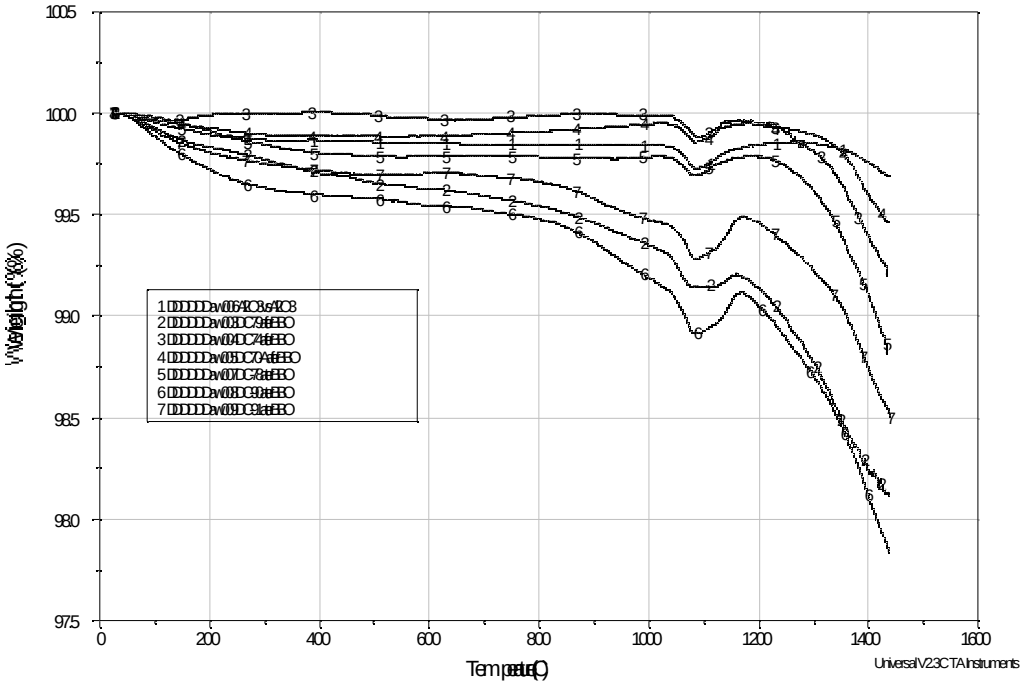

Fig. 3. Thermal gravimetric analysis (TGA) results on composite powders after binder burnout. (The instrument had an anomaly at ~1050°C to 1150°C, which also was present in the Al_2O_3 standard sample.)

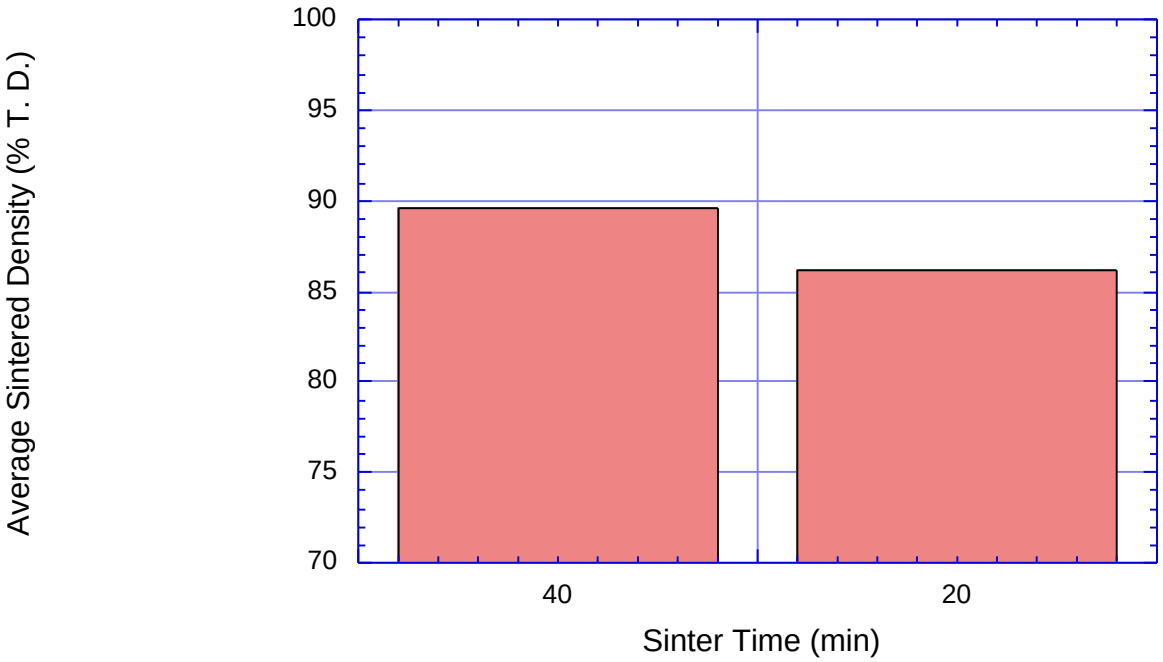

Fig. 4. Effect of sintering time on average density of TiC-Ni_3Al composites.

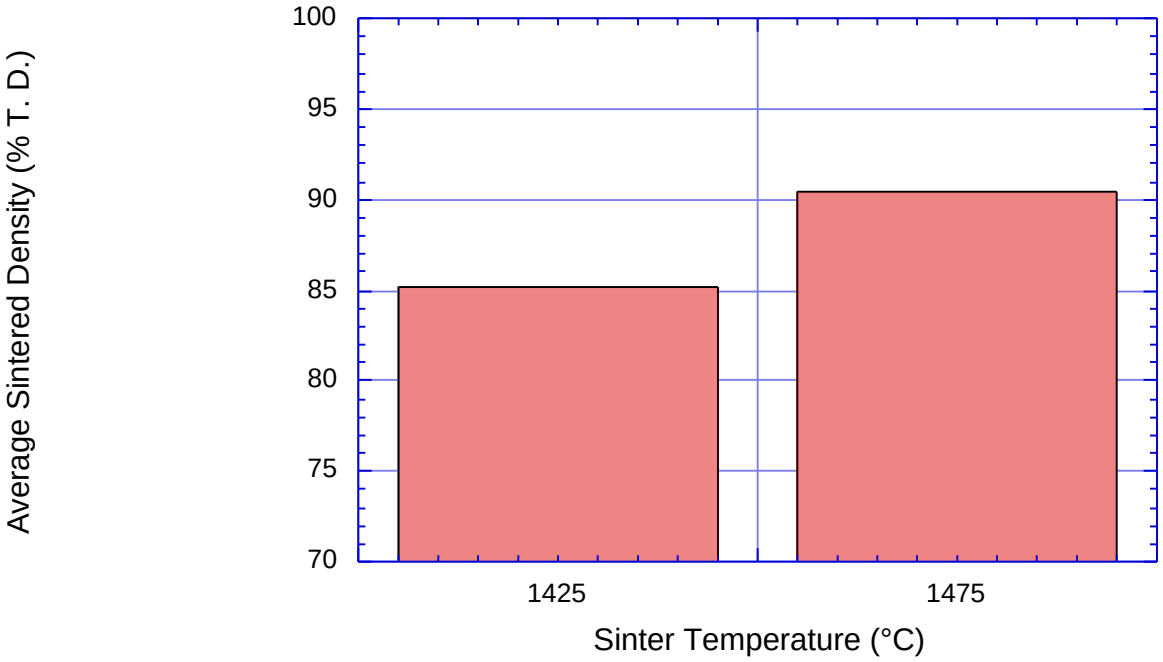

Fig. 5. Effect of sintering temperature on average density of TiC-Ni_3Al composites.

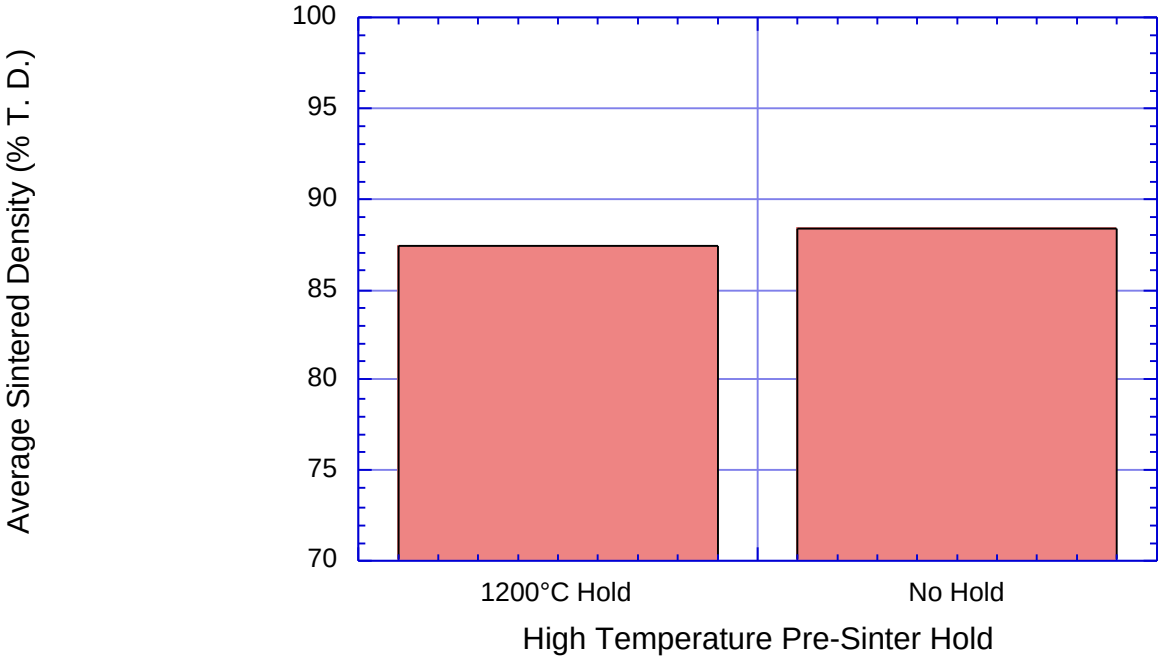

Fig. 6. Effect of 1200°C pre-sinter hold on average density of TiC-Ni_3Al composites.

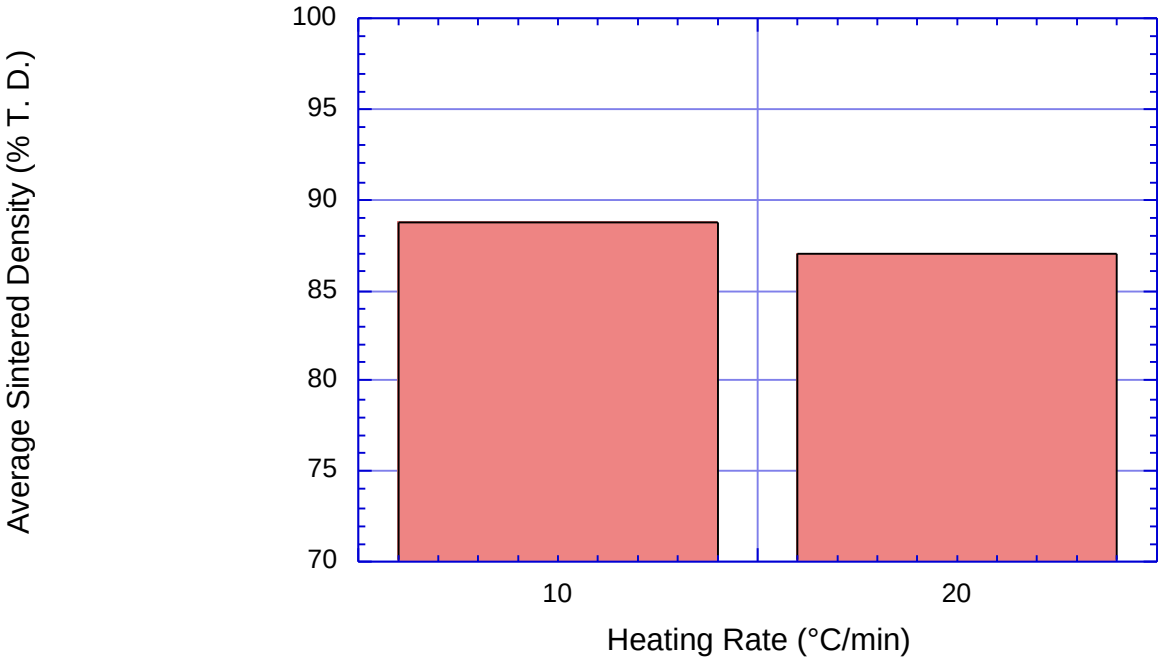

Fig. 7. Effect of heating rate on average density of TiC-Ni_3Al composites.

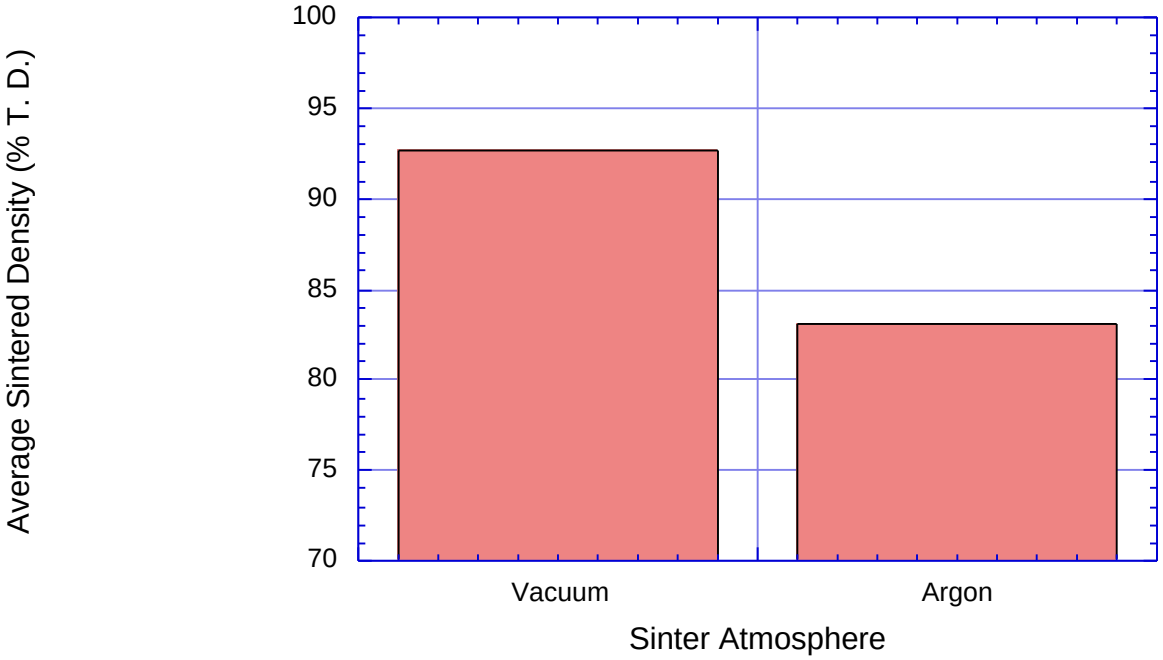

Fig.8. Effect of sintering atmosphere on average density of TiC-Ni_3Al composites.

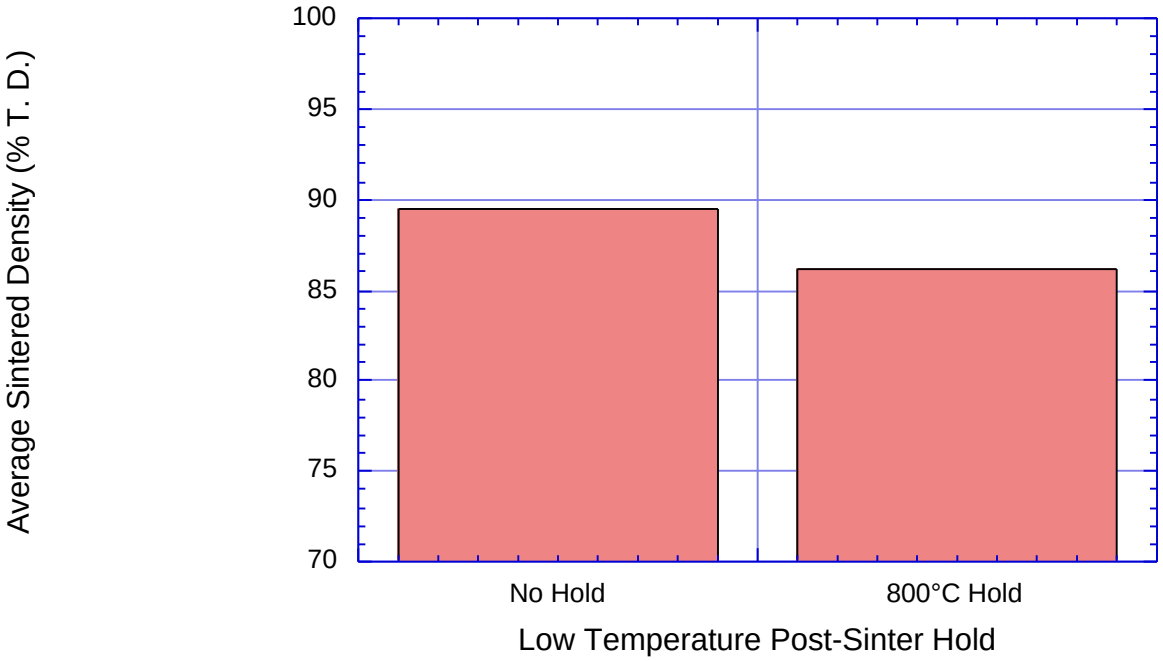

Fig. 9. Effect of 800°C post-sinter hold on average density of TiC-Ni_3Al composites.

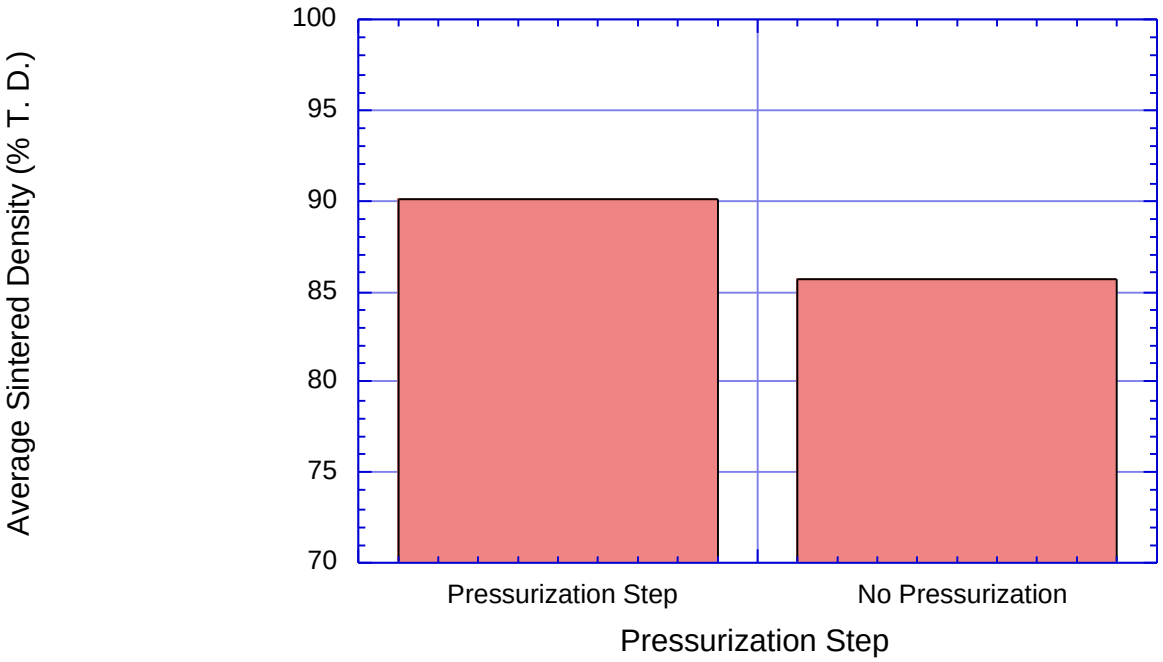

Fig. 10. Effect of 1 MPa pressurization step on average density of TiC-Ni_3Al composites.

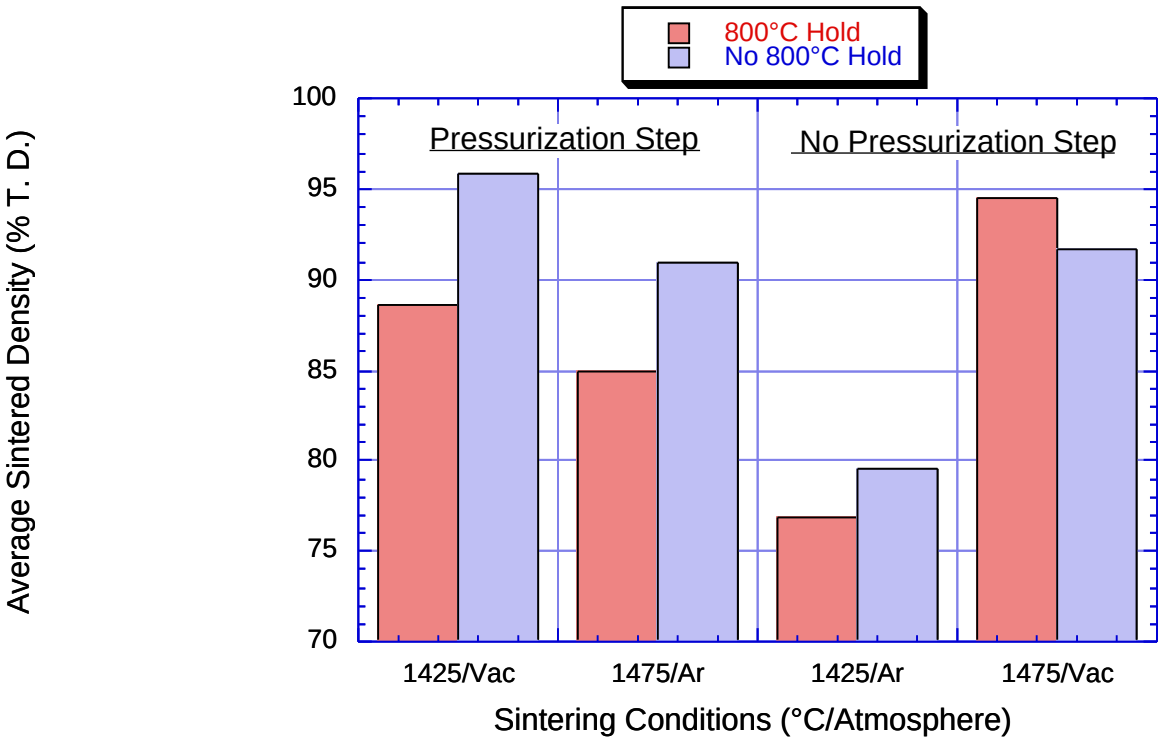

Fig. 11. Comparison of average sintered densities for 800°C hold at different conditions.