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Materials characterization in the development of combustion-based methods for synThesis of niobium silicides

Edgar Maguregui

University of Texas at El Paso, emagu94@gmail.com

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MATERIALS CHARACTERIZATION IN THE DEVELOPMENT OF
COMBUSTION-BASED METHODS FOR SYNTHESIS OF
NIOBIUM SILICIDES

EDGAR J. MAGUREGUI

Master's Program in Mechanical Engineering

APPROVED:

Evgeny Shafirovich, Ph.D., Chair

Arturo Bronson, Ph.D.

David Roberson, Ph.D.

Charles Ambler, Ph.D.
Dean of the Graduate School

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2019

Dedication

To Brisa, for being there for me all this time I could not have done it without you.

My mom for supporting and encouraging me.

And for the one that was with me when no one else was.

MATERIALS CHARACTERIZATION IN THE DEVELOPMENT OF
COMBUSTION-BASED METHODS FOR SYNTHESIS OF
NIOBIUM SILICIDES

by

EDGAR J. MAGUREGUI, B.S.

THESIS

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of the Requirements
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MASTER OF SCIENCE

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Abstract

The use of characterization techniques is essential for a better understanding of novel manufacturing processes and for investigating how the process parameters affect the products. Mechanically activated self-propagating high-temperature synthesis (MASHS) is an attractive method for the production of high-temperature structural materials. In the present work, it was used to fabricate Nb_5Si_3 compound and $\text{Nb}_5\text{Si}_3/\text{Nb}$ composites. It has been shown that for mechanical activation of Nb/Si mixtures, a planetary ball mill is more effective than a shaker ball mill used in prior research on MASHS of Nb_5Si_3 . The influence of mixture composition and experimental parameters, such as milling time and pellet diameter, on the formation of α , β , and γ phases of Nb_5Si_3 was determined. This study shows how the variation of process parameters and use of different ignition methods affect the final composition of niobium silicide-based composites obtained by MASHS.

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Chapter 1: Introduction

1.1 Manufacturing of high-temperature structural materials for gas-turbine applications

Gas turbines are widely used for propulsion and power generation. A decrease in fuel consumption of gas-turbine engines is an important goal, which could be achieved by increasing the thermal efficiency of the engines. According to the Carnot theory, this requires increasing the operating temperatures. Currently, gas-turbine components made of nickel-based superalloys can reach temperatures approaching 1150 °C. Gas temperatures within the turbines, which define the engine operating temperature, are much higher, but the components are protected by air cooling and ceramic thermal barrier coatings. However, cooling consumes energy and hence decreases the efficiency. It is estimated that the operation at 1300 °C without auxiliary cooling would increase the output power by almost 50 % [1]. In addition, that would simplify manufacturing and eliminate weight and complexity of auxiliary cooling equipment.

Niobium silicide based composites are promising high-temperature structural materials for replacing nickel-based superalloys in gas turbines. However, a large-scale fabrication of niobium silicides is difficult. The desired balance of properties could be achieved using additives and creating a certain microstructure, which should remain stable under extreme conditions of high temperature and stress. Innovative powder metallurgy processing is an effective approach to achieve large-scale synthesis of uniform multiphase microstructures. Mechanically activated self-propagating high-temperature synthesis (MASHS) is one of such methods. In the present work, MASHS of Nb_5Si_3 compound and $\text{Nb}_5\text{Si}_3/\text{Nb}$ composites was investigated.

1.2 Research on Nb₅Si₃ and Nb₅Si₃/Nb composites

Niobium silicide-based composites are promising for high-temperature structural applications because of their low density, high fracture toughness, and good fatigue behavior [2]. However, for industrial application, such as gas turbines, their oxidation resistance and creep performance must be improved. To achieve an ideal balance of mechanical properties and oxidation resistance for niobium silicide-based materials, a combination of various additives is used to enhance niobium silicide phases.

There are three stable phases of niobium silicides: Nb₃Si, Nb₅Si₃, and NbSi₂ [3]. Among them, Nb₅Si₃ appears to be the most promising as it has the highest melting point, 2515 °C, and is thermodynamically stable when mixed with excess niobium, molybdenum, and other refractory metals. This makes Nb₅Si₃ an attractive phase for forming composite materials for high-temperature structural applications.

The Nb-Si binary phase diagram (Figure 1.1) shows two stable phases of Nb₅Si₃: the low-temperature α -phase and the high-temperature β -phase (both are tetragonal) [3]. Previous studies have reported the appearance of a metastable and hexagonal γ -phase, which was stabilized by interstitial impurities. Recent computational studies of (α , β , γ)-Nb₅Si₃ phases, however, have shown that all these phases are stable, with α -phase possessing the highest structural stability [4]. The data on the elastic constants and elastic modulus, obtained in that work, indicate that α and β phases are brittle, while γ phase is ductile and has a lower hardness.

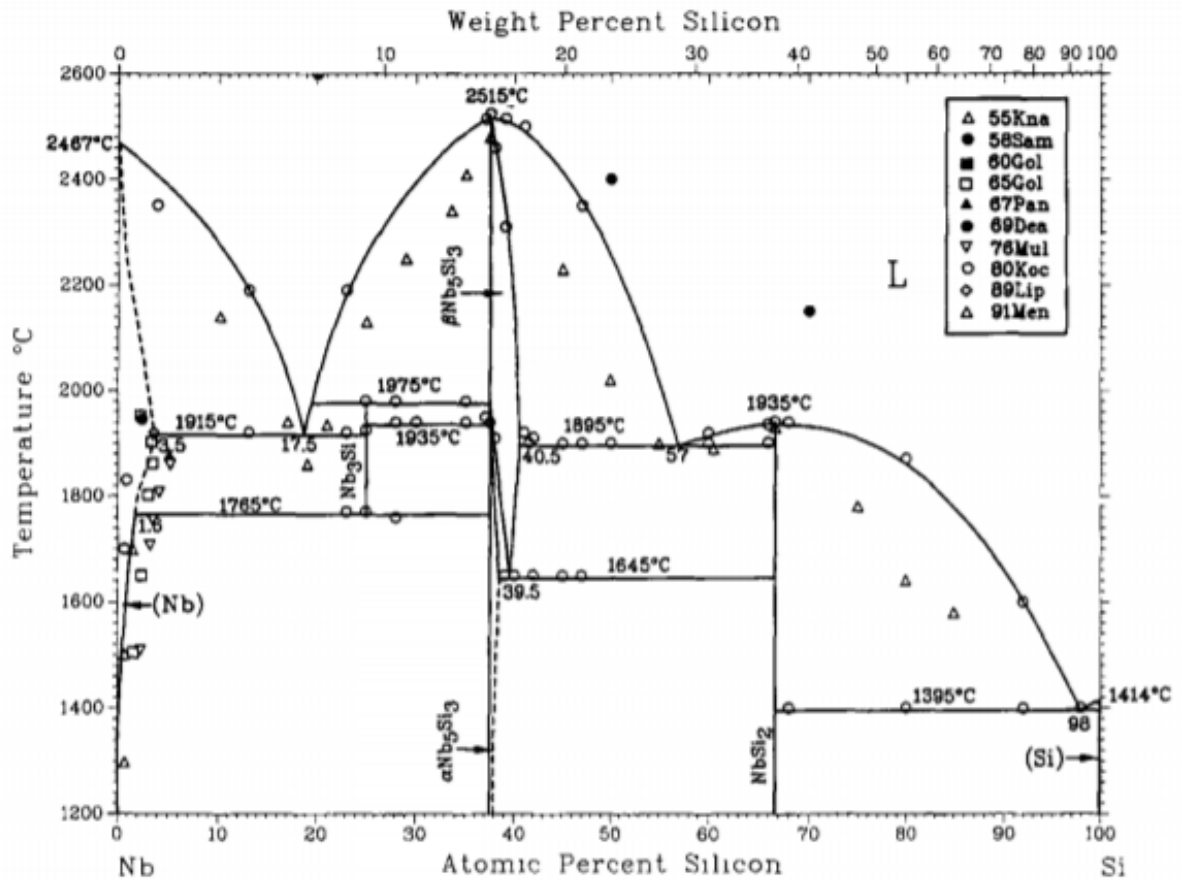


Figure 1.1 Nb-Si binary phase diagram

A significant issue in the development of niobium silicide-based composites is processing. To achieve the desired balance of properties, a specific microstructure needs to be created, and this microstructure should remain stable under extreme conditions of high temperature and stress. Conventional processing modifies the microstructure. The challenge is to develop processing methods that yield the desired final microstructure during initial alloy synthesis [1]. Powder metallurgy processing is viewed as an innovative and practical approach to achieve a large-scale synthesis of uniform multiphase microstructures.

A well-known approach to improving toughness in the brittle Nb_5Si_3 is to make a composite with a more ductile phase, such as Nb [2, 5]. In such a composite, grains of Nb solid solution in the Nb_5Si_3 matrix provide toughness at ambient temperature, while the silicide supplies strength at high temperatures.

1.3 Self-Propagating High-Temperature Synthesis (SHS)

An attractive method for fabricating advanced materials is self-propagating high-temperature synthesis (SHS) [6, 7]. The SHS process takes advantage of the chemical energy released in high-exothermic mixtures and synthesizes materials with low input of external energy. Other advantages of SHS are simple equipment, high purity of products, and a tailored microstructure. The process of SHS entails three stages as shown in Figure 1.2. In the first stage, the initial mixture is ignited locally by an external energy source, in this case a hot wire. Then the combustion front propagates along the pellet forming a new product. In the last stage, the final product cools down to room temperature.

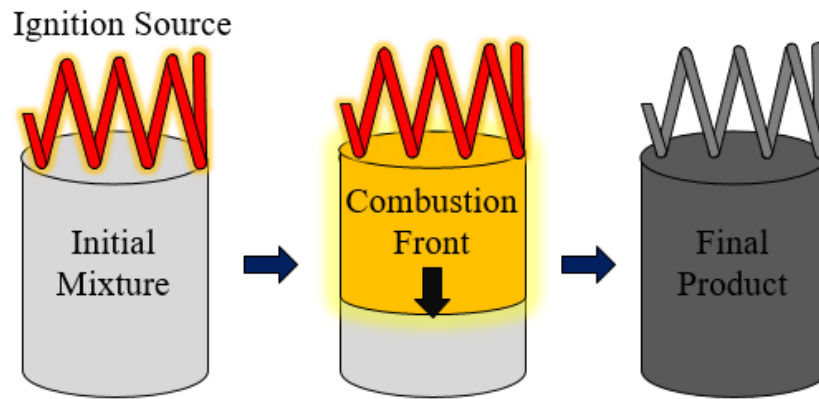


Figure 1.2 Self-propagating high-temperature synthesis

The formation of niobium silicides with SHS has been previously studied [8, 9]. Surprisingly, despite the relatively high adiabatic flame temperatures (over 2000 °C for Nb₅Si₃), a self-sustained combustion was achieved only after preheating the mixtures. The mixture of 5 mol Nb and 3 mol Si required preheating between 200°C and 450 °C and the products contained NbSi₂, Nb, and two phases (α and β) of Nb₅Si₃ [8,11-14, 19-20].

More recently, SHS of Nb₅Si₃ with preheating was studied [10, 11]. It was reported that preheating at 300 °C allowed for the mixture to be ignited, which led to the formation of α -Nb₅Si₃ and β -Nb₅Si₃ phases. Limited data on the SHS (with preheating) of Nb₅Si₃/Nb composites were also reported [10]. The presented XRD pattern of the obtained composite with 10 mol% Nb shows peaks of α -Nb₅Si₃, β -Nb₅Si₃, and Nb phases.

To enable combustion synthesis of Nb₅Si₃ with no preheating, the addition of Joule heating to the reaction zone has been investigated [12]. Specifically, the so-called field-activated combustion synthesis (FACS) was used, where an electric field is applied perpendicular to the direction of the combustion wave. The mode of wave propagation and the nature of the obtained product depended on the field magnitude. At lower fields, between 7.4 and 11.1 V cm⁻¹ [12], a spinning combustion wave was observed, leading to the formation of a multiphase product that included α -Nb₅Si₃, NbSi₂, and unreacted Nb. At higher fields, a steady propagation of a planar combustion front occurred, and the product contained α and β modifications of Nb₅Si₃, with no other phases. The relative concentrations of α and β phases were dependent on the applied field and the mixture density.

Later, the same team had performed simultaneous synthesis and densification of niobium silicide/niobium composites using two techniques – FACS and spark plasma sintering (SPS) [13]. The two techniques are actually similar to each other. The utilized SPS facility involved a pulsed

DC power supply, which generated 15 V, 5000 A, while the FACS applied 60 Hz AC, 10 V, and a 1750 A current. Each facility included a uniaxial 100 kN press. Dense Nb₅Si₃ and Nb₅Si₃/Nb composites were obtained. It should be noted that SPS and FACS are feasible only for mixtures that are good electric conductors. For example, the attempt to use FACS for synthesis of NbSi₂ failed because of a very low electrical conductivity of the mixture [13].

1.4 Mechanically Activated Self-Propagating High Temperature Synthesis (MASHS)

Another approach to enabling SHS of niobium silicides with no preheating is based on the use of mechanical activation of the reacting mixture. Mechanical activation is a short-time, high-energy ball milling step before the SHS process. It has been shown that mechanical activation facilitates the ignition and ensures a stable combustion of low-exothermic mixtures. The entire process is commonly called mechanical activation-assisted SHS or mechanically activated SHS (MASHS) [6, 7].

MASHS of Nb₅Si₃ and NbSi₂ have been conducted using a shaker mill (SPEX CertiPrep 8000) [14]. For Nb₅Si₃, the combustion process of the mechanically activated mixture led to the formation of α , β , and γ phases of Nb₅Si₃. The phases of NbSi₂, Nb, and traces of Si were also detected for the mixtures milled for 80 min, but not in the mixtures milled for 120 min or longer. Increasing the milling time from 120 to 285 min significantly increased the amounts of β and γ phase with respect to α phase.

Maglia et al. [14] have provided insight into understanding the difficult ignition of Nb/Si mixtures and explained the observed positive effect of mechanical activation. Briefly, two factors may be responsible for the poor ignition of the Nb-Si system despite the relatively high

exothermicity. First, the solubility of Nb in molten Si is limited and this decreases the rate of this dissolution. Second, the melting points of both Nb_5Si_3 and NbSi_2 are much higher than the combustion temperatures. It has been suggested that the first step in the reaction mechanism, in the composition Nb:Si = 5:3, is the reaction of liquid Si with abundant solid Nb, leading to the formation of NbSi_2 . After that, the formed solid NbSi_2 slowly reacts with the residual solid Nb. This explains the observed difficulty of obtaining Nb_5Si_3 phase by combustion despite its significant negative enthalpy of formation and high adiabatic flame temperature. The mechanical activation step increases the surface contact area of the powders and decreases the critical diffusional lengths required for completion of the solid-state reaction, thereby enhancing the overall reactivity of the Nb-Si system.

1.5 Research Goals

The overarching goal of the present research is to develop a novel technique for fabricating niobium silicide-based composites for high-temperature structural applications. The specific objective is to determine, through the use of materials characterization techniques, the effects of process parameters, such as the milling time and the pellet diameter, on the phase composition of Nb_5Si_3 and $\text{Nb}_5\text{Si}_3/\text{Nb}$ composites obtained by mechanically activated self-propagating high-temperature synthesis (MASHS).

Chapter 2: Experimental Procedures

2.1 Sample Preparation

This section explains the procedures and equipment used for the preparation of the powders and combustion synthesis as well as the instruments used for the characterization of the obtained materials.

2.1.1 Mixing

Niobium (−325 mesh, 99.8% pure, Alfa Aesar) and silicon (−325 mesh, 99.5% pure, Alfa Aesar) powders were used as starting materials. To prepare the stoichiometric mixture, the niobium and silicon powders were mixed according to a stoichiometric mole ratio of 5:3. Niobium was added to the Nb_5Si_3 to prepare $\text{Nb}_5\text{Si}_3/\text{Nb}$ composites according to the compositions given in Table 2.1.

The powders were mixed in a three-dimensional inversion kinematic tumbler mixer (Inversina 2L, Bioengineering, Figure 2.1). To avoid oxidation, mixing was conducted in a sealed container filled with ultra-high purity argon. The total mass of the prepared mixture was 6 g in all experiments.



Figure 2.1 Mixer (Inversina 2L, Bioengineering) with (a) closed and (b) open protective shield

2.1.2 Mechanical Activation

The mixed powders were mechanically activated in a high-energy planetary ball mill (Fritsch Pulverisette 7 Premium Line, Figure 2.2.a) using zirconia-coated grinding bowls (Figure 2.2.b) and zirconia grinding balls (diameter: 5 mm). The balls-mixture mass ratio was 5:1. Before milling, the bowls were purged with ultra-high purity argon to avoid oxidation of Nb inside the bowl during mechanical activation. The milling speed was 1000 rpm and four milling times were used: 1, 2, 5, and 10 min. To prevent high temperatures and reaction during the milling process, a 60-min cooling period was given after every minute of milling.



Figure 2.2 Milling equipment (a) planetary mill (Fritsch Pulverisette 7 Premium Line) and (b) grinding bowl with purging valves

2.1.3 Compacting

After the milling step, the bowl was opened and powders were extracted inside a glovebox (Terra Universal, Series 300) in an atmosphere composed of 5% O₂ and 95% N₂. The pressing was conducted in a uniaxial hydraulic press, shown in Fig. 2.3. Powder was deposited within the die and pressed at 1.2 metric tons for the 6-mm diameter pellet, 3 metric tons for 13-mm and 7.6 metric tons for the 25-mm pellet. After compaction, a channel was drilled perpendicularly to the pellet axis, approximately midway through the sample. This channel was used to insert a thermocouple and measure the combustion temperature of the pellet. It should be noted that in some of the preliminary experiments with stoichiometric and composite mixtures, a booster pellet of titanium/boron mixture (1:2 molar ratio), compacted at the same pressing parameters, was placed at the top of the sample.



(a)



(b)

Figure 2.3 Pressing equipment: (a) die set for 13mm and (b) uniaxial hydraulic press

2.2 Combustion Synthesis

The combustion synthesis was conducted inside a windowed steel chamber (Figure 2.4), connected to a compressed argon cylinder and a vacuum pump. All experiments were conducted in a 1 atm argon environment. The pellet was placed inside the chamber on top of thick thermal paper (Fiberfrax) and ignited using a hand wound tungsten coil (Midwest Tungsten Service Inc.) heated by a DC power supply (Mastech) set at 15 V. The combustion temperature in the middle of the pellet was measured by a type C thermocouple (WRe 5% WRe26%, wire diameter 76 μm , Omega Engineering). The thermocouple was inserted in the previously mentioned drilled hole of the pellet.

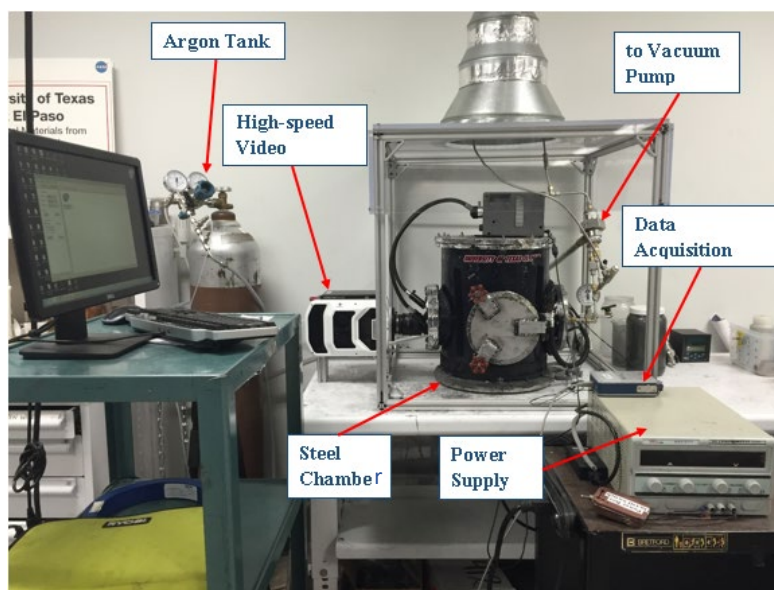


Figure 2.4 Hot-wire ignition setup

2.4 Characterization of Materials.

The characterization of the materials was performed using three techniques: laser diffraction particle size analysis, X-ray diffraction analysis (XRD), and scanning electron microscopy (SEM).

2.4.1 Laser Diffraction Particle Size Analysis

Particle size distribution of the powders were conducted in a laser diffraction particle size analyzer (Microtrac Bluewave, Figure 2.5). To avoid oxidation or dissolution of the powders, isopropyl alcohol (VWR International) was used.



Figure 2.5 Particle size analyzer (Microtrac Bluewave)

2.4.2 X-Ray Diffraction Analysis

Compositions of the powders were investigated by using X-ray diffraction analysis (Bruker D8 Discover XRD, Fig. 2.6.a, and Rigaku MiniFlex II Desktop X-ray Diffractometer, Figure 2.6.b).



(a)



(b)

Figure 2.6 (a) Bruker D8 Discover XRD and (b) Rigaku MiniFlex II

2.4.3 Scanning Electron Microscopy / Energy Dispersive Spectroscopy

Morphology and chemical composition of samples were conducted using a TM-1000 Tabletop Microscope (Figure 2.7.a) and Hitachi S-4800 Scanning Electron Microscope (Figure 2.7.b). The samples were set up using the “Sprinkling method” which consists of applying a water-soluble carbon paste (Electron Microscopy Sciences, CCC Carbon Adhesive) on the specimen stub. Before the paste dries, powder was collected with a cotton swab and sprinkled onto the paste. Once the paste was completely dry, the excess powder was blown off to remove loose powders and minimize the contamination of the internal sample chamber of the instrument.



(a)



(b)

Figure 2.7 (a) TM - 1000 Tabletop Microscope and (b) Hitachi S-4800 Scanning Electron Microscope

Chapter 3: Results and Discussion

3.1 Preliminary Experiments on SHS of Nb_5Si_3

To understand the influence of mechanical activation and select the optimal milling parameters, different milling times were executed, and the results were compared. The initial experiments were conducted with 13-mm diameter pellets, ignited with a booster pellet. In the experiments with the non-activated Nb/Si mixture, the combustion front propagation stopped soon after the ignition, which correlates with prior studies [8-11] where preheating was required. Mechanical activation for 1 min has enabled the combustion front to propagate to the bottom of the sample.

As it was found that mechanical activation allowed for full propagation of the sample, the experiments were then executed with no booster pellet. The mixture activated for 1 min ignited, but the combustion front stopped midway. For milling times 2, 5, and 10 min, the sample burned to completion. Figure 3.1 shows images of the combustion propagation in the experiments with the mixtures milled for 2, 5, and 10 minutes. It is seen that with increasing the milling time from 2 to 10 min, the front velocity doubles. However, after burning, for products milled for 5 and 10 min, instead of losing brightness, an afterglow was emerging from the sample. This suggests a further phase transformation during which the metastable compounds are slowly converting to the final products. This is taking place in bulk, which also has been noticed in previous studies [10-11, 19-20].

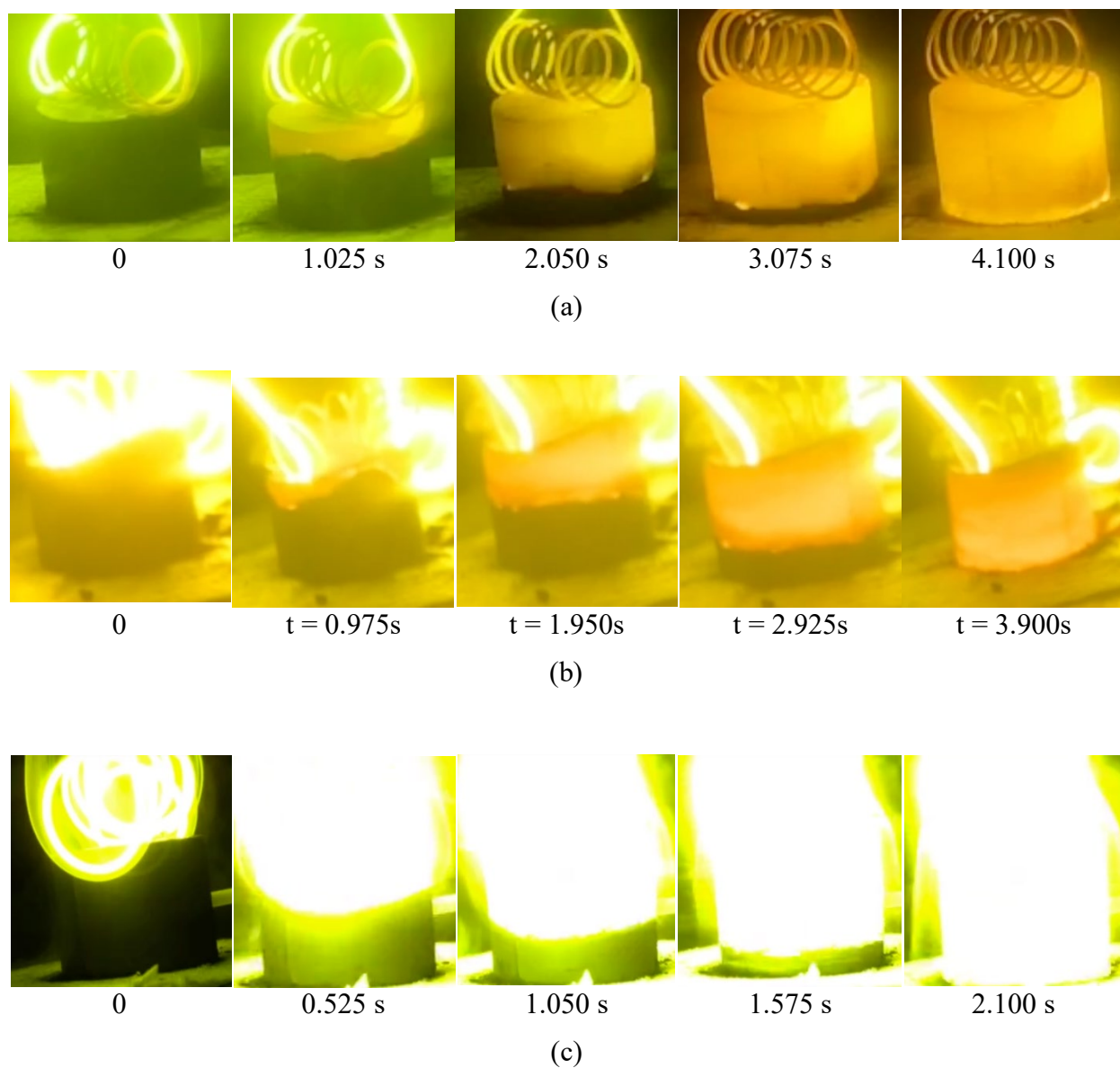


Figure 3.1 Images of combustion propagation over Nb/Si mixture (5:3 mole ratio), mechanically activated for (a) 2 min, (b) 5 min and (c) 10 min. Time zero was set arbitrarily

3.2 The Effect of Milling Time on MASHS of Nb₅Si₃

To further understand the influence of the milling time, XRD analysis was conducted on samples that were milled for 2, 5, and 10 min. Figures 3.2-3.4 show the XRD patterns of products obtained by combustion of mixtures activated for 2, 5, and 10 min. It is seen that the combustion products of the mixtures activated for 2 or 5 min contain four phases: α -Nb₅Si₃, γ -Nb₅Si₃, NbSi₂, and Nb. Note that the presence of unreacted Nb correlates with the formation of NbSi₂, which contains much more Si than Nb₅Si₃. By increasing the milling time from 2 min to 5 min, the concentrations of both NbSi₂ and Nb decrease. At a milling time of 10 min, the product contains only α -Nb₅Si₃ and γ -Nb₅Si₃ phases. This indicates that 10 min of milling was sufficient for the complete formation of Nb₅Si₃.

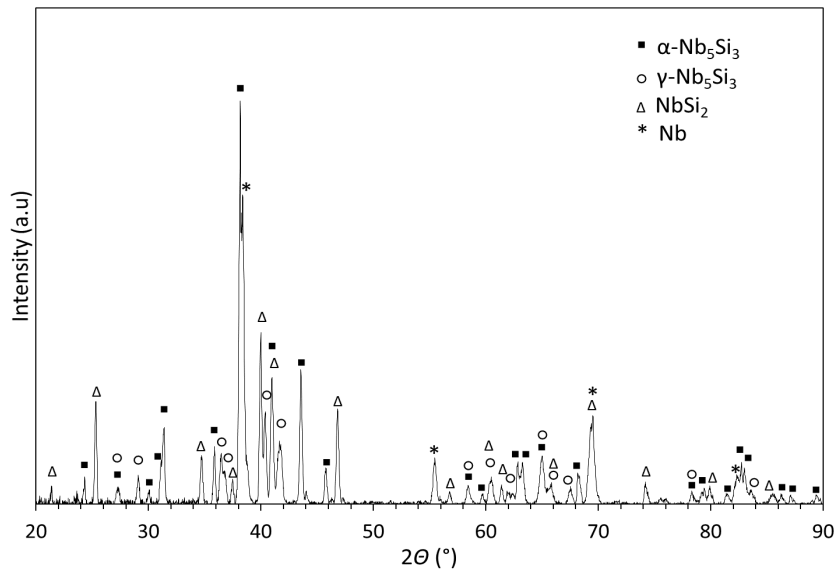


Figure 3.2 XRD pattern of combustion products of Nb/Si mixture milled for 2 min

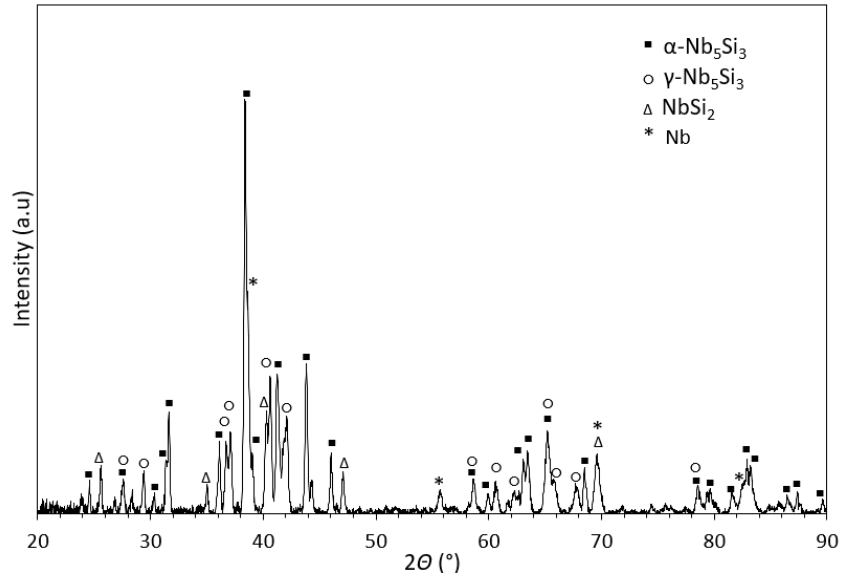


Figure 3.3 XRD pattern of combustion products of Nb/Si mixture milled for 5 min

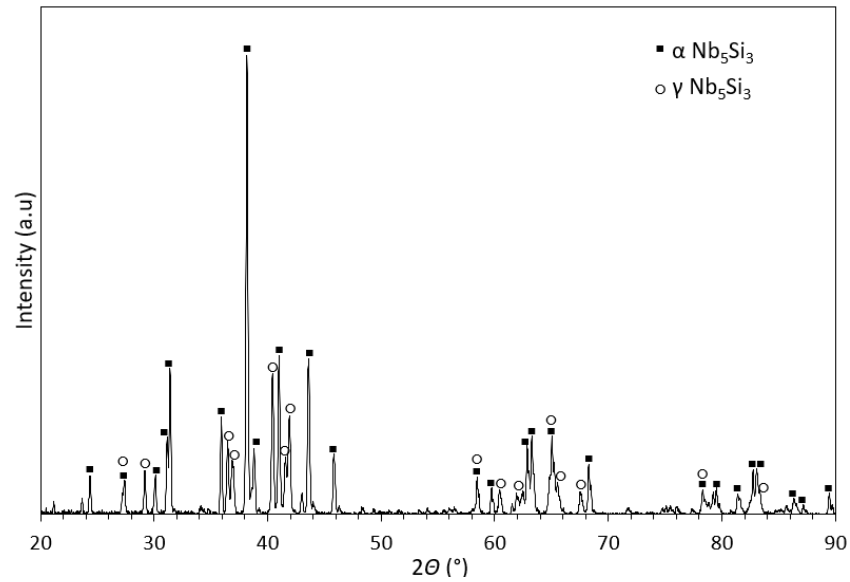


Figure 3.4 XRD pattern of combustion products of Nb/Si mixture milled for 10 min

One of the effects of mechanical activation is increasing the surface contact area of the powders by decreasing the particle size. With this in mind, particle size analysis was conducted after each of the milling times 2 min, 5 min, and 10 min. In order to perform this analysis, the software of the analyzer needs information on whether the particle shape is spherical or irregular. It also requires the refractive index (RI) of the particle material. For this test, all samples were

assumed to be irregular in shape. The refractive indices (RI) used for each material are as follows: $RI_{Nb} = 2.84$. For $RI_{Si} = 3.88$. Samples were also analyzed as absorbing ones, which does not require the knowledge of an RI. It should be noted that small variations of the refractive index usually do not influence the measurements of the particle size distribution.

Two modes of testing were used. In one mode, the run lasted 30 s, the instrument did two measurements, and the output was their average. In the other mode, the time was 60 s and the average of four measurements was obtained from the instrument.

Six samples of each specimen were taken for the 2, 5 and 10 min and only four for Si and Nb (one as absorbing and other with its respective refractive index) following the scheme shown in Table 3.1.

Table 3.1 Scheme of the tests conducted for each specimen. N is the number of measurements during the test.

Run #	1	2	3	4	5	6
Time, s	30	60	30	60	30	60
N	2	4	2	4	2	4
RI	AB	AB	2.84	2.84	3.88	3.88

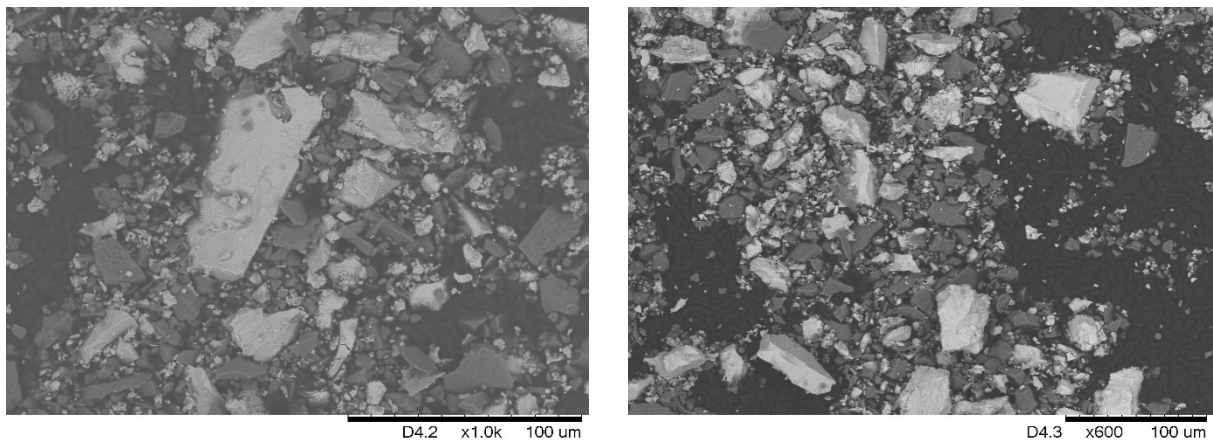
Based on the obtained data, Table 3.2 was created. It shows the parameters that are commonly used for the characterization of powders: the mean volume diameter, the median diameter, and the surface area per unit volume. The latter parameter was calculated by the software assuming that all particles are spherical, while the other two parameters were analyzed according to the selected particle shape, in this case irregular. If the density is known, the specific surface area (i.e. per unit mass) can be calculated. It also should be noted that all specimens showed a unimodal particle size distribution.

Table 3.2 Particle size distribution parameters

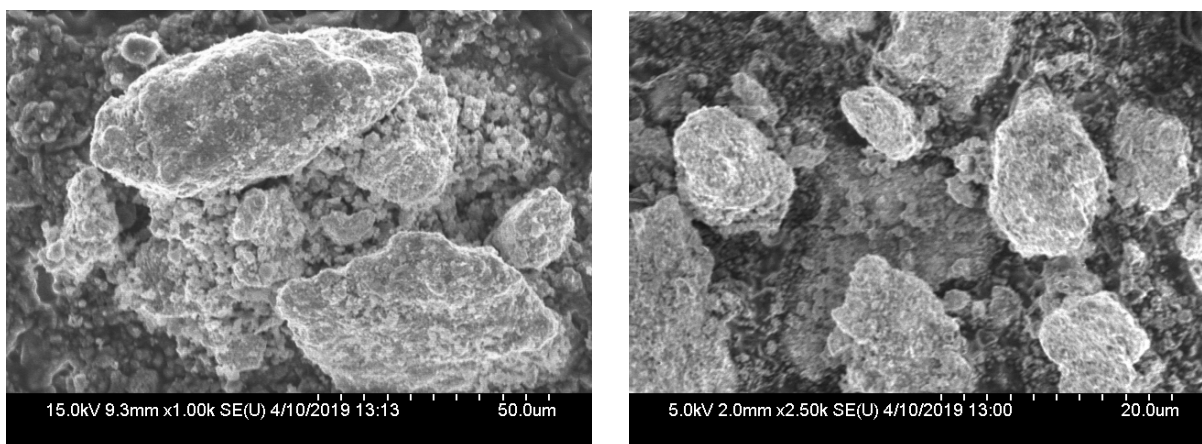
Specimen	Mean Volume Diameter				Median Diameter				Surface Area per Unit Volume			
	μm	μm	μm	μm	μm	μm	μm	μm	m^2/cm^3	m^2/cm^3	m^2/cm^3	m^2/cm^3
	AB	2.84	3.88	Avg.	AB	2.84	3.88	Avg.	AB	2.84	3.88	Avg.
Nb	16.12	15.81	n/a	15.96	2.23	3.04	n/a	2.63	0.803	0.740	n/a	0.771
Si	13.24	n/a	14.31	13.77	2.29	n/a	4.33	3.31	0.779	n/a	0.654	0.716
Nb/Si	14.20	15.30	16.05	15.18	2.89	3.70	3.64	3.41	0.823	0.717	0.712	0.751
2 min	17.78	18.39	17.01	17.73	0.85	1.49	1.48	1.27	1.39	1.01	1.06	1.15
5 min	19.41	20.47	20.52	20.13	0.78	1.42	1.39	1.20	1.22	0.846	0.884	0.97
10 min	12.76	14.20	14.68	13.88	0.94	2.14	2.11	1.73	1.27	0.872	0.871	1.004

For the results obtained for Nb, Si, and Nb/Si, it is seen that the RI used for the analysis does not have a great impact on the particle size obtained in different runs of each sample. However, compared to the analysis done with the AB option, there is a variation of around $1\ \mu\text{m}$ for the mean volume diameter and the median diameter. Also, there is only about $1\ \text{m}^2/\text{cm}^3$ of difference between the results of the surface area per unit volume. It should be noted that as the milling time increases, the surface area of the powder increases. This is not the case for the mean volume diameter as it has an increase of $2\ \mu\text{m}$ for 2 min and another $2\ \mu\text{m}$ at 5 min. However, when a longer milling time of 10 min is employed, a slightly smaller mean volume diameter was found.

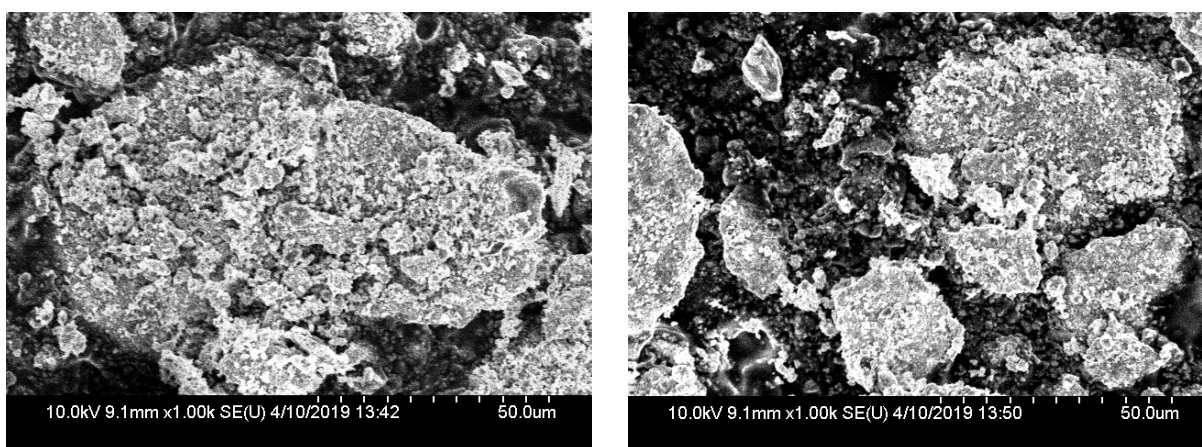
Figure 3.5 shows SEM images of non-activated mixture and of mixtures milled for 2, 5, and 10 min. It should be noted the images for the non-activated mixture and for the 10-min-milled sample were obtained with the TM-1000 instrument, while the mixtures milled for 2 and 5 min were analyzed with the Hitachi S-4800. Since the SEM images are captured by backscatter electrons the TM-1000 and by secondary electrons for the Hitachi S-480, the difference in contrast makes it difficult to compare the images obtained with the different instruments. However, since the non-activated mixture and the 10-min-milled sample were studied using the same SEM instrument, they can be compared to each other. In the non-activated mixture, a clear difference can be seen between the Si powder (gray) and the Nb powder (white), while in the 10-min-milled sample the particles are of the same shade though of different sizes, which suggests uniform mixing and agglomeration of the milled powder. All SEM images in Fig. 3.5 clearly demonstrate irregular shape of particles. In the images of milled powders (Figs. 5b, 5c, and 5d), significant agglomeration is seen.



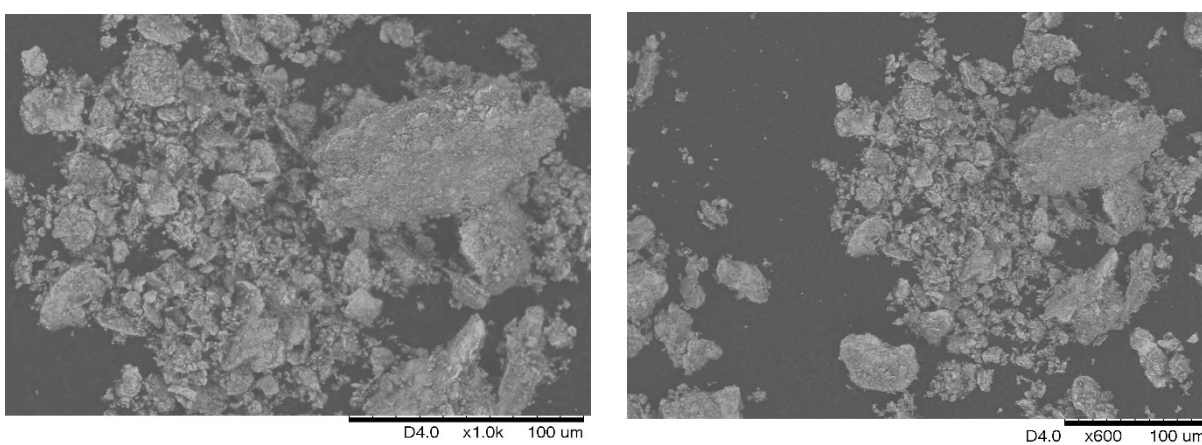
(a)



(b)



(c)



(d)

Figure 3.5 SEM images of (a) non-activated mixture and mixtures milled for (b) 2 min, (c) 5 min, and (d) 10 min

3.3 The Effect of Pellet Size on MASHS of Mg_5Si_3

As seen in the XRD pattern of products obtained from 10-min milled mixture (Fig. 3-4), in contrast with the prior studies on SHS of Nb_5Si_3 [8-14], no β phase was detected. On the other hand, γ phase was always present, correlating to a prior MASHS study by Maglia et al. [14]. The formation of the possibly metastable γ phase may be related to a relatively long cooling period after the SHS process. Since the cooling rate is dependent on the pellet diameter, the experiments with pellets of smaller and larger diameters (i.e. 6 and 25 mm) were performed. The milling time was 10 min. Booster pellets were not used as it was found that they do not influence the SHS process for stoichiometric mixtures milled for 10 min. Table 3.3 shows the dimensions of the pellets, the pressing force, and the pressure calculated based on the force and diameter. The relative density was in the range of 53–60% for all pellets.

Table 3.3 Pellet dimensions, pressing force, and pressure

Diameter	Height	Force	Pressure
mm	mm	kN	MPa
6	8	12.7	451
13	10	29.4	222
25	18.3	74.5	152

Figures 3.6 and 3.7 show the XRD patterns of products obtained by combustion of the samples with different pellet diameters, 6 and 25 mm. It is seen that the combustion products for the samples with 6 mm in diameter contain three phases: $\alpha\text{-Nb}_5\text{Si}_3$, $\gamma\text{-Nb}_5\text{Si}_3$, Nb_3Si , while for both 13 mm and 25 mm the products contained only $\alpha\text{-Nb}_5\text{Si}_3$ and $\gamma\text{-Nb}_5\text{Si}_3$.

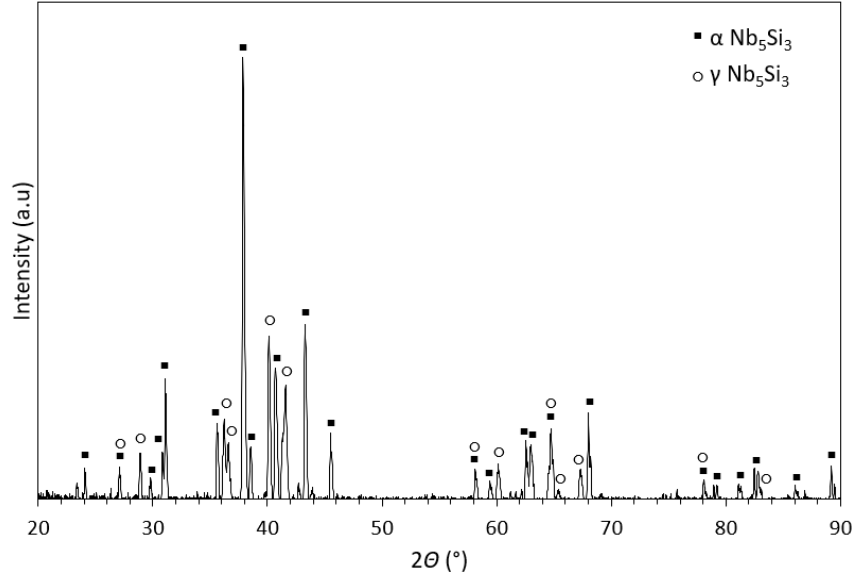


Figure 3.6 XRD pattern of combusted 25 mm pellet diameter milled for 10 min

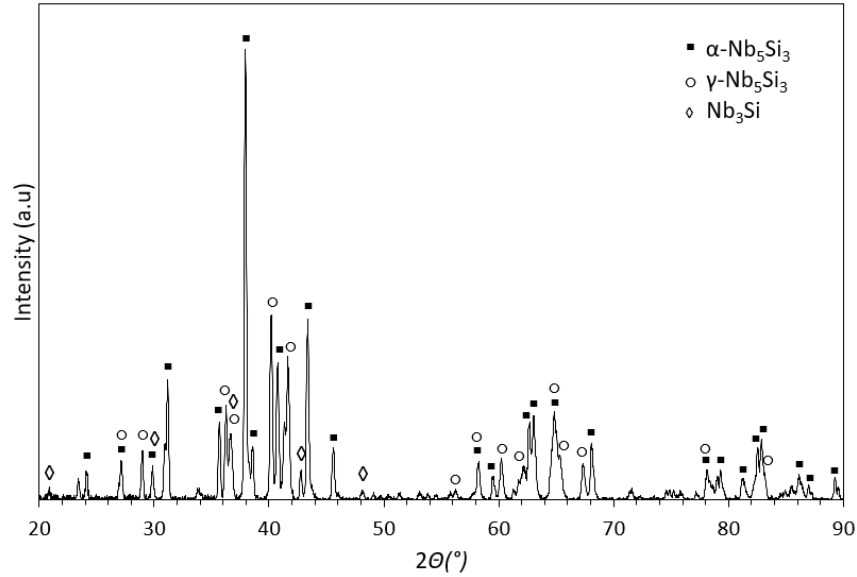


Figure 3.7 XRD pattern of combusted 6 mm pellet diameter milled for 10 min

Figure 3.8 shows the intensity ratio of the highest peak of γ phase to the highest peak of α phase as a function of the pellet diameter. It is seen that the decrease in the diameter from 13 to 6 mm resulted in a higher average γ -to- α ratio. Since the cooling rate increases with decreasing the diameter, the observed increase in the concentration of possibly metastable γ phase is

understandable. However, the increase in the diameter from 13 to 25 mm did not lead to the expected decrease in the concentration of the γ phase. Instead, the average γ - α ratio increased.

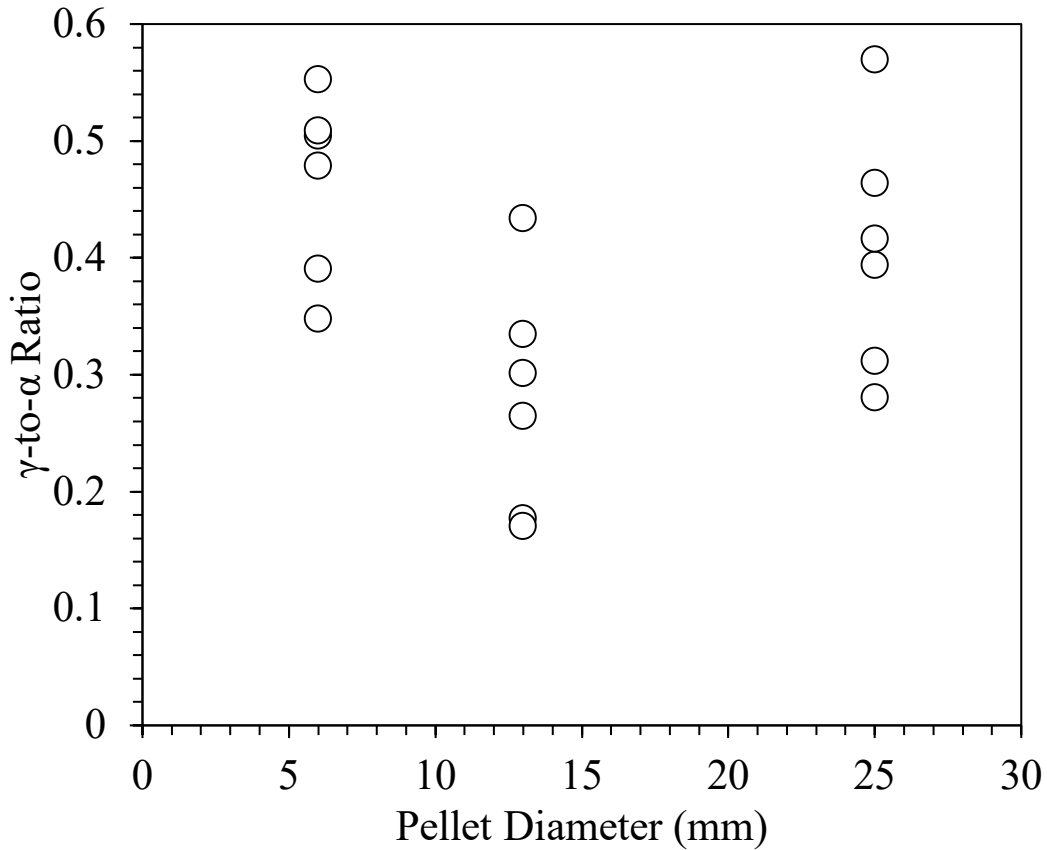


Figure 3.8 The γ -to- α peak ratio in the combustion products of Nb/Si mixture milled for 10 min as a function of the pellet diameter

This effect of the milling duration on the phases obtained during the combustion process agrees with the results of a prior study on MASHS of Nb_5Si_3 , where the mixture was mechanically activated in a shaker ball mill at 875 cycles/min [14]. It was shown that longer milling leads to a higher temperature and a faster propagation of the combustion wave. The measured temperatures for samples are shown in Fig 3.9. It should be noted that, because of the small size of the 6-mm pellet, the thermocouple could not be inserted to obtain an accurate sample temperature and due

to the time consuming and high material usage for a 25-mm pellet, only three temperature measurements were taken.

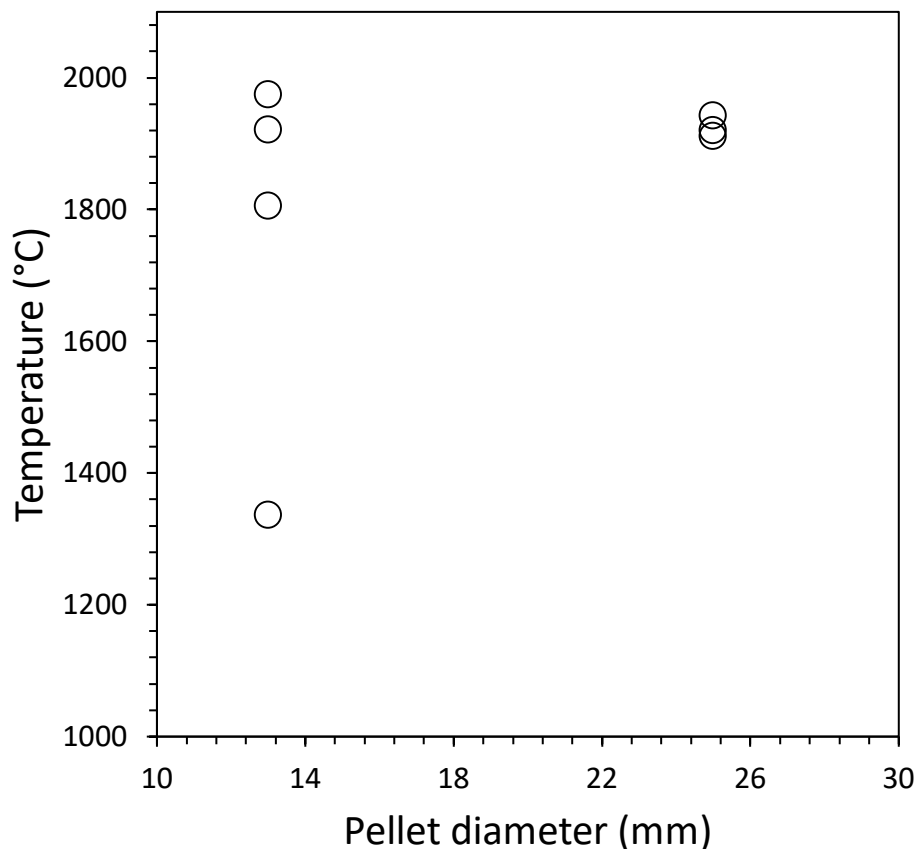


Figure 3.9 Temperature measurements for 13-mm and 25-mm samples

These temperatures were found to be higher than the lowest eutectic point [10-11, 18] in the Nb-Si system and the melting point of silicon (1414°C). This indicates that melting of Si is apparently the first step in the Nb/Si reaction process. On the other hand, the temperature was below the melting point of Nb (2469°C) meaning there is a reaction between solid Nb and liquid Si. This correlates with the results obtained for the previous 2-min and 5-min milled samples where the molten silicon reacts with the solid Nb generating NbSi₂. There, milling time was not sufficient for NbSi₂ to fully react with the rest of Nb and Si to generate the desired Nb₅Si₃.

3.4 MASHS of Mg_5Si_3 via Chemical Oven Technique

In addition, the so-called “chemical oven” technique was used, where the tested mixture is ignited by the combustion of a more exothermic mixture, which is wrapped around the sample. For this to be done, chemical oven pellets were prepared with a core made of Nb/Si (5:3 mole ratio) mixture and a shell made of Ti/B mixture. The pellet was milled and made with the same parameters as for 10-min milled, 13-mm diameter pellets. This pellet was then submerged into a Ti/B mixture inside a 25-mm die and pressed again. This pellet was later ignited using the same procedure as in previous experiments.

Figure 3.10 shows the XRD pattern of the product obtained in the chemical oven experiment. The Ti/B shell was removed and only the mixture that was activated for 10 min was analyzed. It is seen that α phase is dominant and the concentration of γ phase is much less intense than in the case of using hot-wire ignition. In the chemical oven experiment, the temperature of the Nb/Si mixture was much higher and the cooling time was much longer. Apparently, these two factors are responsible for the observed lower concentration of γ phase.

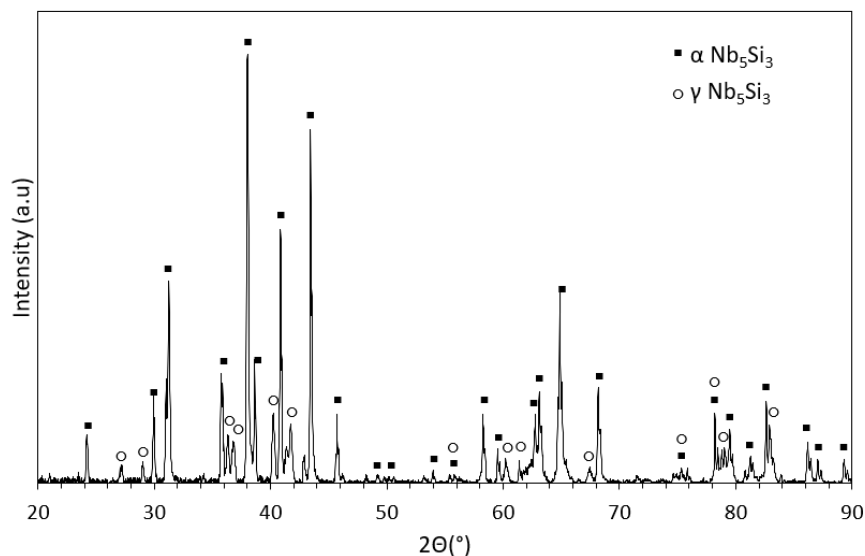


Figure 3.10 XRD pattern of combustion products of Nb/Si mixture obtained using the chemical oven technique

3.5 MASHS of Nb₅Si₃/Nb composites

In the experiments, the mole fraction of additional Nb was increased incrementally (by 0.1) from a zero (Nb:Si = 5:3 mole ratio) to 0.4. Mechanical activation was performed as ten cycles with the total milling time of 10 min.

Table 3.4 Comomposition of Nb₅Si₃/Nb composite

System	Nb	Si
	Moles	
Nb ₅ Si ₃	5.078	0.922
90% Nb ₅ Si ₃ + 10% Nb	5.096	0.904
80% Nb ₅ Si ₃ + 20% Nb	5.116	0.884
70% Nb ₅ Si ₃ + 30% Nb	5.141	0.859
60% Nb ₅ Si ₃ + 40% Nb	5.172	0.828

To understand the impact that excess niobium has in the mixture, XRD analysis was done to all the Nb₅Si₃/Nb samples. Figures 3.12-3.15 show the XRD patterns of products obtained by

combustion of mixture with 10, 20, 30, and 40 mol% excess niobium. It is seen that for the mixture with 10 mol% Nb, the analysis shows peaks of α -Nb₅Si₃, β -Nb₅Si₃, and γ -Nb₅Si₃. This correlates with previous studies on SHS of Nb₅Si₃/Nb composite [10,11]. When the mixture includes 20-30 mol% excess Nb, the products are similar to those for the stoichiometric mixture, there is no trace of the β phase, but a small trace of Nb is present. This is an expected result because increasing the amount of niobium in the mixture leaves some of it unreacted with silicon. As the concentration of excess Nb in the mixture increases to 40 mol%, the XRD shows that the products include Nb₃Si.

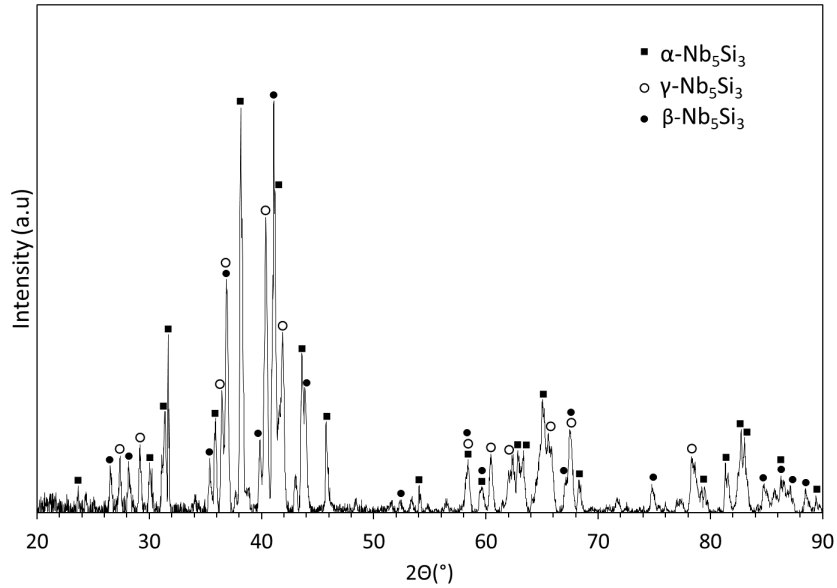


Figure 3.11 XRD pattern of combustion products of 90 mol% Nb₅Si₃ – 10 mol% Nb

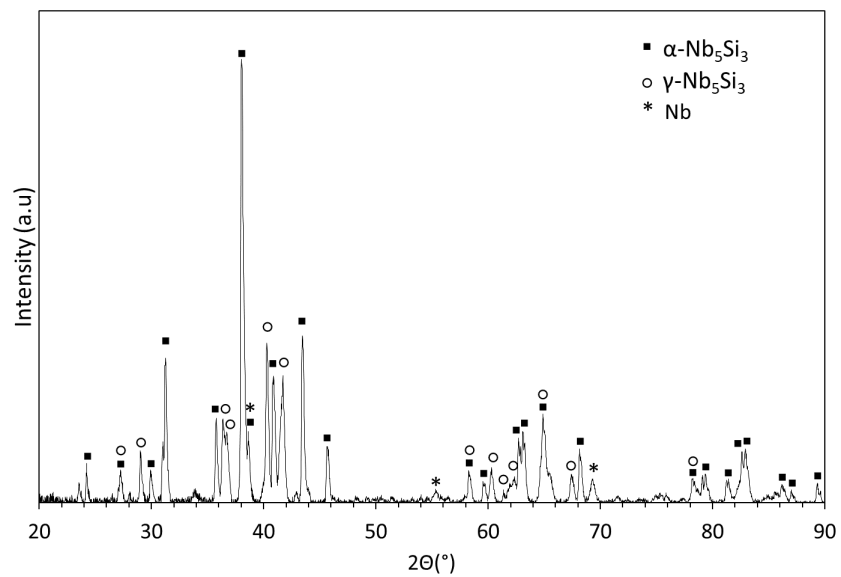


Figure 3.12 XRD pattern of combustion products 80 mol% Nb₅Si₃ - 20 mol% Nb

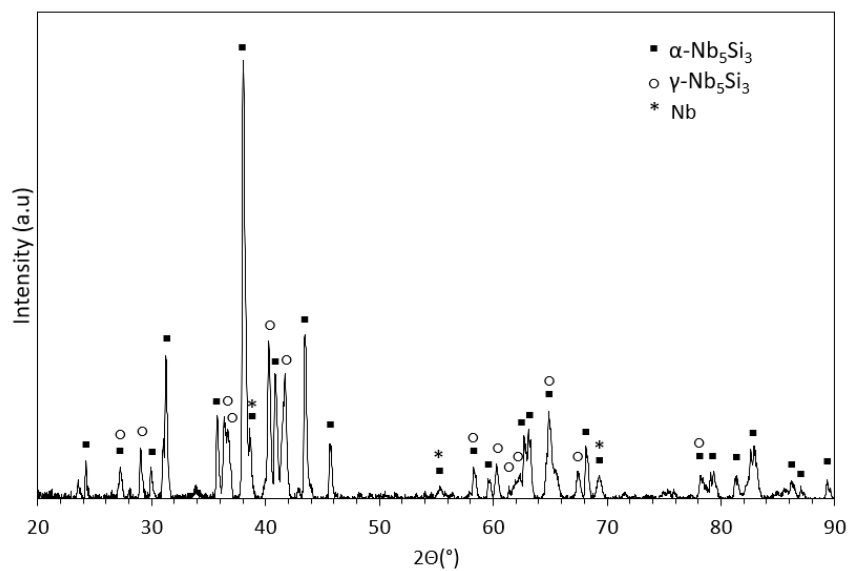


Figure 3.13 XRD pattern of combustion products of 70 mol% Nb₅Si₃ - 30 mol% Nb

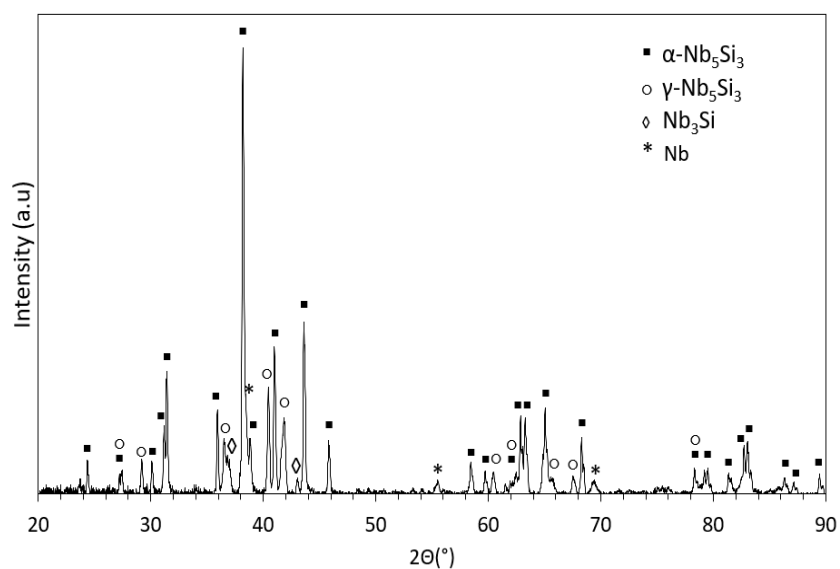
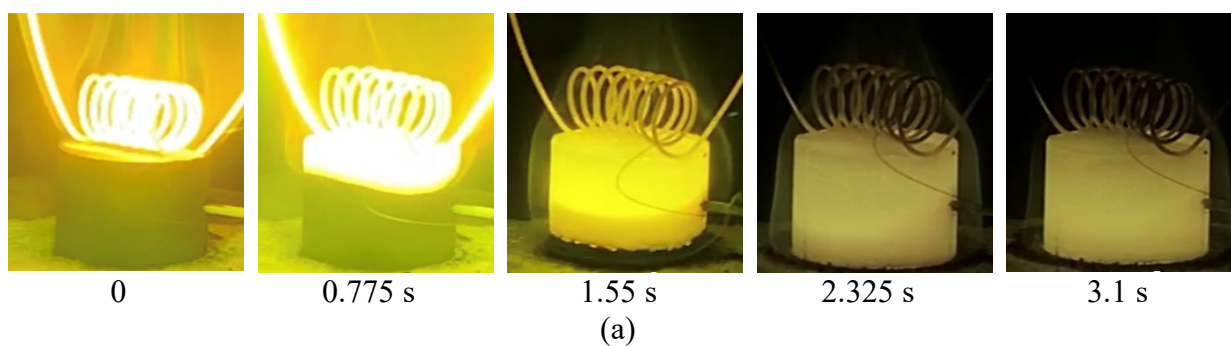


Figure 3.14 XRD pattern of combustion products of 60 mol% Nb₅Si₃ - 40 mol% Nb

It was noticed that with the addition of excess Nb to the mixture, a long ignition time is needed compared to the stoichiometric mixture. A careful insight into this effect has shown that the tungsten coil was short cut by the pellet, obviously because of a high electric conductivity of niobium. This can be seen in Figure 3.16 where part of the coil appears brighter than the rest.



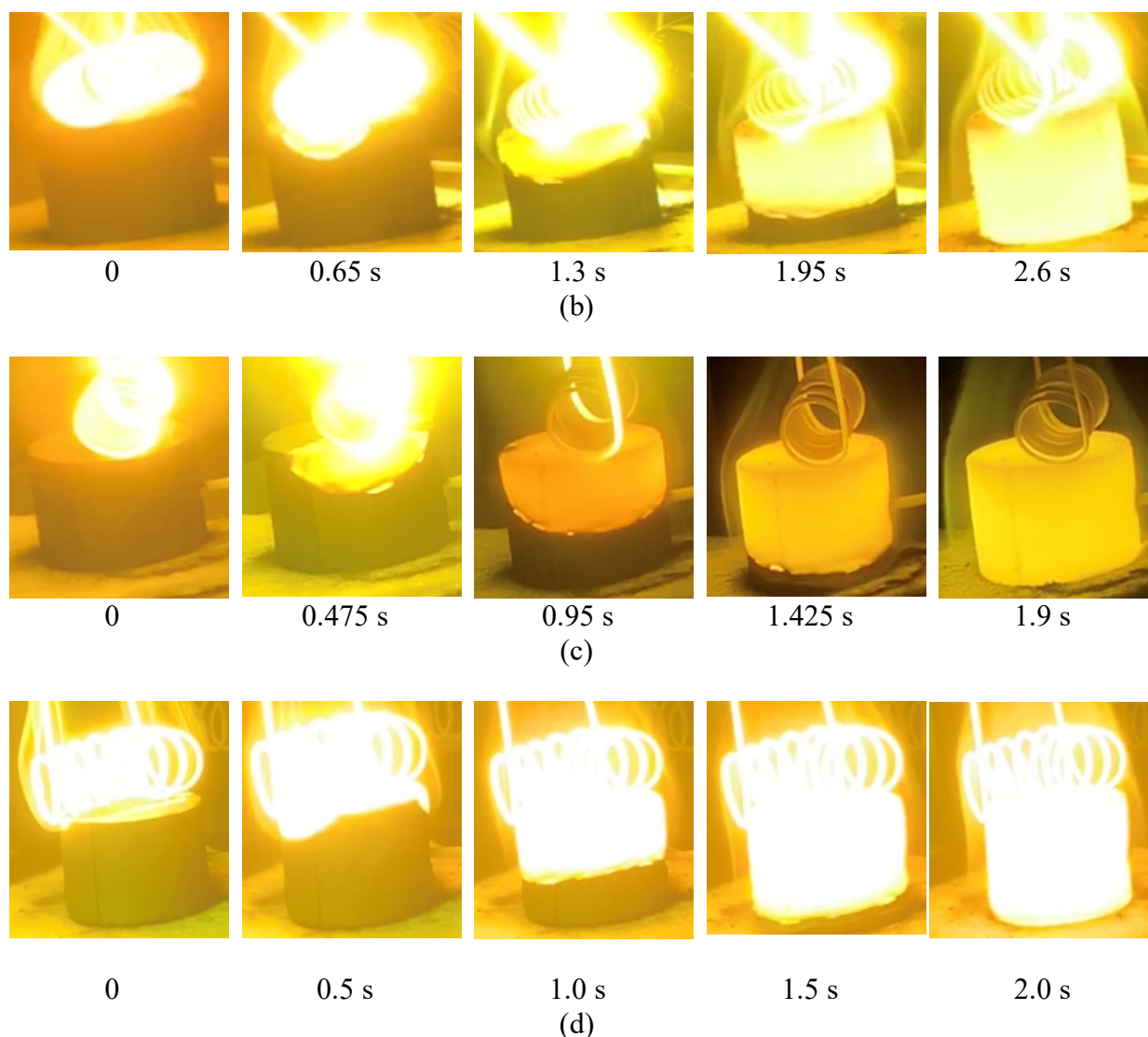


Figure 3.15 Images of combustion propagation over Nb₅Si₃/Nb mechanically activated mixture in mol% (a) 90-10, (b) 80-20, (c) 70-30 and (d) 60-40 without booster pellet. Time zero was selected arbitrarily

Because of the short circuit, it was decided to use a Ti/B booster pellet in subsequent experiments. The use of a booster pellet ensures that the electric current is not flowing through the sample and eliminates the longer ignition time so that preheating is not a factor.

The next step was to repeat the composite experiments, this time with 1g of Ti/B booster pellet on top. Figures 3.17-3.20 show the XRD patterns of products obtained by combustion of

mixture with 10, 20, 30, and 40 mol% extra niobium. It is seen that for the mixture with 10 mol% Nb, the analysis shows peaks of α -Nb₅Si₃, β -Nb₅Si₃, and γ -Nb₅Si₃ as in the previous experiments. However, there has been a decrease in the abundance of the β -Nb₅Si₃ product, from being the most prominent phase in the experiment without a booster to be surpassed by α -Nb₅Si₃ as the most prominent one. When the mixture includes 20 mol% Nb, the products are similar to those of the stoichiometric mixture and there is no trace of the β phase. As the concentration of excess Nb increases to 30 mol%, the XRD shows the resultant products include Nb₃Si. This did not happen in the previous experiment but, opposed to not using the booster, no trace of Nb was found in this experiment. It is not until 40 mol% of excess Nb that the mixture shows a trace of unreacted Nb as well as Nb₃Si.

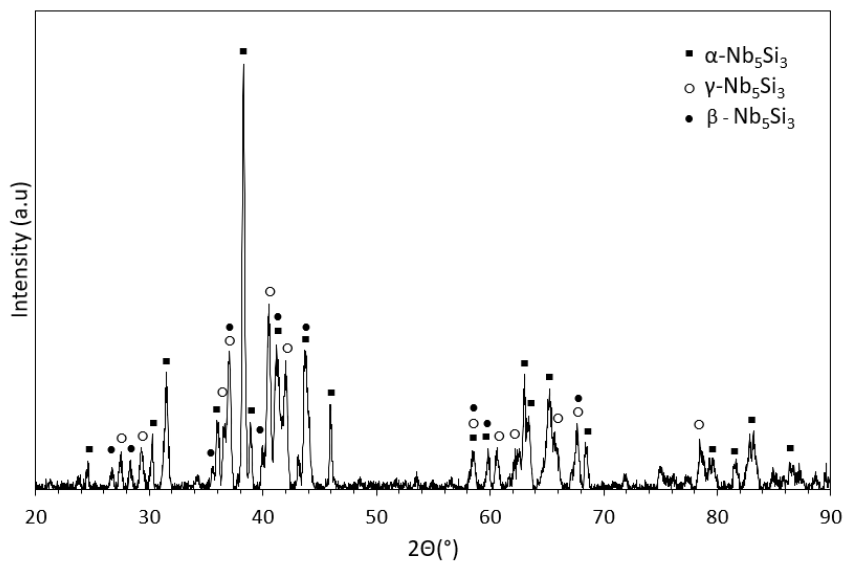


Figure 3.16 XRD pattern of combustion products of 90 mol% Nb₅Si₃ - 10 mol% Nb using a booster pellet

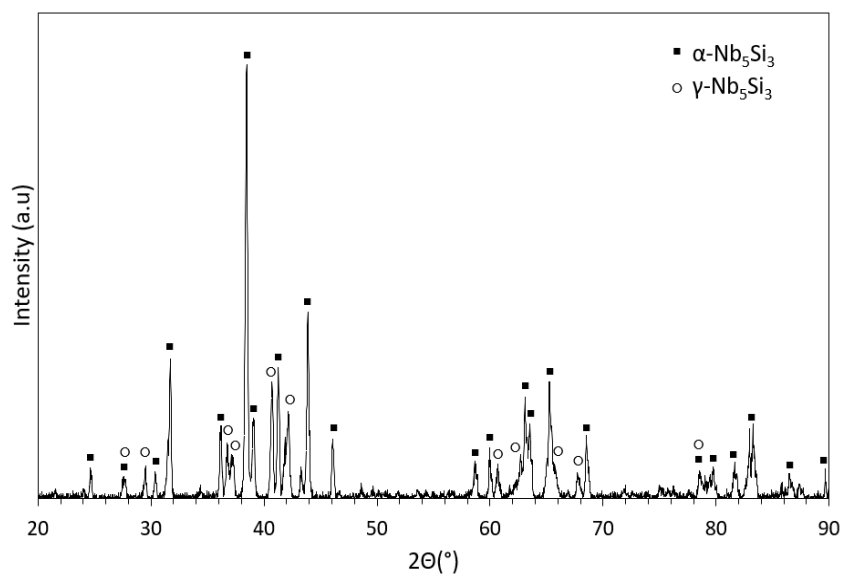


Figure 3.17 XRD pattern of combustion products of 80 mol% Nb₅Si₃ - 20 mol% Nb using a booster pellet

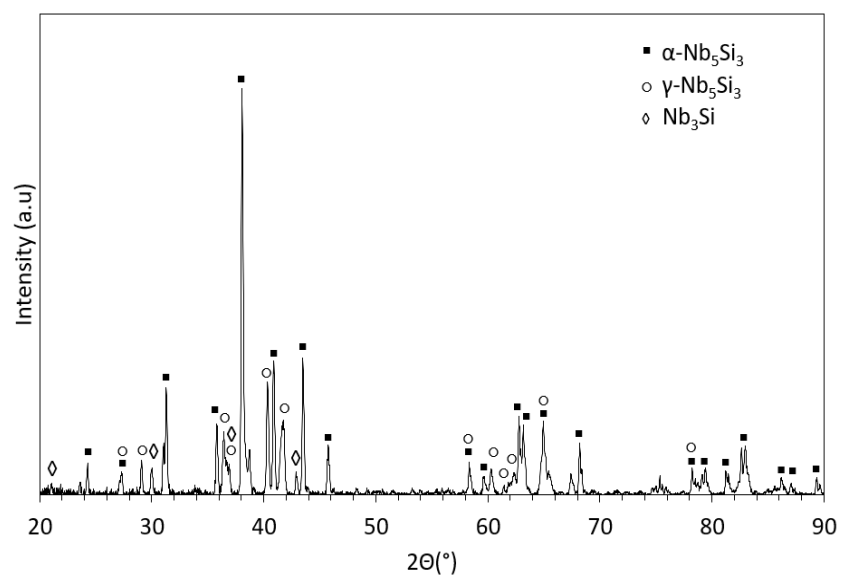


Figure 3.18 XRD pattern of combustion products of 70 mol% Nb₅Si₃ - 30 mol% Nb using a booster pellet

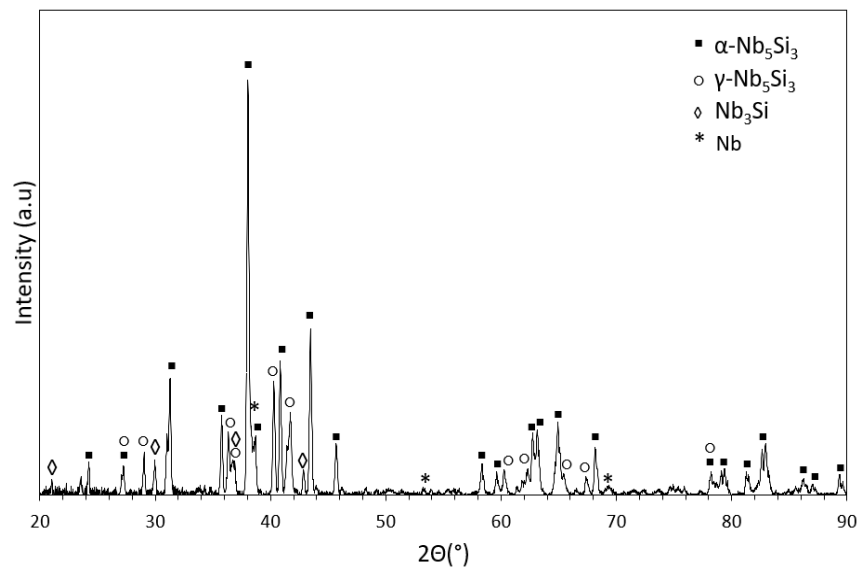
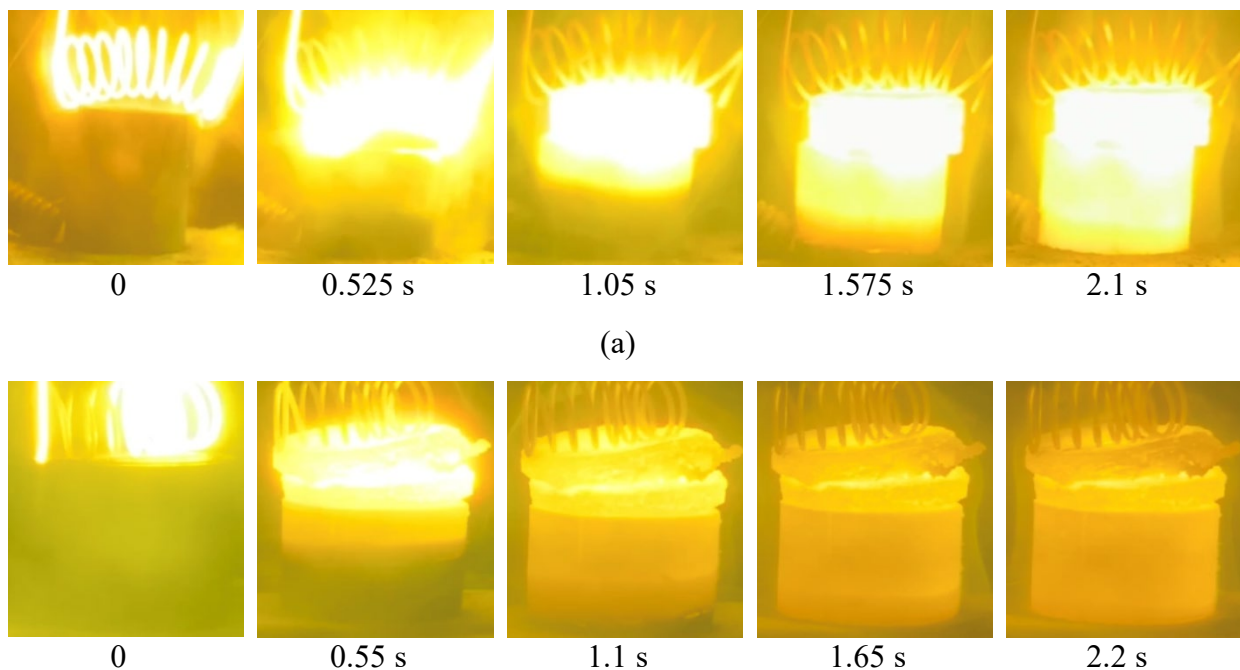


Figure 3.19 XRD pattern of combustion products of 60 mol% Nb₅Si₃ - 40 mol% Nb using a booster pellet

When using the booster pellet, the voltage of 15 V at the coil was sufficient to cause the ignition of the booster pellet and allow the combustion front to propagate through the pellet. Figure 3.21 shows the burning process of all the tested pellets. It is seen that the combustion front reached the bottom of the pellet at around the same time for all concentrations of Nb.



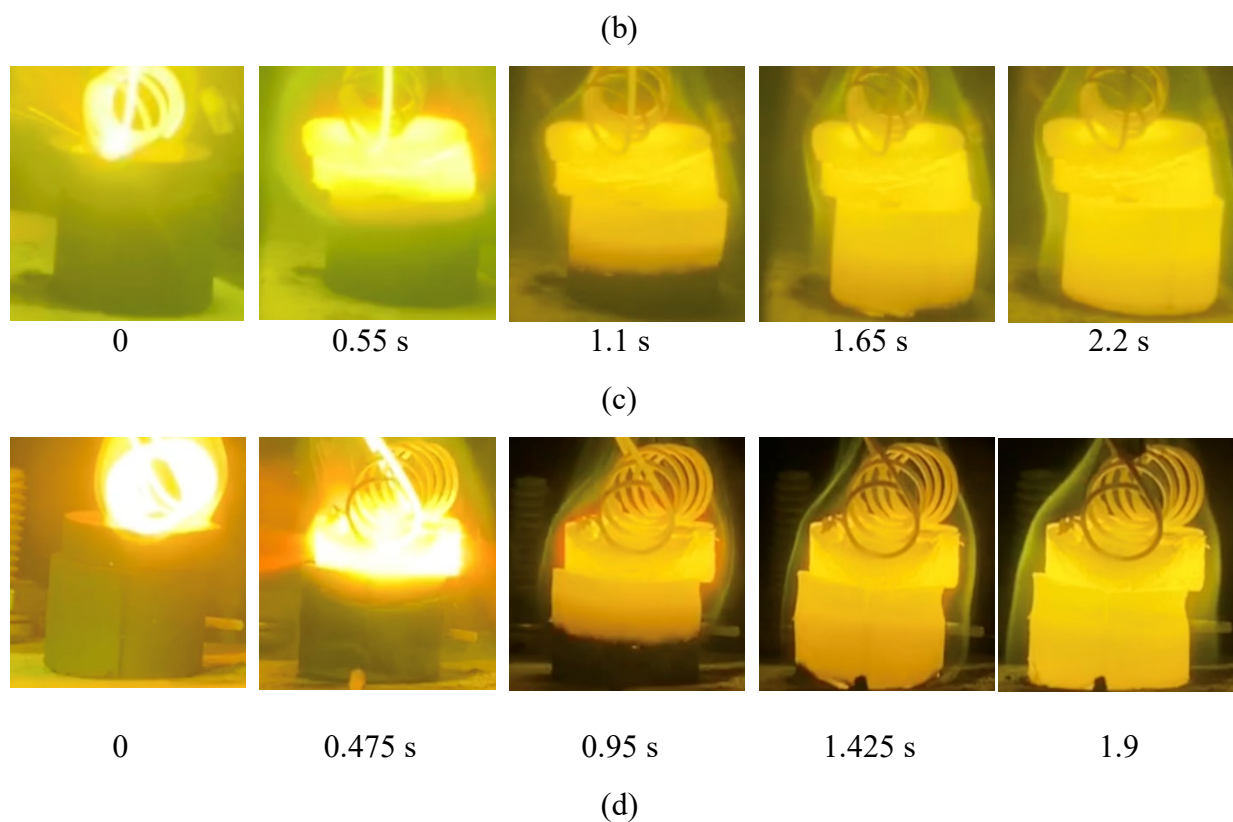


Figure 3.20 Images of combustion propagation over $\text{Nb}_5\text{Si}_3/\text{Nb}$ mechanically activated with booster pellet in mol% for (a) 90-10, (b) 80-20, (c) 70-30 and (d) 60-40. Time zero was selected arbitrarily

Chapter 4: Conclusion

The experiments have shown that 10-min milling of the stoichiometric Nb/Si (5:3 mole ratio) mixture in a planetary ball mill at 1000 rpm enables its complete conversion to Nb₅Si₃ during subsequent SHS process. This milling time is much shorter than 120 min required in prior research with a shaker ball mill.

The obtained products of the stoichiometric mixture contain only α -Nb₅Si₃ and γ -Nb₅Si₃ with no traces of β -Nb₅Si₃. The absence of the β phase is understandable because the combustion temperature was close to the α - β conversion temperature of 1935°C in the Nb-Si phase diagram. Although the appearance of γ phase is not quite understood and the main hypothesis is that the fast cooling of the pellet does not provide enough time for the transition into α .

The effect of the sample size was investigated using pellets with diameters 6 mm, 13 mm and 25 mm. It was found that the 6-mm pellet produced the highest γ -to- α peak ratio, apparently because of a faster cooling rate. However, the 25-mm pellet also had a higher γ -to- α peak ratio than the 13-mm one.

In the experiments with the “chemical oven” technique, where the tested mixture is ignited by combustion of a more exothermic mixture, wrapped around the sample, have produced powders where α phase is dominant and the concentration of γ phase is less intense than in the case of using hot-wire ignition. Apparently, the higher temperature, generated in this technique, significantly increased the cooling time, which led to the observed lower concentration of γ phase.

Since a full conversion of the stoichiometric mixture was possible at 10 min milling time and 13 mm diameter, the fabrication of Nb₅Si₃/Nb composites was conducted at these parameters. In the initial experiments, a tungsten coil with no booster pellet was used for ignition. At 10, 20, 30 and 40 mol% of excess Nb, the pellet burned fully and Nb₅Si₃/Nb composite was obtained.

A problem with the ignition of the mixtures with high concentrations of Nb was short circuit of the coil due to the high electric conductivity of the pellet and energy absorption by the mixture, which created an uncertainty with the required energy input into the sample. This was fixed by adding a Ti/B booster pellet, which eliminated the short circuit and enabled maintaining a constant energy input in all samples. It was shown that increasing the concentration of excess Nb to 30-40 mol% leads to the formation of Nb_3Si phase along with the desired Nb_5Si_3 and Nb.

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Vita

Edgar J. Maguregui was born in El Paso, TX, graduating from Preparatoria El Chamizal, Cd.Juarez, Chihuahua, Mexico. He attended the University of Texas at El Paso from the Fall of 2012. In the Spring of 2013, he started working on the University Library in the Media and Microforms department under the supervising of Juana Rivas. He graduated Cum Laude with his Bachelor of Science in Mechanical Engineering in Spring 2017. He continued at UTEP in pursuit of a master's degree, working with Dr. Evgeny Shafirovich and the Center for Space Exploration and Technology Research (CSETR) at UTEP, with a focus on characterization of high-temperature materials. He presented his work at the Southwest Emerging Technology Symposium in 2018 and the 148th Annual Meeting of the Minerals, Metals & Materials Society (TMS) in 2019.

Contact email: emagu94@gmail.com