The Role of Rapid Solidification Processing in the Fabrication of Fiber Reinforced Metal Matrix Composites

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THE ROLE OF RAPID SOLIDIFICATION PROCESSING IN
THE FABRICATION OF FIBER REINFORCED METAL
MATRIX COMPOSITES

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Summary

Advanced composite processing techniques for fiber reinforced metal matrix composites require the flexibility to meet several widespread objectives. The development of uniquely desired matrix microstructures and uniformly arrayed fiber spacings with sufficient bonding between fiber and matrix to transmit load between them without degradation to the fiber or matrix are the minimum requirements necessary of any fabrication process. For most applications these criteria can be met by fabricating composite monotapes which are then consolidated into composite panels or more complicated components such as fiber reinforced turbine blades. Regardless of the end component, composite monotapes are the building blocks from which near net shape composite structures can be formed. The most common methods for forming composite monotapes are the powder cloth, foil/fiber, plasma spray and arc spray processes. These practices, however, employ rapid solidification techniques in processing of the composite matrix phase. Consequently, rapid solidification processes play a vital and yet generally overlooked role in composite fabrication. The present roles and future potential of rapid solidification processing in fabrication of continuous length fiber reinforced metal matrix composites will be discussed in the following paper.

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Introduction

Continuous length fiber reinforced metal matrix composites are a family of materials which are beginning to gain acceptance in the aerospace industry, where increased performance and not necessarily economics can dictate the use of new materials. These composites combine the high strength and stiffness of modern fibers with the environmental resistance and toughness of a metallic matrix in order to create a component with better overall material performance than possible with present monolithic metals. Gains in terms of higher strength-to-weight ratios, combined with high temperature corrosion and oxidation resistance are expected with the use of continuous fiber composites. These types of advanced materials have significant potential for use in aerospace propulsion and structural applications (1-3) and advanced space power systems (4-5).

More than just an experimental curiosity, rapid solidification processes (RSP) are coming into there own as a viable materials fabrication alternative as evident from the numerous conferences and topical reviews recently dedicated to this subject (6-22). As apparent from these references and Table 1, rapid solidification encompasses a broad spectrum of technologies, from powder producing atomization techniques to the plasma spray process. Therefore, as interest in fiber reinforced metal matrix composite materials is rejuvenated, processing of continuous length fiber composites and the field of rapid solidification are beginning to merge. Whether used to create novel microstructures e.g. by melt spinning or simply because of the convenience of the fabrication technique such as the thermal spray processes, rapid solidification techniques have become an intimate part of the overall fabrication scheme for metal matrix composites.

While methods for processing metallic materials have been established for many years, the fabrication of fiber reinforced metal matrix composites for structural applications has only reached a preliminary stage of development. Optimal solutions to many processing problems still remain to be solved. Special problems associated with the fabrication of
Continuous fiber composites include the control of fiber spacing, complete densification of the matrix while maintaining matrix purity, and optimal bonding of the matrix to the fiber (good chemical bonding without excessive reaction). It is our intention in this chapter to demonstrate the viability of metal matrix composite fabrication and the solution to many of the aforementioned problems through the use of rapid solidification processing techniques for composite matrix development.

At this stage in composite technology very little can be said about large scale production processes for fabrication of continuous fiber composites though a number of techniques have been developed on a laboratory or pilot plant scale. Some of the more common techniques include unidirectional solidification of eutectic or constitutionally appropriate alloys, liquid metal infiltration, conventional powder metallurgy processes, hot pressure bonding of a suitable matrix phase around fiber bundles or mats via the powder cloth or fiber/foil technique, or consolidation of matrix pre-coated fibers (e.g. by thermal spraying or plating).

The first of these processes, unidirectional solidification or the generation of in-situ composites, has a number of naturally imposed restrictions which limits its usefulness as a manufacturing procedure. The number and type of materials which can be fabricated into composites by this technique is generally limited to eutectic or other constitutionally appropriate alloys. The fiber volume fraction in most of these systems is low, being controlled by the thermodynamic phase relationships of the system, and cannot be varied significantly (23,24). Finally, off-axis properties such as transverse strength and ductility are generally poor (25-27) with no convenient method for modifying off-axis properties through angle ply procedures.

With liquid infiltration techniques, proper wetting between fibers and matrix without significant degradation of the fibers is important and yet difficult to achieve (28,29). The relative instability of available advanced filaments and their reactive nature in most metal melts has minimized the practicality of liquid state composite fabrication. Furthermore, fiber spacing is extremely difficult if not impossible to control. This technique may be useful for
producing small volumes of discontinuous fiber composite materials using metals with low melting points such as magnesium and aluminum alloys. It would, however, be impractical to infiltrate presently available fibers with refractory metals or high melting point intermetallic compounds because of severe chemical attack of the fibers (29).

Presently, components under consideration for aerospace applications such as B/Al composite panels (30) or W/Superalloy turbine blades (31-33) are preferably produced by diffusion bonding or hot pressure consolidation of prefabricated monotapes. Monotape production is one area where rapid solidification techniques can have a great impact on the fabrication scheme of metal matrix composites. Thermal spray processes such as arc spray and plasma spray techniques inherently involve rapid solidification. These techniques can be directly utilized to produce composite monotapes which can then be cut, molded and bonded into appropriate composite structures. Monotapes or simple composite plates can also be fabricated from rapidly solidified constituents by the powder cloth or foil/fiber technique. Whether the use of an RS material as a composite matrix phase is intentional, taking advantage of the benefits gained from having a rapidly solidified microstructure, or because a rapid solidification process is the most convenient process available for matrix processing, RS processes are becoming increasingly important to composite fabrication.

Detailed composite fabrication process parameters are almost universally considered proprietary or restricted information. Therefore, the authors' intent in this paper is to describe general rapid solidification processes and their advantages followed by a discussion of the application of rapid solidification processing to composite monotape and component fabrication.
Rapid Solidification Processes

Over a quarter of a century ago a new frontier for the processing of materials was established by the efforts of Paul Duwez (34-38) and others (39-42). While not the first to investigate rapid quench rate techniques (43-44), it was the efforts of Duwez which are recognized for beginning the revolution in rapid solidification technology. During one of his initial experiments Duwez melted a small amount of metal in the bottom of a tube. By sudden gas pressurization the molten metal was ejected onto a copper plate resulting in a "splat" of frozen metal with a solidification rate on the order of $10^6$ K/s. Since then, thousands of technical papers have been published in the area of rapid solidification technology (RST) and everyday new commercial applications are emerging (45-53).

Today the term "rapid solidification" which is defined as a "rapid" quenching from the liquid state, covers a broad range of material processes. Traditionally, for a process to be considered in the rapid solidification regime its cooling rate would have to have been on the order of $10^4$ K/s or greater. Now the concept of rapid solidification is more general and processes with lower cooling rates such as some powder producing techniques have been included under the RST definition.

Rapid solidification technology, therefore, incorporates a large number of different processes. These processes can be classified either as a function of their resulting products (e.g. powder producing techniques), as a function of the resulting microstructure (grain and particle size), or as a function of cooling rate (generally measured by secondary dendrite arm spacing). A useful comparison of secondary dendrite arm spacing versus solidification rate for several different alloys is shown in Figure 1 (54-56). Superimposed on the figure are some common processing techniques, indicating the range in homogenization which can be achieved for different processes.

For solidification rates in excess of about $10^5$ K/s (as observed during melt spinning) the resulting microstructure becomes cellular rather than dendritic. Figure 2, a transmission electron bright field image, shows the cellular structure formed in a melt spun NiAl alloy.
containing 0.5 at.% W. A fine dispersion of tungsten particles helps delineate the cell and grain boundaries.

Common products obtained by rapid solidification techniques include powders, flakes, ribbons, wires and foils. An essential factor associated with almost all current rapid solidification techniques is that the as-solidified product is very small (micron size) in at least one dimension. In other words the surface to volume ratio for the product is very large. This is essential in obtaining very large cooling or solidification rates.

An important objective of all rapid solidification processes is to produce a solid phase of uniform composition with no "micro" or "macro" scale segregation of alloying elements (57). Other effects which may result from rapid solidification rates are: an increase in solid solubility of alloying elements, a significant decrease in grain size, and possibly formation of unusual metastable crystalline phases or production of non-crystalline (amorphous) phases. For most applications, however, rapidly solidified alloys must be consolidated into bulk forms, either monolithic or composite. The consolidation processes and parameters (especially time and temperature) are very critical since many of the microstructures exhibited by RS materials are metastable. Many RS materials are intended for use at elevated temperature, therefore, prolonged exposure at elevated temperature during both consolidation and service could destroy any benefits accrued from the microstructural modifications introduced by RS processing. The addition of insoluble elements or those which will form fine precipitates can result in both pinning of the grain boundaries, controlling grain coarsening during the consolidation process, and increased strength of the alloy (58-60). Thus increased homogeneity, grain refinement and strengthening effects remain the primary advantages of RS materials as applied to high temperature structural applications. The main techniques available for rapid solidification processing are summarized in Table 1 and the more common techniques are also shown schematically in Figure 3. Numerous reviews describing these techniques have been published (24,45-53,61-62), therefore, only a brief description of the processes most relevant to composite fabrication is included here. Details on the numerous
processing parameters which can affect final product quality such as melt composition, melt superheat, chamber atmosphere, crucible composition, crucible configuration and substrate condition, composition and temperature can be found in the references listed in Table 1. For simplicity, the different processes have been divided into two main categories; (i) atomization methods and (ii) chill methods. A third general category for rapid quenching is surface techniques which includes such processes as laser surface melting. This category is not included in the following discussion since it is not relevant to composite fabrication.

Elemental and prealloyed powders used in typical powder metallurgy processes are commonly produced by atomization techniques. Several examples of the morphology and microstructure of powders produced by atomization methods are shown in Figure 4. The common feature of all atomization processes is that they are based on the disruption of a molten metal stream by external forces such as another fluid (gas or water), mechanical disturbances, or electric fields.

Figure 3a is a schematic representation of a two-fluid atomization process. This process consists of a high pressure fluid impacting a continuous stream of liquid metal resulting in a broad distribution of particle sizes. Figures 4a1 and 4a2 are examples of the morphology and microstructure of NiCrAlY powder produced by argon gas atomization. Ultrasonic and supersonic atomization techniques can greatly reduce the range in particle size distribution and also increase cooling rate. This is accomplished by use of high velocity gas pulses which break the molten metal stream into very fine droplets (< 30 \mu m). The fine liquid droplets then solidify convectively at high rates resulting in a narrow size range of fine powder.

Rotary methods are also very common atomization type processes. The rotating electrode process (REP) is one such method for producing high quality, spherical powders. This process, illustrated in Figure 3b, is based on the melting of an alloy electrode rotated at a relatively high rate of speed. The molten alloy droplets are then ejected centrifugally and solidify in an inert environment. Figures 4b1 and 4b2 are examples of the extremely spherical nature of Ti-24Al-11Nb (at%) powders produced by this technique. Several variants
of the rotary process exist. One of the higher cooling rate processes, the rapid solidification rate (RSR) process, consists of a rotating disk which is used to break up a molten metal stream ejecting the droplets into a bed of high pressure gas cooling jets.

The chill methods, based on the work of Duwez, obtain their high cooling rates by heat extraction through a substrate. Solidification rates in excess of $10^6$ K/s are readily achievable by these systems. The chill techniques normally make use of a moving substrate so that localized heating of the substrate and the deposit is minimized. The most common technique is the Chill Block Melt Spinning (CBMS) method and its variations, Free Fall Melt Spinning (FFMS) and Planar Flow Melt Spinning (PFMS). Figure 3d is a schematic setup of the CBMS process. During the CBMS process the molten metal is ejected from the crucible in which it was melted, through a nozzle and onto a rotating wheel with solidification occurring during contact with the substrate. The wheel can be either flat, producing ribbon, or notched, resulting in flake production. The product then flies off into a catcher device before one complete revolution of the wheel. This process is presently being used as a research tool as well as on a pilot plant scale production basis to produce RS material. Melt overflow (Figure 3e) and melt drag processes avoid the use of ceramic crucibles with built in orifices by making use of water cooled Cu hearths, thereby minimizing contamination of the melt. With the elimination of ceramic molds it is possible to more cleanly melt reactive metals such as titanium and silicon based alloys. Both of these modified chill block methods are being used quite successfully on a commercial basis. With the increased demand of high melting point refractory metal and intermetallic compounds for aerospace applications new melting techniques and crucible innovations are being combined with the melt spinning techniques. Arc melting, plasma melting and levitation processes are just a few of the innovations being implemented within the melt spinning process.

The main drawback in using rapidly solidified products is the need to safely handle and consolidate the RS materials into full density bulk components. Several general techniques are used for consolidation such as hot pressing, hot isostatic pressing, forging, extrusion, and
dynamic and explosive compaction processes (16). However, near net shape materials can also be formed by thermal spray processes. With these processes a continuous and controlled deposition of atomized product is sprayed onto a substrate to build up multiple layers of rapidly solidified material. Several techniques have been developed for thermal spraying with near net shape products in mind. They include spray atomization techniques such as the Osprey process (46,62), plasma spraying (42) and the arc spray process (63). The latter two processes are already used on a regular basis for the fabrication of composite monotapes (63-64). Fabrication of composite components and monotapes by the thermal spray processes as well as from RS products such as flake, ribbon and powder will be described in the following sections.

Use of Rapidly Solidified Constituents in Monotape or Composite Fabrication: Powder Cloth and Foil/Fiber Techniques

Any useful composite fabrication technique must provide a component which meets minimum prescribed design parameters and yet still be versatile enough to create parts of complex shape. For example, a common requirement in many components designated for composite reinforcement is the incorporation of hollow cooling or weight reduction passages (65-67). The entire fabrication scheme must also be cost effective and reproducible.

The powder cloth and fiber/foil techniques come as close as any process in meeting these requirements and are the most cost effective (68) and readily adaptable techniques for commercial exploitation (69). These processes are generally known as hot pressure bonding techniques because the individual composite components, matrix and fiber, are formed into composite monotapes or panels by a static pressure consolidation process carried out at elevated temperature. The general concept is shown schematically in Figure 5. From this process, simple sheets or plates can be formed and utilized as honeycomb facing or creep formed into cylindrical or complex blade shapes (70). This process is also an important source of monolayer filament tapes or monotapes which are used to form complex composite shapes
by laminate layering and pressing techniques (31,65-67).

Monotape fabrication by the powder cloth technique simply consists of sandwiching a fiber mat between two metal powder filled "cloths" and consolidating. The entire processing sequence from matrix alloy selection to finished composite monotape is shown schematically in Figure 6. The powder cloth is formed by combining the prealloyed matrix powder (produced by any of the techniques described previously) with a suitable organic binder, usually Teflon powder (71-72), and blending the mixture with the aid of a high purity stoddard solution (72). Once the slurry of powder, binder and stoddard solution is appropriately mixed the majority of the stoddard solution is evaporated off by the application of low heat. The remaining dough like mixture is then rolled into a pliable powder cloth. During the blending and rolling process the polymeric binder forms an interlocking network holding the powder particles together in a cloth like sheet. A typical powder cloth, an example of which is shown in Figure 7, generally contains 4-15% organic binder by weight.

The SiC fiber mat shown in Figure 7 is also held together by a fugitive binder. The fibers are first wound onto a lathe mounted drum or mandrel using a translating wire guide assembly to provide a desired uniform spacing of the fibers. Then an organic binder dissolved in a suitable solvent, for example polystyrene dissolved in toluene (71,73-74), is sprayed or painted over the fibers. The organic binder can also be applied directly to the filaments during the winding procedure by passing the fibers through the binder solution just before they are wound onto the mandrel (74). As the solvent evaporates a polymer film is left, encasing the fibers. The fiber mat is then removed from the drum and cut into segments which fit into the hot press.

A monotape is formed by sandwiching the fiber mat between powder cloths and consolidating. Several layers of alternating powder cloths and fiber mats can also be laid up at the same time to form a composite panel. The binder removal or thermal debinding step can take place in the hot press, under a vacuum or a low pressure inert gas atmosphere, usually without leaving a residue (71,73). A light retaining pressure is first applied to the
stack of powder cloths and fiber mats when introduced into the hot press to hold everything in place during the binder burnout stage before the final pressing temperature and pressure is reached (73). Therefore, both binder removal and partial or complete consolidation of the monotape or composite panel can occur in a single step (73,75). A pictorial review of the steps involved in the powder cloth technique for composite fabrication is shown in Figure 8. More complex components (other than simple plates) can be formed by stacking cut monotapes in desired orientations and then hot pressure bonding them together as illustrated in Figure 9 (76). This process is described in more detail in a later section.

The powder cloth process is one of the most versatile methods for producing both fiber composite finished products and "building block" materials in the form of composite monotapes. Almost all metals and ceramics can be produced in powder form so that the choice of matrix material for this process is limitless. The powder cloth technique as described above or with slight variations has been used in the past on W/superalloy (77-78), aluminide intermetallic matrix (72,75), W/FeCrAlY (65,68,71), and UO$_2$/W composites (79-82). These and other composite systems made by the powder cloth technique are listed in Table II. Examples of more recent composite systems fabricated by the powder cloth technique are shown in Figure 10. It should be noted that the SiC/Ti-24Al-11Nb composite in Figure 10 was fabricated from the same REP powders as shown in Figure 4b and the W/NiAl composite was produced from the vacuum atomized powder shown in Figure 4c.

The minimum requirement for judging the viability of a composite fabrication technique for a system with continuous aligned fibers should be the attainment of a rule-of-mixtures (ROM) strength. If attained, this would indicate that sufficient bonding between the matrix and fiber has occurred to permit load transmittal between the matrix and fiber phases. No loss of strength (compared to ROM) would also mean that bonding occurred without severe reaction between the fiber and matrix phases, that the fibers were not damaged during the hot pressing procedure and that the matrix was not embrittled during processing. In other words, if a rule-of-mixtures strength is obtained then the composite processing technique is
capable of producing a composite part without significantly degrading the strengths of any of the individual components of the composite (fiber or matrix).

Viability of the powder cloth technique for producing intermetallic matrix composites has been demonstrated by Brindley (83) by attainment of near rule-of-mixtures strengths in the SiC/Ti-24Al-11Nb system when low oxygen starting materials were used. These results are shown in Figure 11. Near rule-of-mixtures strengths have been reported in other composite systems fabricated by the powder cloth process as well (71).

Almost all composite systems fabricated to date by the powder cloth technique, including those illustrated in Figure 10, have made use of this technique because it was convenient. However, fine grain sizes which can be achieved by RS processing can also be extremely beneficial for properties. Schulson and Barker (84) have shown that fine grain sizes are preferable for low temperature ductility in intermetallics, while Whittenberger (85) has shown that a fine grain size can even increase the elevated temperature strength of nickel aluminides. With this in mind, a fine grained NiAl alloy was produced by melt spinning for use as a composite matrix phase and is presently under investigation at NASA Lewis Research Center. In preliminary studies a composite produced with this fine grained NiAl alloy has demonstrated improved thermal cycling resistance over NiAl composites made from conventional powders. An example of a NiAl based composite made from melt spun ribbon is shown in Figure 12. Submicron size tungsten particles are responsible for pinning the grain boundaries and retention of the fine grain size in this alloy even after high temperature consolidation (58,86).

The foil/fiber process for forming composites or monotapes is very similar to the powder cloth technique just discussed. Foil/filament arrays are formed by winding fibers with a predetermined filament spacing onto a large diameter mandrel forming a fiber mat (Figure 7) or by winding fibers directly onto the surface of the matrix foil which is placed over the mandrel or drum. A fugitive binder, e.g. polystyrene or an acrylic (71,73-74,87) is then used
to hold the filaments in place before the consolidation process. This time, however, the matrix is in the form of a dense foil instead of a powder cloth. With the application of heat and pressure the binder phase is removed by volatilization and the matrix is forced to flow between the filaments until opposite surfaces meet and all remaining voids are filled (87). Diffusion bonding will occur if the foil surfaces are clean and oxide free. Optimum fabrication parameters (time, temperature, pressure), determined primarily by trial and error (73, 88), are dependent upon matrix composition, filament type and filament spacing. Foil thickness and filament spacing dictate the volume fraction of reinforcement.

Rapid solidification is not the only method or even the most common process for forming thin foils of metals. Before the advent of RSP, thin foils primarily of Al and Al alloys were made by conventional rolling techniques for use in composite fabrication by the foil/fiber process (89-98). The benefit of RS processed foils lies in improvements in mechanical properties due to microstructural refinement, as well as the economic advantages gained from producing foils by RS techniques compared to wrought methods (99). Furthermore, some alloys including many of the high temperature alloys of interest as matrix materials cannot be mechanically worked into foils thin enough for use in composite fabrication. On the other hand, almost any alloy can be melted and cast into thin foils by modified melt spinning or melt overflow type techniques.

Presently, RS titanium alloy foils are the primary material of interest for further fabrication into continuous fiber composites using the foil/fiber process (99-100). The major reason for this is that two major problems encountered in titanium metal matrix composite fabrication can be solved by use of rapid solidification technology. The first problem is the relatively high cost of wrought titanium alloy foil which involves numerous cycles of vacuum annealing and cold rolling using a low reduction ratio in order to prevent cracking. In contrast, RS technology can be economically advantageous by producing thin sheet directly from the melt (99). The second major problem is the magnitude of the matrix/fiber reaction zone which typically occurs during processing, resulting in severe degradation of composite
properties. Higher loads at lower temperatures cannot be used to correct for this problem because the maximum pressing load is controlled by the diametral compression strength of the fiber. However, plastic flow occurs in fine grained RS foils at lower temperatures than wrought foils. This results in less reaction zone growth (99) and less chance in damaging ceramic fibers during the pressing procedure because of the lower loads and temperatures necessary for consolidation.

Composite plates suitable for mechanical testing or as structural panels can be fabricated in a single step by laying up alternate layers of foil sheets and fiber mats and subsequently consolidating. RS foils can even be cast directly onto the fibers by a melt overflow technique which would also lend itself to a semi-continuous type of process. Other minor variations on the powder cloth and fiber/foil techniques exist (e.g 65,74,101,108) but the basic principles are similar to what has been described.
Thermal Spray Techniques for Monotape Fabrication

The use of thermal spray processes, to fabricate composite monotapes is a natural extension of forming structural components (102) and coatings (103-104) by plasma spray deposition. These processes are considered rapid solidification techniques because cooling rates, even though varying from about $10^3$-$10^6$ K/s, fall well within the rapid solidification regime. This wide variation in cooling rate is primarily due to differences in distance between the spray gun and substrate as well as substrate temperature. In fact one of the first techniques used to study the rapid solidification of materials was plasma spraying (42) and it is still used today as a tool to study rapidly quenched metals (105).

Kreider (106-109) was the first person to optimize a thermal spray technique for continuous fiber composite fabrication and did so primarily for aluminum matrix composites using a plasma spray process. Today there are basically two types of thermal spray processes used for composite monotape fabrication. These are the plasma spray process (106-110), shown in figure 3f, and a more recent technique developed by Westfall (111-112) known as the arc spray process which is described in Figure 13. These and the previously discussed hot pressure bonding techniques for composite fabrication are compared in Table III.

The primary difference between the two thermal spray techniques is the design of the spray gun and the type of feedstock necessary for the spraying process. For a plasma spray system, fine spherical powder is used as the feed material for spraying. The powder to be deposited is injected into a plasma stream usually within the throat of the gun as illustrated in Figure 3f. The plasma is generally at 10,000 K and travelling on the order of Mach III (102). Therefore, if the powder is too coarse in size it will not melt before impacting the substrate and if too fine in size it will vaporize in the plasma stream. General practice is to use powder screened to a particular mesh size e.g. -400 mesh or an average diameter of about 37 μm (102).

For the arc spray technique, the feed material for the matrix phase is in the form of continuous wire, generally 0.16- 0.32 cm (0.0625-0.125") in diameter. During this process,
two wire feeds of opposite charge are forced through the arc spray gun at a controlled rate. This causes an electric arc to be struck between the wires melting the wire tips. The resulting molten metal droplets are then sprayed onto the substrate by a stream of argon gas which passes through the gun and directly past the arc (4). An advantage of the arc spray process over plasma spraying is that the as-deposited matrix material has a much lower oxygen content because the starting material (wire vs. powder) will almost always be cleaner (113). As-consolidated oxygen levels for arc sprayed composites is generally on the order of several hundred ppm (4,113) while for plasma sprayed materials the oxygen level is an order of magnitude higher (113). The primary disadvantage in the arc spray process is that it is not always convenient or even possible to procure continuous strands of prealloyed wire of brittle alloys. Clad bimetallic and hollow core elemental powder filled composite wires, however, can potentially be used for creating most desired matrix compositions. For example, W/nickel aluminide monotapes have been successfully fabricated by the arc spray process using a composite wire formed from elemental constituents as feed stock for the spray gun (114).

A flow diagram of the general processing scheme used for monotape fabrication by thermal spray processes is shown in Figure 14. A protective foil wrapped drum or mandrel is covered with a predetermined spaced array of fibers, (similar to forming a fiber mat), which are then sprayed with a layer of matrix material. The mandrel is usually rotated and traversed in front of a stationary spray gun to ensure spraying of an even layer of matrix alloy. This sprayed matrix material mechanically bonds the wires in place by filling the interstices between and even to a limited extent behind the fibers. The monotape can then be removed from the mandrel or it can be overwrapped with another layer of fibers and resprayed forming a unidirectional composite panel. A typical example of a thermally sprayed W/Nb monotape and the resulting RS microstructure can be observed in Figure 15. The as-sprayed monotapes contain 10-30% porosity depending on spraying conditions and drum speed (70,112). Hot consolidation processes are then used to fully consolidate the monotape or composite component.
Component Fabrication from Composite Monotapes

Thermal spray processes and the hot pressure bonding techniques are a convenient source of prefabricated components (monotapes) which can be easily processed into composite parts with angle-ply structures. Although potential exists for high purity product, monotapes are currently being produced with a range of interstitial impurity levels depending upon fabrication method. Residual oxygen levels resulting from the plasma spray process, at about 2000-5000 ppm depending on the alloy being deposited (113,115), can be an order of magnitude greater than for any of the other techniques (4,72,75,113). This can be a problem in some materials since high oxygen contents can have a devastating effect on matrix alloys prone to oxygen embrittlement such as titanium based alloys (113,115) and intermetallics (118). The powder cloth, foil/fiber, and arc spray processes can all produce monotapes with oxygen levels in the hundreds of ppm range (4,72,75,113). While the arc spray process has the lowest oxygen pickup of the thermal spray techniques the foil/fiber process is potentially the cleanest of all the techniques, especially if grooved foils are used to hold the fibers in place instead of organic binders. While all the binder can be theoretically burned off in the powder cloth and foil/fiber processes there is a tendency with these processes for a slight pickup in C (20-500 ppm) (72,75) due to the presence of any trapped organic binder. Carbon pickup is not a problem associated with any of the thermal spray processes.

An advantage to fabrication of monotapes by thermal spray processes is the elimination of the initial hot press and binder removal step necessary with the hot pressure bonding procedures. This can result in savings of both fabrication time and cost (112). Another advantage of the thermal spray processes is that the matrix material can be sprayed onto relatively complex shapes. Shapes of revolution can be produced simply by winding, and more complex shapes can be produced by winding fiber onto flexible frames and then deforming or orienting the frames (106). Experimental rocket nozzles of tungsten wire and tungsten matrix have been produced by this process (110) demonstrating the versatility inherent in the thermal spray techniques.
Hot consolidation of preforms or stacks of monotapes produced by any of the techniques previously discussed has been extensively used to form plate or sheet type composite components (for examples see Table II). Even when restricting structures to this simple geometry there is considerable room for flexibility. Figure 16 is an example of the cross section of a structural panel made from a SiC/Fe-40Al(at%) composite containing stainless steel cooling passages. This particular panel was fabricated by the powder cloth technique to demonstrate the versatility of the process.

The use of monotapes to form more complex components has been demonstrated by the fabrication of composite turbine blades (31,65,119-120). Figure 9 is an illustration of a simplified version of this process. However, even this process is capable of producing solid blade shapes that are close to final dimensions and in need of only limited touch up machining (31,65,119). Intricate demonstration components such as a composite turbine blade containing internal cooling passages and trailing edge cooling slots have also been fabricated (31). Furthermore, an economic assessment of the processing routine (121) indicates that the manufacturing cost of a W fiber reinforced turbine blade should be competitive with current blade production costs using a directional solidification technique. Further details on the fabrication of fiber reinforced turbine blades can be found in the article by D. Petrasek in this same volume.

All the composite fabrication techniques discussed, have the advantage of maintaining accurately controlled fiber volume fractions and fiber distribution. This is because the spacing between fibers in any particular layer is extremely uniform and can be fixed to whatever distance is deemed appropriate. Furthermore, the thickness or total volume of the matrix phase applied can also be accurately controlled. This is a significant advantage over conventional powder metallurgy techniques such as extrusion and molten metal infiltration techniques in which fiber placement and spacing cannot be controlled. In addition, a
structural component can even be produced with a gradient of fiber reinforcement through the thickness of the part. This can be easily accomplished in all of the techniques discussed by simply varying the spacing between fibers in the different layers.

Conclusions

In this paper we have attempted to point out the advantages and versatility of composite fabrication techniques which in one form or another involve the use of rapid solidification technology. Because composite fabrication and RSP have become so interrelated it is to the advantage of the processing engineer to make the best use of the RS processing stage in order to optimize not only the composite processing procedure but composite properties as well. Potential for new composite processing schemes incorporating state-of-the-art RSP and the creation of "designer microstructures" developed for future matrix phases of engineered composite materials are nearly limitless.
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References


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Table 1
Rapid Solidification Techniques

<table>
<thead>
<tr>
<th>Process Name</th>
<th>Description</th>
<th>Product/Dimensions</th>
<th>Cooling Rate K/s</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid Atomization</td>
<td>High Pressure fluid impacting a continuous stream of liquid metal.</td>
<td>For Gas: Low O2 contamination</td>
<td>Gas: 10^2-10^3</td>
<td></td>
</tr>
<tr>
<td>(Normally twin jets)</td>
<td></td>
<td>Spherical/Smooth powder</td>
<td>SGEA: up to 10^4</td>
<td></td>
</tr>
<tr>
<td>- Gas (Ar, N₂)</td>
<td>Ultrasonic G.A: Desintegration occurs by high intensity pulsed waves.</td>
<td>Supersonic G.A: 10-50 μm</td>
<td>USCA: 10^5</td>
<td></td>
</tr>
<tr>
<td>- Water</td>
<td>For Water: High O₂ Contamination</td>
<td>Ultrasonic G.A: &lt;30 μm</td>
<td>Water: 10^2-10^4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spherical powder 40/150 μm Dia</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Irregular particulates 75/200 μm Dia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum Atomization</td>
<td>Molten metal supersaturated with gas under pressure is suddenly exposed to vacuum, gas expands</td>
<td>Spherical powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(solvated Gas)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gas atomized droplets</td>
<td>10^4-10^5</td>
<td>53,133</td>
</tr>
<tr>
<td></td>
<td></td>
<td>directed to impinge on a rotating</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>drum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drum Splat Quenching</td>
<td>Gas atomized droplets directed to impinge on a rotating drum.</td>
<td>Flakes 50/100 μm thick 1-3 mm Dia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotating Electrode Process (REP)</td>
<td>Alloy in electrode form is rotated (~250 rps) while it is melted by arc plasma/beam. Molten metal is</td>
<td>Spherical/Smooth Powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ejected centrifugally and solidifies</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>in an inert gas filled chamber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rapid Solidification Rate (RSR)</td>
<td>Molten metal is ejected into a rotating water cooled cup/disk resulting in fine droplets cooled by high</td>
<td>Spherical Powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Centrifugal Atomization)</td>
<td></td>
<td>100 μm Dia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Twin Roll Atomization</td>
<td>Mechanical Atomization Process where stream of molten metal is directed to a high speed contra</td>
<td>Variable Powder/Flake</td>
<td>10^5-10^6</td>
<td>134-141</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200 μm thick</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laser-Melting/Spin Atomization</td>
<td>Focussed (CO₂) laser beam is used to melt the top of a rotating rod. Droplets are expelled by the</td>
<td>Spherical particles</td>
<td>&gt;10^8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>40 μm Dia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrohydrodynamic Atomization</td>
<td>Electric field is applied to the surface of liquid metal and cause a droplet to be emitted.</td>
<td>Droplets &gt; 0.01 to 150 μm Dia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EHDA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spark Erosion Technique</td>
<td>Repetitive Spark Discharge between two electrodes immersed in dielectric fluid. Spark vaporizes a</td>
<td>&gt; 0.5 μm Dia</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>small amount of metal that</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>immediately freezes.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron Beam Melting Combined</td>
<td>A focussed electron-beam melts the bottom tip, molten drops fall onto the surface of a rotating disk.</td>
<td>Flakes 50 μm Dia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>with Splat quenching</td>
<td></td>
<td>50 μm thick</td>
<td>10^5</td>
<td>129,144</td>
</tr>
</tbody>
</table>
### Table 1 Concluded

<table>
<thead>
<tr>
<th>Process Name</th>
<th>Description</th>
<th>Product/Dimensions</th>
<th>Cooling Rate</th>
<th>2ω-β</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chill Methods</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt Spinning (CSMS)</td>
<td>Molten metal is expelled out onto a rotating wheel (flat or notched).</td>
<td>Ribbons 25/50 μm thick</td>
<td>10^5-10^7</td>
<td>145-152</td>
</tr>
<tr>
<td>Crucible Melt Extraction (CME)</td>
<td>Molten metal solidifies on the edge of a water-cooled disk and flies off.</td>
<td>Filaments or fibers 20-100 μm thick</td>
<td>10^5-10^6</td>
<td>153-155</td>
</tr>
<tr>
<td>Melt Drag (Overflow)</td>
<td>Overflow of a molten metal from a reservoir onto a chill rotating surface.</td>
<td>Filaments, Foils, Particulates</td>
<td>10^4-10^5</td>
<td>155-157</td>
</tr>
<tr>
<td>Pendant Drop (POME)</td>
<td>Filament is extracted from molten end of a rod suspended just above the rotating wheel.</td>
<td>Filaments, Fibers</td>
<td>10^5-10^6</td>
<td>156</td>
</tr>
<tr>
<td>Rapid Spinning Cup (RSC)</td>
<td>Stream of molten metal is ejected onto a thick layer of rotating liquid located in the interior wall of a spinning cup.</td>
<td>Spherical to irregular powder/flakes 50 μm Dia 50 μm thick</td>
<td>10^6</td>
<td>154-155</td>
</tr>
<tr>
<td>Piston and Anvil Twin Pistons</td>
<td>Droplet of molten metal is impacted by piston(s).</td>
<td>Splat 5-300 μm thick</td>
<td>10^4-10^6</td>
<td>41, 161</td>
</tr>
<tr>
<td>Plasma Spray Deposition</td>
<td>Molten metal is propelled onto a substrate by a hot ionized gas emanating from the plasma torch. If deposited layers are kept very thin, rapid solidification is possible. Potential for near net shape. Coherent Deposit.</td>
<td>Porous layer &gt; 50 μm thick</td>
<td>10^2-10^5</td>
<td>102-102, 103-103</td>
</tr>
<tr>
<td>Arc Spray</td>
<td>Electrically opposed charged wires of the alloy to be sprayed are fed together to produce a controlled arc. The molten metal is atomized and by a stream of gas is projected onto a substrate.</td>
<td>Porous film &gt; 50 μm thick</td>
<td>10^2-10^5</td>
<td>111-112</td>
</tr>
</tbody>
</table>
Table 2  
Fabrication Of Fiber Reinforced Composite Systems

<table>
<thead>
<tr>
<th>Process</th>
<th>Composite System Fiber/Matrix</th>
<th>Product form</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Cloth</td>
<td>W (1.5% HfO&lt;sub&gt;y&lt;/sub&gt;)/FeCrAlY</td>
<td>JT8D-7F Turbine/Blade Plates</td>
<td>31, 65, 120</td>
</tr>
<tr>
<td>Powder Cloth</td>
<td>SiC/11-26AI-1Nb</td>
<td>Plates</td>
<td>72, 33, 160</td>
</tr>
<tr>
<td>Powder Cloth</td>
<td>WNial, SiC/Nial</td>
<td>Plates</td>
<td>75</td>
</tr>
<tr>
<td>Powder Cloth</td>
<td>SiC-NiAl2O/f/e-40AI</td>
<td>Plates</td>
<td>75, 166</td>
</tr>
<tr>
<td>Powder Cloth</td>
<td>W/Superalloy</td>
<td>Plates</td>
<td>77, 78</td>
</tr>
<tr>
<td>Powder Cloth</td>
<td>UO&lt;sub&gt;2&lt;/sub&gt;/W</td>
<td>Honeycomb Structural Panels</td>
<td>79-82</td>
</tr>
<tr>
<td>Powder Cloth</td>
<td>HfC-SiC/Superalloy</td>
<td>Plates</td>
<td>101</td>
</tr>
<tr>
<td>Foil/Fiber (RG Foil by PME)</td>
<td>Borsic/SiC/BiC/ Ti-6Al-4V</td>
<td>Plates</td>
<td>99</td>
</tr>
<tr>
<td>Foil/Fiber (W)</td>
<td>W/Superalloy</td>
<td>Plates</td>
<td>77, 78</td>
</tr>
<tr>
<td>Foil/Fiber (W)</td>
<td>B/Al</td>
<td>Plates</td>
<td>89-92, 96, 109, 160, 169, 170</td>
</tr>
<tr>
<td>Foil/Fiber (W)</td>
<td>Borsic/Al</td>
<td>Plates</td>
<td>93-95, 109</td>
</tr>
<tr>
<td>Foil/Fiber (W)</td>
<td>Be/Al</td>
<td>Plates</td>
<td>96</td>
</tr>
<tr>
<td>Foil/Fiber (W)</td>
<td>Stainless Steel/Al</td>
<td>Plates</td>
<td>97</td>
</tr>
<tr>
<td>Foil/Fiber (W)</td>
<td>SiC/Al</td>
<td>Plates</td>
<td>98</td>
</tr>
<tr>
<td>Foil/Fiber (W)</td>
<td>Borsic/Ti-6Al-4V</td>
<td>Plates</td>
<td>109</td>
</tr>
<tr>
<td>Combination: Foil/Fiber and Powder Cloth</td>
<td>Borsic/Ti-6Al-4V</td>
<td>LPI Fan Blade</td>
<td>76, 171</td>
</tr>
<tr>
<td>Combination: Foil/Fiber and Plasma Spray</td>
<td>Borsic/Al (powder)</td>
<td>Plates</td>
<td>108</td>
</tr>
<tr>
<td>Plasma Spray</td>
<td>B/Ti-6Al-4V</td>
<td>Ring Structure</td>
<td>74</td>
</tr>
<tr>
<td>Plasma Spray</td>
<td>Borsic/Ti-6Al-4V</td>
<td>Plates</td>
<td>109</td>
</tr>
<tr>
<td>Plasma Spray</td>
<td>W/N</td>
<td>Rocket Nozzle Inserts</td>
<td>110</td>
</tr>
<tr>
<td>Plasma Spray</td>
<td>SiC/Al</td>
<td>Missile Body Casings Structural Panel 2-Stiffeners</td>
<td>172</td>
</tr>
<tr>
<td>Arc Spray</td>
<td>W/Cu</td>
<td>Combustion Liner</td>
<td>3</td>
</tr>
<tr>
<td>Arc Spray</td>
<td>W/Nb or Nb-12r</td>
<td>Plates, Tubes</td>
<td>4, 174</td>
</tr>
<tr>
<td>Arc Spray</td>
<td>W/FeCrAlY</td>
<td>Plates</td>
<td>31, 33, 66, 111, 112, 175, 176</td>
</tr>
<tr>
<td>Arc Spray</td>
<td>W/Ni707</td>
<td>Plates</td>
<td>33, 173-176</td>
</tr>
<tr>
<td>Arc Spray</td>
<td>W/Inconel 907</td>
<td>Plates</td>
<td>33, 173-176</td>
</tr>
<tr>
<td>Arc Spray</td>
<td>W/Inconel 907</td>
<td>Plates</td>
<td>33, 173-176</td>
</tr>
</tbody>
</table>

All Compositions in At.%
Table 3

General Comparison of Monotape Fabrication Techniques

<table>
<thead>
<tr>
<th></th>
<th>Powder Cloth</th>
<th>Foil/Fiber</th>
<th>Arc Spray</th>
<th>Plasma Spray</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Contamination</td>
<td>Low to intermediate</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Starting Cond. of Matrix</td>
<td>Powder</td>
<td>Foil or sheet</td>
<td>Wire</td>
<td>Powder</td>
</tr>
<tr>
<td>Limiting Size of Monotape</td>
<td>Hot press die (cm²)</td>
<td>Hot press die (cm²)</td>
<td>Fiber wound drum (cm²)</td>
<td>Fiber wound drum (cm²)</td>
</tr>
<tr>
<td>Min. Equipment Requirements</td>
<td>Vacuum hot press</td>
<td>Vacuum hot Press</td>
<td>Arc spray Facility + HIP or Hot Press</td>
<td>Plasma spray Facility + HIP or Hot Press</td>
</tr>
</tbody>
</table>

CONVENTIONAL RAPID SOLIDIFICATION SOLIDIFICATION

FIGURE 1. - DEPENDENCE OF SECONDARY DENDRITE ARM SPACING ON COOLING RATE FOR SEVERAL ALLOYS54-56.

FIGURE 2. - TEM BRIGHT FIELD IMAGE OF A MELT-SPUN NiAl ALLOY WITH 0.5 AT.% W ADDITION SHOWING A CELLULAR STRUCTURE.
Figure 3. - Schematic representation of RS powder and ribbon producing techniques.
(a) NiCrAlY Powders produced by argon atomization.

Figure 4. - Examples of the morphology\(^{(1)}\) and microstructure\(^{(2)}\) of powders prepared by various atomization techniques.

(b) Ti-24Al-11Nb powders produced by the rotating electrode process.

Figure 4. - Continued.
NiAl Powders Produced by Vacuum Atomization.

**Figure 4, Concluded.**

**Figure 5.** Hot Pressure Bonding Technique for Composite Fabrication.
PREALLOYED POWDER

SPINNING

ALLOY RIBBON OR FLAKE

PULVERIZE

SIEVE

BLEND POWDER WITH FUGITIVE BINDER AND STODDARD SOLUTION

PROCURE FIBER

ROLL POWDER CLOTH

FABRICATE FIBER MATS USING FUGITIVE BINDER

COMBINE POWDER CLOTHS AND FIBER MATS

VACUUM HOT PRESS (THERMAL DEBINDING)

COMPOSITE MONOTAPE

FIGURE 6. - COMPOSITE MONOTAPE FABRICATION FROM RAPIDLY SOLIDIFIED CONSTITUENTS.
Figure 7. Examples of an actual powder cloth and fiber mat used in the hot pressure bonding process of composite fabrication.

Figure 8. Powder cloth method of composite fabrication.
STACK UP CONSTRUCTION FOR GAS TURBINE BUCKET OR BLADE

STACKING OF MONOTAPES

FIGURE 9. - COMPLEX SHAPED PARTS CAN BE FABRICATED BY BONDING OF STACKED MONOTAPES.

INTERMETALLIC MATRIX COMPOSITES PRODUCED BY THE POWDER CLOTH TECHNIQUE.

FIGURE 10.
FIGURE 11. - TENSILE STRENGTH VERSUS TEMPERATURE FOR SiC FIBERS, Ti-24Al-11Nb MATRIX AND SiC/Ti-24Al-11Nb COMPOSITE INDICATING CLOSE AGREEMENT TO RULE-OF-MIXTURES STRENGTHS FOR LOW OXYGEN CONTAINING COMPOSITES.

FIGURE 12. - (a) SiC/NiAl+0.5 at. % W COMPOSITE MADE FROM PULVERIZED MELT SPUN RIBBON BY THE POWDER CLOTH TECHNIQUE AND (b) TEM IMAGE OF NiAl+0.5 at. % W MELT SPUN RIBBON AFTER ANNEALING AT 1300 °C FOR 1 HR. SHOWING GRAIN BOUNDARIES PINNED BY W PARTICLES.
FIBER WINDING

ARC SPRAYING

SPRAYED MONOTAPE

HOT ISOSTATIC PRESSING

FIGURE 13. - ARC SPRAY METHOD OF COMPOSITE FABRICATION.
CHOOSE MATRIX ALLOY

PROCURE OR FABRICATE ALLOY OR COMPOSITE WIRE

PROCURE FIBERS

OBTAIN ALLOY POWDER

MOUNT FIBERS ON MANDREL OR ROTATING DRUM

ARC SPRAY

PLASMA SPRAY

COMPOSITE MONOTAPE

FIGURE 14. - MONOTAPE FABRICATION FOR THERMAL SPRAY PROCESSES.

FIGURE 15. - W/NO MONOTAPE PREPARED BY THE ARC SPRAY PROCESS.

FIGURE 16. - COMPOSITE PANEL WITH COOLING PASSAGES PREPARED BY THE POWDER CLOTH TECHNIQUE.
Advanced composite processing techniques for fiber reinforced metal matrix composites require the flexibility to meet several widespread objectives. The development of uniquely desired matrix microstructures and uniformly arrayed fiber spacing with sufficient bonding between fiber and matrix to transmit load between them without degradation to the fiber or matrix are the minimum requirements necessary of any fabrication process. For most applications these criteria can be met by fabricating composite monotapes which are then consolidated into composite panels or more complicated components such as fiber reinforced turbine blades. Regardless of the end component, composite monotapes are the building blocks from which near net shape composite structures can be formed. The most common methods for forming composite monotapes are the powder cloth, foil/fiber, plasma spray and arc spray processes. These practices, however, employ rapid solidification techniques in processing of the composite matrix phase. Consequently, rapid solidification processes play a vital and yet generally overlooked role in composite fabrication. The present roles and future potential of rapid solidification processing in fabrication of continuous length fiber reinforced metal matrix composites is discussed in the following paper.