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Synthesis, consolidation and properties of Nb$_5$Si$_3$ and laminated Nb$_5$Si$_3$/Nb composites

Kajuch, Jan, Ph.D.

Case Western Reserve University, 1993
SYNTHESIS, CONSOLIDATION AND PROPERTIES OF Nb$_3$Si$_4$

AND LAMINATED Nb$_3$Si$_4$/Nb COMPOSITES

by

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Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

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May 1993
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(chair)

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SYNTHESIS, CONSOLIDATION AND PROPERTIES OF Nb$_2$Si$_3$
AND LAMINATED Nb$_2$Si$_3$/Nb COMPOSITES

Abstract

by

JAN KAJUCH

Formation of Nb$_2$Si$_3$ from elemental Nb and Si powders was studied using a mechanical alloying (MA) process. It is shown that compound formation proceeds by a self-propagating exothermic reaction in both interrupted and continuous milling processes, but in the interrupted process reaction is completed in a much shorter time. The kinetics of compound formation in both processes were investigated.

X-ray diffraction, scanning electron microscope (SEM) examination and transmission electron microscope (TEM) imaging and diffraction were utilized to characterize changes in the milled powders. Differential Thermal Analysis (DTA) was utilized to determine the critical and onset temperature of reaction as a function of milling time. On the basis of experimental results, a kinetic model was proposed for the formation of Nb$_2$Si$_3$ via the interrupted and continuous milling process. It is suggested that precipitation of Nb$_2$Si$_3$ particles during cooling in the interrupted process was responsible for the exothermic reaction when milling resumed, while self-
propagating high temperature synthesis (SHS) is the driving force for the compound formation in the continuous milling process.

In addition to the MA process, the Reactive Sintering (RS) technique was employed for the production of the monolithic NbSi₃ and composite Nb₅Si₇/Nb compacts from elemental Nb and Si powder mixtures. The homogeneity of the Nb-Si powder blend, particle size and the heating rates significantly affected microstructures produced after hot-press consolidation. The RS process may prove to be an effective alternative for producing both monolithic and ductile-phase reinforced Nb₅Si₇ as opposed to in situ and arc melting and casting processes.

Model laminates of mechanically alloyed Nb₅Si₇ and nominally pure niobium were prepared via vacuum hot pressing and structural adhesive bonding. Room temperature toughness tests were conducted inside a SEM equipped with a deformation stage to evaluate the effect of niobium reinforcement on the composite fracture behavior. Significant (5 fold) toughness increases were obtained in the laminates produced by both the diffusion and structural adhesive bonding method.

The mechanical behavior of the Nb reinforcement in Nb₅Si₇/Nb laminates was also investigated under a variety of stress states and test temperatures. Tests were conducted at room temperature (298 K) and liquid nitrogen (77 K) on as-received Nb foils, on Nb₅Si₇/Nb laminates, Nb foils extracted from the hot-pressed laminates, and those simply exposed to vacuum at high temperature (1473 K/5 h). It is shown that Nb grain size, solid solution of Si in Nb, degree of constraint, and test temperature
significantly affect the mechanical behavior of Nb. Unconstrained Nb foils failed in a ductile manner at room temperature, while a mixture of cleavage and ductile fracture was exhibited by the constrained Nb present in the diffusion bonded laminates. A similar ductile-to-brittle transition in fracture appearance was observed in tests conducted at 77 K, however the toughness of the laminates was relatively unaffected by this change in fracture mode.
DEDICATION

To these United States of America which accepted my family and me with open arms and provided opportunities never dreamed of by a little boy in a mountain village of Slovakia.

Extreme gratitude to Anna, my wife and all three children, who supported and encouraged me in my last three academic adventures.
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CHAPTER 1

INTRODUCTION

1.1 Definition of Intermetallics

Intermetallic phases (also intermetallic compounds, or intermetallics) are solid solutions or compounds of two or more metals with crystal structure different from that of each pure component [1.1]. Intermetallic compounds which form with the exact stoichiometric ratio of initial metals are called line compounds. Some intermetallic compounds exist over a range of compositions with a significant deviation from the stoichiometric ratio. For example, the D8\textsubscript{c} chromium silicide (Cr\textsubscript{5}Si\textsubscript{3}) phase field extends several atomic percent around the ideal ratio (Figure 1.1) [1.2]. To maintain ordering, these chemical deviations must be accommodated by lattice defects which are required to maintain the number of electrons per unit cell at a constant value, i.e. vacancies, interstitial atoms, or the A atoms on B sites and vice versa. Since intermetallic compounds belong to a group of long-range-ordered alloys (LRO), in addition to exhibiting a fixed location of the atomic sites (crystal structure), the occupation order of the sites (ordering) by specific types of atoms is given. The driving force for the ordering is the greater strength of the A-B atom bonds created on ordering rather than of A-A and B-B bonds in the initial components. These materials often have very complex crystal structures with partial metallic bonding.
thereby retaining some of the metallic properties such as the metallic luster and high thermal and electrical conductivity.

1.2 Role and Use of Intermetallics

The capability of maintaining long-range order up to the melting point makes the use of intermetallic compounds very attractive for structural components that are subjected to high stresses at elevated temperatures. At the present time no single phase intermetallic compounds are being used in such applications, although the Ni-base superalloys consist of as much as 60 vol. % of the L1₂ (cP4) intermetallic phase Ni₃(Al, Ti) [1.3]. It is this phase that provides high-temperature strength by the thermally activated immobilization of screw dislocations through cross-slip from \{111\} glide-planes onto \{100\} [1.4]. The application of intermetallic compounds is not solely restricted to structural components. For example, steels and superalloys alloyed with Cr are protected against high-temperature oxidation through the formation of a dense adherent oxide film, Cr₂O₃. Intermetallic compounds of chromium such as NbCr₂ (Laves phase with C15 structure) and TiCr₂ are thus oxidation resistant. It should be noted that TiCr₂ has been considered for high-temperature applications, although not at temperatures in excess of 1273 K due to the high vapor pressure of Cr₂O₃ [1.5].

For temperatures exceeding 1273 K, the addition of aluminum promotes the formation of an adherent scale of Al₂O₃, thus intermetallics containing Al, especially
Ni-Al intermetallics (e.g., NiAl) are being considered as turbine blade coatings in order to increase the oxidation resistance [1.6]. Another element providing oxidation resistance is silicon. Here, oxidation resistance is provided by the formation of SiO₂. It has been found that Si-rich alloys of the transition metals are resistant to oxidation. In particular, MoSi₂ has an excellent oxidation resistance and is used as a heating element [1.7]. NiTi and other intermetallic compounds (NiAl, CuZn) are also used in devices where the shape memory effect [1.8] may be utilized. These compounds are characterized by a body-centered-cubic structure which undergoes a reversible martensitic transformation, thus the material remembers its original shape and returns to it upon heating [1.9]. Permanent magnets and superconductors are other examples in which intermetallics are being presently used.

1.3 Advantages of Intermetallics

With respect to material properties, intermetallic compounds combine aspects of metallic alloys and ceramics. The ultimate goal in the materials community is to combine the best of both materials classes, (e.g., the ductility of metals and the strength and oxidation resistance of ceramics). In comparison to disordered alloys, intermetallic compounds have a number of properties that make them appealing for high temperature applications [1.10]. First, intermetallic compounds have high melting temperatures. In many phase diagrams, intermetallic compounds have melting temperatures exceeding those of the constituent elements. One of the most desirable
properties of intermetallic materials is their high melting temperature, for it offers the possibility of operating at higher temperatures than current superalloys. Because of their strong bonding, high temperature intermetallics have high elastic modulus which tends to decrease more slowly with increasing temperature than that of disordered alloys. Also many intermetallics have low densities, therefore many have a high specific stiffness (E/p). This is an important property primarily for rotating structural parts of high temperature engines. Intermetallic compounds tend to be intrinsically very strong (high yield or fracture stress) and the strength tends to be maintained up to high temperatures. Some intermetallic compounds show an increasing yield strength with increasing temperature, as in Ni₃Al [1.11]. Dividing the strength and modulus of elasticity by the density we obtain interesting properties of specific strength and specific stiffness. High values are very desirable for aerospace structural applications [1.12].

Since intermetallic compounds are ordered structures, they tend to have much lower self-diffusion coefficients than do disordered alloys [1.13]. Low values for self-diffusion often manifests itself in microstructural stability at elevated temperatures and improved creep strength [1.14].

1.4 Inherent Problems of Intermetallics

Despite the advantages of increased strength, modulus of elasticity, low density, structural stability and high creep strength of intermetallics, there is a problem
of low ductility at ambient temperatures. Ambient temperature failure often is intergranular or cleavage. This brittle behavior can be attributed to the type of crystal structures possessed by intermetallic compounds. A large slip vector, restricted cross-slip, inability to slip across grain boundaries [1.15] and a limited number of active slip systems [1.16] are a number of the factors responsible for low ductility.

Although there is a transition from brittle to ductile fracture with increasing temperature, very low ductility (e.g., $\varepsilon_f < 1\%$) is often obtained at lower temperatures. As previously mentioned, one source of limited ductility in polycrystalline materials is that there are a limited number of active slip systems. Single crystals of intermetallics can be quite ductile at room temperature in contrast to polycrystals. For example, NiAl single crystals exhibited 5% [1.17] and 10% [1.18] strain to failure in compression respectively, while polycrystalline NiAl exhibited not measurable strain to failure in compression. Since grain boundaries are strong barriers to the spread of deformation, and stress concentration at grain boundaries tends to increase with the larger grain size, it has been proposed that polycrystalline ductility can be obtained in intermetallic phases provided the grain size is below that of "critical grain size" [1.19]. For example, by refining the grain size of NiAl to below $\approx 20 \mu m$, the ductility in tension at 673 K increased from $\approx 2\%$ to over 40% [1.19]. Other efforts to improve ductility has concentrated on micro- and/or macro-alloying. One consequence of such changes in chemistry may be loss in some of the high temperature properties. In such cases, compositing is being explored to increase the low temperature toughness of
brittle intermetallics.

1.5 Toughening of Intermetallics

1.5.1 Intrinsic toughening.

Intrinsic toughening relies in trying to change the fundamental deformation characteristics of a material and can be accomplished via alloying. Some remarkable improvements in the ductility of some intermetallics have been achieved via microalloying. Additions of B to Ni$_3$Al produced an increase in tensile elongation from 1-2% to as high as 50% [1.20]. In these cases, it has been proposed that B acts to strengthen the grain boundaries, thereby preventing intergranular fracture at low strain.

1.5.2 Extrinsic toughening.

In cases where intrinsic toughening mechanisms are inadequate to toughen the material, extrinsic toughening mechanisms (e.g., compositing) may be employed. In such cases, brittle solids can be toughened by incorporating brittle fibers/whiskers and ductile reinforcements in the form of particles or continuous ligaments. The toughening of brittle solids by brittle fibers and/or whiskers is controlled by debonding at the fiber/matrix interface. In its simplest form, debonding causes crack tip blunting, thereby reducing the stress concentration at the fiber and leaving the fiber intact in the crack wake. Cracking of the fiber itself is controlled by the largest defect
size in the fiber. Since the distribution of surface defects on the fiber is randomly distributed, initial fiber fracture should also occur randomly throughout the composite thickness during tension testing. Interface friction during fiber pull-out acts to provide a crack closure behind the crack tip, leading to an increase in the composite toughness.

The toughening afforded by the incorporation of ductile phases depends on the plastic properties of the reinforcement, on its volume fraction, and on the strength of the interface between the ductile reinforcement and the brittle matrix [1,21]. Constraints imposed on the particle by the rigid matrix suppresses plastic deformation of the particle at the crack tip, so that the main contribution to composite toughness comes from the formation of ligaments in the matrix and their fracture behind advancing crack front. In some cases, additional extrinsic toughening is also provided by crack deflection and branching induced by the particles. The energy absorbed in stretching the ligaments contributes to the increase in toughness of the composite as compared to that of a monolithic brittle matrix. The toughness \( \Delta K_{\text{isc}} \) increases with an increase in the length of the ductile bridge zone and reaches steady-state level \( \Delta K_{\text{ss}} \) at the maximum bridge length.

There are however no "ready-for-use" intermetallic compounds for high temperature applications (\( > 1473 \) K) utilizing the ductile phase toughening approach. Only in the last three years have there been studies to develop "tough" composites by integrating continuous ductile fibers and/or foils. Some examples of materials systems
where ductile phase toughening has been somewhat successful are cases of toughening of $\gamma$-TiAl by Nb or TiNb particulates [1.22], by wires [1.23] or by plates [1.24], MoSi$_2$ toughened with ductile Nb plates and filaments [1.25] and particulates [1.26], toughening of Al$_2$O$_3$ by Al particulates and whiskers [1.27] and toughening of Nb$_3$Si$_3$ by Nb particulates [1.28] and [1.29].

1.6 Summary

Intermetallic compounds offer number of desirable properties for use in structural applications at temperatures above the range of superalloys. Unfortunately, they often exhibit inherent room temperature brittleness, which has a negative impact on various processing and fabrication aspects. Extrinsic toughening via bridging is one of the most potent ways to improve composite toughness. Although research in this area has accelerated in recent years, a detailed mechanism of bridging via ductile ligaments is still not fully understood, although it has been shown that the homogeneity and microstructure of the intermetallic matrix has a pronounced impact on the details of crack initiation and propagation. Since these materials possess a high melting temperature, their synthesis and consolidation constitutes a critical manufacturing step. Novel methods of rapid solidification, mechanical alloying, reactive sintering or self-propagating high temperature synthesis are possible ways to minimize impurity contamination and microstructural segregation. Powder metallurgy approaches also offer low waste, near-net shape dimensions and production of
complicated shapes, thus potentially offering a lower cost of production.

1.7 The Nb-Si as a Model System for Research

Figure 1.2 shows a plot of melting temperature (°C) vs. density (g/cm³) for many refractory intermetallic compounds [1.30]. The dotted vertical line showing the specific density of Ni designates a limit of density for the superalloys, while the dotted horizontal line designates the minimum desired melting temperature based on the need for 1600°C (1873 K) operational temperature. These guidelines define materials needs which combine a density below that of Ni, and a melting temperature above 2,068°C (2,341 K). As can be seen from Figure 1.2 the Nb₅Si₃ compound has the highest melting temperature and a reasonable density among all refractory silicides. On this basis, a number of the silicides are being explored as potential replacements for nickel and cobalt superalloys in high temperature (1473-1873 K) applications. However, the oxidation resistance of many of the refractory based silicides is still not sufficient for structural use at elevated temperatures.

Figure 1.3 shows the Nb-Si phase diagram [1.2]. The Nb₅Si₃ compound, designated here as a γ phase, is a line compound. As such, it has a high melting temperature (2757 K) and exact stoichiometry (37.5 at.% Si). However, this compound has three allotropic modifications as can be seen in Table 1.1. The α-phase exists at temperatures below 1923 K, the β-phase for temperatures above 1923 K, and the γ-phase for an impure (ternary) compound. The α and β phases are body centered
tetragonal structures, while the γ phase is a primitive hexagonal structure. Since the
 Nb₃Si₃ compound is brittle at room temperature, compositing via refractory "ductile
 reinforcement" is a viable way to increase the damage tolerance. The Nb-Si system
 is one of only three refractory metal-silicon systems, where there is thermodynamic
 stability between the Nb reinforcement and the intermetallic compound. As suggested
 by the phase diagram, there should be no reaction products at the interface between
 Nb₃Si₃ and Nb(ss) at temperatures up to 1873 K. Such characteristics make the Nb-Si
 system a model system for evaluating the role of interface strength and the extent of
 interface debonding on the fracture toughness of the composites.

1.8 Scope/Goal of this Thesis

There are two principal areas of work presented in this thesis. The first is the
 investigation of the synthesis of Nb₃Si₃, by the use of Mechanical Alloying (MA) and
 a kinetic model of compound formation is presented. In addition to the MA work,
 Reactive Sintering is utilized in combination with hot pressing to produce the Nb₃Si₃
 compound and Nb₃Si₃/Nb particulate composites.

The second area of investigation concerns the role of matrix constraint on the
 mechanical behavior of the ductile reinforcement and its resultant effect on the
 fracture toughness of the composite. Tri-layer laminates were designed and produced
to study the effect of the interface strength on the crack propagation path. Recommendations for designing "tough" composites using ductile reinforcements are
included.
1.9 References


Figure 1.1 Cr-Si phase diagram.
Figure 1.2 Properties of refractory intermetallic compounds.

Figure 1.3 Nb-Si phase diagram.
<table>
<thead>
<tr>
<th>PHASE</th>
<th>STRUCTURE TYPE</th>
<th>PEARSON SYMBOL</th>
<th>c (nm)</th>
<th>a (nm)</th>
<th>c/a</th>
<th>REMARKS/ STABILITY</th>
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<td>α-Nb₅Si₃</td>
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<td>0.6570</td>
<td></td>
<td>&gt;1923 K</td>
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<tr>
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<td>1.0026</td>
<td>0.5059</td>
<td>&lt;1923 K</td>
</tr>
<tr>
<td>γ-Nb₅Si₃</td>
<td>Mn₃Si₂</td>
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<td>0.5249</td>
<td>0.7536</td>
<td>0.6965</td>
<td>Impure</td>
</tr>
</tbody>
</table>

Table 1.1 Allotropic phases of Nb₅Si₃ compound.
CHAPTER 2
LITERATURE REVIEW

2.1 Mechanical Alloying

2.1.1 Oxide-dispersion-strengthened (ODS) materials.

Traditionally, metallurgists concentrated their efforts in the development of new alloys based on the phase diagram of potential systems of interest. Systems which exhibit acceptable solubilities in the liquid and solid states were traditionally explored, while those which had very low or non-existent solubilities in the solid state were not investigated in detail. A novel technique was developed during the 1960’s and 1970’s, resulting in the non-equilibrium processing of materials and thus creating metastable structures with unique properties. One of the methods is Rapid Solidification, which can modify the materials by refining the microstructure, extend the solid solubilities, thereby enabling the creation of metastable crystalline phases.

Mechanical Alloying (MA) is also a non-equilibrium processing technique analogous to Rapid Solidification (RS). In contrast to the RS process, the MA process is entirely a solid state process operating at or near room temperature. The MA process was developed by Benjamin and his co-workers at the International Nickel Co., in late 1960’s with the sole purpose of producing complex oxide-dispersion-strengthened (ODS) alloys [2.1]. One result of their efforts was the development of
high-strength superalloys for jet engines. This effort can be appreciated only when there is a good understanding of the challenge to produce new class of materials in which the long-sought combination of dispersion strengthening and age-hardening is realized. This is precisely what Benjamin and his co-workers achieved. Use of the mechanical alloying technique allowed the alloying of Ni with reactive elements (Al, Ti) without the formation of oxides and a close control of oxygen. The precipitation of γ' Ni₃(Al,Ti) particles during age hardening contributes to a significant increase in the strength of the alloy at low temperature. Incorporation of refractory oxide in a high melting point matrix, (e.g.,ThO₂ or Y₂O₃ particles less than 0.1 μm in size) increases the high temperature strength of the alloy up to the melting temperature of the matrix. In the intermediate temperature range, 977 to 1,090 K two strengthening mechanisms are operative. Several commercially available alloys were developed, including Inconel MA 754, MA 6000 and MA 956.

2.1.2 Physics of mechanical alloying.

The MA process has been defined as a dry, high energy ball milling process that produces composite metal powders with extremely fine microstructures. Interdispersion of the powders occurs by the repeated cold welding and fracturing process of the free powder particles, trapped between two colliding steel balls (Figure 2.1) [2,2]. The force of the impact deforms the particles and creates atomically clean surfaces, which, weld together on contact. The milling operation is often carried out
in inert gas atmosphere to prevent oxidation of these surfaces. Refinement of the structure is approximately a logarithmic function of time and depends on the mechanical energy input into the milling process and the work hardening of powders being processed [2.3]. Benjamin and Volin here studied the microstructural refinement process in their work on ductile/brittle components and have categorized the MA process into 5 time intervals:

1. initial period of particles welding to the balls
2. powder welding
3. formation of equiaxed particles
4. period of random welding
5. steady-state distribution of powder particle size.

The amount of time required to develop a given structure in any system depends on the initial particle sizes and their characteristics, particular equipment used and the processing parameters. In all cases, however, microstructural refinement continues into the steady-state period even though the particle hardness saturates and a constant particle size distribution is achieved.

C.C. Koch provides an excellent overview of the work done by various authors in the area of ductile/ductile, ductile/brittle and brittle/brittle components [2.4]. His interest is concentrated in the area of the amorphization of the crystalline phases (Nb-Sn system) [2.5]. According to the theory of the Mechanical Alloying process, alloying occurs by the continuous welding and fracturing process of particles, which
requires sufficient ductility of one component. At the same time, the second component (i.e. brittle particles) are fractured by the milling process and are trapped at the boundaries between the ductile particles. With continued milling, the lamellar spacing is continuously refined until a terminal dispersion or alloying occurs. In brittle/brittle systems, although there is an apparent lack of the ductility of both components particles, Davis and Koch have demonstrated in the Si-Ge system, that a solid solution of Si in Ge forms [2.6]. The microstructural evolution during milling in the Si-Ge system differs from that of the lamellar morphology of the ductile/brittle components, retaining a granual morphology. Koch speculates that there is a relative difference in the "ductility" between Si and Ge to the extent that the Si particle are imbedded in the "softer" Ge [2.5].

Although the MA process is used on a commercial basis, the process has been described more qualitatively than quantitatively. The first systematic effort to describe the physics of mechanical alloying was reported by Davis, McDermont and Koch using brittle/brittle components [2.7]. Combining videotape of the collision of Spex mill balls with computer modeling enabled the authors to calculate the number of ball impacts per specific time of milling operation and the temperature rises during an impact. They conclude that thermal activation is required for the mechanical alloying of the Si-Ge system and that the temperature rise in typical powder alloys during MA in the Spex mill was estimated to be $\leq 350$ K.

The first attempt to describe the basic geometry, mechanism and physics of the
MA process based on Hertzian contact between the grinding media was reported by Maurice and Courtney [2.8]. This geometry of Hertzian contact [2.9] defines the volume of powder material affected per collision, and from this information and the characteristics of the specific milling apparatus and material being processed, milling times were estimated. These results correlate very well with the observed milling times. However, all calculations are based on the assumption that both metals are ductile, thus microstructural refinement calculations are based on the uniform decrease in the interlamellar distance. Regardless of these concerns, the works of Davis and Maurice provide a sufficient physical model of the mechanical alloying process.

2.1.3 Non-equilibrium systems.

From the initial work on production of the ODS alloys, the MA process was extended to other applications, as summarized below:

a. alloys where one element has a very high melting point and the second one a low melting point,

b. immiscible alloy systems, where there is no solubility between elements,

c. amorphous structures, and

d. intermetallic compound production.

The superconducting intermetallic Nb₃Sn is a good example of a system where the fabrication by normal melting techniques is difficult due to the very large difference between melting points of Nb and Sn. MA of a mixture of elemental powders yield
\( \text{Nb}_{2}\text{Sn} \) with the required homogeneity [2.10].

There are several liquid and solid immiscible systems that are difficult to process by conventional pyrometallurgy, (*e.g.*, liquid immiscible Cu-Pb system and a solid immiscible Cu-Fe system) where heavy segregation occurs on solidification from the liquid phase. Eloquent work was done by Uenishi and Kobayashi [2.11] on the Ag-Cu system. Mechanical alloying by ball milling and repeated rolling produced a super-saturated solid solution in the entire composition range, demonstrating that the MA process is as effective as the Rapid Quenching (RQ) technique. The elevation of free energy is caused not only by the stored energy of defects but also by the effect of mixing the immiscible components in the nanometer scale. This elevation of free energy by the MA process is equivalent to solidification below the \( T_s \) curve in rapid quenching.

The most studied but least understood phenomena is the amorphization process. Schwarz and Koch defined solid state amorphization as a process which involves the fast diffusion of one component and a large negative heat of mixing of the alloy [2.12]. However, on the basis of experimental evidence available, these two conditions do not seem to be sufficient for amorphization. There are many instances where systems exhibit a large negative heat of mixing but amorphization does not occur. For example, crystalline \( \text{Nb}_2\text{Si}_3 \) compound forms directly, while \( \text{Ta}_2\text{Si}_3 \) transforms directly to an amorphous product from elemental powders [2.13]. Mechanical alloying is characterized by the severe plastic deformation and the potential for a high density of
defects during the milling process which can raise the free energy of the deformed crystalline phase to that of the amorphous alloy as demonstrated in Figure 2.2 [2.4]. The role of large plastic deformation on the crystalline-to-amorphous state transition as investigated by Palvov also needs to be considered [2.14].

2.1.4 Synthesis of intermetallics by MA process.

Several authors have studied the formation of intermetallic compounds by mechanical alloying processes. The capability for producing intermetallics by MA starting from elemental powders has been established [2.6]. Atzmon determined the parameters affecting phase formation in the Al-Ni system. In his experiments, the NiAl formed by an explosive, self propagating reaction, while Al₃Ni formed in a reaction with layer diffusion as a predominant factor [2.15]. Morris followed the evolution of Cr₂Nb compound by ball milling elemental Cr and Nb powders as a function of time [2.16]. There exists very little work on the production of the intermetallic compounds of Nb-Si by the use of the MA process. Kumar and his co-workers at Martin Marietta Laboratories were the first to methodically study the mechanism of MA alloying in group V transition metal/silicon systems [2.13] and [2.17]. Their work was instrumental in the production of NbₓSiₙ from the elemental Nb and Si powders. Mechanical alloying of the powders was studied primarily by the use of the x-ray diffraction method and supplemented by the SEM and TEM work for the study of the particle morphology. In order to study the progress of mechanical
alloying, the ball mill was stopped periodically and left to cool to room temperature in order to remove a small amount of the powder for analysis. This "interrupted process" resulted in the formation of Nb₂Si₃ compound in 75 minutes, while at 73 minutes, x-ray diffraction shows only peaks of the elemental Nb and Si. The explanation of the instantaneous nature of compound formation by thermodynamics alone was questioned. Whittenberger in his analysis of the solid state processing of high temperature alloys and composites believes that the so called "enhanced diffusivity" plays a major role in the alloying process [2.18]. Here, "enhancement" of the diffusivity is due to a large increase of the dislocation density and the higher homologous temperature at the impact point as compared to the "average" powder temperature in the milling vial. Thadhani, Costello and Song showed by the DTA analysis that Nb-Si powders form the intermetallic compound by an exothermic reaction initiated at approximately 1523 K (1250°C) [2.19].

2.2 Reactive Sintering (RS) or Self-propagating High-temperature Synthesis (SHS).

2.2.1 Characteristics.

Processing powder materials with mechanical alloying or other conventional powder consolidation methods (i.e. hot pressing) involves the expense of time and energy. A novel processing technique termed self-propagating high-temperature synthesis (SHS), combustion synthesis or reactive sintering (RS) has been used for the production of high temperature intermetallic compounds. The driving force for these
processes is the strong exothermic reaction between the powder constituents. Although such reactions must be highly exothermic to be self-sustaining, they need additional energy for reaction initiation. It is the initiation of the reaction which makes a distinction between the above mentioned SHS and RS processes. In such cases, the reaction can be initiated at one end of the powder compact by thermal radiation or through the use of laser energy. The exothermic reaction self-propagates in a wave form through the whole volume of powder compact (Figure 2.3), thereby explaining the term self-propagating high-temperature synthesis [2.20]. Since this process has characteristics close to that of standard sintering processes, variables such as particle size ratios, blending methods, stoichiometry, and green density influence the as reacted microstructure. SHS synthesis is being used due to its practical alternatives to conventional methods [2.20], as following:

1. simplicity and low energy requirement,
2. high purity of reactive products,
3. complex or metastable phases capability,
4. combination of compound formation and densification.

Process simplicity and low energy requirements stem from the lack of need for complicated equipment. Furthermore, once the reaction is initiated, no additional energy input is needed. A high purity product is associated with the high temperature of the combustion wave and the consequent volatization of impurities. The possibility of formation of metastable phases is based on the rapid cooling rates of the
combustion process. If SHS synthesis is coupled with the densification process (i.e. hot pressing, dynamic compaction, etc.), near net shape products can be manufactured.

Several studies have investigated the mechanisms and characteristics of the SHS process. Atzmon studied the influence of diffusion processes between the planar layers of two metallic elements, and the presence of interfacial contaminants and heating rate on the ignition temperature of compacted Al-Ni mixtures. It was shown that the ignition temperature increases with an increase in the layer thickness, keeping other parameters constant [2.21]. A numerical model for the SHS process of a system that forms a nonstoichiometric alloy without porosity has been developed by Lakshmikantha et al., [2.22]. The variation of the combustion velocity and temperature was studied as a function of the heat of reaction (Q), the activation energy (E), thermal conductivity (K'), initial temperature (T₀), and the frequency factor (K₀). An increase in thermal conductivity may lead to a decrease in the combustion velocity. Higher initial temperatures increase both the combustion velocity and temperature. An increased activation energy reduces the combustion velocity, but has no impact on the combustion temperature. Decreased heat of reaction and an increased activation energy will eventually lead to extinction of reaction [2.22]. The propagation of a steady, planar combustion wave and a prediction of the parameters above which this stability is lost to nonsteady modes of combustion were mathematically modeled by Margolis [2.23]. Again, as in the work of Lakshmikantha, higher activation energies and lower combustion temperatures were chosen to enhance
the loss of stability (*i.e.* planar combustion wave propagation). The role of activation energy on the combustion velocity propagation was translated into SHS diagrams, where, depending on the initial temperature $T_0$ and the alloy composition, various areas of stable and unstable SHS were constructed [2.24].

If, the powder compact is heated in a furnace until the reaction occurs instantaneously throughout the compact, the term thermal explosion or reactive sintering (RS) is used. The schematic in Figure 2.4 [2.25] shows that in general, reactive sintering involves the formation of a transient liquid of a lower melting component [2.26]. Since it is possible to control the thermal processing variables in a reactive sintering process, in addition to the fact that there is ample information on reactive sintering employing the transient liquid phase, reactive sintering is being employed in the production of a variety of intermetallic compounds. However, important processing parameters which have a pronounced impact on as reacted microstructure, such as particle size ratio, heating rates, stoichiometric control, and use of vacuum need to be taken into consideration [2.26]. Variation of the reactive sintering process involves simultaneous hot pressing and pressure-assisted sintering.

2.2.2 Synthesis of intermetallics by SHS or RS process.

The majority of the investigations on the synthesis of intermetallic phases has focused on a variety of aluminides, including titanium nitride, shape-memory alloys, and other metallic phases [2.20]. It is interesting to note that the major contribution
to the understanding of the SHS and RS processes comes from the scientists of the
former Soviet Union. Stoloff and Alman describe the effects of various processing
factors on the fabrication of Ni$_2$Al, NiAl, TaAl$_3$, and MoSi$_2$ [2.25]. Their contribution
comes mainly from a variant process involving reactive sintering coupled with the
simultaneous pressurization in a hot isostatic press, termed reactive hot isostatic
pressing (RHIP). This process resulted in a full density of compacts, especially in
systems with a weak exothermic reaction. More detailed studies on reactive sintering
and reactive hot isostatic pressing of Ni$_2$Al were conducted by Misiolek and German
[2.27]. The atmosphere and the green density effect on sintered density was
determined. Vacuum processing provides the best theoretical densities (97.5%), while
green densities in excess of 75% are needed. In order for aluminum to form an
interconnected network around Ni particles, a particle ratio of 2.4 to 1 (Ni to Al) was
required, confirming work done by Biggs [2.28]. This is also close to results obtained
by Bose who demonstrated that the best single phase, fully-reacted, low-porosity
microstructures were developed from powders with the agglomerated size of
aluminum to nickel of approximately 0.3 [2.29]. Combustion synthesis of Fe$_3$Al in a
hot isostatic press from elemental powders, the microstructural development, and the
room temperature tensile properties for various conditions was conducted by Rabin
and Wright [2.30]. The presence of grain boundary aluminum oxides is observed to
suppress grain growth, which in turn is responsible for the significant strengthening
of these materials. A new method for the production of titanium diboride (TiB$_2$) by
combining reactive sintering with dynamic compaction is reported by Hoke et al., [2.31]. The main objective of this process is to use inherited product material ductility resulting from the high temperature obtained during synthesis, which is well above its ductile-to-brittle transition temperature (DBTT). However, the authors concluded that micro- and macrocracking occurring during and after consolidation is a major problem for the successful production of TiB₂ using dynamic compaction. Similar work was done on the synthesis of TiC by Vecchio et al., [2.32]. Densification of TiC was compared to that of hot-pressed TiC with comparable results.

2.2.3 Formation of composites.

It is only natural to extend the concept of SHS and RS processes from the formation of intermetallic compounds to that of composites. There are two possible approaches to composite formation:

1. Use of pure elemental powders for intermetallic matrix formation mixed with particulate or fiber reinforcement, or

2. Use of naturally occurring and less expensive materials, for example:

\[ \text{MoO}_3 + 2\text{Al} + 2\text{Si} = \text{MoSi}_2 + \text{Al}_2\text{O}_3, \]

instead of using pure Mo which adds to the cost of production [2.20]. Attempts to produce Ni₃Al based composites reinforced with 5% chopped Al₂O₃ fibers or Y₂O₃ powders failed to yield increased mechanical properties as compared to the monolithic matrix due to the decohesion at the matrix-fiber interface. Since consolidation
becomes more difficult in the presence of a reinforcing phase, generation of connected two-phase microstructures analogous to cemented carbides could possibly circumvent these difficulties [2.33]. In a similar study, reinforcement of SHS-produced Ni<sub>3</sub>Al with Al<sub>2</sub>O<sub>3</sub> or SiC whiskers resulted in rapidly increased porosity with a lower green compact density and higher volume fraction of Al<sub>2</sub>O<sub>3</sub>, or SiC whiskers with diminishing degree of reaction completeness [2.34]. The reactive hot isostatic pressing was successfully used to synthesize NiAl reinforced with 10 and 20% TiB<sub>2</sub>, with appreciable strengthening attributed to the refinement of grain size from the TiB<sub>2</sub> and surface oxides from the powders in the compact [2.35]. The emergence of reactive sintering as one of the newest techniques for the production of intermetallics justifies the need for more theoretical work done in an attempt to ensure its application to the production of various composite systems.

2.3. Ductile Phase Toughening of Brittle Matrix Materials

2.3.1 Concept.

As mentioned in chapter 1, the brittleness of intermetallics due to their strong atomic bonding can be alleviated by intrinsic or extrinsic means. One consequence of intrinsic toughening which involves micro or macroalloying can be a significant loss of high temperature properties. A more effective and practical approach may be the use of ductile phase toughening. Ductile reinforcements may be in the form of particles, or continuous ligaments. Mechanisms contributing to the toughness include
crack trapping [2.36], crack shielding and plastic dissipation within a plastic zone [2.37] and crack bridging [2.38], [2.39], [2.40], and [2.41]. Experimental results indicate that crack bridging is the most potent mechanism. The toughening depends on the plastic properties of the reinforcement, its volume fraction, and on the strength of the interface between the ductile reinforcement and the brittle matrix. Constraints imposed on the particle by the rigid matrix suppress plastic deformation of the particle at the crack tip so that the main contribution to composite toughness comes from ligament formation in the matrix and their deformation and fracture behind advancing crack front [2.38]. The physical mechanism of toughening is quite simple. As a crack propagates in the brittle matrix, ductile ligaments are formed and must stretch as the crack opens until they fracture or decohere, as illustrated in Figure 2.5 [2.42]. The energy absorbed in stretching the ligament contributes to the increase in toughness of the composite as compared to that of a monolithic brittle matrix. The toughness increases with an increase in the length of the ductile bridge zone and reaches a steady-state level at the maximum bridge length. At this point ligament rupture occurs at the end of the bridge zone while new ligament forms ahead of advancing crack tip. At this point, the steady-state increase in toughness, \( \Delta G_c \), [2.40] and [2.42] is given by:

\[
\Delta G_c = f \sigma_0 a_0 \chi
\]  

(1)

where \( f \) is the area fraction of ductile material on the fracture surface, \( \sigma_0 \) and \( a_0 \), are the uniaxial yield stress, and the cross-sectional radius of reinforcement respectively,
and $\chi$ is a "work of rupture" function, which depends on the debond length at the reinforcement/matrix interface, plastic displacement at ligament failure $u^*$ and work hardening coefficient $n$. Here, the interfacial strength of ductile reinforcement/matrix plays a critical role. If the reinforcement is very weakly bonded to the matrix there is a very small contribution to the toughness. If the reinforcement is strongly bonded to the matrix, the matrix constraint prevents the reinforcement from plastically deforming producing a small toughness increment. It is desirable to have an "optimal" amount of debonding, where the relaxed constraint results in an increased gauge length of the reinforcement and thus greater plastic deformation. Mataga obtained value of $\chi$ numerically using:

$$\chi = \int_0^{u/a_0} \frac{\sigma}{\sigma_0} \, d(\omega/a_0)$$

where $a_0$ is the radius of ligament, $\sigma_0$ initial yield stress of the ductile phase and $\sigma$ the nominal stress carried by the stretching particle for a given crack opening $u$.

We can determine $\chi$ by obtaining normalized stress $\sigma/\sigma_0$ vs. normalized crack-opening $u/a_0$ and compute the area under the curve (Figure 2.6) [2.40], or by the use of inverted relationship:

$$\chi = \frac{1}{f \sigma_0 a_0} \left\{ \frac{(1-v^2)K^2}{E} - \frac{(1-f)(1-v^2)K_m^2}{E_m} \right\}$$
where the strain energy release rates are expressed in terms of plane strain fracture toughness and elastic properties for the matrix \( (K_m, \ E_m, \ \nu_m) \) and composite \( (K, \ E, \ \nu) \). The ligament failure mechanism will determine the extent of the \( \sigma - u \) curve, specifically failure stretch of ligament u*. For continuous ductile fibers (Pb) in a brittle matrix (glass), Ashby, Blunt and Bannister [2.40] determined the increase in fracture toughness as:

\[
\Delta K_{IC} = E \left[ C \ V_f \ \frac{\sigma_0}{E} \ a_0 \right]^{1/2}
\]

where \( V_f \) is the area fraction of ductile material intersected by the crack plane. The constant C depends on the degree of debonding and is equal to 1.6 for complete bonding with no matrix fracture and equal to 6 with limited debonding or matrix fracture. The greatest toughening is obtained from particles or ligaments with a high modulus \( E \), a high strength \( \sigma_0/E \), and a large diameter.

**2.3.2 Experimental results.**

Numerous studies have been conducted in the last three years to study the effects of ductile phase reinforcement on the fracture toughness of brittle intermetallics, (e.g., silicides and aluminides). In most of these systems there are reaction layers formed between the reinforcement and the matrix during the consolidation process. This has a direct impact on the degree of interfacial debonding, and thus the value of C. There are only a few thermodynamically stable systems where there is no reaction between
the reinforcement and the matrix. The Nb-Si system is one such system, as it provides a model system where interfacial strength can be experimentally varied without such difficulties. Two manufacturing processes were recently used for the production of composite Nb/Nb$_2$Si$_3$:

1. Melting and arc-casting of Nb-Si with various compositions in order to obtain in-situ Nb/Nb$_2$Si$_3$ composites with a varying amount of Nb phase, [2.43], [2.44], [2.45], [2.46] and [2.47].

2. Hot pressing of a blend of Nb and Nb$_2$Si$_3$ powders followed by heat treatment or heat treatment and extrusion, [2.48].

Mendiratta and Lewandowski produced in-situ composites consisting of a brittle Nb$_2$Si$_3$ intermetallic matrix and ductile Nb particles by the use of an arc-casting technique. Their results showed that the fracture toughness of notched bend samples increased with an increase in volume fraction of the ductile Nb phase. At the same time, the bend strength increased with increasing Si content. The impact of the heat treatment history of cast samples on the mechanical properties of the composite (strength, ductility and toughness) was investigated by the same authors. The properties obtained and the fractographic analyses indicate that in the extruded form, the terminal Nb solid solution can provide significant toughening of the Nb$_2$Si$_3$ matrix by combination of plastic stretching of the particles, interface-debonding and crack bridging. The fractography of the hot-extruded material reveal that the fracture mode of the Nb reinforcement changed from predominately brittle transgranular in the as-
cast condition to predominately ductile in the hot-extruded condition.

Studies of composites reinforced with ductile particles include TiAl with Nb or Ti-6Al-4V pancakes [2.49], MoSi$_2$ reinforced with Nb [2.50] and MoSi$_2$ reinforced with Ta pancakes produced by plasma spraying [2.51]. Elliott showed that both Nb and Ti-6Al-4V pancakes increase the toughness of γ-TiAl. The Ti-6Al-4V pancakes do not exhibit a significant resistance curve and only moderate toughness (=12.4 MPa$\sqrt{m}$), while the Nb composites (=16 volume %) showed a strong resistance curve and higher steady-state toughness ≈16 MPa$\sqrt{m}$ in crack arrestor orientation. In the work of Lu et al., [2.50], composites of MoSi$_2$ reinforced with 20 volume % of Nb particles had a work of rupture $\chi$ almost four times larger than the unreinforced MoSi$_2$ matrix.

There were also several studies conducted on toughening of intermetallics by ductile continuous fibers and foils. Cao et al., proposed a test procedure for characterizing the toughening of brittle intermetallics by ductile reinforcements [2.52]. Cylindrical test specimens were produced by HIPing and a method for tensile testing of samples was established. The proposed test method involved testing actual composites of γ-TiAl reinforced with Nb and Ti-33 at.% Nb alloys in the form of wire. The toughening was expressed in terms of the reinforcement strength, ductility, notch type, interface reaction layers and loss of constraint. Nb reinforcements increased the "work of rupture" $\chi$ depending on the notch design to a value of 2.6, while Ti-33 at.% Nb reinforcements showed $\chi$ to be ≈0.75. However, comparison to
the results obtained on constrained Pb wires in glass matrix [2.40] to the results obtained on Ti-Nb alloy reinforcements showed large differences in $\chi$ values. The authors rationalized this difference as due to the multiple cracking of the matrix, a phenomenon not observed in the constrained Pb wires. Single layer laminates of MoSi$_2$ with 130 $\mu$m thick Nb foils either coated with Y$_2$O$_3$ or uncoated were studied by Lu, Evans, Hecht and Mehrabian [2.50]. The toughness of composites was measured using a chevron notched three-point flexural samples in an SEM deformation stage. In both cases, uncoated laminates or yttria coated laminates, extensive debonding along interface was observed with resultant work of rupture $\chi$, $\approx 6.3$ and $5.7$ respectively. Multilayer laminated composites of 250 $\mu$m thick Nb foils in MoSi$_2$ matrix were produced by Xiao, Kim, Abbaschian and Hecht [2.53]. Nb foils were uncoated or coated with Al$_2$O$_3$ or ZrO$_2$. All three conditions showed an improved damage tolerance with $K_{ic}$ around 14-15 MPa$\sqrt{\text{m}}$ for uncoated and alumina coated Nb foils and 8.6 MPa$\sqrt{\text{m}}$ for zirconia coated foils. However, lower damage tolerance of zirconia coated Nb composites was manifested by brittle cleavage fracture of the Nb foils. Again, the importance of the fracture mode of the reinforcement in the toughness of the composite material need be addressed. Deve, Evans, Odette and Mehrabian, [2.54], conducted similar studies on single layer laminate composites combining 120 to 170 $\mu$m thick Nb and Ti-33 at.% Nb foils. The reinforcement foils were either uncoated or coated with alumina or zirconia. The toughness of the composites was again evaluated as a function of interfacial debonding using uniaxial
tension tests and the debond fracture energies were measured using four-point flexure after the crack was introduced into the interface. It is concluded that the work of rupture $\chi$ exhibits a linear dependence on the debond length. Inert oxide coatings, having low fracture energy, enhance debonding length thus leading to enhanced values of $\chi$.

2.4 Conclusions

Although the work of Benjamin and his co-workers in using the mechanical alloying process to develop stronger superalloys seemed to be an exotic means for its time, there has recently been an increasing use of this process for the development of other materials, particularly those where conventional melting and casting processes could not guarantee required properties. Mechanical alloying and subsequent consolidation of metal powders led the way to the understanding of non-equilibrium processes, such as metal powder alloying and sintering, and ultimately to other processes where exothermic reaction between metal constituents provides the energy required for compound formation. Mechanical alloying in combination with hot pressing or hot isostatic pressing provides one avenue for the production of some compounds and/or alloys where other metal processing techniques fail. Other derivatives of this process, including reactive sintering or self-propagating high-temperature synthesis alone and/or in combination with other densification processes offer other possibilities for the production of high temperature materials, including
intermetallics and composites. The advantage of the powder processing techniques over that of melting and casting lies in the ease of incorporation of the reinforcements in the metal matrix, chemical cleanliness, and compositional control. It is well established that the improved toughness of brittle intermetallics is achieved more successfully by extrinsic approaches rather than intrinsic approaches (macro or micro-alloying). From all of the factors contributing to the increased toughness of composite materials, "ductile phase toughening" is one of the most promising. However, the conventional wisdom of requiring a strong interface bonding for the high strength of materials is not appropriate for such materials. It is only appropriate to expect that some new high temperature materials are going to be a combination of brittle ceramics or intermetallics reinforced by ductile metals. This can provide the required formability and damage tolerance at low temperatures and all properties required for the high temperature operation.

The literature on compound formation of Nb₅Si₃ by mechanical alloying (MA) indicates that for the interrupted milling process, the reaction is exothermic and explosive in nature. This investigation focuses on the nature of the reaction in both the interrupted and continuous milling process in order to develop a kinetic model of compound formation. The feasibility of an "enhanced diffusivity" model and precipitation mechanism, will be addressed.

Extrinsic toughening of brittle matrices by ductile reinforcements has been accomplished using refractory metal reinforcements. The mechanical behavior of
refractory metals, having a bcc structure, is sensitive to changes in test temperature, strain rate, and the matrix constraint imposed by composite structures. The role of these variables on the fracture toughness of laminated composites and fracture mode of the Nb reinforcement will be addressed, as will the interfacial strength which was modified by diffusion bonding and structural adhesive bonding of the Nb reinforcement to the Nb$_2$Si$_3$ matrix.
2.5. References


Figure 2.1 Schematic of powder welding process.

Figure 2.2 Free energy of crystalline and amorphous phases.
Figure 2.3 Schematic of SHS process.

\[ A + B \rightarrow AB + \text{heat (mixed powder)} \]

Figure 2.4 Schematic of reactive sintering.
Figure 2.5 Crack bridging by ductile ligaments.

Figure 2.6 Normalized stress-strain curve for work of rupture $\chi$. 
CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Mechanical Alloying

3.1.1 Spex mill configuration.

Mechanical alloying was carried out in a Spex model 8000 high-intensity mixer/mill with a tungsten carbide vial (38x51 mm diameter), 100 g of hardened 52100 steel balls (12 mm in diameter) and 10 g of elemental powders for a 10:1 balls/powder weight ratio. The schematic in Figure 3.1 shows the Spex mill and the clamp-type fixture for securing the vial in place. The clamp assembly is powered by an electric motor operating at approximate 1725 rpm through a cam shaft, allowing the fixture to rotate in three orthogonal directions. Elemental powders with a proper ratio for the formation of Nb$_2$Si$_3$ (Nb-37.5 at.% Si) were weighed (e.g., 8.465 g Nb, 1.535 g Si) and placed into the vial while in an argon-gas-filled glove box. Powder removal from the vial after interrupted milling processes was also done in the glove box. The ends of the vial were sealed with neoprene gaskets to prevent the powders oxidation during the milling process. In addition, a plexiglass enclosure was built around the Spex mill in order to control the vial temperature and to permit the use of different gases for some experimental runs. An electric fan was additionally utilized to cool the vial during milling. The vial temperature was monitored with a portable
digital thermometer model 450 (Marlin Manufacturing Corp.,) with a contact
termocouple type J probe. In order to assure the same processing conditions for each
batch of powders, the tungsten carbide vial and the balls were cleaned with alcohol
or acetone after each batch by running the Spex mill for at least 15 minutes. The
resulting contaminated liquids were collected for proper disposal. The original Spex
mill timer with a capacity of 30 minutes was replaced by another one, which allowed
the Spex mill to operate for extended times (e.g. 24 hrs maximum).

3.1.2 Starting materials.

Elemental silicon powder was purchased from the Aldrich Chemical Co., with
particle size of -325 mesh (< 44 μm) and a nominal purity exceeding 99%. Niobium
powders were purchased from Johnson Matthey Inc., and Cabot Corp., with -325 mesh
(<44 μm) particle size and a nominal purity exceeding 99.8%. For the reactive
sintering studies, niobium powder with -60 mesh (= 150 μm) and a nominal purity
exceeding 99.8% was purchased from the Aldrich Chemical Co.

3.1.3 Test matrix.

In the Nb-Si system, Nb is a ductile component. During the mechanical alloying
(MA) process, welding and fracturing of the Nb powder particles is responsible for
microstructural refinement. In addition to particle welding, there is welding of the Nb
to tungsten carbide (WC) vial walls and to the steel balls. This could cause significant
contamination of the Nb powder by interstitial impurities. In this system, the \( \gamma \) phase \( \text{Nb}_2\text{Si}_3 \) is stabilized by interstitial impurities such as carbon [3.1]. In order to determine the degree of contamination arising from sample milling, pure Nb powders were milled for 1, 3, 6 and 9 hrs in either air or argon atmospheres. Mechanical alloying of the Nb-Si powders to study formation of the \( \text{Nb}_2\text{Si}_3 \) compound was accomplished using two approaches:

1. **Interrupted milling**, in which samples of powders were cooled after different milling times before further milling of the same batch of powders was resumed. Figure 3.2 shows the schematic of such a process.

2. **Continuous milling**, in which different samples of powder were continuously milled for different lengths of time, followed by examination at the conclusion of each particular milling condition, as shown in Figure 3.3.

In addition to using MA to produce \( \text{Nb}_2\text{Si}_3 \), Nb-Si mixtures were alloyed for times less than that required for compound formation (e.g., less than 3.25 h). These batches were MA for 2 h and later blended in a horizontal roller mixer for 2 h, to be used for reactive sintering and hot press consolidation experiments.

### 3.1.4 Preparation of MA Nb-Si powders for SEM examination

In order to examine a progress of the microstructural refinement in mechanically alloyed Nb-Si powders, samples of polished cross-sectional powders were employed. Sample mounting was especially critical in order to avoid exposing the powder
particles to excessive heat. First Buehler Co., cold mounting epoxy was used to produced standard size (31.75 mm in diameter) mold without any powder. Then a 6 mm hole in the center of mold was drilled to a depth of 13 mm. A small amount of powder was then mixed with a new batch of epoxy and poured into mold cavity and consequently cured at room temperature. Resulting powder samples were prepared by a standard metallographic technique to 0.05 μm finish and carbon coated for the SEM examination.

3.1.5 Examination of Powders

3.1.5.1 X-ray diffraction.

A Philips X-ray Autodiffractometer operated in the continuous scanning mode using a Cu Kα radiation source (λ = 1.5418 Å) was used for the X-ray analyses. All powder samples were set on a metallized frame of a powder sample holder by double stick Scotch tape. Nb and Si elemental powders as well as powders mechanically alloyed for a various periods of time were scanned at speed of 0.02°s⁻¹ and 0.05° step from 2Θ=20° to 2Θ=50° to verify existence of either elemental Nb and Si powders, Nb₅Si₃ compound, or other Nb-Si system compounds in comparison with corresponding Joint Committee on Powder Diffraction cards (JCPD’s). For the studies of a kinetic model of Nb₅Si₃ compound formation, determination of the lattice parameters of Nb and Si elements required very slow peak scan at 0.01°s⁻¹ speed and 0.01° step for all peaks occurring in the 2Θ range of 20-145°. X-ray diffractometer
output was stored on diskettes for further analysis on IBM or Vax computers. Several samples of consolidated powder were also scanned. The same parameters of scanning as those used for the phase identification of powder samples were employed.

X-ray diffraction data of the continuously scanned samples were processed with the use of an IBM QuatroPro program which consists of spreadsheet and graphic function. Scan peaks of Nb and Si elemental powders and milled Nb-Si powder mixtures were analyzed by the use of a proprietary Lotus program which allowed determination of the precise 2θ angle of each peak.

3.1.5.2 Scanning electron microscopy (SEM) and optical metallography.

The powder particle size, microstructural refinement of milled Nb-Si powder mixtures, and the post failure analysis of laminates was conducted in a JEOL 840A scanning electron microscope using secondary electron (SE) or back scattered electron (BE) mode with 25 kV acceleration voltage and 1x10⁻⁹ A current. The back scattered electron mode was particularly effective in the determination of the microstructural refinement of Nb and Si milled powders due to the large difference in the atomic weights of Nb and Si. The energy-dispersive X-ray analysis (EDAX) was used to determine the presence of unreacted niobium in compacts obtained by the reactive sintering method and from prealloyed Nb and Si powders. Montages were taken of the fracture surfaces of laminates tested in three point bending, while stereo-imaging was additionally used to determine the failure locus of the Nb foil reinforcement.
The microstructural analyses of consolidated compacts produced under various powder milling and hot pressing conditions and of Nb foil in AR, VHT, Nb(ss) and (Constrained Nb(ss)) conditions were conducted on a Nikon optical microscope. Both reflected light and Nomarski interference modes were utilized.

3.1.5.3 Transmission electron microscopy (TEM).

A JEOL 200CX transmission electron microscope was used for the microstructural evaluation of the Nb-Si milled powders produced by interrupted and continuous milling. The powders were dispersed on a piece of carbon film which was supported on a copper grid (3 mm in diameter). An additional layer of carbon film was deposited on top of the dispersed powders in order to avoid contamination of the microscope. Both bright field and dark field imaging techniques were employed to observe and identify the particles.

3.1.5.4 Differential thermal analysis.

Differential Thermal Analysis (DTA) uses the principle of measuring the temperature difference between the sample of interest and a standard alumina crucible (Al₂O₃) to determine a solid state phase transformation. Thermocouples used for temperature measurements are connected in series so that any exothermic reaction will cause a positive temperature difference, while an endothermic reaction will produce a negative temperature differential. The first series of Nb-Si powders milled from 0.5
h to 3.5 h utilized a NASA Lewis Research Center Netzsch STA 429/409 DTA unit. For each test, a small amount of powder (= 500 mg) was placed into the alumina crucible. The DTA unit was then evacuated, followed by purging with helium gas (30 cc/min) throughout the test duration. A constant heating rate of 10°C/min was employed. Temperature differential versus DTA furnace temperature was recorded with a chart recorder. A DTA computer analyzed the data to give information on the nature of transformation (exothermic or endothermic), on the critical temperature, onset and peak temperature, as well as the peak area. The critical reaction temperature is defined as the temperature at which the heat of reaction is large enough to cause a positive increase in the temperature difference between the sample and the reference thermocouple. The onset temperature is designated as the temperature at which the reaction is self-propagating, as shown in Figure 3.10.

In the study of the kinetics of Nb₃Si₃ compound formation, there was a need for DTA analyses of 1 h milled Nb-Si powders immediately after the milling and after aging at room temperature up to 1000 h. Due to the difficulty with timely access to the NASA DTA unit, a modified DTA unit was built at Case Western Reserve University. A Lindberg company 6 zone tubular furnace with a 1473 K maximum temperature capacity was employed. An alumina boat crucible was used for the sample and the thermocouples attachment. The output of all thermocouples, (furnace, sample and alumina standard) was recorded with a Hewlett Packard model 7132A two pen recorder. A cold junction (0°C) was placed between the thermocouple leads and
the pen recorder. Powder samples (2 to 5 gr) were cold pressed into small disks and a center hole was drilled for the insertion of a K type ( Chromel/Alumel) thermocouple, while another K type thermocouple was placed in the alumina crucible as a reference. Argon gas was used to prevent powder oxidation during the analysis and post-analysis cooling. The end zones of the furnace were held at 573 K, allowing the sample to "quench" during the analysis for the subsequent x-ray diffraction to determine the phase evolution during the DTA analysis.

3.2 Powder Consolidation

3.2.1 Hot press configuration.

Powder consolidation was accomplished with a GCA/Vacuum Industries Inc., 3600 series Vacuum Hot Press capable of operating at up to 66 MPa pressure and 2573 K using graphite dies and punches and a graphite resistance heating element (Figure 3.4). The room temperature vacuum capability of the hot press was on the order of 1.2 x 10^{-6} \text{ torr}, and decreased to 1x10^{4} \text{ torr} with an increase in the operational temperature. The hot press control thermocouple (W/5\%Re-W/26\%Re) was placed between the resistance heating element and the graphite die at approximately half the height of the die. To get a precise die temperature reading, a Leeds & Northrup optical pyrometer was employed. However, since the sighting port is located on the top of the hot press, only the die's top surface temperature could be measured accurately.
The hot press configuration permitted use of a graphite die of 12.7 cm O.D., 5.08 cm I.D., and 15.24 cm in height. In order to prevent carbon diffusion into the consolidated powders, the graphite die was lined with 0.127 mm thick tantalum foil. The upper and lower punch surfaces were also lined with 0.25 mm thick graphite foil to allow for easy separation from the Ta foil.

3.2.2 Processing parameters.

The general hot pressing scheme is shown schematically in Figure 3.5. The degassing stage at 1123 K for 1-4 h may be particularly important for powders prepared by the MA process, as significant microcracking was observed in compacts not degassed for sufficient time at this temperature. A pressure of 55 MPa was applied after the degassing cycle was completed and was held constant during the consolidation process to enhance densification. Since the Nb₅Si₃ compound has a ductile-to-brittle transition temperature at 1873 K (1650°C) [3.2], maintaining the pressure during cooling was unnecessary, but the cooling rate was kept below that of 5°C/min in order to avoid residual stress build-up in consolidated samples. The process summarized in Figure 3.5 including hot press loading, powder degassing, consolidation, and cooling required 2 working days per batch.

3.2.3 Reactive sintering and hot pressing.

In addition to consolidation of MA powders, the vacuum hot press was also used
for reactive sintering experiments. Since reactive sintering is associated with liquid phase sintering, there is a significant volume change associated with the reaction. In order to determine the onset reaction temperature, LVDT's were installed on the hot press upper and lower rams. The LVDT's combined output was monitored via the use of a digital strain gage conditioner.

In comparison with the consolidation process used for the MA powders which contain a high volume of argon gas filled pores, reactive sintering of blended elemental powders did not require extensive degassing. All other processing parameters were the same as those used for the consolidation process used on the MA powders as shown in Figure 3.5.

### 3.2.4 Density measurements

The Archimedes immersion density method was employed for the density determination of powder compacts consolidated under various milling and hot pressing conditions. In this simple method, a sample is first weighed in air (weight A), and then with the electronic balance reset to 0, weighed again in water (weight P). For best results distilled water brought to the boiling point and then cooled to 293-303 K was used in order to lower the amount of absorbed air in the water. The water temperature was measured with a mercury thermometer for an accurate determination of the water density ($\rho_w$). The absolute density of the measured sample was then calculated by:
\[ \rho_{\text{sample}} = \frac{P}{A} \times \rho_{\infty} \]  

(6)

The theoretical density of \( \text{Nb}_3\text{Si}_3 \) was calculated using the unit cell lattice parameter and the number of Nb and Si atoms according to the equation:

\[ \rho = \frac{\text{number of atoms/unit cell} \times \text{atomic weight}}{\text{Avogadro number} \times \text{unit cell volume}} \]  

(7)

The space group of \( \alpha \) and \( \beta \) phase of \( \text{Nb}_3\text{Si}_3 \) compound is \( \text{tI}32 \) with 20 atoms/unit cell of Nb and 12 atoms/unit cell of Si. \( \text{Nb}_3\text{Si}_3 \) unit cell lattice parameters are:

- \( \alpha \)-phase: \( a = 1.0026 \text{ nm} \)
- \( \beta \)-phase: \( a = 0.6570 \text{ nm} \)
- \( c = 0.5072 \text{ nm} \)
- \( c = 1.1884 \text{ nm} \)

The calculated theoretical density is 7.107 gr cm\(^{-3}\) for \( \alpha \)-phase and 7.151 gr cm\(^{-3}\) for \( \beta \)-phase. The relative density of the measured sample is its absolute density divided by the theoretical density of given compound phase.

3.3 \( \text{Nb}_3\text{Si}_3/Nb \) Laminate Production

3.3.1 Diffusion bonding of laminates.

A general schematic of the diffusion bonding process used to produce tri-layer \( \text{Nb}_3\text{Si}_3/Nb/\text{Nb}_3\text{Si}_3 \) laminates is shown in Figure 3.6. The MA \( \text{Nb}_3\text{Si}_3 \) powders consolidated via vacuum hot pressing into compacts of 50 mm diameter and 21 mm height were electro-discharge machined into disks 4 mm in thickness. The disks were subsequently ground on Buehler wet grinding wheel with 320 grit SiC abrasive for
removal of the damaged layer produced by EDM as well as ensure the sides were flat and parallel to enable a good contact between the Nb$_2$Si$_3$ matrix and the reinforcing Nb foil. The Nb foil (0.25 mm thick) with a nominal purity exceeding 99.8% purchased from Aldrich Chemical Co., was cut into a disk 50 mm in diameter. One Nb foil and two Nb$_2$Si$_3$ plates were degreased in acetone and placed into a Ta foil lined graphite die. Diffusion bonding was accomplished in the vacuum hot press at 10 MPa and 1473 K for 5h. The diffusion cycle of 1473 K/5 h was chosen to minimize the amount of Si diffusion while providing good bonding and was based on the theoretical calculations of Si diffusion into Nb shown in Figure 3.7. Figure 3.7 was derived using data developed by Sirotta and Sokolov who investigated the diffusion of semiconductor grade Si from the vapor phase into 99.7% pure polycrystalline Nb specimens [3.3]. Over the temperature range 1073-1373 K, the layer thickness increase in their work was described by the following:

$$D_0 = 0.78 \text{ cm}^2\text{sec}^{-1}, \ Q = 68.2 \pm 3.4 \text{ kcal mole}^{-1}.$$  

From the given data, the diffusion coefficient at 1473 K was calculated to be $D = 5.62 \times 10^{-11} \text{ cm}^2\text{sec}^{-1}$. To calculate the Si concentration profile at this diffusion bonding temperature, a model of 2 semi-infinite Nb and Si blocks using an error function was used:
\[ C = \frac{C_1 + C_2}{2} - \left( \frac{C_1 - C_2}{2} \right) \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \] (5)

As can be seen in Figure 3.7, 5 h at 1473 K produces Si penetration up to 50 \( \mu \)m from the interface.

A 5 h hot pressing time was selected to limit the extent of Si diffusion into Nb while allowing sufficient Nb self-diffusion to provide strong interface bonding. Using data from Lundy: \( D_0 = 1.1 \text{ cm}^2\text{sec}^{-1}, Q = 96 \text{ kcal mole}^{-1} \) for a temperature range 1151-2668 K, the interdiffusion thickness for Nb using approximated relationship \( x = \sqrt{Dt} \) was calculated and plotted in Figure 3.8 [Lundy, 1965].

3.3.2 Adhesive bonding of laminates.

In order to modify the Nb\(_2\)Si\(_3\)/Nb interfacial strength in a controlled way, three layer laminates were produced using the structural adhesive EC 1386 produced by 3M. The two different laminate constructions differed only in the condition of the Nb reinforcement. In the first one, we used as-received Nb foil (AR-Nb) with a grain size of 10 \( \mu \)m, while the second laminate incorporated Nb foil which was vacuum heat treated (VHT-Nb) at 1473 K/5 h to produce an identical grain size to that obtained in the Nb reinforcement from diffusion bonding the laminate. Electro-discharge machined Nb\(_2\)Si\(_3\) disks 2 mm in thickness were ground to 320 grit by the use of SiC abrasive papers. A disk 50 mm in diameter was cut from the Nb foil. All surfaces
were degreased with acetone before application of the adhesive. Thin layers of EC 1386 adhesive were applied to the Nb foil surfaces and sandwiched with two Nb₂Si₃ compound disks. The sandwiched sample was placed into a special Tinius Olsen Co., steel fixture which featured a self-aligning bottom anvil. In order to prevent sticking of the excess adhesive to the anvils, a graphite foil was placed at the bottom and top surface of the laminate. The curing cycle consisted of heating to 449.7 K (350°F) at rate of 278.5 K/min (10°F/min), holding for 60 minutes at that temperature, and then slow cooling to below 394.1 K (200°F) under applied pressure of 0.16 MPa (25 psi).

3.4 Mechanical Test Sample Preparation

3.4.1 Single edge notched and double edge notched monolithic and laminated samples.

The schematic in Figure 3.9 shows the sample configurations for the three point bend test and the uniaxial tension test. Samples were electro-discharge machined and single edge notched (SEN) or double edge notched (DEN) specimens were tested in the crack arrestor direction in accordance with the ASTM E 399 - 83, Standard Test Methods for Plane-Strain Fracture Toughness of Metallic Materials. Due to an EDM wire size limitation, the obtained notch root radius was in the order of 125 μm. In some samples a wire was used to extended the notch with a 50-60 μm root radius. All notches were placed at 125-250 μm distance from the matrix/reinforcement interface.

Bend bars were also electro-discharge machined from the monolithic Nb₂Si₃,
compacts obtained under a various mechanical alloying and consolidation techniques. The specimens had a cross-sectional area of 2 mm x 4 mm, and were single edge notched (SEN) to a depth of 2 mm with a notch root radius of 125 μm.

As-machined and notched samples were subsequently ground and polished to 0.05 μm finish using SiC paper and an Al₂O₃ suspension. Both surfaces were polished to enable observation of crack propagation in the SEM deformation stage.

Special care was exercised in the preparation of samples for X-ray diffraction and density tests. Due to diffusion between the Ta foil and Nb₃Si₃ matrix, the surfaces exposed to the Ta foil were ground to a depth of 10 μm or more to remove any Ta metal contamination.

3.4.2 Uniaxial tension test samples of Nb reinforcement.

In addition to the as-received Nb foil (AR-Nb), the foil was heat treated to obtain following conditions:

1. Vacuum Heat Treated - (VHT)

2. Vacuum Heat Treated/Si in Solid Solution - {Nb(ss)}

3. Nb₃Si₃/Nb laminate - {Constrained Nb(ss)}.

All heat treatments were conducted in the vacuum hot press. To obtain the VHT condition, Nb foils were wrapped with a Ta foil and the 1473 K/5 h cycle was used. For the Nb(ss) condition, the same conditions as those used for the diffusion bonding cycle excluding the applied punch pressure were used. This allowed an easy foil
separation from the silicide plates. For the uniaxial tension tests conducted at 298 K, Nb foil samples were machined in accordance with the Standard Methods of Tension Testing of Metallic Materials - ASTM E8-83 with a gage section of 6 mm x 0.25 mm x 12.7 mm, and 3 mm x 0.25 mm x 20 mm gage section for the tests at 77 K. Special care was taken in the de-burring of the gage section edges in order not to provide any surface defects for the ease of crack propagation.

3.5 Mechanical Properties Testing

3.5.1 In-situ SEM test.

Mechanical testing was accomplished in a JEOL 840A scanning electron microscope equipped with an Oxford Instruments deformation stage. The Nb$_3$Si$_y$/Nb laminates were tested in either three point bending (i.e., SEN) or in tension (i.e., DEN) at a loading rate of 1 $\mu$m s$^{-1}$. In-situ monitoring of fracture events combined with a real time load-time recording enabled accurate calculation of fracture initiation loads and monitoring of the behavior of the niobium ligament. In order to minimize the possibility of the catastrophic crack propagation as the result of high elastic energy stored in the sample during photography of interested area, the applied load was manually decreased. Testing in the SEM was limited to 80 kg force load, thus requiring the use of the Instron testing system for samples requiring in excess of 80 kg force.
3.5.2 Samples tested with the Instron.

3.5.2.1 Nb foil.

Mechanical testing of tensile samples which were machined from the AR, VHT and Nb(ss) materials was conducted on a screw driven Instron 1125 Universal Testing machine at an initial strain rate of $1 \times 10^{-3}$. Load and displacement were recorded for each tension test. Mechanical testing was conducted at 298 K as well as 77 K (liquid nitrogen).

3.5.2.2 Laminates.

Since the SEM deformation stage was limited to room temperature, additional laminates and Constrained Nb(ss) samples were tested at 77 K using the Instron testing machine at the loading rate of $1 \mu m \ s^{-1}$. A clip gage was placed across the notch in the case of three point bend testing to monitor the crack opening displacement (COD). The loading span was 46 mm.

3.5.2.3 Nb$_3$Si$_2$.

Three-point bend tests of the bend bars of monolithic Nb$_3$Si$_2$ compound were also conducted on the Instron testing machine at the loading rate of $1 \mu m \ s^{-1}$ with the load and displacement recorded for each test.
3.11 References

3.1 JCPD card #8-422.


Figure 3.1 Schematic of Spex mill clamp-type fixture and loaded vial.

Figure 3.2 Flow chart of interrupted milling process.
Figure 3.3 Flow chart of continuous milling process.

Figure 3.4 Schematic of hot press.
CONSOLIDATED POWDERS:  
- Mechanical alloyed Nb + Si mixture
- Mechanical alloyed NbSi3
- Blended Nb + Si powders

![Diagram of hot pressing cycle](image)

Figure 3.5 Schematic of hot pressing cycle.

![Diagram of diffusion bonding cycle](image)

Figure 3.6 Schematic of diffusion bonding cycle.
Figure 3.7 Diffusion of Si in Nb.

Figure 3.8 Nb self-diffusion in Nb$_3$Si$_y$/Nb laminate bonding.
Figure 3.9 Laminate sample dimensions and notch orientation.

Figure 3.10 Schematic of the critical and onset temperature determination.
CHAPTER 4

RESULTS

4.1 Mechanical Alloying

4.1.1 Initial powders.

The initial powder particle sizes and shapes of the Nb and Si powders are illustrated in Figure 4.1 and Figure 4.2 respectively. The Nb had a uniform particle size of 44 µm as specified by Aldrich Chemical Co., while the Si particle size varied from 44 µm down to 1 µm. The X-ray diffraction patterns taken from the as-received elemental Nb and Si powders are shown in Figures 4.3 & 4.4, and confirm that body centered cubic Nb is present in the former while a diamond cubic structure for the Si in the later. The calculated lattice parameter of Nb, 3.3065 Å, obtained from the x-ray diffraction results nearly identical to that given in JCPD card #35-789 (i.e. 3.3066 Å). The lattice parameter calculated for Si (5.4365 Å) was slightly higher than given in JCPD card #35-1158 (5.4309 Å).

4.1.2 Mechanical milling of Nb powders.

Mechanical milling of pure Nb in air and argon atmosphere was conducted in order to study the impact of the vial atmosphere on the lattice parameter of Nb. Some material pull-out from the walls of the vial was evident during milling of the pure Nb
powder. A plexiglass enclosure was filled with argon for the milling of Nb in an argon filled vial in order to minimize oxygen contamination. Table 4.1 and Figure 4.5 shows the lattice parameter of Nb as a function of the milling time and the vial atmosphere. For milling times up to 4.5 h, lattice parameter increase is higher for milling in argon than an air atmosphere. It was also observed during the milling of pure Nb in argon that a substantially higher operating temperature of the tungsten carbide vial was obtained (e.g. 50°C in air and 75°C in argon). This is due to the lower specific heat capacity (0.124 vs. 0.2401 cal g⁻¹ K⁻¹) and thermal conductivity (41.33 vs. 60 cal sec⁻¹ cm⁻¹ C⁻¹) of argon gas as compared to air. For the longer milling times, oxygen contamination becomes predominant. X-ray diffraction patterns of the milled Nb show both peak shifts and line broadening, as shown in Figure 4.6. SEM micrographs of the Nb particles taken at different milling times are shown in Figure 4.7, revealing the significant decrease in Nb particle size with increased milling.

On the other hand, oxygen has limited solubility in silicon, while the Si particles do not weld to the vial walls and steel balls. Oxygen contamination of Si is therefore not expected to be very significant, as discussed in section 4.1.5 on the lattice parameter changes observed in the Nb and Si in the MA mixtures.

4.1.3 Nb,Si, compound formation.

4.1.3.1 Interrupted milling process.
Figure 4.8 shows a schematic summarizing the results of interrupted milling experiments using an argon gas filled vial and fan air cooling of the Spex mill. It was found that the silicide compound formed in an average time of 75-120 minutes, depending on the length of interruption between milling periods. Each milling segment in the interrupted process was 30 minutes. Figure 4.9 shows the measured vial temperature for various milling conditions where the starting powders were Nb and Si. The vial temperature increased with milling time for each milling cycle in the interrupted process, and a sharp rise in the vial temperature was detected upon resumption of milling for the third period, apparently due to the exothermic reaction which accompanies compound formation. Figure 4.10 shows x-ray diffraction patterns taken from a Nb-Si mixture just before (i.e. 60 min) and just after Nb₃Si₁ formation (i.e. 75 min). It is evident from Figure 4.10 that the elemental Nb and Si peaks disappeared after 75 minutes of interrupted milling, being replaced by the Nb₃Si₁ compound. All conditions of milling were kept constant, except for the cooling time of the interruptions. Figure 4.11 shows the SEM micrographs of the Nb-Si mixture just before (i.e. 60 min) and just after (i.e. 75 min) compound formation. The particle size is uniform and less than 10 \( \mu \text{m} \) after 60 minutes of milling, due to accumulated cold work. After the exothermic reaction occurred (i.e. 75 min), Figure 4.11 B shows that the particles exhibit a non-uniform distribution of particle sizes, and the presence of some large fused agglomerates that are 20-30 \( \mu \text{m} \) in size and larger. Additional milling breaks these agglomerates into finer particles without changing the
composition.

4.1.3.2 Continuous milling process.

Figure 4.12 summarizes the continuous milling experiments conducted on the Nb and Si powders. In these experiments the Nb-Si mixture was loaded into the vial under an argon atmosphere, while vial cooling during milling was accomplished by the use of fan. In the continuous milling process, the repeated coalescence and fragmentation of the Nb and Si particles creates a layered structure. The inter-layer distance between Nb and Si atoms decreases with increasing milling time at which point compound formation occurs, as shown in Figure 4.13. Figure 4.14 shows SEM micrographs of the Nb-Si mixture just before (i.e. 3 h) and just after (i.e. 3.25 h) Nb₅Si₃ formation. Corresponding x-ray diffraction patterns are shown in Figure 4.15.

The temperature measurements taken on the outside cylindrical wall of the vial during milling, Figure 4.9 b, show that the temperature rises during milling and it takes approximately 30 minutes of continuous milling to reach a steady-state temperature rise of 50°C. This temperature rise of 50°C is attributed to the dissipation of the kinetic energy of steel balls impacting the powder particles and the walls of the vial. This was checked by simply running the mill with the steel balls and without the Nb and Si powders. The temperature rise in this case was 50°C. The dashed line in Figure 4.9 b represents the speculated temperature rise accompanying compound formation, which is exothermic. This temperature rise, using the enthalpy of reaction
of 108 kcal/mole, was calculated to be 34°C.

4.1.4 DTA of milled Nb-Si powders.

Figure 4.16 shows a DTA trace of a Nb-Si (1:1 at. % ratio) powder mixture heated from 298 K to 1673 K [2.19]. The formation of Nb₅Si₁₅ commenced at approximately 1250°C (1523 K), as indicated by the abrupt discontinuity in the DTA trace shown in Figure 4.16. In the MA process utilized presently, this reaction occurs at relatively low vial temperatures (e.g. 50-80°C). However, as estimated by Maurice and Courtney [2.8], the temperature rise at powders trapped between two colliding steel balls may be much higher (e.g. 600-900 K). DTA analyses were used on powders milled for various times in order to determine the critical and onset temperatures of Nb₅Si₁₅ compound formation. Figure 4.17 summarizes the DTA tracings obtained from Nb-Si powders MA for times ranging from 1 to 3.5 hours. Table 4.2 and Figure 4.18 show that while the reaction temperature decreases with increased milling time, the largest decrease occurs in the first hour of milling. The designation "NASA DATA" corresponds to experiments conducted at NASA Lewis Research Center while those denoted "CASE DATA" indicate data obtained at CWRU on the apparatus described earlier.

The DTA trace obtained from the NASA DTA unit on the Nb-Si mixture milled for 1 hour indicated three distinct peaks, as shown in Figure 4.19. In order to identify the phases associated with each peak, the Case modified DTA unit was employed with
a "quench" capability during the DTA analysis. Here, "quench" designates capability of cooling the sample after each DTA peak by placing the DTA ceramic boat in the end zone of the furnace kept at 300°C. Quenched samples were crushed and x-rayed to determine the phase evolution during DTA analysis. Figure 4.20 shows the diffraction patterns and corresponding phases obtained from powders quenched after each of the peaks labeled in Figure 4.19. The first peak in Figure 4.19 corresponds to the formation of NbSi₂. An increase in the furnace temperature enables the NbSi₂ compound to react with any unreacted Nb, thereby forming Nb₅Si₇, corresponding to the second diffraction peak in Figure 4.20. A further increase in the DTA furnace temperature beyond the second peak in Figure 4.19 promotes diffusion of Si into any other unreacted Nb resulting in the formation of additional Nb₅Si₇ as demonstrated by third diffraction peak shown in Figure 4.20. Increased furnace temperature to form additional Nb₅Si₇ is required due to a low diffusivity of Si through Nb₅Si₇ (i.e. 7x10⁻¹⁵ cm² sec⁻¹ at 721°C). Figure 4.21 shows that the microstructural refinement after 1 hour of MA is non-uniform. Based on the above, the subsequent DTA experiment on such a structure is proposed to occur as follows:

a. Nb and Si react to form NbSi₂

b. NbSi₂ and unreacted Nb react to form Nb₅Si₇

c. NbSi₂ and residual unreacted Nb react to form Nb₅Si₇.

It was observed that the length of cooling time after milling has a pronounced impact on formation of Nb₅Si₇ upon resumption of milling in the interrupted process.
For example, milling for 1 hour followed by cooling for 45 minutes and remilling for additional 30 minutes produced only Nb and Si, while cooling for an additional 105 minutes in an identical specimen produced Nb$_2$Si$_3$ after only 5 minutes of additional milling upon resumption of milling. This is summarized below:

Condition 1: Nb+Si milled 1 hour/ Cooled for 45 minutes/ Remilled for 30 minutes/ Result - Nb+Si.

Condition 1: Nb+Si milled 1 hour/ Cooled 150 minutes/ Remilled for 5 minutes/ Result - Nb$_2$Si$_3$.

The experiments described were repeated numerous times in order to analyse such phenomena. DTA analyses were conducted on powders milled for a total time of 1 hour immediately after the milling process was stopped as well as after room temperature "aging" for up to 1000 hours as shown in Figure 4.22. Milling for 1 hour produces only Nb+Si as illustrated by x-ray measurements. Figure 4.23 shows the onset reaction temperature of Nb$_2$Si$_3$ vs. "aging" time at room temperature. Aging for times up to 1000 hours at room temperature produced a total temperature differential of less than 9°C. This small reaction temperature drop due to "aging" at room temperature suggests that enhanced diffusivity occurred as proposed by Whittenberger. However, it does not play a significant role in compound formation in the interrupted process. A more significant decrease in the onset temperature would indicate that room temperature "aging" is associated with enhanced Si diffusion into Nb particles as the result of the accumulated high density of defects (e.g. dislocations).
4.1.5 Lattice parameters of Nb and Si in MA mixtures.

The observation of Nb-Si$_2$ formation in the interrupted milling process at times significantly less than that in continuous milling indicates that some mechanism of Nb$_2$Si$_3$ formation may occur during powder cooling to room temperature prior to resumption of milling. One possible mechanism is precipitation of Nb$_2$Si$_3$. In order to examine this, powders of elemental Nb and Si, as well as Nb-Si mixtures were milled for 1 hour period in an argon-filled WC vial. X-ray diffraction was immediately performed on the milled elemental Nb and Si powders and prealloyed powders using the continuous step scanning mode. A very slow peak scan was performed for all Nb and Si peaks from 2θ=20° to 2θ=145°. Each scan thus provided 600 points for determination of the precise 2θ angle of each peak. From the given value of peaks angle and corresponding plane hkl indices, the lattice parameters, a, were calculated and plotted against the Nelson-Riley function ($\cos^2\Theta/\sin^2\Theta + \cos^2\Theta/\Theta$). The least square method, Cohen modified least square method, and Nelson-Riley method are the statistical methods of the best fit of the experimentally determined lattice parameters. However, Nelson-Riley function is recommended in the situations were only few diffraction peaks are available. Extrapolation of the measured a values to the Nelson-Riley function at 0 (e.g. Θ=90°) gives the true lattice parameter, a. Figures 4.24 and 4.25 show the Nb and Si lattice parameters plotted against the Nelson-Riley function, respectively. Table 4.3 and Figure 4.26 show the extrapolated values of Nb lattice parameters for milled elemental Nb and for milled Nb-Si mixtures as a function
of milling time. It appears that the change in the lattice parameter with milling time is the result of powder contamination during milling and not due to solution of Si in Nb. Table 4.4 and Figure 4.27 show extrapolated values of the lattice parameter $a_0$ of Si for milled elemental Si and milled Nb-Si mixtures as a function of milling time. It is evident from these values that elemental Si milled in argon filled vial maintains its purity. However, the lattice parameter of Si in the milled Nb-Si mixtures shows a significant increase (e.g. 0.04%), suggesting a solid solution of Nb in Si.

4.1.6 TEM of MA Nb-Si powders.

The resolution of X-ray diffraction is only about 5 volume percent. Thus, in order to accurately determine the presence of Nb$_2$Si$_3$ compound formation, transmission electron microscopy (TEM) of Nb-Si mixtures milled for a period of 1 hour and those milled in the continuous milling process for a time period just prior to compound formation (i.e. 3 hours) was conducted. Figure 4.28 shows TEM micrographs and electron diffraction patterns of the MA Nb-Si powder which was milled for 1 hour. The majority of particles examined comprised a mixture of elemental Nb and Si particles, as determined by analysis of the electron diffraction patterns, after 1 hour milling time. However, Nb$_2$Si$_3$ particles were also present. Figure 4.29 shows TEM micrographs and indexed diffraction patterns taken from Nb-Si powders milled for 3 hours, which is just before extensive compound formation. The existence of elemental Nb and Si mixtures before compound formation was also confirmed with x-ray
diffraction and DTA analyses. The bulk of the powders primarily consisted of a mixture of elemental Nb and Si particles, with a small volume fraction of Nb$_2$Si$_3$.

4.2 Powder Consolidation

4.2.1 Metallography/grain size.

4.2.1.1 Monolithic Nb$_2$Si$_3$ compacts.

Figures 4.30 and 4.31 show optical micrographs of as-polished and as-etched compacts obtained from the various powder processing techniques outlined earlier. Compacts produced from mechanically alloyed Nb$_2$Si$_3$ exhibited a single-phase microstructure (Nb$_2$Si$_3$) with an average grain size of 5 μm as shown in Figure 4.31. Compact hot pressed from Nb and Si powders prealloyed for times ranging from 3.5 to 5 hours and blended for 2 hours contained a small amount (less than 3 vol.% of unreacted niobium, confirmed by scanning electron microscopy and energy-dispersive X-ray analysis (EDAX), with the remaining microstructure consisting of Nb$_2$Si$_3$, with an average grain size of 5 μm. However, compact obtained from prealloyed Nb-Si powders Spex milled for 2 hours and blended for 2 hours exhibited a single-phase Nb$_2$Si$_3$ microstructure with an average grain size of 4 μm. The reactive sintered (RS) compacts, in addition to exhibiting a larger volume percentage of unreacted niobium (i.e., 5 vol.%), displayed a bimodal Nb$_2$Si$_3$ grain size distribution with average grain sizes of ranging from 2-3 μm to 15 μm. These RS compacts were produced from Nb and Si powders with a particle size ratio of 1:1 (≤44 μm).
Additional RS compacts were produced with a Si/Nb particles ratio of 0.3 resulting in the microstructure shown in Figure 4.32. The microstructure consists of unreacted Nb particles of average size of 50 μm, a continuous Nb$_2$Si$_3$ matrix, and a network of a eutectic mixture of NbSi$_2$ and Si. The large Nb grain size and the slow heating rates obtained in the vacuum hot press are responsible for incomplete reaction for otherwise expected single-phase, low-porosity microstructure of Nb$_2$Si$_3$.

4.2.1.2 Nb$_2$Si$_3$/Nb composites.

Reactive sintering and hot pressing techniques were also used for the production of the Nb$_2$Si$_3$/Nb composite compacts. Elemental Nb and Si powders with average size ≤44 μm were blended in a horizontal roller blender for 75 hours prior to reactive sintering in ratio such that 30 vol. % Nb was in excess. Figure 4.33 shows the resulting microstructure. The microstructure consists of somewhat clustered Nb particles (*i.e.* light colored phase in Figure 4.33) in the continuous Nb$_2$Si$_3$ matrix (*i.e.* gray colored phase). The tendency of the Nb particles to clustering is probably a result of blending process inefficiency. In contrast to compacts obtained from Nb$_2$Si$_3$ and prealloyed Nb-Si powders, the reactive sintering method provides compact with very small residual porosity as evident in Figure 4.33.

4.2.2 X-ray diffraction.

Figure 4.34 shows the X-ray diffraction patterns of the consolidated compacts
obtained from the various powder processing techniques. Comparison of the
diffraction spectra with the JCPD card file shows that Nb$_3$Si$_3$ exists as both the $\alpha$
phase (unmarked peaks) and carbon-stabilized $\gamma$ phase (filled squares) in the RS
material. In contrast, MA-processed material contains the $\beta$ phase ($\Theta$ marked) as well
as the $\alpha$ and $\gamma$ phases. The $\beta$ phase is a high temperature phase stabilized by the
accumulated cold work experienced during the MA process, while carbon in the
graphite die is responsible for the formation of the carbon-stabilized $\gamma$ phase. Since
the hot press consolidation temperature was below that of the $\alpha$-to-$\beta$ phase
transformation, the $\beta$ phase was retained in the compacts. Figure 4.35 compares the
x-ray diffraction pattern of the composite Nb$_3$Si$_3$/Nb compact to those of monolithic
Nb$_3$Si$_3$ compacts. The presence of excess Nb is shown by the Nb (110) diffraction
peak.

4.2.3 Density.

The results of immersion density measurements are reported in Table 4.5. The
density of the MA processed powders exceeded 97.4% of theoretical density aided by
the fact that the hot press consolidation was conducted at or above the ductile to
brittle transition temperature of 1650°C for Nb$_3$Si$_3$. Densities in excess of 99% were
achieved for reactive sintered Nb$_3$Si$_3$ and Nb$_3$Si$_3$/Nb compacts at much lower
densification temperature (e.g. 1300°C) utilized, as shown in Figure 4.36. All
micrographs shown in Figure 4.30 illustrate porosity levels which suggest that
densities lower than 98% theoretical density are present. However, subsequent work has shown that the additional "holes" and porosity are produced by silicide grain pull-out during metallographic preparation.

4.2.4 Chemical Analysis.

4.2.4.1 Initial powders.

Chemical analyses on the initial powders were obtained by the verification of the chemistry. Elemental silicon powder was purchased from the Aldrich Chemical Co., with a nominal purity exceeding 99%. Niobium powders were purchased from Johnson Matthey Inc., and Cabot Corp., with a nominal purity exceeding 99.8%. For the reactive sintering studies, niobium powder with a nominal purity exceeding 99.8% was purchased from the Aldrich Chemical Co. In addition, precise lattice parameters of Nb and Si powders were determined with the x-ray diffraction method as reported in Tables 4.3 and 4.4, indicating that both Nb and Si were reasonably pure.

4.2.4.2 Mechanically alloyed mixtures.

Table 4.6 shows the chemical composition of MA Nb-Si mixtures for various alloying times. Powder contamination, especially with carbon and iron, increases with increasing milling time. One potential source of contamination are the 52100 hardened steel balls, which is supported by the noticeable weight loss from the balls. The presence of oxygen contamination indicates that either the neoprene gaskets did not
provide a completely air-tight seal as originally expected, or that oxidation of the powder occurred while the powders were stored in air for 2 months prior to chemical analyses at NASA Lewis Research Center.

4.2.4.3 Consolidated compacts.

Table 4.7 shows the chemical composition of the consolidated compacts obtained from the MA Nb<sub>5</sub>Si<sub>3</sub> powders and the RS Nb-Si powders. The RS compacts exhibited significantly lower contamination of oxygen, iron, and carbon in comparison to the MA Nb<sub>5</sub>Si<sub>3</sub> compacts. This is in general agreement with the observation of increased purity achieved during reactive sintering processing in comparison to mechanical alloying or other conventional powder consolidation methods [2.20].

4.2.4.4 Nb foil and Nb<sub>5</sub>Si<sub>3</sub> matrix.

Table 4.8 shows the grain size and the impurity level in the Nb foil reinforcement and the Nb<sub>5</sub>Si<sub>3</sub> matrix used for the laminate construction. The impurity content of the as-received Nb foil was providee by Aldrich Chemical Co., and that of VHT and Nb(ss) samples by Analytical Associates Inc., excluding silicon which was determined by Herron Testing Laboratories Inc. Chemical characterization of the Nb<sub>5</sub>Si<sub>3</sub> matrix used for the Nb<sub>5</sub>Si<sub>3</sub>/Nb laminates and the Nb(ss) condition was performed at NASA Lewis Research Center.
4.3 Bonding of Laminates

4.3.1 Diffusion bonding.

Figure 4.37 shows the SEM micrograph of the Nb$_3$Si$_2$/Nb/Nb$_2$Si$_3$ laminate and the laminate interfacial region. No interfacial reactions between Nb$_3$Si$_2$ and niobium were observed. Also, no cracks were observed in the as-electrodischarge-machined specimens.

4.3.2 Structural adhesive bonding.

The SEM micrographs of the Nb$_3$Si$_2$/Nb/Nb$_2$Si$_3$ laminate using the structural adhesive EC 1386 are shown in Figure 4.38. Following the recommended curing cycle by 3M company, a 10-13 µm thick adhesive layer between the Nb foil and the Nb$_2$Si$_3$ matrix was obtained. The variance in adhesive layer thickness is the result of the thickness variation of the Nb foil as shown in Figure 4.38.

4.4 Mechanical Testing

4.4.1 Tensile properties of unconstrained Nb reinforcement.

Diffusion bonding of the laminates resulted not only in the recrystallization of the Nb foil, but also in forming of the solid solution of Si in Nb (Nb(ss)). In order to determine the effect of grain size and/or Si solid solution in Nb on the mechanical properties of Nb, additional Nb foils were heat treated in vacuum in the hot press at 1473 K/5 hr. Figure 4.39 shows typical etched optical microstructures of Nb in the
as-received (AR), vacuum heat treated (VHT), and solid solution Nb(ss) condition. The AR-Nb had elongated grains 10 \mu m in width perpendicular to the rolling direction. Exposure of the Nb to 1473 K/5 hr promoted recrystallization and grain growth, producing grains 210 \mu m in diameter, and extending through the Nb foil for both VHT and Nb(ss) specimens. Mechanical testing was conducted at room temperature (298 K) as well as liquid nitrogen temperature (77 K) on tensile samples which were machined from the AR, VHT, and Nb(ss) materials. Figures 4.40 and 4.41 show the typical engineering stress-strain curves obtained on the Nb foils tested under the conditions summarized in Table 4.9.

4.4.2 Tensile properties of constrained Nb reinforcement.

In addition to the diffusion bonded laminates, laminates employing structural adhesive EC 1386 were produced. The AR-Nb and VHT-Nb foils were used as the reinforcement. Table 4.10 shows constrained Nb tensile properties obtained on double-notched laminated tension specimens using Nb$_3$Si$_3$ and either the, Nb(ss), AR-Nb, or VHT-Nb conditions.

4.4.3 $K_{ic}$ of monolithic Nb$_3$Si$_3$.

Table 4.11 shows $K_{ic}$ values of hot pressed monolithic Nb$_3$Si$_3$ compacts produced from MA Nb$_3$Si$_3$ powders, prealloyed Nb-Si mixtures, and reactive sintered elemental Nb and Si powders. Nb$_3$Si$_3$/Nb laminates were produced only from the compacts
produced from the MA monolithic Nb$_2$Si$_3$ powders. As evident from the $K_{lc}$ values, the presence of some unreacted Nb in the RS and prealloyed Nb-Si powder compacts (e.g., Table 4.5) does not significantly affect the fracture toughness of Nb$_2$Si$_3$. The $K_{lc}$ values verify the very brittle nature of Nb$_2$Si$_3$ at room temperature.

4.4.4 Fracture toughness of laminated Nb$_2$Si$_3$.

4.4.4.1 Diffusion bonded laminates.

Figure 4.42 shows the load-displacement trace obtained on the laminate tested in three point bending inside the scanning electron microscope, while Figure 4.43 presents a sequence of photographs taken at the locations marked in Figure 4.42. The shaded area in Figure 4.42 represents the notch-bend behavior of monolithic Nb$_2$Si$_3$. The significant toughness increase (e.g., area under the load-displacement trace) results from the niobium ligament and its ability to blunt propagating cracks in the Nb$_2$Si$_3$ as shown in Figure 4.43. The location and the orientation of machined notch has a significant effect on obtained fracture toughness values. Figure 4.44 shows the load-displacement trace obtained on a laminate with the notch placed inside the Nb ligament in the crack arrestor orientation. The calculated value $K_Q=10.3$ MPa√m based on the maximum load as shown in Table 4.12 is significantly higher that $K_Q=7.1$ MPa√m obtained on identical sample when notch was placed in Nb$_2$Si$_3$ 112 μm from the Nb$_2$Si$_3$/Nb interface (e.g., Figure 4.42). The lowest toughness value of $K_Q=1.9$ MPa√m was obtained on a laminate tested with the notch placed in the divider.
orientation, as shown in Figure 4.45.

Figure 4.46 shows the load-displacement trace of a laminate tested in three-point bending at 77 K (liquid nitrogen) with the notch placed in the Nb$_3$Si$_3$ matrix in the arrestor orientation. The first two load drops in figure 4.46 are associated with crack propagation in the Nb$_3$Si$_3$ matrix above and below the Nb ligament.

4.4.4.2 Structural adhesive bonded laminates.

The AR-Nb and VHT-Nb foils were used for the construction of laminates using the structural adhesive EC 1386. Three-point bend tests (3 PBT) were conducted on four laminates with the AR-Nb reinforcement. Two of the laminates were of 4x4x30 mm dimensions, and two other laminates were of 4x2x36 mm dimensions. Figure 4.47 shows a representative load-displacement trace obtained on the laminate with 4x2x36 mm dimension. The significant toughness increase, as measured by area under load-displacement curve, results from the Nb ligament deformation and its ability to blunt propagating cracks in Nb$_3$Si$_3$, as shown in Figure 4.48. The photographs in Figure 4.48 were taken at the positions noted in Figure 4.47. Three laminates with VHT-Nb reinforcements and 4x2x16 mm dimensions were tested in three point bending, with the representative load-displacement trace shown in Figure 4.49. The deformation of the Nb ligament at load points designated A, B, C, and D in Figure 4.49 is shown in Figure 4.50. Table 4.13 summarizes the test conditions, sample dimensions, and calculated values of $K_q$ for both group of laminates.
As indicated in section 4.4.4.1, all laminates were constructed incorporating 0.25 mm thick Nb foil. With an average notch root distance of 0.25 mm from the Nb$_3$Si$_2$/Nb interface, this Nb reinforcement represents 10 volume % of the laminate.

4.4.5 R curve behavior of Nb$_3$Si$_2$/Nb composites.

4.4.5.1 Laminates composites.

SEM observations of the notched bend tests conducted on the laminates with 0.25 mm thick Nb foil indicated that the initiation fracture toughness in the Nb$_3$Si$_2$ matrix above the notch was of the same magnitude as the fracture toughness of monolithic Nb$_3$Si$_2$, (i.e. 1.5-2.0 MPa$\sqrt{m}$). However, due to tractions imposed by the Nb ligament, the crack nucleates at the other ligament/matrix interface at higher loads (e.g., average $K_Q$ of 8.6 MPa$\sqrt{m}$ for diffusion bonded and 7.8 MPa$\sqrt{m}$ for structural adhesive bonded laminates) and then propagates catastrophically throughout the length of sample, leaving the Nb ligament intact.

4.4.5.2 Reactive sintered and hot pressed Nb particulate Nb$_3$Si$_2$/Nb composites.

Figure 4.51 plots $K_Q$ vs crack length for the composite produced by reactive sintering and hot pressing of elemental Nb and Si powders. The microstructure contained up to 30 volume % of Nb as shown in Figure 4.33. Tests conducted on three samples show that the initiation toughness varied from 3 to 6 MPa$\sqrt{m}$, increasing to an average value of 7.5 MPa$\sqrt{m}$ for crack extensions up to 250 $\mu$m.
The crack branching, crack blunting, and crack bridging by Nb particles shown in Figure 4.52 produces the measured toughness increase. However, the values of $K_G$ remain lower than those obtained in the laminated samples which contained only 10 vol.% of Nb reinforcement.

4.4.6 Fractography.

4.4.6.1 Dual deformation mode of Nb reinforcement.

Table 4.14 summarizes the effect of test conditions on the fracture mode of the Nb reinforcement. All unconstrained Nb foils exhibited high ductility (e.g., RA > 75%) at 298 K (e.g., Table 4.9) and failed by 100% ductile fracture, as shown in Figure 4.53. Examination of the fracture surfaces obtained from the diffusion bonded laminate tested at 298 K (Figure 4.54) indicates that the niobium exhibits both cleavage and ductile fracture in the proportion of 45% and 55% respectively. The arrested microcracks in the niobium ligament shown in Figure 4.43 are cleavage microcracks which are blunted by the ductile niobium. However, examination of the fracture surfaces obtained from the structural adhesive bonded laminates reinforced with AR-Nb and VHT-Nb foils tested at 298 K indicate that Nb exhibits 100% ductile fracture, as shown in Figure 4.55.

At 77 K, unconstrained AR-Nb foils failed in 100% ductile mode, while VHT and Nb(ss) samples failed by 100% cleavage mode, Figure 4.56. This difference in fracture mode is attributed to the large grain size difference (10 $\mu$m for AR vs. 210
μm for VHT and Nb(ss). The constrained Nb(ss) foils exhibited the same cleavage
type as did the unconstrained VHT and Nb(ss) specimens as shown in Figure 4.57.

In addition to calculating the percentage of cleavage using comparison of the
relative areas and using the linear method of the fracture mode of diffusion bonded
SEN samples tested in bending at 298 K (e.g., Table 4.14), stereo-imaging was
employed to determine the fracture mode of the Nb reinforcement depending on the
bonded/debonded length of the matrix/reinforcement interface, as shown in Table 4.15.

4.4.6.2 Fracture mode of Nb, Si,

The Nb, Si, matrix used for the laminate construction was produced from MA
Nb, Si, powders. As such, it exhibits porosity associated with the densification of the
powders in hot press, as shown in Figure 4.58. The fracture surface exhibits
transgranular cleavage failure, associated with the strong bonding of the Nb and Si
atoms in the unit cell of Nb, Si,
Figure 4.1 SEM micrograph of initial Nb powders.

Figure 4.2 SEM micrograph of initial Si powders.
Figure 4.3 X-ray diffraction pattern of initial Nb powders.

Figure 4.4 X-ray diffraction pattern of initial Si powders.
<table>
<thead>
<tr>
<th>MILLING TIME (hrs)</th>
<th>MA IN AIR LAT. PAR. $a_0$ (Å)</th>
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<td>3.31557</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3.32311</td>
<td>3.31822</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3.32707</td>
<td>3.32083</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 Lattice parameter of Nb milled in argon and air atmosphere.

![Graph showing Nb lattice parameter vs. milling time.](image)

Figure 4.5 Nb lattice parameter vs. milling time.
Figure 4.6 X-ray diffraction pattern of Nb powders milled in air.
Figure 4.7 SEM micrographs of Nb powders milled in air:
A) 1 hour  B) 3 hrs  C) 6 hrs  D) 9 hrs.
Figure 4.8 Flowchart of interrupted milling process.

Figure 4.10 X-ray diffraction patterns of Nb-Si mixture milled in the interrupted process.
Figure 4.9 Vial temperature vs. milling time:
A) Interrupted milling process  B) Continuous milling process.
Figure 4.11 SEM micrographs of Nb-Si mixture milled in the interrupted process: 
A) Just before (60 min)  B) Just after (75 min) compound formation.
Figure 4.12 Flowchart of continuous milling process.

Figure 4.14 SEM micrograph of Nb-Si mixture milled in the continuous process:
A) Just before (3 hrs) B) Just after (3.25 hrs) compound formation.
Figure 4.13 Inter-particle spacing as a function of milling time.
1) 1 hr  2) 2 hr  3) 3 hr  4) 3.5 hr.
Figure 4.15 X-ray diffraction patterns of Nb-Si mixture milled in the continuous milling.

Figure 4.16 DTA tracing of Nb-Si mixture.
Figure 4.17 DTA tracing of MA Nb-Si powders.

<table>
<thead>
<tr>
<th>MILLING TIME (hrs)</th>
<th>NASA DTA $T_{on}$ (K)</th>
<th>NASA DTA $T_{off}$ (K)</th>
<th>CASE DTA $T_{off}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1523</td>
<td>1633</td>
<td>1633</td>
</tr>
<tr>
<td>0.5</td>
<td>1223</td>
<td>1303</td>
<td>1343</td>
</tr>
<tr>
<td>1</td>
<td>923</td>
<td>995</td>
<td>1020</td>
</tr>
<tr>
<td>2</td>
<td>913</td>
<td>969</td>
<td>934</td>
</tr>
<tr>
<td>2.5</td>
<td>898</td>
<td>957</td>
<td>937</td>
</tr>
<tr>
<td>3</td>
<td>898</td>
<td>954</td>
<td>922</td>
</tr>
<tr>
<td>3.5</td>
<td>873</td>
<td>945</td>
<td>897</td>
</tr>
</tbody>
</table>

Table 4.2 Critical and onset reaction temperature vs. milling time.
Figure 4.18 $T_{\text{cr}}$ and $T_{\text{onset}}$ of Nb$_2$Si$_3$ compound formation vs. milling time.

Figure 4.19 DTA trace of 1 hr MA Nb-Si mixture in NASA DTA unit.
Figure 4.20 Phase evolution in MA Nb-Si mixture for 1 hr during DTA test.

Figure 4.21 SEM micrograph of Nb-Si mixture milled for 1 hr.
Figure 4.22 DTA traces of interrupted milling of Nb-Si mixtures.

Figure 4.23 Onset reaction temperature vs. RT aging time.
Figure 4.24 Nb lattice parameter vs. Nelson-Riley function.

Figure 4.25 Si lattice parameter vs. Nelson-Riley function.
<table>
<thead>
<tr>
<th>MILLING TIME (hrs)</th>
<th>ALDRICH Nb $a_0$ (Å)</th>
<th>CABOT Nb-Si $a_0$ (Å)</th>
<th>JCPD #35-789 $a_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.3065</td>
<td>3.3077</td>
<td>3.3066</td>
</tr>
<tr>
<td>1</td>
<td>3.3078</td>
<td>3.3090</td>
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<tr>
<td>3</td>
<td>3.3178</td>
<td>3.3161</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3 Nb lattice parameter vs. milling time.

<table>
<thead>
<tr>
<th>MILLING TIME (hrs)</th>
<th>ALDRICH Si $a_0$ (Å)</th>
<th>CABOT Nb-Si $a_0$ (Å)</th>
<th>JCPD#27-1402 $a_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.4365</td>
<td>5.4365</td>
<td>5.4309</td>
</tr>
<tr>
<td>1</td>
<td>5.4366</td>
<td>5.4388</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4 Si lattice parameter vs. milling time.
Figure 4.26 Nb lattice parameter vs. milling time.

Figure 4.27 Si lattice parameter vs. milling time.
Figure 4.28 TEM micrograph and diffraction of MA Nb-Si mixture (1 hr).
Nb-Si mixture \hspace{1cm} \alpha\text{-}Nb_2Si_3

Figure 4.29 TEM micrograph and diffraction of MA Nb-Si mixture (3 hrs).
Figure 4.30 Optical micrographs of as-polished hot pressed compacts.
Figure 4.31 Optical micrographs of as-etched hot pressed compacts.
Figure 4.32 Optical micrograph of as-etched RS+HP compact.
Figure 4.33 SEM micrograph of Nb$_2$Si$_3$/30 vol.% Nb composite.
Figure 4.34 X-ray diffraction patterns of consolidated compacts.

Figure 4.35 X-ray diffraction patterns of monolithic and composite compacts.
### HOT PRESSING TEMPERATURE 1873 K

<table>
<thead>
<tr>
<th>INITIAL POWDERS</th>
<th>PROCESSING CODE</th>
<th>DENSITY % THEORETICAL</th>
<th>X-RAY DIFFRACTION</th>
<th>OPTICAL MICROSTRUCTURE</th>
<th>GRAIN SIZE (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb+Si POWDER BLEND (24 HR)</td>
<td>RSH1P1</td>
<td>99.1</td>
<td>Nb₃Si₁ α, γ</td>
<td>Nb₃Si₁ + Nb (-5 vol. %)</td>
<td>DUAL DISTR. 5 - 12.5</td>
</tr>
<tr>
<td>Nb₃Si₁</td>
<td>N553HP3</td>
<td>98.7</td>
<td>Nb₃Si₁ α, γ</td>
<td>Nb₃Si₁</td>
<td>-6</td>
</tr>
<tr>
<td>Nb+Si MA MIXT. (3.5-5.0 HR)</td>
<td>PPH1P1</td>
<td>97.7</td>
<td>Nb₃Si₁ α, γ</td>
<td>Nb₃Si₁ + Nb (3 vol. %)</td>
<td>-5</td>
</tr>
</tbody>
</table>

### HOT PRESSING TEMPERATURE 1873 K

<table>
<thead>
<tr>
<th>INITIAL POWDERS</th>
<th>PROCESSING CODE</th>
<th>DENSITY % THEORETICAL</th>
<th>X-RAY DIFFRACTION</th>
<th>OPTICAL MICROSTRUCTURE</th>
<th>GRAIN SIZE (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb+Si POWDER BLEND (60 HR)</td>
<td>RSH1P3</td>
<td>99.5</td>
<td>Nb₃Si₁ α, γ</td>
<td>Nb₃Si₁ + Nb (-8 vol. %)</td>
<td>DUAL DISTR. 5 - 12.5</td>
</tr>
<tr>
<td>Nb₃Si₁</td>
<td>N553HP4</td>
<td>97.4</td>
<td>Nb₃Si₁ α, γ</td>
<td>Nb₃Si₁</td>
<td>-3</td>
</tr>
<tr>
<td>Nb+Si MA MIXT. (2 HR)</td>
<td>PP2HP2</td>
<td>98.1</td>
<td>Nb₃Si₁ α, γ</td>
<td>Nb₃Si₁</td>
<td>-4</td>
</tr>
<tr>
<td>Nb+Si POWDER BLEND (75 HR) 30 VOL % Nb</td>
<td>RHPCOMP1</td>
<td>99.8</td>
<td>Nb₃Si₁ + Nb α, γ</td>
<td>Nb₃Si₁ + Nb (30 vol. %)</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 4.5 Properties of monolithic Nb₃Si₁ and Nb₃Si₁/Nb composite.
Figure 4.36 LVDT vs. temperature for reactive sintered and hot pressed compact.

<table>
<thead>
<tr>
<th>SAMPLE I.D.</th>
<th>CARBON wt.%</th>
<th>OXYGEN wt.%</th>
<th>IRON wt.%</th>
<th>COBALT wt.%</th>
<th>TUNGSTEN wt.%</th>
<th>NIOBIUM wt.%</th>
<th>SILICON wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA-1 HR</td>
<td>0.0325</td>
<td>1.50</td>
<td>0.3</td>
<td>&lt;0.01</td>
<td>&lt;0.02</td>
<td>80.8</td>
<td>17.3</td>
</tr>
<tr>
<td>MA-3 HR</td>
<td>0.0744</td>
<td>1.18</td>
<td>0.5</td>
<td>&lt;0.01</td>
<td>0.20</td>
<td>81.0</td>
<td>16.9</td>
</tr>
<tr>
<td>MA-3.25 HR</td>
<td>0.0544</td>
<td>1.26</td>
<td>1.0</td>
<td>&lt;0.01</td>
<td>&lt;0.02</td>
<td>80.8</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Table 4.6 Chemical analysis of MA Nb-Si mixtures.
<table>
<thead>
<tr>
<th>SAMPLE I.D</th>
<th>CARBON wt.%</th>
<th>OXYGEN wt.%</th>
<th>IRON wt.%</th>
<th>COBALT wt.%</th>
<th>TUNGSTEN wt.%</th>
<th>NIOBUM wt.%</th>
<th>SILICON wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA-Nb,Si&lt;sub&gt;1&lt;/sub&gt;</td>
<td>0.9980</td>
<td>1.26</td>
<td>0.4</td>
<td>&lt;0.01</td>
<td>&lt;0.02</td>
<td>81.3</td>
<td>16.9</td>
</tr>
<tr>
<td>RS+HP</td>
<td>0.0296</td>
<td>0.4175</td>
<td>0.1</td>
<td>&lt;0.01</td>
<td>&lt;0.02</td>
<td>82.0</td>
<td>17.2</td>
</tr>
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</table>

Table 4.7 Chemical analysis of hot pressed compacts.

<table>
<thead>
<tr>
<th>MATERIAL &amp; CONDITION</th>
<th>GRAIN SIZE (µm)</th>
<th>C (ppm)</th>
<th>O&lt;sub&gt;2&lt;/sub&gt; (ppm)</th>
<th>N&lt;sub&gt;2&lt;/sub&gt; (ppm)</th>
<th>H&lt;sub&gt;2&lt;/sub&gt; (ppm)</th>
<th>Si (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>10</td>
<td>&lt;10</td>
<td>&lt;125</td>
<td>&lt;50</td>
<td>&lt;5</td>
<td>&lt;100</td>
</tr>
<tr>
<td>VHT</td>
<td>210</td>
<td>420</td>
<td>490</td>
<td>120</td>
<td>NA</td>
<td>90</td>
</tr>
<tr>
<td>Nb(ss)</td>
<td>210</td>
<td>210</td>
<td>1300</td>
<td>190</td>
<td>NA</td>
<td>1050</td>
</tr>
<tr>
<td>Nb,Si&lt;sub&gt;1&lt;/sub&gt;</td>
<td>5</td>
<td>980</td>
<td>1260</td>
<td>NA</td>
<td>NA</td>
<td>16.9wt%</td>
</tr>
</tbody>
</table>

Table 4.8 Impurity content of Nb foil and Nb<sub>5</sub>Si<sub>3</sub> matrix.
Figure 4.37 Diffusion bonded Nb<sub>3</sub>Si<sub>3</sub>/Nb interface.
Figure 4.38 Structural adhesive bonded Nb$_2$Si$_y$/Nb interface.
Figure 4.39 Grain size of Nb foil in AR, VHT, and Nb(ss) condition.  
1) AR-Nb  2) VHT-Nb  3) Nb(ss).
Figure 4.40 Tensile properties of Nb at room RT (298 K).

Figure 4.41 Tensile properties of Nb at liquid nitrogen (77 K) temperature.
Table 4.9 Tensile properties of unconstrained Nb.

<table>
<thead>
<tr>
<th>MATERIAL &amp; CONDITION</th>
<th>GRAIN SIZE (µm)</th>
<th>TEST TEMP. (K)</th>
<th>0.2% Y.S (MPa)</th>
<th>UTS (MPa)</th>
<th>AREA REDUCTION (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-AR</td>
<td>10</td>
<td>298</td>
<td>268</td>
<td>358</td>
<td>78</td>
</tr>
<tr>
<td>Nb-VHT</td>
<td>210</td>
<td>298</td>
<td>186</td>
<td>222</td>
<td>79</td>
</tr>
<tr>
<td>Nb(ss)</td>
<td>210</td>
<td>298</td>
<td>363</td>
<td>390</td>
<td>76</td>
</tr>
<tr>
<td>Nb-AR</td>
<td>10</td>
<td>77</td>
<td>730</td>
<td>822</td>
<td>93</td>
</tr>
<tr>
<td>Nb-VHT</td>
<td>210</td>
<td>77</td>
<td>661</td>
<td>765</td>
<td>6</td>
</tr>
<tr>
<td>Nb(ss)</td>
<td>210</td>
<td>77</td>
<td>844</td>
<td>898</td>
<td>8</td>
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</tbody>
</table>

Table 4.10 Tensile properties of constrained Nb.

<table>
<thead>
<tr>
<th>MATERIAL &amp; CONDITION</th>
<th>TEST TEMP. (K)</th>
<th>0.2% Y.S (MPa)</th>
<th>UTS (MPa)</th>
<th>AREA REDUCTION (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIFF. BOND. Nb(SS)</td>
<td>298</td>
<td>371</td>
<td>481</td>
<td>8</td>
</tr>
<tr>
<td>DIFF. BOND. Nb(ss)</td>
<td>77</td>
<td>1341</td>
<td>1341</td>
<td>4</td>
</tr>
<tr>
<td>STRUCT. ADH. AR-Nb</td>
<td>298</td>
<td>215</td>
<td>345</td>
<td>98</td>
</tr>
<tr>
<td>STRUCT. ADH. VHT-Nb</td>
<td>298</td>
<td>100</td>
<td>209</td>
<td>99</td>
</tr>
<tr>
<td>PROCESSING DESIGNATION</td>
<td>PROCESSING DESCRIPTION</td>
<td>$P_e$ (kg)</td>
<td>$K_e$ (MPa m)</td>
<td>AVERAGE $K_e$ (MPa m)</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------</td>
<td>------------</td>
<td>---------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>RSHP1 1700°C</td>
<td>REACTIVE SINTERED &amp; HOT PRESSED Nb-Si POWDER MIXTURE (24hr)</td>
<td>0.9</td>
<td>2.3</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.12</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.74</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>PPHP1 1700°C</td>
<td>PREALLOYED Nb-Si POWDERS (3.5-5 hr) &amp; HOT PRESSED</td>
<td>0.498</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.54</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.63</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>N5S3HP3 1700°C</td>
<td>Nb$_3$Si$_3$ HOT PRESSED</td>
<td>0.8</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.43</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>RSHP3 1600°C</td>
<td>REACTIVE SINTERED &amp; HOT PRESSED Nb-Si POWDER MIXTURE (69 hr)</td>
<td>1.2</td>
<td>1.9</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.55</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.77</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>PP2HP2 1600°C</td>
<td>PREALLOYED Nb-Si POWDERS (2 hr) &amp; HOT PRESSED</td>
<td>0.52</td>
<td>1.0</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.78</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.11 $K_e$ of monolithic Nb$_3$Si$_3$ powder compacts.
Figure 4.42 Load-displacement trace of 3 PBT sample with notch placed in Nb$_3$Si$_3$ in the crack arrester direction.
Figure 4.43 SEM micrographs of Nb ligament deformation at loads marked A, B, C, and D respectively in Figure 4.42. Arrows indicate arrested cleavage microcracks in Nb.
Figure 4.44 Load-displacement trace of 3 PBT sample with notch in Nb ligament.
Figure 4.45 Load-displacement trace of 3 PBT with notch in the crack divider direction.
<table>
<thead>
<tr>
<th>SAMPLE NUMBER</th>
<th>DISTANCE FROM ( \text{Nb}_3\text{Si}_2/\text{Nb} ) INTERFACE</th>
<th>TEST TEMP. (K)</th>
<th>DIMENSIONS (mm)</th>
<th>( P_0 ) (kg)</th>
<th>( K_0 ) (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 µm in Nb</td>
<td>298</td>
<td>8x4x44</td>
<td>25.0</td>
<td>10.3</td>
</tr>
<tr>
<td>2</td>
<td>112 µm in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>8x4x40</td>
<td>20.8</td>
<td>7.1</td>
</tr>
<tr>
<td>3</td>
<td>240 µm in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>8x4x40</td>
<td>28.3</td>
<td>8.9</td>
</tr>
<tr>
<td>4</td>
<td>145 µm in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>8x4x40</td>
<td>23.1</td>
<td>7.4</td>
</tr>
<tr>
<td>5</td>
<td>20 µm in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>8x4x20</td>
<td>46.2</td>
<td>8.4</td>
</tr>
<tr>
<td>6</td>
<td>20 µm in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>8x4x20</td>
<td>59.1</td>
<td>11.4</td>
</tr>
<tr>
<td>7</td>
<td>275 µm in ( \text{Nb}_3\text{Si}_2 )</td>
<td>77</td>
<td>8x4x46</td>
<td>15.7</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Table 4.12 \( K_0 \) values of diffusion bonded laminates.

Figure 4.46 Load-displacement trace of 3 PBT sample tested at 77 K.
Figure 4.47 Load-displacement trace of 3 PBT of structural adhesive bonded (SAB) laminate with AR-Nb reinforcement.

Figure 4.49 Load-displacement trace of 3 PBT of SAB laminate with VHT-Nb reinforcement.
Figure 4.48 SEM micrographs of AR-Nb ligament deformation at load points designated A, B, C, and D in Figure 4.47.
Figure 4.50 SEM micrographs of VHT-Nb ligament deformation at load points designated A, B, C, and D in Figure 4.49.
### Table 4.13 \( K_Q \) values of the structural adhesive bonded laminates.

<table>
<thead>
<tr>
<th>SAMPLE NUMBER</th>
<th>DISTANCE FROM ( \text{Nb}_3\text{Si}_2/\text{Nb} ) INTERFACE</th>
<th>TEST TEMP. (K)</th>
<th>DIMENSIONS (mm)</th>
<th>( P_Q ) (kg)</th>
<th>( K_Q ) (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 AR-Nb</td>
<td>270 ( \mu \text{m} ) in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>4x4x30</td>
<td>8.8</td>
<td>5.5</td>
</tr>
<tr>
<td>2 AR-Nb</td>
<td>189 ( \mu \text{m} ) in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>4x4x30</td>
<td>10.5</td>
<td>6.5</td>
</tr>
<tr>
<td>3 AR-Nb</td>
<td>200 ( \mu \text{m} ) in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>4x2x36</td>
<td>4.9</td>
<td>7.4</td>
</tr>
<tr>
<td>4 AR-Nb</td>
<td>203 ( \mu \text{m} ) in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>4x2x36</td>
<td>5.9</td>
<td>8.9</td>
</tr>
<tr>
<td>5 VHT-Nb</td>
<td>166 ( \mu \text{m} ) in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>4x2x16</td>
<td>12.0</td>
<td>8.2</td>
</tr>
<tr>
<td>6 VHT-Nb</td>
<td>245 ( \mu \text{m} ) in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>4x2x16</td>
<td>13.3</td>
<td>8.8</td>
</tr>
<tr>
<td>7 VHT-Nb</td>
<td>185 ( \mu \text{m} ) in ( \text{Nb}_3\text{Si}_2 )</td>
<td>298</td>
<td>4x2x16</td>
<td>9.7</td>
<td>6.4</td>
</tr>
</tbody>
</table>

**Figure 4.51** \( K_Q \) vs. crack length \( \Delta a \) of the Nb particulate reinforced composite.
Figure 4.52 SEM micrographs of crack propagation in RS Nb$_3$Si$_4$/30 vol.% Nb composite.
Figure 4.53 SEM micrographs of fracture surface of the unconstrained Nb tested at 298 K.

1) AR-Nb  2) VHT-Nb  3) Nb(ss).
Figure 4.54 Fracture surface of Nb ligament in diffusion bonded laminate at 298 K.
Figure 4.55 Fracture surface of Nb ligament in structural adhesive bonded laminate tested at 298 K, 1) AR-Nb  2) VHT-Nb.
<table>
<thead>
<tr>
<th>MATERIAL &amp; CONDITION</th>
<th>TEST TEMPERATURE (K)</th>
<th>CLEAVAGE FRACTURE (%)</th>
<th>DUCTILE FRACTURE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-AR</td>
<td>298</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Nb-VHT</td>
<td>298</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Nb(ss)</td>
<td>298</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Constrained Nb(ss)</td>
<td>298</td>
<td>31.0</td>
<td>69.0</td>
</tr>
<tr>
<td>(DEN sample)</td>
<td></td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Diff. bond</td>
<td>77</td>
<td>95.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Constrained Nb(ss)</td>
<td>298</td>
<td>45.0</td>
<td>55.0</td>
</tr>
<tr>
<td>(SEN sample)</td>
<td></td>
<td>84.0</td>
<td>16.0</td>
</tr>
<tr>
<td>Diff. bond</td>
<td>77</td>
<td>99.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Constrained AR-Nb</td>
<td>298</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>(DEN &amp; SEN samples)</td>
<td>Structural adhesive</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constrained VHT-Nb</td>
<td>298</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>(DEN &amp; SEN samples)</td>
<td>Structural adhesive</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.14 Fracture mode of Nb reinforcement in AR, VHT, and Nb(ss) condition.
Figure 4.56 Fracture surface of unconstrained Nb tested at 77 K: 1) AR-Nb 2) VHT-Nb 3) Nb(ss)
<table>
<thead>
<tr>
<th>SAMPLE I.D.</th>
<th>% CLEAVAGE</th>
<th>% DUCTILE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPTI-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-D Method</td>
<td>61.0</td>
<td>39.0</td>
</tr>
<tr>
<td>Linear Method</td>
<td>68.2</td>
<td>31.2</td>
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<tr>
<td>Area Measurement</td>
<td>45.0</td>
<td>55.0</td>
</tr>
<tr>
<td>CPTI-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-D Method</td>
<td>75.4</td>
<td>24.6</td>
</tr>
<tr>
<td>Linear Method</td>
<td>60.8</td>
<td>39.2</td>
</tr>
<tr>
<td>Area Measurement</td>
<td>84.0</td>
<td>16.0</td>
</tr>
</tbody>
</table>

Table 4.15 Fracture mode determination of Nb ligament in diffusion bonded laminate tested in 3 PBT at 298 K.

Figure 4.57 Fracture surface of Nb ligament in diffusion bonded laminate tested at 77 K.
Figure 4.58 Fracture surface of Nb$_2$Si$_3$ matrix.
CHAPTER 5

DISCUSSION

5.1 Contamination of Nb and Si Powders

5.1.1 Mechanically alloyed Nb-Si mixtures.

While the mechanical alloying process offers improved cleanliness of products as compared to in situ and arc melting and casting processes, it is not immune to some degree of contamination. Potential powder contaminants include tungsten, cobalt, and carbon, as they are components of the tungsten carbide vial, with iron and carbon contaminants possible from the 52100 hardened steel balls, and argon or air due to the vial atmosphere. Weight loss from the steel balls was confirmed by periodic weighing. After processing 88 batches of powders, 8.33 grams (i.e., equivalent to the weight of one 12 mm diameter steel ball) of material was abraded in the milling process, corresponding to 0.0956 g/batch. Taking a total powder weight per batch of 10 grams, this represents a contamination at the 0.95 wt.% level. However, as shown in Table 4.6 the contamination level of MA Nb-Si mixtures was approximately half the amount calculated from the steel balls weight loss. The mechanical milling of pure Nb powders in the initial experiments resulted in excessive welding of Nb particles to the tungsten vial walls and the steel balls, possibly accounting for a higher abrasion of steel balls. In addition to the weight loss from the steel balls, material pull-out from
the walls of the vial (e.g., tungsten and carbon) was evident and confirmed by chemical analysis as shown in Table 4.6 for the Nb-Si mixture milled for 3 hours. Oxygen contamination of the milled powders was higher than anticipated. Although milling was carried out in an argon gas filled vial and the ends of the vial were sealed with neoprene gaskets, there was clear loosening of the end caps after the milling process was complete, leading to a loss of sealing pressure. In addition to oxygen contamination accompanying the milling process, additional oxygen contamination could have been produced from powder oxidation prior to the chemical analyses at NASA Lewis Research Center.

5.1.2 Consolidated compacts.

Table 4.7 provides the chemical analyses of the two hot pressed compacts. Compacts obtained from Nb$_2$Si$_3$ mechanically alloyed (MA-Nb$_2$Si$_3$) for 3.25 hours exhibits impurity levels comparable to those of the MA Nb-Si powders shown in Table 4.6, with the exception of the carbon levels. Additional carbon contamination resulted from powder consolidation in the vacuum hot press which utilized a tantalum-lined graphite die and punches, while the increased carbon levels were not as extensive in comparison to the iron and oxygen levels.

The reactive sintered (i.e. elemental Nb and Si powders) and hot pressed compacts exhibited impurity levels substantially lower than that of the MA Nb$_2$Si$_3$ powder compacts. Oxygen contamination is a result of the limited vacuum of 10$^4$ torr at the
consolidation temperature, and the residual oxide present on the elemental Nb powders.

5.2 Kinetics of Nb₂Si₃ Compound Formation

5.2.1 Interrupted milling process.

From the results of several interrupted milling experiments as depicted in Figure 4.8, two major variables controlling Nb₂Si₃ compound formation were identified. In order to ensure formation of Nb₂Si₃, a minimum milling time of 1 hour and a minimum cooling time of 2 hours was required prior to resumption of milling, as shown in Figure 5.1. The following observations were analyzed to determine the reason for the critical milling time and hold time at room temperature.

Figure 4.21 shows the microstructural refinement in a Nb-Si agglomerate after MA for 1 hour. Particles within the agglomerate are not uniformly refined, with an average inter-particle spacing on the order of 1 μm, although there are areas where refinement is on a much smaller scale. According to the theory of mechanical alloying [2.2], true alloying occurs when the microstructural refinement is no longer visible in an optical microscope, (i.e. roughly a particle spacing of 0.5 μm). This suggests that there are small areas where the intensive MA energy input promoted solid solubility between Nb and Si, thereby creating a supersaturated solid solution with respect to its equilibrium solubility at low (e.g. 600-900 K) processing temperatures. Upon cooling, a small amount of Nb₂Si₃ particles could precipitate from solid solution. Upon
resumption of milling, a self-propagating exothermic reaction takes place, due to the large heat of formation release upon growth of Nb$_2$Si$_3$ particles.

In order to determine which specific solid solution, \textit{i.e.} Si in Nb, Nb in Si) is formed, the lattice parameters of the milled elemental Nb and Si powders and those of the mechanically alloyed Nb-Si mixtures were determined. Figures 4.24 and 4.25 show plots of the Nb and Si lattice parameters, respectively, obtained from individual scanned peaks of the pure elements and those of milled Nb-Si mixtures. The extrapolated values of the lattice parameter $a_0$ at $\Theta=90^\circ$ $(\cos^2\Theta/\sin\Theta+\cos^2\Theta/\Theta=0)$ shown in Tables 4.3 and 4.4 and plotted in Figures 4.26 and 4.27 suggest Nb solution in Si occurs in the milling process. While there is an increase in the lattice parameter of Nb for both pure Nb and Nb-Si mixture with an increase milling time, the difference is very small. If the Si solid solubility in Nb is minuscule, it is not detectable with the x-ray diffraction method, and the Nb lattice parameter increase is the result of contamination with elements of the vial and steel ball. The lattice parameter of Si as plotted in Figure 4.27 shows that upon milling of pure Si, contamination with the vial’s elements did not occur. However, there is a large difference in the Si lattice parameter upon milling of Nb-Si mixture, indicating that a possible Nb solid solubility in Si occurred. It is, however, difficult to substantiate this conclusion since as indicated in the Nb-Si phase diagram in Figure 1.3, Si-rich regions are not clearly delineated. The question must be raised on the role of Nb in the mechanical alloying process of Nb-Si mixtures on the lattice parameter of Si, as well as the role of the
high-energy non-equilibrium conditions during the MA process on the formation of amorphous, and metastable phases.

Differential Thermal Analyses (DTA) conducted on powders milled and "aged" at room temperature for up to 1000 hours show that such "aging" only decreased the reaction onset temperature of Nb$_2$Si$_3$ by less than 9°C, Figure 4.23. This small drop in the reaction temperature indicates that room temperature "enhanced diffusivity" due to the increased dislocation density in the milled powders does not significantly affect Nb$_2$Si$_3$ compound formation in the interrupted process. In order for the reaction to take place as shown in Figure 4.18, enhanced diffusivity would have to decrease the local critical reaction temperature on the order of 50°C.

TEM electron diffraction images of Nb-Si powders milled for 1 hour (e.g., Figure 4.28) show finely mixed particles of Nb-Si mixture as well as isolated Nb$_2$Si$_3$, further suggesting that Nb$_2$Si$_3$ particle precipitation may occur during the cooling cycle in the interrupted milling process. Considering that the mechanical alloying process is the solid state transformation process, we can assume that the nucleation of the Nb$_2$Si$_3$ particles is heterogeneous. As such, there are many suitable nucleation sites available, such as excess vacancies, dislocations, grain boundaries, inclusions, and free surfaces. Heterogeneous nucleation depends on driving force $\Delta G_\nu$, which is a function of the concentration gradient of the super-saturated solid solution, and the undercooling $\Delta T$ (K). However, critical nucleus growth depends on the solute concentration gradient $\Delta X$, which is the function of temperature, and the diffusion rate of solute, which is
controlled by the interdiffusion coefficient $D$ (cm$^2$ sec$^{-1}$). Therefore, optimum time and the undercooling will result in the maximum grow rate of precipitates. In the case of Nb$_3$Si$_3$ precipitation in the interrupted process, we can speculate that the long cooling time is required for both the nucleation and growth to occur due to a small inter-diffusion coefficient of Si in Nb and small $\Delta X$.

No other metastable, amorphous, or equilibrium phases were detected. The existence of Nb-Si mixtures and that of Nb$_3$Si$_3$ were determined from the indexing of the electron diffraction images as shown in the Appendix.

### 5.2.2 Continuous milling process

Figure 4.12 shows that 3.25 hours of milling time was required for formation of Nb$_3$Si$_3$ in continuous milling. In a more detailed series of experimental runs, it was found that milling for 3 hours and 2 minutes produced the Nb-Si mixture (as verified by the x-ray diffraction), while milling for 3 hours and 5 minutes resulted in complete Nb$_3$Si$_3$ compound formation by a self-propagating exothermic reaction. However, in contrast to the interrupted milling process, the lack of cooling to room temperature in the continuous milling process suggest that compound formation must be initiated under different conditions.

In the continuous milling process, repeated coalescence and fragmentation of the Nb and Si particles creates a layered structure. With increasing milling time, the inter-particle distance between Nb and Si atoms decreases continuously to the point where
the optical resolution of individual particles is difficult, as shown in Figure 4.13. This decrease in inter-particle spacing produces a decrease in the critical and onset reaction temperature, as shown in Table 4.2 and Figure 4.18. Ultimately, the point is reached when the local temperature rise of the powders trapped between two colliding balls exceeds the reaction onset temperature and the compound forms spontaneously as illustrated in Figure 5.2 and 5.3. This process is analogous to the self-propagating high-temperature synthesis (SHS) where after an initial energy input for the start of reaction (electrical spark or laser beam), the reaction proceeds through the whole volume of unreacted powders due to the formation of a transient liquid of the lower melting component. In the present case, the low melting component is Si, while the activation energy for the reaction is supplied by the cold work accumulated in the milled powders, particle size refinement, and the local temperature rise of the powders trapped between the colliding steel balls.

TEM observations of powders continuously milled for 3 hours (e.g. Figure 4.29) and cooled to room temperature for approximately 10 hours also exhibited of Nb₂Si₃. This suggests that Nb₂Si₃ precipitation occurred during the cooling to room temperature. If the Nb₂Si₃ precipitates were formed during the continuous milling, conditions for rapid growth of precipitates (e.g. local temperature rise and supplied mechanical energy) exist for the reaction to occur in the same time as in the interrupted milling. However, for the continuous milling process it requires 3 hours and 5 minutes of continuous milling for the reaction to occur, suggesting that the
reaction is initiated through self-propagating high-temperature synthesis (SHS) process.

5.3 Powder Consolidation process

5.3.1 Nb₃Si₃ powders.

The continuous milling process as established in Figure 4.12 indicated that a minimum milling time of 3.25 hours is required for complete Nb₃Si₃ compound formation. All batches of Nb-Si powders were mechanically alloyed for this length of time. Powder consolidation was accomplished according to the general hot pressing scheme as shown schematically in Figure 3.5. The degassing stage at 1123 K for times up to 4 hours proved important for powders prepared by the MA process, as significant cracking was observed on the first two compacts not degassed at this temperature. In order to determine the impact of the consolidation temperature on the obtained microstructures and the density, consolidation temperatures of 1973 K and 1873 K respectively were used. It was found that holding times of 1 to 2 hours at the consolidation temperature did not significantly affect the compact properties. Thus, most of the consolidations were done with a 1 hour holding time, while a cooling rate of 5°C/minute or less was maintained in order not to build-up residual stresses in compacts. Due to the high consolidation temperature, the silver colored tantalum foil reacted with the carbon of the graphite die, creating a gold colored tantalum carbide which was fused to the Nb₃Si₃ compact and required removal by the electro-discharge
machining process (EDM).

5.3.2 Nb-Si prealloyed mixtures.

In the experiments on MA Nb-Si mixtures in the interrupted and continuous process, several batches of powders did not react to Nb₃Si, and remained as elemental Nb and Si prealloyed mixture after milling process was terminated. The twenty-one batches of prealloyed Nb-Si mixtures were blended for 2 hours in a horizontal roller mixer, then consolidated in the vacuum hot press using the hot pressing scheme shown in Figure 3.5. The resulting compact microstructure consisted of Nb₃Si, phase, as confirmed by x-ray diffraction. A similar approach of using a combination of MA and RS processes was also investigated. All batches of Nb-Si mixtures were mechanically alloyed for times less than that required for compound formation \(i.e. \ 3.25\ \text{h}\). In this case, 45 batches were mechanically alloyed for 2 hours, blended in a horizontal roller mixer for 2 hours, then reactive sintered and consolidated in the vacuum hot press. The resulting powder mixture, prior to hot pressing, contained an intimate blend of elemental niobium and silicon powders as confirmed by x-ray diffraction, Figure 4.34.

5.3.3 Reactive sintering of Nb-Si blends.

Elemental powders of niobium and silicon with approximately the same particle size \(i.e. \leq 44 \ \mu m\) and in the proper ratio for Nb₃Si₃ formation \(i.e. \ 15.35\)
wt.\% Si) were also blended for 24 hours using a horizontal roller mixer. As the powder homogeneity and/or segregation in a blending operation depends on various factors related to the blending equipment, and the size, density and volume percent fill of elemental powders, a standard blending time of 24 h was selected for this work to produce a sufficient mixture. It is assumed that a more homogeneous blend will be obtained with longer blending times. As-blended powders were consolidated in a vacuum hot press under the same conditions as the MA Nb$_3$Si$_3$ powders and the prealloyed Nb-Si mixtures. It is of interest to note here that precise monitoring of the hot press operating parameters revealed a significant deterioration of vacuum for a short period of time (e.g. 1 to 2 minutes) at approximately 1250°C, which is associated with the critical reaction temperature of Nb$_3$Si$_3$ compound formation. However, the Nb-Si blended mixture did not required as long a degassing time as needed for the mechanically alloyed powders. X-ray diffraction patterns of the consolidated compacts shown in Figure 4.34 indicate the presence of α and γ phase Nb$_3$Si$_3$. Since Nb-Si powders were not exposed to the mechanical energy of the MA process, β phase is absent in the reactive sintered compacts.

Bose [2.29] demonstrated that the best single phase, fully-reacted, low-porosity microstructures of Ni$_3$Al were developed from powders with an agglomerate size of aluminum to nickel of approximately 0.3 [2.29]. In an attempt to apply this result to the Nb-Si system a ratio of Si/Nb of 0.3 was employed. That is, Si powders with a particle size of ≤ 44 μm and Nb powders with particle sizes of ≈150 μm were
blended. The powders were heated at a rate of 8.8°C/min up to the Nb₃Si₅ compound reaction initiation (=1200°C), while a pressure of 7000 psi (46.7 MPa) was applied at 850°C and maintain during the consolidation process until the cooling cycle commenced. Figure 4.32 shows the resulting microstructure of unreacted Nb particles (i.e. average size = 50 μm), surrounded by the Nb₃Si₅ matrix and the residual network of a eutectic mixture of NbSi₂ and Si. While it seems that all of the necessary requirements for the development of single phase Nb₃Si₅ were satisfied, it appears that the Nb particle size was too large to enable Si diffusion throughout the Nb grains. Although RS of elemental powders typically involves the formation of a transient liquid phase (e.g., silicon in Nb-Si mixture), the formation of the desired phase is controlled by the mass transport of atoms with higher diffusivity. In the Nb-Si system, silicon (melting point 1687 K) diffusion into niobium grains controls the formation of Nb₃Si₅. Using a value of Dₛⁱ = 3.38 × 10⁻¹⁰ cm² sec⁻¹ in Nb₃Si₅ at 1773 K, calculated from the values from the work of Lu and Evans [2.50], it would take 145 hours to complete the reaction of 150 μm diameter Nb particles to Nb₃Si₅. Decreasing the niobium particle size to 44μm would decrease the time needed for a full reaction to 12.5 hours, while niobium particle sizes of 18 μm would result in complete reaction to Nb₃Si₅ in 2 hours at 1773 K. Successful reactive sintering of Nb-Si powders would require Nb particles of 18 μm in diameter and Si particles of 5.4 μm in diameter for a desired ratio of Si/Nb of 0.3. However, commercial availability of such Nb and Si powders are very limited and costly.
5.4 Compacts Properties vs. Processing Parameters

Table 4.5 summarizes the properties of the monolithic Nb$_2$Si$_3$ and Nb$_2$Si$_3$/Nb composites. A change of the consolidation temperature from 1973 K to 1873 K did not significantly affect the density, grain size, or the microstructure of the compacts. This high consolidation temperature was chosen based on the knowledge that the ductile-to-brittle transition temperature of Nb$_2$Si$_3$ is approximately 1923 K (1650°C). Thus, consolidation temperatures chosen to be above or below the DBTT could affect the resulting compact density. However, the temperature readings using the optical pyrometer were done on the top of the graphite die, and are only approximate, since the center of the die may posses an actual temperature of 50-100°C higher. It is therefore conceivable that the consolidation temperature was above the DBTT for all compacts, as reflected in the negligible differences in densities. However, the difference of 100°C in consolidation temperature was confirmed by the smaller grain size of compacts obtained from MA Nb$_2$Si$_3$ powders and prealloyed Nb-Si mixtures. The reactive sintered compacts exhibited densities close to theoretical, combined with a dual distribution of grain sizes. In the reactive sintering operation, Nb$_2$Si$_3$ reaction and consolidation is completed around 1600 K as shown in Figure 4.36. Increasing the consolidation temperature by 200-300 K enhanced the densification process and promoted some grain growth, as demonstrated by the dual distribution of grain sizes (i.e. 5-12.5 μm) shown in Figure 4.31.
The microstructural evolution is largely dependent on the Nb-Si powder refinement in the MA process, and the Nb/Si particle ratio and distribution in the reactive sintering operation, as demonstrated by the amount of residual unreacted Nb in the prealloyed Nb-Si mixture (PPHP1) and in the reactive sintered compacts (RSHP1 and RSHP3). In mechanically prealloyed Nb-Si mixtures, the niobium and silicon inter-particle spacing is somewhat smaller than that of the simply blended material used for RS. Thus, the amount of unreacted niobium is somewhat less than that of the reactive sintered powder.

5.5 Laminate Composite Processing

5.5.1 Diffusion bonded laminates.

Diffusion bonding of the Nb foil with Nb₃Si₃ plates according to the schematic in Figure 3.6 produced strong interfacial bond, free of other reaction products and cracks as shown in Figure 4.37. The diffusion cycle of 1473 K/5 h was based on the theoretical calculations of silicon diffusion into the Nb foil, using a model of 2 semi-infinite Nb and Si blocks. The calculated silicon concentration profile plotted in Figure 3.7 indicates silicon penetration to a depth of 50 μm, which is equivalent to the silicon concentration of 8.6 wt.%. This high Si concentration would result in the Nb₃Si₃ formation, since the Si solubility in Nb at diffusion bonding temperature of 1473 K is less than 0.1 wt%. However, the chemical analysis of Nb foil removed from the laminate after diffusion bonding indicates silicon concentration of 0.105
wt.% (1050 ppm) as shown in Table 4.8. This lower value of silicon concentration is expected, since silicon must diffuse from the Nb₃Si, compound, where strong bonding exists between the niobium and silicon atoms.

5.5.2 Structural adhesive bonded laminates.

The structural adhesive EC 1386 manufactured by 3M is a thermosetting liquid adhesive. It offers exceptionally high strength properties up to 370 K, higher impact, peel and bond strength properties than normally attainable in epoxy based adhesives. A structurally sound bonding obtained at a curing temperature of 350°F/1 h under an applied pressure of 0.17 MPa (25 psi) is shown in Figure 4.38. The combined thickness of the 20-25 μm of adhesive layer on both sides of the Nb foil represents only 10% of the Nb reinforcement thickness (250 μm), and should not have a significant impact on the mechanical properties of the Nb reinforcement. However, structural adhesive bonding offers easy of debonding at the reinforcement/matrix interface, thus having a significant impact on the fracture toughness properties of the laminate.

5.6 Mechanical Properties of Nb Reinforcement

5.6.1 Effect of heat treatment.

Table 4.9 summarizes the effect of grain size and silicon diffusion on the properties of the 250 μm thick niobium foils. Nb foils simply exposed to vacuum at
1473 K/5 h (i.e., VHT-Nb) exhibited a significant drop in yield strength in comparison to AR-Nb, consistent with the large change in grain size from 10 μm (AR) to 210 μm (VHT), and the Hall-Petch relation for the change in $\sigma_y$, according to the equation $\sigma_y = \sigma_0 + k d^{-1/2}$. In contrast, Nb foils exposed to Nb, at 1473 K/5 h (i.e., Nb(ss)), exhibited significantly higher yield and ultimate tensile strengths than both the AR and VHT specimens tested at 298 K. Silicon is a solid solution strengthenener of Nb [5.1], and significantly increases the yield strength of the smooth tension specimens at 298 K without a significant loss of ductility. As shown in Table 4.9, the ductility of all of the smooth specimens tested at 298 K was very high, with reductions in area in excess of 75%. The comparison of the energy (i.e. area under stress-strain curves in Figure 4.40) of smooth Nb specimens in AR-Nb, VHT-Nb and Nb(ss) condition indicates smaller energy value of AR-Nb as compared with VHT-Nb and Nb(ss) (i.e. 53.3% of VHT-Nb and 34.8% of Nb(ss)). This energy differences are associated with the condition of instability during the tensile deformation and the difference in the dimensions of AR-Nb specimens and those of VHT-Nb and Nb(ss) specimens. The shorter gage length of VHT-Nb and Nb(ss) resulted in greater percentage of elongation as shown in Figure 4.30. The AR-Nb exhibited a small localized necking before 45° fracture occurred. In contrast, VHT-Nb and N(ss) exhibited first the diffuse necking, followed by localized necking. However, elongation and the reduction of area measure different type of material behavior. The elongation is influenced by uniform elongation and is dependent on the strain-hardening capacity of the material, while
5.6.2 Effect of test temperature.

Figures 4.40 and 4.41 show the typical engineering stress-strain curves obtained on the Nb foils tested at 298 K and 77 K. Consistent with the behavior of bcc metals [5.2], Figure 4.41 and Table 4.9 illustrates the considerable increase in yield strength and UTS for the smooth tension tests conducted at 77 K. Consistent with the tests conducted at 298 K, the large grain VHT-Nb specimens exhibited a lower yield strength than either the AR-Nb or Nb(ss) specimens. However, a large difference in ductility was observed between specimens tested at 77 K as shown in Figure 4.56. While the AR-Nb specimen again exhibited high ductility (e.g., RA > 90%), both VHT-Nb and Nb(ss) specimens exhibited little necking and low ductility (e.g., RA < 10%). A comparison of the energy (e.g., area under the curves in Figure 4.40 and 4.41) between specimens tested at 298 K and 77 K reveals that while fine grained AR-Nb exhibited only 9% decrease at 77 K, the VHT-Nb and Nb(ss) exhibited drop of 53% and 40% respectively. Materials containing large grains typically exhibit a greater tendency for cleavage fracture since the cleavage fracture stress decreases with an increase in grain size [5.3].

5.6.3 Effects of constraint.
Table 4.10 indicates that laminated specimens (e.g., Constrained Nb(ss)) tested at 298 K produced by the diffusion bonding process exhibited an additional increase in the yield and UTS in comparison to the smooth Nb(ss) specimens (i.e., Table 4.9), although the former also exhibited a much lower ductility (e.g., RA = 8% vs 75%). At 77 K, the Constrained Nb(ss) specimens exhibited a yield strength of 1340 MPa, considerably in excess of the smooth Nb(ss) specimens which also exhibited a yield strength of 844 MPa. The reduction in area at 77 K was similarly reduced by constraint (e.g., 4% vs 8%).

Constrained AR-Nb and VHT-Nb specimens produced in the structural adhesive bonding process exhibited a slightly lower yield and UTS at 298 K in comparison to the smooth AR-Nb and VHT-Nb specimens (e.g., Table 4.9), while the reduction in area was considerably higher (98% vs 78%). In both cases, the knife edge appearance of the fracture is indicative of a ductile fracture mode, as shown in Figure 5.4. The VHT-Nb ligament containing large grains exhibits a non-uniform width reduction in the deformation zone due to grain rotation toward the direction of applied load, while a fine grained (10 μm) AR-Nb shows a uniform width reduction. The significant debonding exhibited at the Nb,Si/Nb interface is shown in Figure 5.5.

The existence of traverse stresses associated with the introduction of the notch into a material raises the average value of longitudinal stress at which yielding occurs. From the Tresca yield criterion $\sigma_0 = \sigma_1 - \sigma_3$, longitudinal stress alone measures yielding in the unnotched (smooth) tension specimens since $\sigma_3 = 0$. However, just
below the notch in the notched specimens, $\sigma_0 = \sigma_y - \sigma_t$. Since the basic material yield strength $\sigma_0$ is the same, whether notched or unnotched, it takes a higher values of longitudinal stress $\sigma_y$ to produce yielding in a notched specimen. A significant debonding associated with the tension testing of the structural adhesive bonded and double-notched laminates removes the triaxial state of stress (e.g. notch effect), resulting in the yield stress of smooth specimens.

5.7 Fracture Toughness of Laminated Nb$_2$Si$_3$

5.7.1 Effects of test temperature.

Table 4.12 summarizes the fracture toughness, $K_{\text{O}}$, values of 3 PBT diffusion bonded laminates tested at 298 K and 77 K. With the exception of the sample where the notch was placed inside the Nb ligament, the average value of 8.6 MPa$\sqrt{m}$ for laminates tested at 298 K represents a 5 fold increase in fracture toughness as compared to that of monolithic Nb$_2$Si$_3$ (1.7 MPa$\sqrt{m}$). Figure 4.42 shows the load-displacement trace obtained on the 3 PBT of laminate tested inside the SEM, with the shaded area representing the notch-bend behavior of monolithic Nb$_2$Si$_3$. The significant toughness increase (e.g. area under the load-displacement trace) results from the Nb ligament and its ability to blunt propagating cracks in Nb$_2$Si$_3$ as shown in Figure 4.43. The laminate tested at 77 K exhibited a fracture toughness of 6.2 MPa$\sqrt{m}$ which indicates a 28.2% decrease from the average value obtained at 298 K. However, while the Nb ligament tested at 298 K exhibited a dual fracture mode (i.e.
Figure 4.54) with approximately 50% cleavage, the sample tested at 77 K exhibit 100% cleavage as shown in Figure 4.57. This indicates that while the test temperature has a significant impact on the fracture mode of Nb reinforcement, the fracture toughness, as calculated using the peak load, is not significantly affected.

5.7.2 Effects of interface strength.

Table 4.13 summarizes the fracture toughness data on the structural adhesive bonded laminates tested at 298 K. In this case, the lower interfacial strength promoted significant debonding between the Nb ligament and the Nb$_2$Si$_3$ matrix. Two groups of structural adhesive bonded laminates were tested where the condition of the Nb reinforcement was different in the two cases. The laminates incorporating as-received Nb foil (AR-Nb) tested at 298 K exhibited an average fracture toughness of 7.1 MPa$\sqrt{m}$, while laminates incorporating vacuum heat treated Nb foil (VHT-Nb) exhibited the average fracture toughness of 7.8 MPa$\sqrt{m}$. It is of interest to note that while fracture toughness values decreased by 17% and 9% respectively as compared to the average value of diffusion bonded laminates, the mechanical properties of the constrained Nb in the diffusion bonded laminates were significantly higher than those of the constrained Nb in structural adhesive laminates, as shown in Table 4.10. However, it was observed that significant debonding in 3 PBT of structural adhesive bonded laminates occurred after the maximum load was reached, and the crack initiated and propagated throughout the Nb$_2$Si$_3$ matrix below the Nb reinforcement.
5.8 Deformation Mode of Nb Reinforcement

The significant toughness increase (e.g., area under the load-displacement trace in Figure 4.42) results from the niobium ligament and its ability to blunt propagating cracks in the Nb₂Si₃, as shown in Figure 4.43. This was also observed in much of the previous work on arc-cast and extruded in situ composites of Nb₂Si₃ [5.1, 5.4-5.7]. The Nb₂Si₃-Nb interface is well bonded, while Figure 4.43 shows arrested microcracks in the niobium. Examination of the fracture surfaces obtained from the laminate tested at 298 K as shown in Figure 4.54 indicates that the niobium exhibits both cleavage and ductile fracture in the proportion of 45% and 55% respectively. The arrested microcracks in the niobium ligaments shown in Figure 4.43 are cleavage microcracks which are blunted by the ductile niobium.

The appearance of room temperature cleavage fracture of Nb in the present test is apparently due to a combination of several factors, as pure Nb does not typically cleave at room temperature [5.8]. The high-temperature vacuum hot-press bonding procedure used to produce laminates enables diffusion of silicon into Nb and grain growth in the Nb ligament. The large grains are shown in Figure 4.39. The effect of grain size on the propensity for cleavage fracture are well documented in ferrous materials [5.3]. Materials containing large grains typically exhibit a greater tendency for cleavage fracture since the cleavage fracture stress decreases with an increase in grain size. The tensile results in Table 4.9 show that large grain size decreases the yield stress of the smooth specimens (VHT-Nb) without significantly decreasing the
ductility. The silicon is a potent solid solution hardener and embrittler of Nb as shown in previous work [5.1, 5.4, 5.5]. However, the results in Table 4.9 show that smooth tension specimens of Nb containing silicon in solid solution (Nb(ss)) are ductile, while notched specimens of the same material exhibit cleavage fracture and much lower ductility (e.g., Table 4.10).

In light of the present results, it appears that the constraint provided by the Nb₃Si₃ is sufficient to elevate the local stresses to levels high enough to induce cleavage in the Nb ligament. Areas of ductile Nb fracture in the diffusion bonded laminates result in part from multiple cracks in the silicide which effectively reduce the constraint locally in the Nb, as shown in Figure 4.43 and similar to other recent work on Pb-glass model system [2.40].

In comparison with the diffusion bonded laminates, Nb ligament in the structural adhesive bonded laminates exhibits 100% ductile fracture mode in both AR-Nb, and VHT-Nb conditions. As shown in Figures 4.48 and 4.50 for the 3 point bend test, and in Figure 5.5 for the tension test, a significant debonding (i.e. 2-3 mm) reduces the constraint in the Nb and creates a large gage length for the plastic deformation to occur. A high ductility (i.e. as measured by the reduction of area) demonstrates itself in the Nb liagment stretching to a knife edge point, as shown in Figure 5.4.
5.9 References


Figure 5.1 Schematic of interrupted milling process.

Figure 5.2 Schematic of compound formation in the continuous milling process.
Figure 5.3 Proposed model of compound formation in continuous milling process.
Figure 5.4 Fracture surfaces of constrained structural adhesive bonded Nb ligaments: 1) AR-Nb  2) VHT-Nb
Figure 5.5 Nb$_2$Si$_3$-Nb interface of structural adhesive bonded laminate.  
1) AR-Nb  2) VHT-Nb.
CHAPTER 6

CONCLUSIONS

1. Nb₃Si₃ compound was processed from elemental Nb and Si powders by mechanical alloying. Nb₃Si₃ compound formation proceeds by a self-propagating exothermic reaction in both the interrupted and continuous milling process.

2. The initiation of Nb₃Si₃ compound reaction in the interrupted milling process apparently occurs via the precipitation of Nb₃Si₃ particles upon cooling from the milling temperature. The precipitation process is caused by the creation of a non-equilibrium supersaturated solid solution. The initiation of Nb₃Si₃ compound formation in the continuous milling process occurred via the self-propagating high-temperature synthesis (SHS).

3. Vacuum hot-press consolidation processing of MA Nb₃Si₃, prealloyed Nb-Si powders, and RS Nb-Si mixtures resulted in crack-free, dense compacts. This technique may be utilized to produce composite microstructures of Nb₃Si₃ and Nb, or other combination of phases in different systems.

4. Nb₃Si₃/Nb laminates were successfully produced via the use of diffusion bonding
and structural adhesive bonding methods. The laminates exhibited significant (5 fold) toughness increases over that of monolithic $\text{Nb}_2\text{Si}_3$.

5. *In situ* fracture monitoring revealed crack blunting by the Nb and stable cleavage microcracks in the Nb. Dual fracture characteristics of Nb were observed in the diffusion bonded laminates, but not in the structural adhesive bonded laminates, indicating strong role of the $\text{Nb}_2\text{Si}_3$ matrix constraint on the fracture mode of the Nb ligament.
CHAPTER 7

RECOMMENDED FUTURE RESEARCH

There were many questions raised by the results obtained in this thesis. It is always a hindsight wisdom of knowing what could have been done. However, results obtained strongly suggest continuity of research effort in the following areas:

- Study the $\text{Nb}_5\text{Si}_3$ particles precipitation mechanism during the interrupted milling process by seeding Nb-Si mixtures with a small amount of $\text{Nb}_5\text{Si}_3$.

- Conduct investigation of composites consolidation from elemental powders combining the reactive sintering, vacuum hot pressing, and heat treatment and/or extrusion processes in order to enhanced the fracture toughness. There is a strong indication that hot working operations, such as extrusion, significantly affect the fracture toughness of composites.

- Conduct study of the role of reinforcement thickness and the multi-layered lamination on the fracture toughness of laminates. With the current three layered laminate we are not able to create a significant bridging with the Nb ligament, and once the $\text{Nb}_5\text{Si}_3$ matrix cracks, we are in principle, conducting
a tension test on Nb ligament. Multi-layered laminates could offer the opportunity to create a steady state bridge length, thus providing a more meaningful way of determining the ductile reinforcement toughening of a brittle matrix.

- Develop the laminated system with a controlled de-lamination length at the reinforcement/matrix interface through the use of combination of selective coating of the Nb ligament with the yttria and alumina.
BIBLIOGRAPHY


3.1 JCPD card #8-422.


APPENDIX

A. Indexing of Electron Diffraction Patterns in Figure 4.28

1. Nb+Si mixture:

There is a combination of diffraction points and rings. Using the formula \( L\lambda = R\, d \), where \( L\lambda \) is the TEM constant determined from the measurement of the gold standard, \( R \) is the distance between the diffraction beam origin and the diffraction point or ring, inter-planar \( d \) spacing can be calculated and compared with JCPD cards for Nb, Si, \( \alpha\)-Nb\_5Si\_3, and \( \beta\)-Nb\_5Si\_3.

\( L\lambda = 21.504 \)

**Diffraction points:**

<table>
<thead>
<tr>
<th>( R_{OA} )</th>
<th>( R_{OB} )</th>
<th>( R_{OC} )</th>
<th>( d )</th>
<th>( d_{si} )</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.80</td>
<td>11.2</td>
<td>12.95</td>
<td>3.132</td>
<td>3.1355</td>
<td>(111)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.902</td>
<td>1.9201</td>
<td>(220)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.645</td>
<td>1.6375</td>
<td>(311)</td>
</tr>
</tbody>
</table>

**JCPD card # 27-1402**

**Diffraction rings:**

<table>
<thead>
<tr>
<th>Ring</th>
<th>( d )</th>
<th>JCPD # 27-1402 (Si)</th>
<th>JCPD # 35-789 (Nb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = 6.8</td>
<td>3.132</td>
<td>( d = 3.1355 ) (111) (Si)</td>
<td></td>
</tr>
<tr>
<td>R = 9.1</td>
<td>2.341</td>
<td>( d = 2.3379 ) (110) (Nb)</td>
<td></td>
</tr>
<tr>
<td>R = 11.2</td>
<td>1.902</td>
<td>( d = 1.9201 ) (220) (Si)</td>
<td></td>
</tr>
</tbody>
</table>

179
\begin{align*}
R &= 12.95 \quad d = 1.645 \\
\quad d &= 1.6375 \ (311) \quad (\text{Si}) \\
\quad d &= 1.6532 \ (200) \quad (\text{Nb}) \\
R &= 15.8 \quad d = 1.338 \\
\quad d &= 1.3577 \ (400) \quad (\text{Si}) \\
\quad d &= 1.3499 \ (211) \quad (\text{Nb})
\end{align*}

The calculated d spacings suggest that the particle is a block of Si with some embedded deformed Nb particles.

\textbf{2. Nb}_{3}\text{Si}_{5}:

\begin{align*}
\text{Diffraction rings} & \quad L \lambda = 21.334 \\
R & \quad d \quad d \quad \text{of } \beta-\text{Nb}_{3}\text{Si}_{5} \\
6.6 & \quad 3.232 \quad 3.243 \ (130) \\
10.35 & \quad 2.067 \quad 2.056 \ (050) \\
11.25 & \quad 1.896 \quad 1.874 \ (322) \\
12.25 & \quad 1.742 \quad 1.755 \ (142) \\
17.25 & \quad 1.236 \quad 1.229 \ (024) \\
18.25 & \quad 1.167 \quad 1.177 \ (134) \\
20.25 & \quad 1.054 \quad 1.071 \ (344)
\end{align*}

The imaged particle is the \(\beta\)-Nb\(_3\)Si\(_5\).

\textbf{B. Indexing of Electron Diffraction Patterns in Figure 4.29}

\textbf{1. Nb+Si mixture:}
Diffraction rings  $L \lambda = 21.334$

<table>
<thead>
<tr>
<th>R</th>
<th>d</th>
<th>Si</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.45</td>
<td>3.307</td>
<td>3.1355 (111)</td>
<td></td>
</tr>
<tr>
<td>9.125</td>
<td>2.338</td>
<td></td>
<td>2.338 (110)</td>
</tr>
<tr>
<td>11.10</td>
<td>1.921</td>
<td>1.9201 (220)</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>1.219</td>
<td>1.2140 (420)</td>
<td></td>
</tr>
<tr>
<td>18.1</td>
<td>1.168</td>
<td></td>
<td>1.168 (220)</td>
</tr>
</tbody>
</table>

Diffraction image suggest an agglomerate of Nb and Si particles.

2. Nb$_3$Si$_3$:

Diffraction points  $L \lambda = 21.328$

<table>
<thead>
<tr>
<th>R</th>
<th>d</th>
<th>d of $\alpha$-Nb$_3$Si$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{OA} = 7.05$</td>
<td>3.02</td>
<td>3.015 (113)</td>
</tr>
<tr>
<td>$R_{OB} = 6.85$</td>
<td>3.14</td>
<td>3.160 (201)</td>
</tr>
<tr>
<td>$R_{OC} = 8.6$</td>
<td>2.48</td>
<td>2.507 (114)</td>
</tr>
<tr>
<td>$R_{OD} = 14.05$</td>
<td>1.52</td>
<td>1.508 (017)</td>
</tr>
</tbody>
</table>

Small discontinuous rings were observed. This means presence of small grains of $\alpha$-Nb$_3$Si$_3$. 