



Mechanically activated SHS of Nb₅Si₃ and Nb₅Si₃/Nb composites

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ABSTRACT

Nb₅Si₃ and Nb are the main components of niobium silicide-based composites, which are promising materials for high-temperature structural applications. Self-propagating high-temperature synthesis (SHS) is an attractive method for fabricating advanced materials from powders via exothermic reactions between the mixture constituents. However, to overcome kinetic difficulties of Nb–Si reaction, SHS of niobium silicides usually requires additional heat input. The present work focuses on a technique that addresses this problem by adding a mechanical activation step before SHS. Specifically, short-term ball milling was used for mechanical activation of Nb/Si mixtures with the goal of conducting SHS of Nb₅Si₃ and Nb₅Si₃/Nb composites with no preheating. The milled mixtures were compacted and ignited in an argon environment. It has been shown that a planetary mill is an effective tool for mechanical activation of Nb/Si mixtures. Milling for 10 min enabled SHS of the product that consisted of α -Nb₅Si₃ and γ -Nb₅Si₃ phases with traces of Nb₃Si. For the first time, Nb₅Si₃/Nb composites were obtained by mechanically activated SHS with no preheating. Combustion took place at an Nb/Si mole ratio as high as 3, i.e. at 25 at% Si in the mixture. At this mole ratio, a spinning propagation of the combustion wave was observed, and the content of the γ phase, which has poor mechanical properties, was dramatically decreased.

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1. Introduction

Niobium silicide-based composites are promising for high-temperature structural applications because of a high melting point, low density, high fracture toughness, and good fatigue behavior [1–3]. However, for use in applications such as gas turbines, their oxidation resistance and creep performance have to be improved. The best balance of mechanical properties and oxidation resistance for niobium silicide-based materials could be achieved by a combination of various additives to niobium silicide phases. Among three stable silicides of niobium (Nb₅Si₃, Nb₃Si, and NbSi₂ [4]), the former has the highest melting point, 2515 °C, and it is thermodynamically stable with Nb, Mo, and other refractory metals. This makes Nb₅Si₃ an attractive phase for forming the composite materials for high-temperature structural applications.

The Nb–Si binary phase diagram shows two stable phases of Nb₅Si₃: the low-temperature α -phase and the high-temperature β -phase (both are tetragonal) [4]. The authors also mentioned prior reports of a metastable hexagonal γ -phase, which apparently was stabilized by interstitial impurities. It has also been shown that this

phase is stabilized by Ti and Hf additives [3]. Recent computational studies of (α , β , γ)-Nb₅Si₃ phases have shown, however, that all these phases are stable, with α -phase possessing the highest structural stability [5]. 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. The γ phase exhibits poor creep performance [3].

A well-known approach to improving toughness in the brittle Nb₅Si₃ is to make a composite with a more ductile phase, such as Nb [1–3,6]. In such a composite, grains of Nb solid solution in the Nb₅Si₃ matrix provide toughness at ambient temperature, while the silicide supplies excellent strength at high temperatures.

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 [7]. Innovative powder metallurgy processing is viewed as a practical approach to achieve a large-scale synthesis of uniform multiphase microstructures.

A promising method from this standpoint is self-propagating high-temperature synthesis (SHS) [8,9]. SHS of niobium silicides

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was first studied as long as 40 years ago [10,11]. Surprisingly, despite the relatively high adiabatic flame temperatures (over 2000 °C for Nb₅Si₃), a self-sustained combustion was achieved only with preheated mixtures. The mixture of 5 mol Nb and 3 mol Si required preheating at 450 °C. Along with two phases (α and β) of Nb₅Si₃, the combustion products contained NbSi₂ and Nb.

More recently, SHS of Nb₅Si₃ with preheating was studied in Refs. [12,13]. 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. In Ref. [12], limited data on the SHS (with preheating) of Nb₅Si₃/Nb composites were also reported. 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 [14]. 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, 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 planar combustion front propagated steadily, forming 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 has performed simultaneous synthesis and densification of niobium silicide/niobium composites using two techniques – FACS and spark plasma sintering (SPS) [15]. The two techniques are actually similar to each other. The used SPS facility involved a pulsed DC power supply, which generated 15 V, 5000 A, while the FACS applied 60 Hz AC, 10 V, 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 electrical conductors. For example, the attempt to use FACS for synthesis of NbSi₂ failed because of the low electrical conductivity of the mixture [15].

Another, universal 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-term, 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) [8,9].

MASHS of Nb₅Si₃ and NbSi₂ has been conducted using a shaker mill (SPEX CertiPrep 8000) for mechanical activation [16]. 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.

The study [16] has also provided insight into the ignition mechanism 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 Nb₅Si₃ and NbSi₂ 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 NbSi₂. After that, the formed solid NbSi₂ slowly reacts

with the residual solid Nb. This explains the observed difficulty of obtaining Nb₅Si₃ 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.

Summarizing this brief review of literature, one can conclude that Nb₅Si₃ can be obtained by MASHS with no preheating, but the required long duration of milling in a shaker mill is a significant drawback. In addition, the multiplicity of the obtained phases of Nb₅Si₃ in the prior SHS experiments is not well understood. It is remarkable that in the SHS with preheating or with an electric field, both α and β phases of Nb₅Si₃ were obtained, while MASHS also produced the γ phase. For successful implementation of SHS approaches, it is important to understand what factors are responsible for the formation of certain phases and how one can tune the operating parameters toward the formation of the desired product.

Further, to our knowledge, there is no information on MASHS of Nb₅Si₃/Nb composites (without preheating) in the literature. Since the addition of Nb above the Nb₅Si₃ stoichiometry should decrease the combustion temperature of the Nb/Si mixture, the question arises about the maximum concentration of Nb at which the mixture remains combustible. This is important because Nb silicide composites typically contain only 12–25 at% Si [1–3].

The objectives of the present work were to investigate the feasibility of decreasing the milling time in the MASHS of Nb₅Si₃ by using a planetary ball mill and to explore the possibility of making Nb₅Si₃/Nb composites by MASHS. The experiments were conducted with mixtures, compositions of which ranged from the Nb₅Si₃ to Nb₃Si stoichiometry, i.e. at Nb/Si mole ratios 1.67–3 (37.5–25 at% Si in the mixture). Special attention was paid to the formation of different Nb–Si phases during the SHS process. Oxidation resistance of the obtained products was examined using thermogravimetric analysis.

2. Experimental

Niobium (–325 mesh, 99.8% pure, Alfa Aesar) and silicon (–325 mesh, 99.5% pure, Alfa Aesar) powders were used as starting materials. The powders, placed in a sealed container filled with argon, were mixed in a three-dimensional inversion kinematics tumbler mixer (Bioengineering Inversina 2L) for 1 h.

The mixed powders were mechanically activated in a planetary ball mill (Fritsch Pulverisette 7 Premium Line) using zirconia-coated grinding bowls (volume: 20 mL and 80 mL) and 5-mm zirconia balls. The balls-powder mass ratio was 5:1. The milling was conducted in an argon environment and included from one to ten milling-cooling cycles (1-min milling at a rotation speed of 1000 rpm followed by 60-min cooling).

The powders were cold-pressed into cylindrical pellets of three different diameters using a uniaxial hydraulic press. The pressing force was 12.7, 29.4, and 74.5 kN for pellet diameters of 6, 13, and 25 mm, respectively (the corresponding pressures were 451, 222, and 152 MPa).

The combustion experiments were conducted in a 30-L stainless steel reaction chamber. A schematic diagram of the setup is shown elsewhere [17]. The pellet was installed vertically on a ceramic fiber insulator (Fiberfrax). The chamber was evacuated and filled with ultrahigh purity argon at 1 atm. The pellet was ignited at the top by a tungsten wire heated with a DC power supply. The combustion process was observed using video recording through a glass window.

In several experiments, thermocouples (95%W/5%Re–74%W/26%Re, type C, wire diameter: 76.2 μ m, Omega Engineering) were

used to measure the temperature in the middle of the sample during the combustion process. The thermocouples, located in two-channel ceramic insulators (Omegatite 450), were inserted into pellets at the bottom through channels, drilled along the pellet axis, approximately midway through the sample. The thermocouples were connected to a USB-based data acquisition system (National Instruments USB-9211).

The obtained products were examined with X-ray diffraction analysis (Bruker D8 Discover XRD) and scanning electron microscopy (Hitachi TM-1000). The particle size distributions in the used and milled powders were determined with a laser diffraction particle size analyzer (Microtrac Bluewave), using isopropyl alcohol as a liquid carrier.

Compression testing was conducted using Instron 5969 Universal Test Machine in accordance with ASTM standard E9. Prior to the test, the pellet was cut using a diamond saw and polished.

Oxidation tests were performed using a thermogravimetric analyzer (Netzsch TGA 209 F1 Iris). Samples were placed in alumina crucibles (diameter: 6 mm) and heated up to 1000 °C at rates of 1 °C/min and 10 °C/min in O₂/Ar (20% O₂) flow.

3. Results and discussion

3.1. MASHS of Nb₅Si₃

The experiments with Nb/Si (5:3 mole ratio) mixtures were conducted with 13-mm-diameter pellets, which had a height of about 10 mm. The relative density was in the range from 53 to 63%. Initially, the pellets were ignited using a 1-g booster pellet (thickness: about 3 mm) at the top. In the experiments with an unmilled Nb/Si mixture, the combustion front propagation stopped soon after the ignition, which correlates with prior studies [10–13] where preheating was required. Mechanical activation for 1 min has enabled the propagation until the bottom of the sample.

Then, experiments were conducted with no booster pellet. The mixture activated for 1 min ignited, but the combustion front stopped in the middle of the pellet. However, mixtures activated for 2, 5, and 10 min burned completely. Fig. 1 shows images of the combustion propagation in the experiments with mixtures milled for 2 and 10 min. It is seen that with increasing the milling time from 2 to 10 min, the front velocity doubled and the light emission increased dramatically.

Figs. 2–4 show the XRD patterns of products obtained by combustion of the mixtures activated for 2, 5, and 10 min. It is seen that the combustion products of the mixtures activated for 2 or

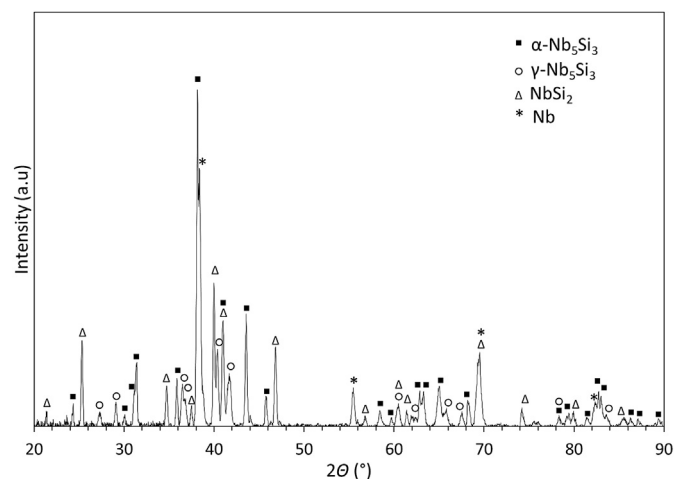


Fig. 2. XRD pattern of combustion products of Nb/Si mixture milled for 2 min.

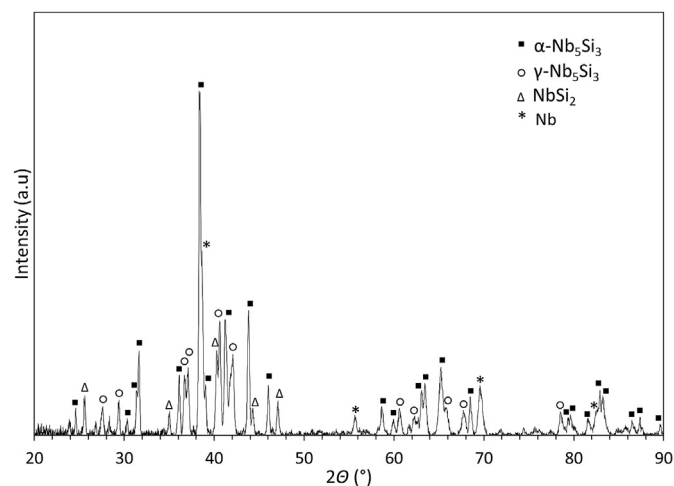


Fig. 3. XRD pattern of combustion products of Nb/Si mixture milled for 5 min.

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. With increasing the milling time from 2 min to 5 min, the concentrations of both

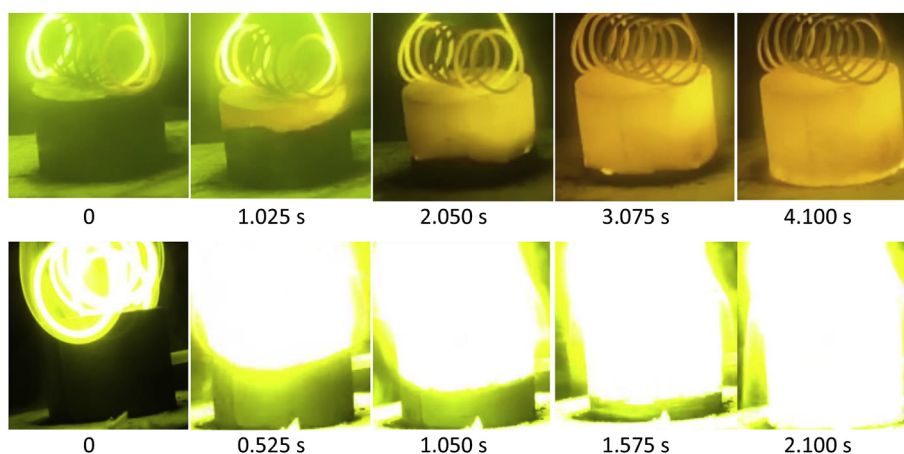


Fig. 1. Images of combustion propagation over Nb/Si mixture (5:3 mole ratio), mechanically activated for (top) 2 min and (bottom) 10 min. Time zero was selected arbitrarily.

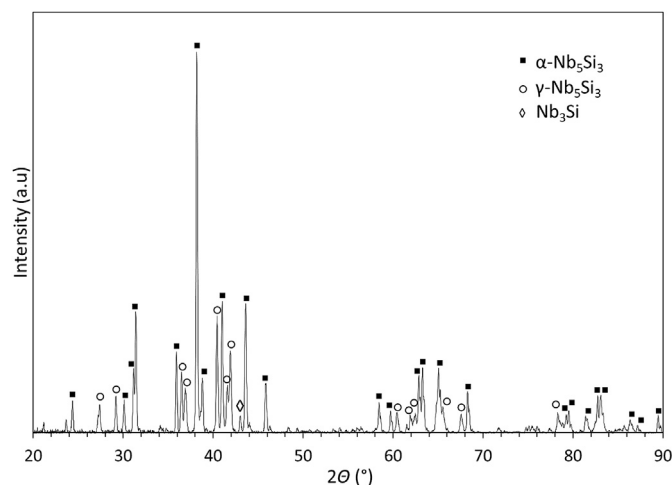


Fig. 4. XRD pattern of combustion products of Nb/Si mixture milled for 10 min.

NbSi₂ and Nb decrease. At a milling time of 10 min, their peaks are not present and a small peak at 43° appears. This peak indicates traces of Nb₃Si (other peaks of this phase overlap with those of α -Nb₅Si₃ and γ -Nb₅Si₃ phases).

Summarizing, the product obtained by MASHS with 10-min milling consists of α -Nb₅Si₃ and γ -Nb₅Si₃ phases with traces of Nb₃Si. Increasing the milling time to 15 min has not changed the product composition. The formation of NbSi₂ at shorter times of milling correlates with the aforementioned mechanism of Nb₅Si₃ synthesis, which includes the formation of NbSi₂ as an intermediate product [16].

This effect of the milling duration on the phases obtained during the combustion process is in qualitative agreement with the prior study on MASHS of Nb₅Si₃, where the mixture was mechanically activated in a shaker ball mill at 875 cycles/min [16]. It was shown in that work that longer milling leads to a higher temperature and a faster propagation of the combustion wave. Since the formation of NbSi₂ is the initial step in the formation mechanism of Nb₅Si₃, it occurs at a relatively low temperature, but complete transformation to the final Nb₅Si₃ product requires a higher temperature. Our observations of the accelerating effect of milling duration on the front propagation align with these results. However, the formation of Nb₅Si₃ phases with no NbSi₂ and Nb required only 10 min of milling in the planetary mill vs. 120 min of milling in the shaker mill [16]. Thus, the use of a planetary mill is more effective for MASHS of Nb₅Si₃ than the use of a shaker mill.

It was shown [16] that the mechanical activation step increases the reactivity of the Nb–Si system by increasing the surface contact area of the powders and decreasing the critical diffusional lengths required for completion of the solid-solid reaction. To investigate how mechanical activation affected the powders in the present work, particle size analysis was conducted for an unmilled Nb/Si mixture and after each of the milling times 2 min, 5 min, and 10 min. The initial Nb and Si powders were examined as well.

The analysis has shown that all tested powders have a unimodal particle size distribution. Table 1 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 (calculated by the instrument's software assuming that all particles are spherical). The data on the median diameter and surface area indicate that the particle size decreased after 2-min milling, but the longer times did not affect it much.

The relatively low decrease in the particle size after milling implies that significant agglomeration could take place. To verify

Table 1
Particle size distribution parameters.

Specimen	Mean Volume Diameter	Median Diameter	Surface Area per Unit Volume
	μm	μm	m^2/cm^3
Nb	16.0	2.63	0.77
Si	13.8	3.31	0.72
Nb/Si, no milling	15.2	3.41	0.75
Nb/Si, 2 min milled	17.7	1.27	1.15
Nb/Si, 5 min milled	20.1	1.20	0.97
Nb/Si, 10 min milled	13.9	1.73	1.00

this, scanning electron microscopy was done. Fig. 5 shows SEM images of an unmilled mixture and of a mixture milled for 10 min. In the former case (Fig. 5a), a clear difference can be seen between the Si (gray) and Nb (white) powders, while in the milled sample (Fig. 5b) the particles are of the same shade though of different sizes, which suggests uniform mixing and significant agglomeration of the milled powder. Apparently, the particle size analysis determined the size of agglomerates and so the surface area was also determined based on the size of agglomerates.

It can be concluded that not only does milling grind coarse particles that are present in the initial powders, but it also creates a powder that consists of agglomerates where the two components, Nb and Si, are uniformly mixed. This clearly improves conditions for effective solid-solid reactions between the two components. It should be noted that mechanical activation is a complex phenomenon that may also include other processes, such as the increase in the dislocation density and crystallographic defect concentrations within the powders, which improves high-temperature diffusion kinetics through short circuit diffusion [8]. The analysis of such processes is beyond the scope of the present work.

In contrast with the prior studies on SHS of Nb₅Si₃ [10–14,16], β phase was not detected in the XRD patterns of the products. It is possible that in the prior studies, preheating [10–13], the Joule heat [14], and a large thermite booster pellet [16] increased the combustion temperature leading to the formation of the high-temperature β phase.

On the other hand, γ phase was always detected in the present work and in the prior MASHS of Nb₅Si₃ [16] as well. The formation of the possibly metastable γ phase could be related to a relatively high cooling rate 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 to verify this hypothesis. The milling time was 10 min.

Fig. 6 shows the intensity ratio of the highest peak of γ phase to the highest peak of α phase in the XRD pattern as a function of the pellet diameter. Each point is the average of values obtained in six experiments, and the error bars show the standard deviations. 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 γ phase supports the explanation based on its metastability.

3.2. MASHS of Nb₅Si₃/Nb composites

Prior to the experiments on MASHS of Nb₅Si₃/Nb composites, thermodynamic calculations of the adiabatic flame temperature and combustion products for Nb/Si mixtures with various mole ratios were conducted using THERMO (version 4.3) software, which

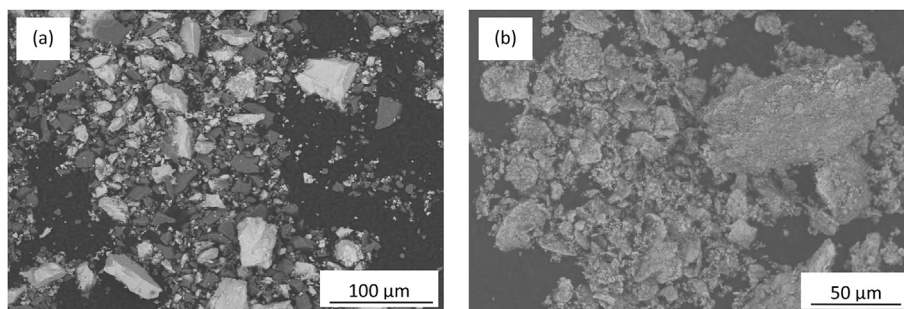


Fig. 5. SEM images of (a) non-activated mixture and (b) mixture milled for 10 min.

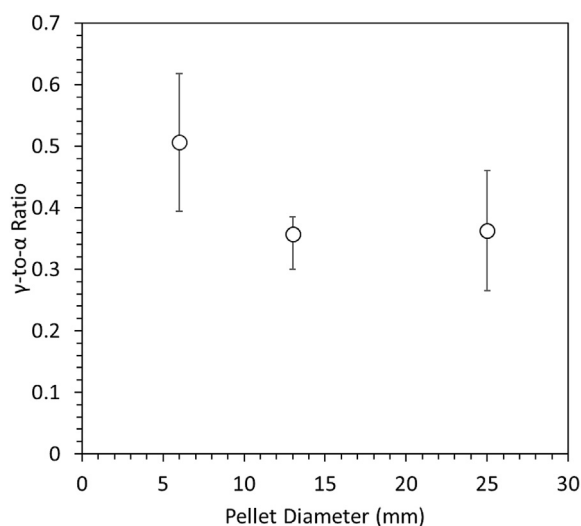


Fig. 6. The γ -to- α peak intensity ratio in the combustion products of Nb/Si mixture vs. the pellet diameter.

is based on the Gibbs free energy minimization and contains a database of approximately 3000 compounds [18]. In the calculations, pressure was 1 atm, and the mole fraction of excess Nb in the initial mixture was varied from 0 to 1 (i.e. no excess Nb means Nb:Si mole ratio is 5:3 = 1.67). The results show that for all mixtures, the combustion products consist of Nb_5Si_3 and Nb. It should be noted, however, that the database of the used software does not include thermochemical properties of Nb_3Si , so caution should be exercised in the analysis of the obtained results.

Fig. 7 presents the adiabatic flame temperature vs. the mole fraction of excess Nb in the initial Nb/Si mixture. It is seen that the adiabatic flame temperature decreases with the addition of more Nb, but the decrease is relatively small up to very high contents of excess Nb. For example, with increasing the mole fraction of excess Nb from 0 to 0.4 (Nb/Si mole ratio in the initial mixture is equal to 1.89) and 0.8 (Nb/Si mole ratio in the initial mixture is equal to 3), the adiabatic flame temperature decreases from 2289 K to 2151 K and 1677 K, respectively. This implies that the mixtures with relatively high contents of excess Nb may remain combustible.

The experiments on MASHS of $\text{Nb}_5\text{Si}_3/\text{Nb}$ composites were conducted with 13-mm-diameter pellets. Initially, the pellet height was about 10 mm and the relative density was 53–63%. The mole fraction of additional Nb was increased incrementally (by 0.1) from a zero to 0.7, which corresponds to increasing the actual Nb/Si mole ratio in the initial mixture from 1.67 to 2.44. Mechanical activation was performed as ten cycles with the total milling time of 10 min.

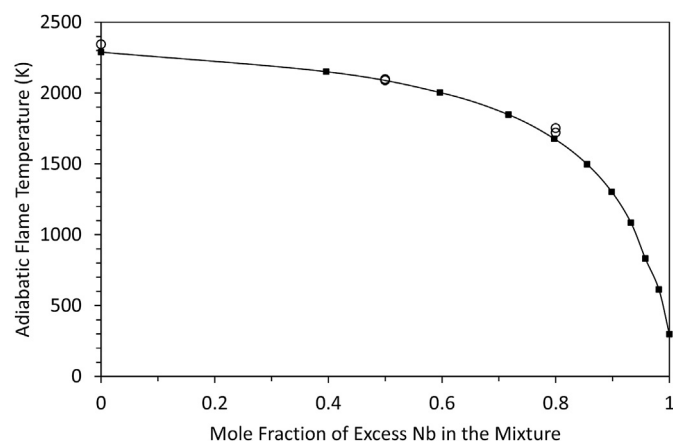


Fig. 7. The adiabatic flame temperature (black squares and the approximating line) and measured maximum temperatures (white circles) vs. the mole fraction of excess Nb in the initial mixture; the two data points at a mole fraction of 0.5 overlap each other.

The initial experiments were conducted without a booster pellet. However, at a certain concentration of Nb, short-circuiting of the tungsten coil by the pellet was noticed, which created an uncertainty in the results due to a longer ignition time and Joule's heat release in the pellet. For this reason, the experiments with excess Nb were conducted with Ti/B (1:2 mole ratio) booster pellets (mass: 1 g). They have shown that increasing the mole fraction of excess Nb to 0.7 has not led to a significant change in the combustion front velocity, which was in the range of 4–5 mm/s for all samples.

The XRD patterns of the products were obtained for all mixtures and compared with that of the product obtained from the stoichiometric (Nb_5Si_3) mixture (Fig. 4). Fig. 8 shows the XRD pattern of products obtained by combustion of a mixture with Nb/Si mole ratio of 2.44, i.e. 70 mol% excess Nb in the expected $\text{Nb}_5\text{Si}_3/\text{Nb}$ mixture. It is seen that, in addition to α - Nb_5Si_3 , γ - Nb_3Si , and Nb_3Si , the peaks of Nb have appeared. XRD patterns of other mixtures show a gradual growth of Nb peaks with adding more Nb (see Fig. S1 – S6 in Supplementary Material). It is also seen that the γ -to- α ratio decreases with increasing more Nb. In addition, β - Nb_5Si_3 was detected in the products obtained from the mixture with Nb/Si mole ratio of 1.70 (Fig. S1 in Supplementary Material). The small peak at 43° , which indicates traces of Nb_3Si , is present in all patterns. It should be noted that the presence of Nb_3Si phase has not been reported in prior research on SHS of Nb_5Si_3 .

Analysis of the SHS experiments described above has shown that the end effects (both the ignition at the top and the heat loss to the support at the bottom) may significantly affect the combustion wave propagation and the product composition. To diminish the

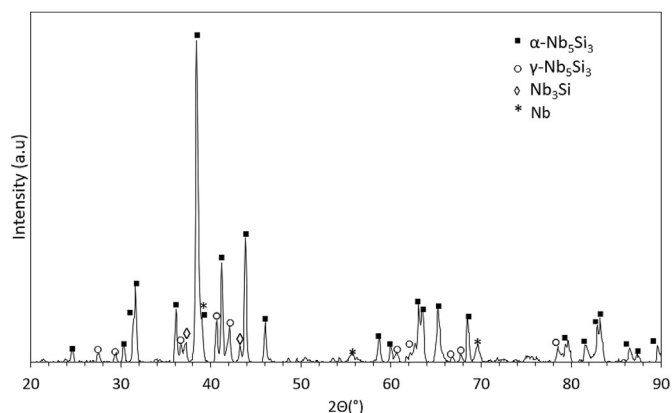


Fig. 8. XRD pattern of combustion products of the mixture with Nb/Si mole ratio of 2.44 (height of the pellet: 10 mm).

end effects, a new series of experiments were conducted where the height of the pellet was increased to 25 ± 2 mm (the diameter remained the same, 13 mm) and the mass of the Ti/B booster pellet was decreased from 1 g to 0.5 g. It is worth noting that the increase in height has led to a higher relative density, 58–70%.

The mixtures with Nb/Si mole ratios of 1.67, 2, and 3 were tested. Note that the ratio of 3 (i.e. 25 at% Si) corresponds to either Nb_3Si or a binary mixture of 20 mol% Nb_5Si_3 and 80 mol% Nb. Fig. 9 shows the images of combustion propagation over the pellets (see also Videos 1–3 in the Supplementary Material). It is seen that adding more Nb decelerates the front propagation. The average velocity of the combustion front propagation was 7 mm/s at Nb/Si = 1.67 and 5 mm/s at Nb/Si = 2. At the Nb/Si mole ratio of 3, a spinning propagation of the combustion wave was observed where hot spots were traveling over the pellet surface and the axial velocity of combustion propagation dropped to 3 mm/s (Fig. 9c). The transition to spin combustion is explained by a lower exothermicity of the

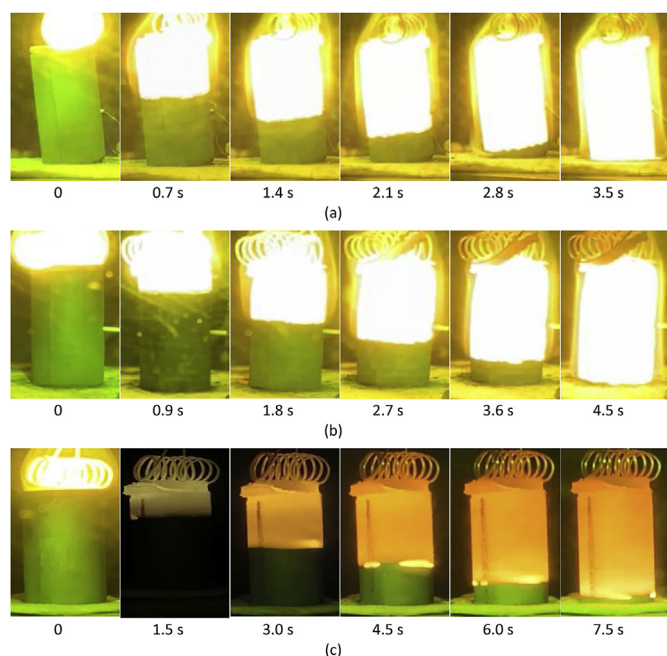


Fig. 9. Images of combustion propagation over Nb/Si mixture pellets (height: 25 ± 2 mm) with Nb/Si mole ratios of (a) 1.67, (b) 2, and (c) 3. Time zero was selected arbitrarily.

initial mixture. Spin combustion of metal/silicon mixtures during MASHS of molybdenum borosilicides has been reported recently [19,20].

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.jallcom.2020.154228>.

For each composition, thermocouple measurements of the temperature in the center of the pellet were conducted during the SHS process. The sample rate was 100 Hz. Fig. 10 shows the measured temperature profiles. The acquisition board shows only the voltage (not the temperature) for a Type C thermocouple, which has a highly non-linear temperature-voltage characteristic. For this reason, the curves show the electromotive force (emf) of the hot junction relative to 0 °C, while the grid lines correspond to the standard temperature-emf relationship for a Type C thermocouple (ASTM E230/E230M – 17). Time “zero” corresponds to the beginning of the temperature rise in each curve.

Thermocouple measurements were conducted in several experiments with the mixture that had Nb/Si mole ratio of 1.67. All emf-time curves exhibited sudden jumps up and down. Apparently, these jumps were caused by interactions between the thermocouple wires and the initial, intermediate, or final products. Note that some of the products (Nb, Nb_5Si_3 , and Nb_3Si) are electrical conductors and some (Si and NbSi_2) could be in the liquid state (the melting point of NbSi_2 is 1935 °C [4]). For clarity, only one of the obtained curves is shown in Fig. 10.

Thermocouple measurements were also conducted with two mixtures that had Nb/Si mole ratio of 2 and with two mixtures that had Nb/Si mole ratio of 3. The curves for Nb/Si = 2 were smooth and similar to each other. The curves for Nb/Si = 3 were also similar to each other; both exhibited fluctuations near the highest point.

The maximum temperatures in the five curves are shown in Fig. 7. It is seen that the measured decrease in the maximum temperature with adding more Nb aligns with the predicted dependence. The obtained data points are close or even higher than the adiabatic flame temperatures calculated for the same mixture ratios. This was surprising because it was expected that heat losses would lead to lower temperatures. The relatively low adiabatic flame temperatures were apparently obtained because of an incorrect value of the standard formation enthalpy of Nb_5Si_3 in the THERMO software database. The used value is -451.764 kJ/mol, or -56.5 kJ/(mole of atoms). The values of this property, calculated by CALPHAD modeling in five different papers, range from -47.7 to -64.8 kJ/(mole of atoms) [21], while the values obtained experimentally are -63.8 ± 11.5 kJ/(mole of atoms) [22] (calorimetry), -64.6 ± 2.4 kJ/(mole of atoms) [23] (calorimetry),

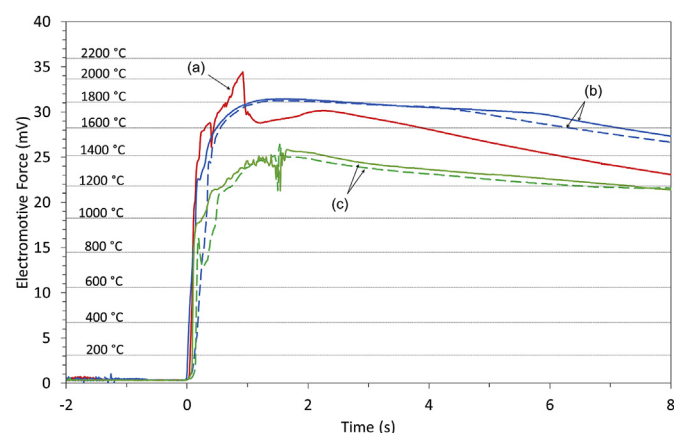


Fig. 10. Temperature records during combustion propagation over Nb/Si mixture pellets (height: 25 mm) with Nb/Si mole ratios of (a) 1.67, (b) 2, and (c) 3.

and -62.2 ± 7.9 kJ/(mole of atoms) [24] (electromotive force measurements). Thus, the formation enthalpy of Nb_5Si_3 used in THERMO is significantly lower (by absolute value) than the experimental values, which explains the low adiabatic flame temperatures obtained in the calculations.

Based on the measured maximum temperatures and combustion front velocities, the apparent activation energy was estimated with the method used in the study on SHS of Nb_5Si_3 with preheating [12]. The obtained value, 60 kJ/mol, is much lower than 259 kJ/mol reported in that study, which reflects the observed strong effect of mechanical activation.

For the SEM and XRD analyses, the product pellets were cut into three parts of equal length. Their analysis has shown that XRD patterns of the top and bottom portions are slightly different from those of the middle parts, which is explained by end effects. For this reason, only XRD patterns and microstructures of the middle parts are shown in the present paper.

Fig. 11 shows SEM images of the products. The products obtained from the mixtures with Nb/Si ratios of 2 and 3 appear to be agglomerates of micron-sized particles, while the Nb/Si = 1.67 mixture also contains large particles of a uniform material with few pores (see Fig. 11d). This difference can be explained based on the temperature measurements and the Nb_5Si_3 formation mechanism [16]. As mentioned in the Introduction, this mechanism includes, as the first step, the formation of NbSi_2 , which then reacts with solid Nb. Since the temperature exceeded the melting point of NbSi_2 , 1935 °C, during combustion of the Nb/Si = 1.67 mixture (see Fig. 10), the formed NbSi_2 phase was in the liquid state, which apparently led to the formation of large particles such as the one seen in Fig. 11d.

Fig. 12 shows the XRD pattern of the products obtained by combustion of the mixture with Nb/Si mole ratio of 1.67. As compared with the product obtained by combustion of a shorter pellet of the same mixture (see Fig. 4), new peaks appeared, and they belong to the β phase of Nb_5Si_3 . The appearance of the β phase may be explained by a higher temperature generated in the middle portion of the 25-mm-high pellet during combustion. Indeed, the maximum temperature measured in the experiment with this mixture (Fig. 10) was 2071 °C, i.e. well above the α - β transition temperature, 1935 °C [4].

Fig. 13 shows the XRD pattern of the products obtained by combustion of the mixture with Nb/Si mole ratio of 2. It is seen that the β phase disappeared. This correlates with the thermocouple measurements, which showed maximum temperatures of 1816 and 1824 °C. Both of these are over 100 °C below the α - β transition

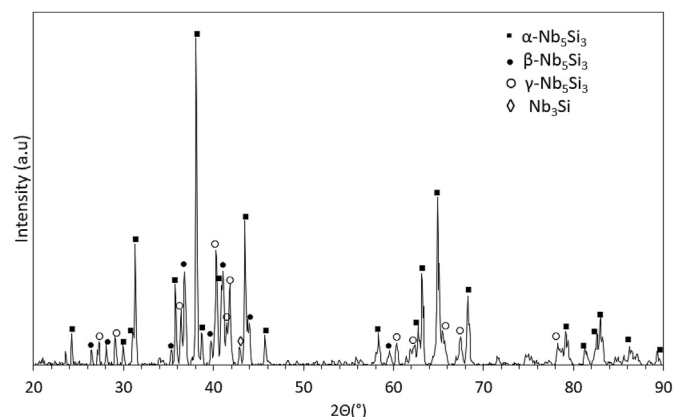


Fig. 12. XRD pattern of combustion products of the mixture with Nb/Si mole ratio of 1.67 (height of the pellet: 25 mm).

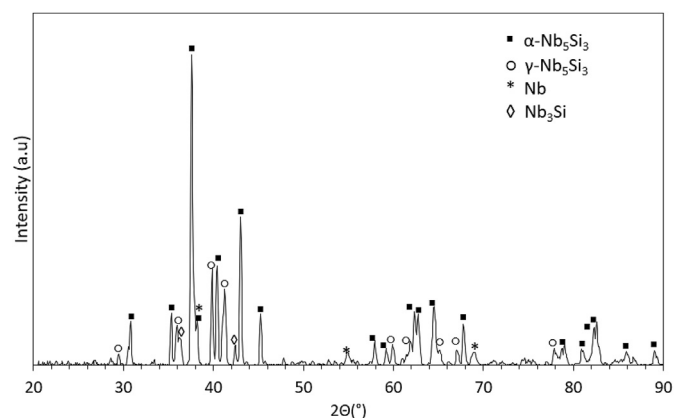


Fig. 13. XRD pattern of combustion products of the mixture with Nb/Si mole ratio of 2 (height of the pellet: 25 mm).

temperature. Instead, Nb is now present, so the products include α - Nb_5Si_3 , γ - Nb_5Si_3 , Nb, and traces of Nb_3Si . The product composition is apparently close to 50 mol% Nb_5Si_3 (both α and γ phases) and 50 mol% Nb.

Finally, Fig. 14 shows the XRD pattern of the products obtained by combustion of the mixture with Nb/Si mole ratio of 3. The content of Nb clearly increased, while the apparent peak of Nb_3Si

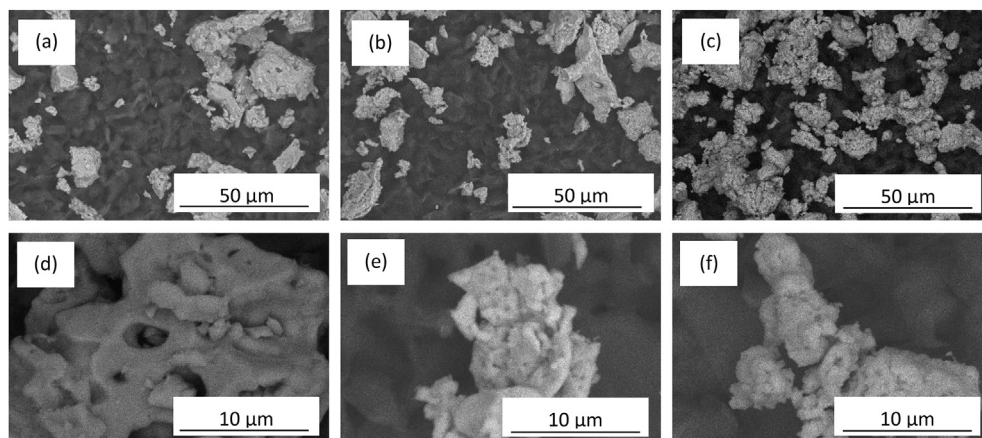


Fig. 11. SEM images of products obtained from mixtures with Nb/Si mole ratios of (a, d) 1.67, (b, e) 2, and (c, f) 3.

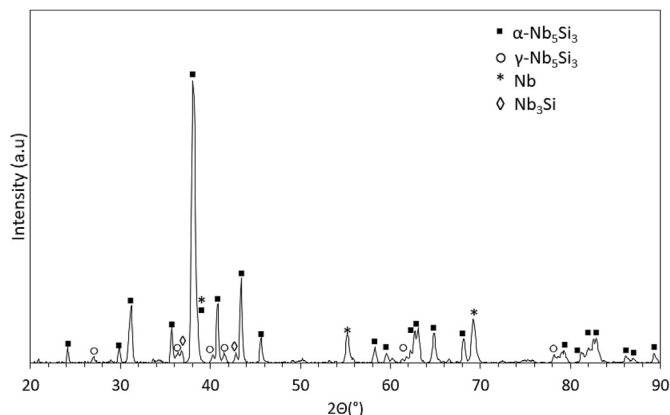


Fig. 14. XRD pattern of combustion products of the mixture with Nb/Si mole ratio of 3 (height of the pellet: 25 mm).

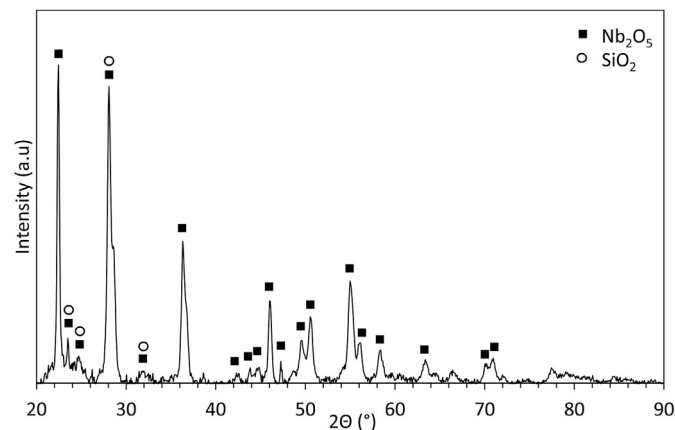


Fig. 15. XRD pattern of combustion products of the mixture with Nb/Si mole ratio of 1.67 after oxidation in TGA.

remained about the same. It is also notable that the peaks of the γ phase became much smaller. The γ -to- α peak intensity ratio was 0.35 and 0.31–0.32 at Nb/Si mole ratio of 1.67 and 2, respectively, and it dropped to 0.03–0.05 at Nb/Si = 3. Clearly, α -Nb₅Si₃ and Nb are dominant phases. Although the mole ratio of 3 corresponds to Nb₃Si, the actual composition is apparently close to 20 mol% Nb₅Si₃ (primarily the α phase) and 80 mol% Nb.

Since the γ phase of Nb₅Si₃ has poor mechanical properties, the MASHS of Nb₅Si₃–Nb composite with a low content of the γ phase is an important result. The decrease in the content of γ phase correlates with decreasing the combustion temperature. Indeed, the measured combustion temperature of the mixture with Nb/Si mole ratio of 3 is less approximately by 500 K than for the Nb/Si = 1.67 mixture and by 300 K than for the Nb/Si = 2 mixture (see Fig. 7). The lower exothermicity of the mixture and the lower temperature lead to the spinning mode of the combustion wave propagation, which is characterized by a lower axial velocity of the front propagation and, accordingly, by a longer duration of the SHS process. The decrease in the yield of the γ phase with increasing the process time implies that the γ phase is metastable, as suggested in Ref. [4], in contrast with the computational study [5].

3.3. Strength and oxidation resistance of Nb₅Si₃ and Nb₅Si₃/Nb composites obtained by MASHS

Handling of the pellets obtained by combustion of mixtures with various Nb/Si mole ratios and crushing them for XRD analysis have shown that the addition of extra Nb to the mixture apparently makes the products stronger. To verify these observations, the compressive strength of the product pellets (diameter: 6 mm) was measured. At the mole ratios of 1.67, 2, and 3, the compressive strength was 78 MPa, 211 MPa, and 169 MPa, respectively. Niobium silicide-based alloys, obtained by conventional metallurgical methods, exhibited compressions strengths over 1500 MPa at room temperature [2]. Therefore, the MASHS products without additional consolidation can hardly compete with them in applications where high strength is required. However, they may be sufficiently strong for various chemical engineering applications. To increase the strength, the materials could be consolidated using hot pressing or spark plasma sintering. In addition, the synthesis could be conducted in the so-called SHS compaction mode, i.e. in a special die with pressing immediately after the synthesis [17,19].

It should be noted that the mixture with Nb/Si mole ratio of 3 burned in the spin combustion mode (see Fig. 9c). The unsteady propagation of the combustion wave over a low-exothermic

mixture may occur in either pulsating or spinning mode [25,26]. Both are usually considered as undesirable combustion modes that may lead to instabilities and non-uniform products. It is thus remarkable that spin combustion of the mixture with Nb/Si mole ratio of 3 led to the formation of a relatively uniform and strong product.

To examine the oxidation resistance of the products obtained by combustion of mixtures with Nb/Si ratios of 1.67, 2, and 3, TGA tests were conducted in O₂/Ar flow, where the samples were heated up to 1000 °C. Prior to the tests, the products were ground to powders using agate mortar and pestle. Fig. 15 shows the XRD pattern of the Nb₅Si₃ product after oxidation (the XRD patterns of oxidized products obtained using the mixtures with excess Nb are similar). Here, Nb₂O₅ includes both orthorhombic and monoclinic phases. A small peak at 39° may indicate the presence of non-oxidized Nb, but it could also belong to Nb₂O₅. Elemental Si has the most intensive lines at around 28°, followed by the lines at 47° and 56°. Since these lines overlap with strong lines of Nb₂O₅, it is difficult to determine whether there is a non-oxidized Si in the sample. In any case, it is clear that the products were heavily oxidized. XRD patterns of oxidized products, obtained from two other mixtures, are similar (see Figs. S7 and S8 in the Supplementary Material).

Fig. 16 shows the TG curves obtained at heating rates of 1 °C/min and 10 °C/min, while Table 2 presents the temperature that corresponds to 50% of the mass change, the measured mass change,

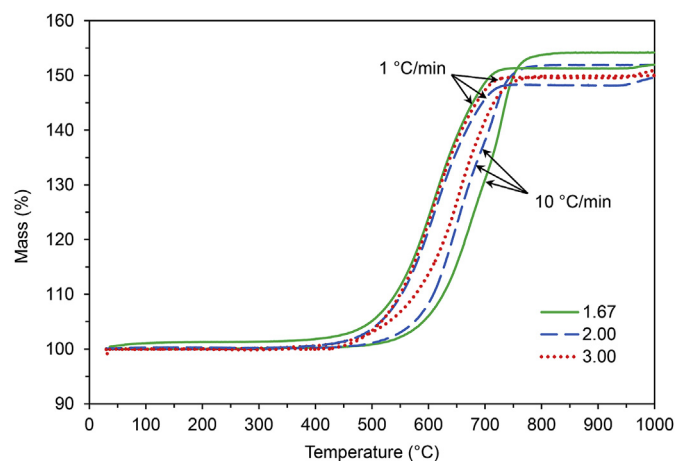


Fig. 16. TG curves for oxidation of products obtained by combustion of Nb/Si mixtures with Nb/Si mole ratios of 1.67, 2, and 3 (height of the pellet: 25 mm).

Table 2

Thermogravimetric parameters for oxidation of products obtained by combustion of Nb/Si mixtures.

Nb/Si Mole Ratio	Temperature at 50% of the Mass Change		Experimental Mass Change		Theoretical Mass Change
	10 °C/ min	1 °C/ min	10 °C/ min	1 °C/ min	
	°C	°C	%	%	
1.67	688	606	54.2	51.9	53.9
2	660	610	51.9	49.6	52.4
3	645	607	49.9	50.9	49.5

and the theoretical mass change calculated for full oxidation of these products to Nb_2O_5 and SiO_2 . It is seen that the difference between the measured and theoretical values of the mass change is within 5%, which indicates that full oxidation took place. For all compositions and heating rates, the oxidation starts at about 500 °C and is complete at about 700 °C. Testing small pieces of the product pellets with no grinding produced similar results.

For comparison, TGA oxidation tests were also conducted with the initial Nb/Si mixtures. Fig. 17 shows the obtained TG curves. It is seen that oxidation occurred sharply upon reaching a temperature of about 470 °C. Therefore, the oxidation of the obtained materials required higher temperatures than for the initial components and was occurring at a lower rate. However, the products were fully oxidized at about 700 °C. Additives and protective coatings [1–3,27–30] are necessary for improving the oxidation resistance of the $\text{Nb}_5\text{Si}_3/\text{Nb}$ composites obtained by MASHS.

4. Conclusions

Mechanical activation in a planetary ball mill at 1000 rpm has enabled SHS of Nb_5Si_3 with no preheating. At a milling time of 2–5 min, the SHS products contained NbSi_2 and Nb in addition to the desired Nb_5Si_3 . When the milling time was 10 min or longer, these impurities were not detected, and the product consisted of Nb_5Si_3 with traces of Nb_3Si . In prior research on MASHS of Nb_5Si_3 , where a shaker mill at 875 cycles/min was used, the required milling time was longer by an order of magnitude. Thus, a planetary mill is more effective for MASHS of Nb_5Si_3 than a shaker mill.

For the first time, $\text{Nb}_5\text{Si}_3/\text{Nb}$ composites have been obtained by MASHS with no preheating. MASHS was conducted at a milling time of 10 min. Combustion took place at an Nb/Si mole ratio as high as 3, i.e. at 25 at% Si in the mixture. At this mole ratio, a

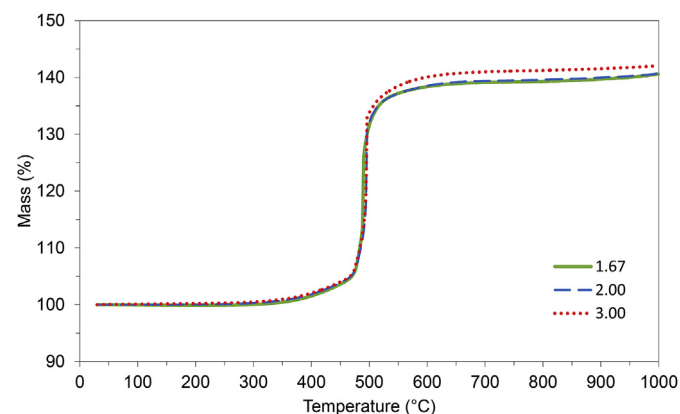


Fig. 17. TG curves for oxidation of the initial Nb/Si mixtures with Nb/Si mole ratios of 1.67, 2, and 3.

spinning propagation of the combustion wave was observed, which is explained by a low exothermicity of the initial mixture.

The products obtained by combustion of a mixture with Nb/Si ratio of 2 contained α and γ phases of Nb_5Si_3 as well as Nb and some amount of Nb_3Si . The β phase was not formed because the reaction temperature was lower than the α - β transition point. The increase in Nb/Si ratio to 3 significantly decreased the content of the γ phase, which may be associated with its metastability and the long duration of the occurring spin combustion process.

The obtained porous products had a compressive strength of approximately 100–200 MPa. Thermogravimetric analysis in an O_2/Ar environment has shown full oxidation; the oxidation starts at about 500 °C and is complete at about 700 °C. Therefore, for use at temperatures over 500 °C, the oxidation resistance of these materials has to be improved by additives and protective coatings.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Reina Trevino: Investigation, Visualization, Writing - original draft. **Edgar Maguregui:** Investigation. **Frank Perez:** Investigation. **Evgeny Shafirovich:** Conceptualization, Funding acquisition, Methodology, Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jallcom.2020.154228>.

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