L. Synthesis of Powders for Titanium Carbide/Nickel Aluminide Cermets

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Objectives

- Develop an understanding of the synthesis of submicron-sized titanium carbide, Ni_3Al, and the composite intermetallic cermet (TiC/Ni_3Al) powder.
- Synthesize titanium carbide, NiAl, Ni_3Al, and TiC/Ni_3Al powders via batch and continuous processing.

Approach

- Investigate the synthesis of these materials on a small scale (1–5 g) using a well characterized thermogravimetric analyzer (TGA).
- Investigate the effects of using diluent materials during the synthesis of nickel aluminides to promote the formation of submicron product powders in a batch process at both a small and large scale (50–150 g). (Diluents are presynthesized powdered forms of nickel aluminides and/or titanium carbide that act to absorb excess heat released during the chemical reaction and to provide extra surface area for melted aluminum to coat.)
- Synthesize both materials using a continuous-flow, aerosol transport tube reactor.

Accomplishments

- Studied the formation of submicron titanium carbide powders as a function of temperature and feed composition in the small-scale batch reactor (TGA).
- Found that diluent materials allow for the synthesis of submicron nickel aluminide powders in the small-scale batch reactor (TGA).
- Synthesized submicron titanium carbide/nickel aluminide composite materials in the small-scale batch reactor (TGA) using a variety of diluent compositions and amounts.
  - The diluent particles participate in the reactions and have their size reduced.
- Synthesized nickel aluminides in the continuous-flow, aerosol transport tube reactor. No diluent materials were used. These experiments served as a base case to help develop an understanding of what effects the diluents will have.

- Studied the synthesis of titanium carbide in the transport tube as a function of temperature and the residence time for the reactants in the reactor.

Future Direction

- Optimize the synthesis of titanium carbide to provide for stoichiometric titanium carbide of low oxygen content.
- Explore finishing the titanium carbide product (after synthesis in the aerosol transport tube) in a second reactor.
- Study the effect of diluent materials on the synthesis of nickel aluminides in the aerosol transport tube. Both nickel aluminide and titanium carbide diluents will be used.
- Synthesize larger quantities of the pure and composite materials so that parts can be made from them and their physical properties tested.

Introduction

Intermetallics and ceramics are attractive materials for applications in many extreme environments. Both have physical and chemical properties that allow them to operate under conditions that many current materials cannot withstand. Intermetallics, unlike alloys (simple solid mixtures of metals), comprise definite atomic ratios of atoms that are chemically bonded together in a crystalline lattice, such as Ni_3Al or $TiAl_3$. They have greater strength, higher melting points, and better corrosion resistance than common alloys. Similarly, ceramics, especially non-oxide ceramics like carbides, exhibit high toughness and hardness, as well as excellent chemical resistance. Composites of these two materials, called cermets, combine the best properties of both to yield exceptional materials.

However, the very properties that make these materials desirable make it difficult to fabricate parts from them. Parts are typically made from aluminides by synthesizing the material in a molten form and then casting the liquid. It is desirable to directly synthesize the intermetallic and cermet (TiC/Ni_3Al) as submicron-sized powders.

The focus of this research is to develop a process for directly synthesizing nickel aluminide and titanium carbide as powders suitable for densification. These materials will preferably be of submicron size and have tight particle size distributions.

Approach

Titanium carbide will be synthesized via the carbothermal reduction of titanium dioxide. The reaction is given in Eq. (1). Nickel aluminide will be synthesized from nickel and aluminum metals. The aluminide reaction is given in Eq. (2). It occurs in two different compositions. In the first, one atom of nickel is reacted with one atom of aluminum to form mononickel aluminide (NiAl). In the second, three atoms of nickel are reacted with one atom of aluminum to form trinickel aluminide (Ni_3Al)

$$TiO_2 + 3\ C \rightarrow TiC + 2\ CO \quad (1)$$
$$(3)\ Ni + Al \rightarrow Ni_3Al \quad (2)$$

The synthesis reactions for both titanium carbide and nickel aluminide were at first studied using a large-capacity (1–5 g) TGA (Figure 1). The TGA is capable of accurately measuring small weight changes in reaction masses (Figure 2). In cases where the reactions generate or consume gases, the weight change is a method to monitor the progress of the reaction. The synthesis of titanium carbide from titanium oxide generates carbon monoxide. However, the synthesis of nickel aluminide from nickel and aluminum results in no weight change.

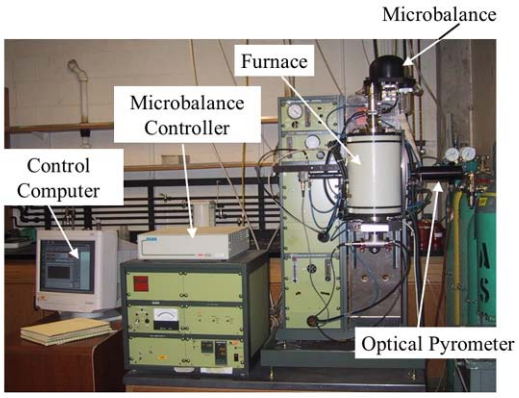

Figure 1. Theta Gravitronic VII TGA.

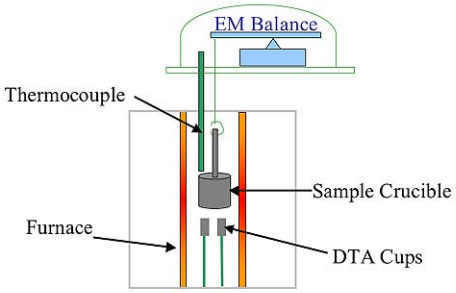

Figure 2. Schematic of TGA.

So for nickel aluminide, the heat evolved by the reaction was monitored using a differential thermal analyzer (DTA).

The first step in the aluminide reaction is to heat the raw materials to the melting point of aluminum (~650°C). The molten aluminum then reacts with the nickel to form the desired aluminide. This reaction releases a substantial quantity of heat, often enough to melt the aluminide that is formed (melting point is ~1450°C). Therein lies the problem with directly making the material as a powder: the molten liquids, both aluminum and aluminide, coalesce to form large droplets, not submicron powders. The strategy for preventing this was the use of diluent materials. Pre-synthesized nickel aluminide and/or titanium carbide was included in the batch reaction formulation. The diluents provided a surface area for the molten aluminum to coat and a heat sink to absorb the excess energy of the reaction. Surprisingly, previous work in this project found that aluminide diluent materials actually participated in the reaction and were reduced from 10–50 micron particles into submicron particles themselves.

The reactions were also studied using an aerosol transport tube reactor (Figure 3). This reactor design is already used industrially to synthesize tungsten carbide powders for use in drill bits in the electronics industry. There is also interest in using this reactor to synthesize boron carbide for use as ceramic armor. The carbothermal reduction of titanium dioxide [Eq. (1)] is analogous to both of these reactions. So it should be possible to synthesize titanium carbide in an aerosol transport tube as well. This reactor design allows for the continuous synthesis of product powders. By controlling the residence time of the materials in the reactor and the temperature of the reactor, the particle size of the products can be controlled: longer residence times and higher temperatures lead to larger particles.

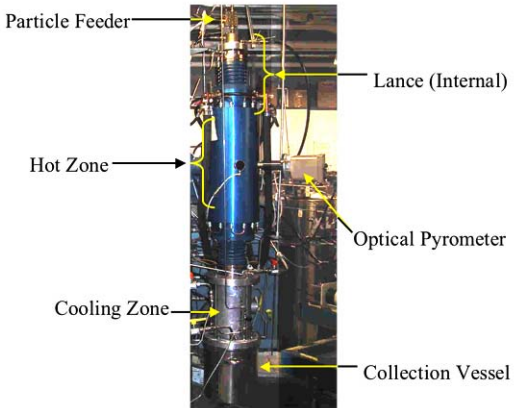

Figure 3. Photograph of aerosol transport tube reactor.

A schematic of the aerosol transport tube reactor is given in Figure 4. A powder consisting of an intimate mixture of the two reactants is entrained in a gas flow and carried to the reactor. It enters the hot zone of the furnace via a water-cooled lance that

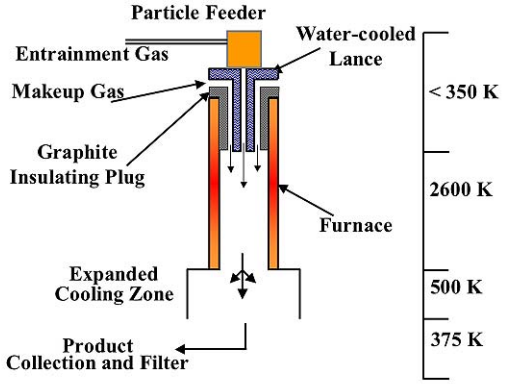

Figure 4. Schematic of aerosol transport tube reactor.

extends down into the furnace. This lance maintains the raw materials at roughly room temperature until they enter the hot zone. At that point, thermal radiation from the walls of the furnace heats the powders to the reaction temperature in a fraction of a second. The raw materials react as they fall through the furnace, and then they enter the expanded cooling zone, where they cool rapidly. From there, the powders settle into the collection vessel.

During this year of the research project, work was performed on the batch processing of aluminides and titanium carbide both to elucidate the reaction pathway further and to investigate the possibilities of scaling the batch process up. Preliminary studies of both reactions were also run in the aerosol transport tube.

Results

Batch Processing

In an effort to further confirm and characterize the breakdown of the diluent materials, experiments were run in the TGA using titanium aluminide as a diluent material. The first experiment, involving titanium aluminide and aluminum, showed that aluminides could, under the proper conditions, absorb aluminum to change the stoichiometric ratios of the substituent atoms. Trititanium aluminide was transformed at least partially into monotitanium aluminide. The second experiment involved using the trititanium aluminide as a diluent for the reaction between nickel and aluminum. The product material was found to consist of titanium dinickel aluminide; the diluent material had in fact participated in the chemical reaction.

The remaining batch experiments were run in the large-scale batch reactor. A significant effort went first into designing and building this reactor, shown in Figures 5 and 6. It is capable of holding 50–150 g of reactants and heating them to 1700°C. The

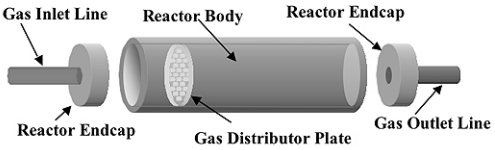

Figure 5. Schematic of horizontal tube batch reactor.

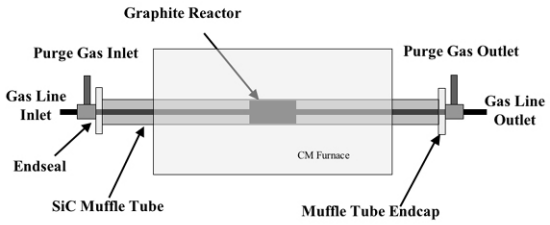

Figure 6. Schematic of horizontal tube furnace with inserted batch reactor.

first experiment involved synthesizing a batch of titanium carbide. Unfortunately, the same issues inherent in the industrial-scale synthesis became apparent: heat transfer into the reaction mass limited the conversion of the raw materials. Hence the product ended up being only 75% titanium carbide; the

remainder was unreacted titanium dioxide and carbon. The remaining experiments therefore focused on the direct synthesis of the cermet material. The reactor was loaded with varying mixtures of titanium carbide and nickel and aluminum powders and heated to 700°C. Each batch showed two types of product morphology. The outer sections were fine powders, while the inner sections were powders that had agglomerated together to form solid masses. The solid mass was smallest in the reaction involving the largest amount of diluent material. These results emphasized the importance of the diluent materials: more diluent resulted in the greatest amount of powdered product. The particle size distributions for the powdered products from the three runs are shown in Figure 7, along with the experimental conditions.

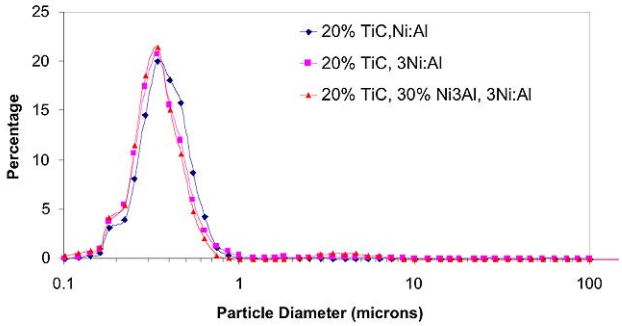

Figure 7. Particle size distribution of intermetallic cermet products.

Continuous Processing

The initial nickel aluminide synthesis experiments were run in the aerosol transport tube reactor without the use of diluent materials. These experiments were to serve as a base case for comparison with the experiments to be run later using diluents. This also simplified the analysis of the products, since in this reactor it is less clear that the raw materials would be in close enough proximity to react. Any product detected would have to have been made by the reaction. The synthesis of both NiAl and Ni_3Al was studied in a 3 × 3 matrix of temperature (1000, 1200, and 1400°C) and residence time (1.0, 2.0, and 3.0 seconds). These 18 experimental runs were analyzed via X-ray diffraction to determine if the products were formed. To varying degrees in all cases, spectrum peaks associated with nickel aluminides were evident; however the peaks did show that there was some variation in the ratio of nickel to aluminum. Also, there were varying degrees of unreacted nickel and aluminum in the samples. However, as previously stated, this is expected to be a base case (and worst case). The use of diluents should help in making a more homogeneous product, as well as helping more of the raw materials to react. The specific surface areas (a measure of the average particle size) for the product powders ranged from 0.04 to 0.83 m^2/g, indicating average particle sizes ranging from 0.5 to 10 microns for the experiments. This compares favorably with the surface areas of the starting materials (0.29 m^2/g for the 1:1 mixture of nickel and aluminum, and 0.39 m^2/g for the 3:1 mixture of nickel to aluminum), since the aluminides are more dense than the weighted averages of the starting materials. Again, this is also the base case for the aluminide synthesis. The use of diluents should allow for higher-surface-area products to be made.

The initial work on the synthesis of titanium carbide in the aerosol transport tube proved to be only marginally successful. The reaction was studied at 1900, 2000, 2100, and 2200°C using a residence time of 1.5 seconds. The products ranged from 14 to 80% pure titanium carbide. These experiments used a feed mixture that contained 5% carbonized starch to act as a binding agent during the feed preparation process. Carbonized starch has previously been found to assist in driving the reaction to completion. Therefore, the next round of experiments used a feed in which all of the carbon was supplied by carbonized starch. In addition, the feed was prepared using a slight

(5%) excess of titanium dioxide. Again, previous work had shown that a higher quality of product was obtained when the feed had excess titanium dioxide. This is apparently because the final carbide morphology then depends on the morphology of the starting titanium dioxide. The Degussa P-25 titanium dioxide is a very fine submicron powder, so it should yield a high-quality titanium carbide product. The excess titanium dioxide can be removed by reacting the titanium carbide with extra carbon at lower temperatures in a batch furnace. This will also allow for the adjustment of the titanium-to-carbon ratio in the finished carbide, a critical parameter for physical properties such as hardness and toughness. As with the aluminide synthesis, a 3×3 matrix of experiments was run at 2100, 2200, and 2300°C and at residence times of 0.5, 1.5, and 2.5 seconds. These experiments yielded much better results. In most of the runs, all the free carbon was converted into the carbide, and in the three runs that did contain free carbon, it was always lower than 3.1%. That is comparable to industrially available carbide. The specific surface areas ranged from 0.57 to 5.0 m^2/g for the products. This size distribution should provide for effective densification into finished parts.

Conclusions

More evidence was found for the chemical participation of diluent materials in the synthesis of intermetallics. This participation allows for the batch synthesis of submicron powders of nickel aluminide. Using this method, it is possible to make smaller quantities of intermetallics for materials testing or other laboratory tests. Composites of intermetallics and ceramics were synthesized in the large-scale batch reactor. Some reactions did not have sufficient diluent materials and formed larger agglomerates in addition to the fine powders; but in the cases where fine powders were formed, the product powders were submicron with a relatively tight particle size distribution. Both titanium carbide and nickel aluminide were successfully synthesized in the continuous aerosol transport tube. The resulting product powders were submicron and, under many conditions, completely consumed the limiting reagent. They appear to have the appropriate physical properties for use in the manufacture of parts for use in extreme environments.