JOURNAL OF MATERIALS SCIENCE **34** (1999) 1477–1482

Effect of partial mechanical alloying on the self-propagating high-temperature synthesis of Ni_3Si

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Self-propagating high-temperature synthesis (SHS) is a new method for economical processing of intermetallic compounds and ceramic materials, as well as composites based on them. On the other hand, mechanical alloying is an effective method for producing highly metastable and, therefore, reactive metal powders. In this paper an overview of partial mechanical alloying is given. The effect of partial mechanical alloying on the self-propagating high-temperature synthesis of Ni_3Si-compounds is studied. The influence of alloying time on powder characteristics, e.g. particle size distribution, is given. The effect of alloying time on the properties of Ni–Si composite powders and on the characteristics of the SHS process, e.g. propagation rate, is reported. Ni_3Si was chosen as the object for this study because of its corrosion and high-temperature oxidation resistance. Like other $L1_2$-type compounds, the strength of Ni_3Si shows an anomalous behaviour as a function of temperature, therefore, it has potential for high-temperature applications. © *1999 Kluwer Academic Publishers*

1. Introduction

The main interest in the field of silicides is focused on $MoSi_2$, because of its excellent high-temperature oxidation resistance. In this paper, the focus is on nickel silicide, Ni_3Si, which is also a potential high-temperature structural material. While $MoSi_2$ is more or less a ceramic material, Ni_3Si can still be characterized as a metallic compound, resulting from the difference in the bonding nature of these compounds [1].

Ni_3Si is a $L1_2$-structured (ordered face centred cubic (fcc), Cu_3Au prototype) intermetallic (metal–metalloid) compound. Like other $L1_2$-type compounds, it possesses an anomalous yield strength as a function of temperature [1]. It is reported to have an excellent corrosion resistance against sulphuric acid and aqueous sulphur dioxide solutions. The high-temperature oxidation resistance of Ni_3Si is good, because of the high silicon content [2]. Mechanical properties of the intermetallic compounds are usually influenced by the ordering effect. The nearer the structure of a material is to perfect long-range order (LRO) the smaller is the symmetry of the crystal and the higher is the strength [3]. The brittleness, which is characteristic for Ni_3Si compounds, can somewhat be improved by Ti-alloying and by B-microalloying, but not entirely without decreasing the LRO (at least the ordering kinetics), which has a noticeable effect on strength [4].

Self-propagating high-temperature synthesis is a promising method for producing intermetallic compounds. In the SHS process the time at high temperatures is short. This has a positive influence on the properties of the product in comparison to other materials-production methods, which include total melting or long annealing times at high temperatures [5]. Even compounds with only moderate properties (as compared with the best conventional materials) may be effectively produced by SHS, because of its flexible nature and its positive effect on the mechanical properties. The method is economical, because no external energy or expensive high-temperature furnaces are needed.

In the SHS process elemental or compound powders are mixed and then cold compacted to a density of 50–80% of the theoretical value. After ignition, the reaction propagates through the powder mixture at a rate of 1–20 $mm\,s^{-1}$. Immediately after reaction, the hot material is compacted by mechanical pressing. Without pressing, porous materials can be produced: compound-based powders can be produced by crushing these sponges. The reaction enthalpy has to be high enough to ensure ignition and propagation of the reaction. If the heat evolved in the reaction zone is insufficient to heat the powder ahead of the reaction front to the ignition temperature, the reaction is not self-sustaining. The second important process parameter is the propagation rate of the reaction [5]. Too high a propagation rate is avoided because of rapid gas formation and subsequent powder blow-out. On the other hand too low a propagation rate makes it difficult to keep the temperature high enough at the surface until the reaction front has reached the bottom of the powder lot.

By mechanical alloying (MA) the thermodynamic properties and the reaction kinetics of metal powders can be modified. MA is a process in which the starting powders are effectively mixed together by high energy ball-milling. Mechanically, the process involves repeated cold deformation, welding and fracture. During this kind of process phase evolution and phase transformation can occur. The low processing temperatures lead to formation of metastable phases [6].

1.1. Partial mechanical alloying

Partial mechanical alloying is a novel and, therefore, rarely used method that is intermediate between conventional mechanical alloying and simple mechanical mixing. In partial mechanical alloying, the process in taken into a stage where a lamellar composite structure is formed into the powder particles. Mechanical alloying is stopped before complete homogenization is reached. By partial mechanical alloying, intimate contact between the alloyed elements can be achieved, avoiding the eventual reactions and phase transformations of milled materials.

The reactivity of the processed materials is an essential feature in the SHS process. By partial MA, the enthalpy, ΔH, of the reaction may be increased and the reaction propagation rate also increased. The reaction ignition becomes easier as a result of these two facts. This improvement originates from the well known fact that MA causes disturbances in milled material's microstructure. MA introduces disordering, decreases grain size, increases dislocation density and produces mechanical stresses, which all cause divergence from the thermodynamically stable state [7]. The extra energy, or enthalpy, can be called disorientation energy or mechanical energy, although actually it can be addressed to the increase of grain boundary energy and similar phenomena. The higher propagation rate is actually related more to the distance between reacting elements than to the thermodynamical metastability of the powder itself. If reasonably low MA efficiencies are used, scaling up to an industrial process can be easily carried out as compared with high energy ball-milling MA in efficient laboratory mills.

Reactive plasma spraying of partially alloyed Ni_3Si powders is reported elsewhere [8]. Enhanced reactivity of mechanically alloyed Ni–Si powders was verified by the fully dense coatings obtained by reactive plasma spraying. The partially alloyed powders have also shown increased reactivity during the opening of alloying vials. These observations were significant, because in earlier studies SHS production of Ni_3Si has not been reported to be possible without high preheating temperatures.

2. Experimental procedure

Self-propagating high-temperature synthesis is commonly performed by using mixed elemental powders. However, in our study partially mechanically alloyed elemental powders were used to modify SHS parameters such as the rate of reaction propagation and the adiabatic temperature T_{ad}. Strictly, the adiabatic temperature cannot be changed considering only the heat of formation, but some extra heat is evolved during reaction by disorientation energy. Partially MA-processed powders consist of particles with lamellar composite microstructure, whereas in mixed powders the elements are still in separate particles.

Near-stoichiometric Ni_3Si composition (13.4 wt % Si) was used to examine the reactivity and the SHS behavior of Ni_3Si intermetallic compound. However, Ti alloying was earlier discovered to retard the ordering of Ni_3Si: therefore, it was expected to have an effect on other mechanical properties, i.e. ductility. Ti alloying may have a positive effect on SHS characteristics because of the higher heat of formation of $Ni_3(Si, Ti)$ compounds compared with the pure Ni_3Si compound, as noticed in this study.

Experiments with different MA times were carried out on the stoichiometric composition (24.4 at %) of Ni_3Si. A planetary ball mill (Fritsch pulverisette 5) and hardened steel balls were used with a ball to powder ratio of 10 : 1. Rotational speeds varying from 160 to 200 r.p.m. were used to ensure controlled processing. All the milling experiments were carried out in argon atmosphere and no process controlling agents were used.

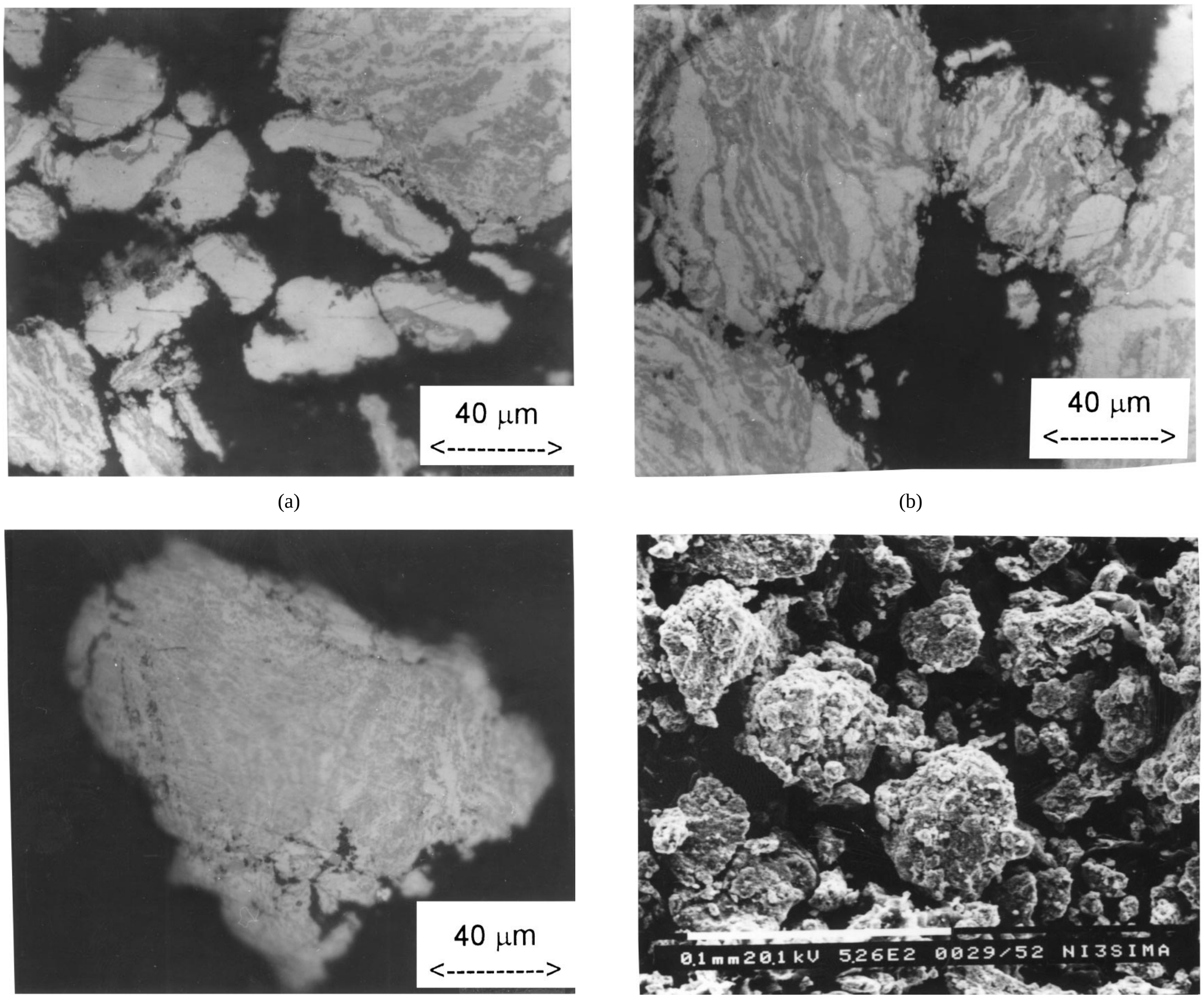
The propagation rate and the adiabatic temperature of the SHS reaction were measured from both cold-pressed powder compacts and from some uncompacted powders inside insulating material using K-type thermoelements. The ignition was performed by a heating coil (Kanthal) heated with an electrical transformer. The size of the cold-pressed compacts was $10 \times 10 \times 70$ mm.

Finally, the partially mechanically alloyed powder was packed in a steel mould to a green density of 40–50% of the theoretical value prior to ignition. After the reaction zone had propagated through the whole precompact, it was densified using a hydraulic press with a pressure of 100 MPa. The time delay between reaction completion and pressing was 3–7 s.

The powders were characterized after milling by optical and scanning electron microscopy (SEM), X-ray diffraction (XRD) with CuK_{α} radiation and by laser diffraction (Sympatec Helos) particle size analysis. The SHS compacts were characterized by XRD and optical microscopy. Both powders and compacts were chemically analysed by energy disperisve spectroscopy (EDX).

3. Results

During mechanical alloying the microstructure of Ni–Si powder particles changed gradually from particles



(a) (b)

(c) (d)

Figure 1 Optical micrographs of the cross-sections of the Ni–Si powder particles mechanically alloyed for 1, 2 and 6 h at 160 r.p.m. (a–c, respectively). The darker phase corresponds to silicon and the lighter to nickel. The samples are unetched. (d) SEM micrograph showing the particle morphology of the powder alloyed for 6 h. Magnifications: (a), (b) and (c) ×465; and (d) ×526.

stuck together to a lamellar composite particle microstructure. Homogenous supersaturated solutions of Ni and Si could have been produced, if the milling had been continued sufficiently long. Fig. 1 presents cross-sectional optical micrographs of Ni–Si particles milled for 1, 2 and 6 h. The evolution of the microstructure as a function of milling time is clearly visible. Fig. 1d presents a scanning electron micrograph of the powder milled for 6 h.

The particle size analysis data of alloyed powders are summarized in Fig. 2. In the figure the 50% cumulative volume distribution level (in micrometres) is presented as a function of MA time. The particle size first increases at the beginning of milling and then decreases during continued milling. The influence of milling time on the phase structure of the powder is presented in the XRD patterns of Fig. 3. Silicon starts to dissolve in nickel right at the beginning of MA. Peaks tend to broaden slightly, indicating a reduction of grain size. In some cases the formation of the compound mixture $Ni_3Si + Ni_{31}Si_{12}$ has occurred during milling with 200 r.p.m. after 5 or 6 h. No compound formation was noticed when milling with a rotational speed of 160 r.p.m.

A differential thermal analysis (DTA) scan was taken for non-alloyed and for 4-h mechanically alloyed powder in order to verify the effect of alloying time on the SHS of the powders. The exothermic peak seen in the curve of the non-milled powder mixture was not

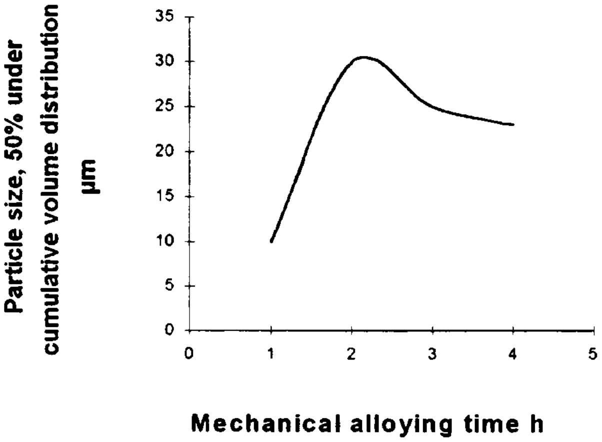


Figure 2 The particle size (50% cumulative volume distribution) of mechanically alloyed Ni–Si powders as a function of milling time (200 r.p.m.).

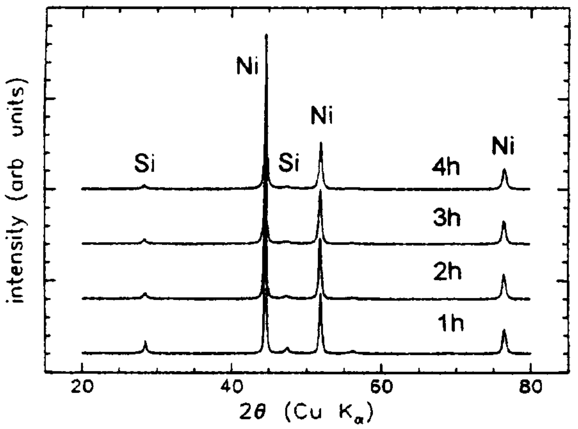


Figure 3 XRD patterns of Ni–Si powders mechanically alloyed for 1, 2, 3 and 4 h (from bottom to top). Powders were alloyed in argon gas using a rotational speed of 200 r.p.m.

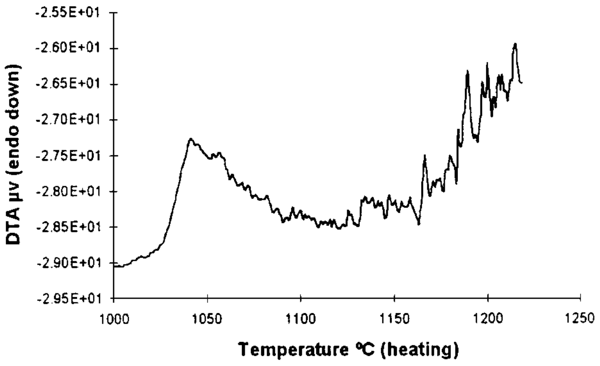


Figure 4 DTA curve for heating non-milled Ni–Si powder mixture (heating rate, 5 °C min^{-1}).

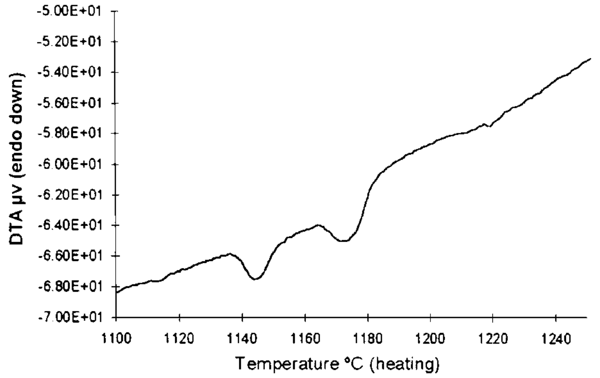


Figure 5 DTA curve for heating 3-h milled Ni–Si powder mixture (heating rate, 5 °C min^{-1}).

visible anymore after 3-h of milling. Only for endothermic peaks can corresponding phase transitions be seen. The DTA scan of non-milled powder is presented in Fig. 4. The DTA scan of 3-h milled powder is presented in Fig. 5. These DTA scans were measured using a heating rate of 5 °C min^{-1}.

The SHS experiments of mechanically alloyed Ni–Si powders revealed that MA is essential for enabling SHS processing at room temperature. The unalloyed or 1- to 2-h milled powders did not react when being heated with a high temperature glow wire. Powders ignited very easily and the reaction propagation rate was higher as compared with conventional SHS after several hours of milling. Normal reaction propagation rates in SHS are considered to be of the order of 10 mm s^{-1}. Propagation rates of the order of 40 mm s^{-1} were measured for alloyed powders in some cases.

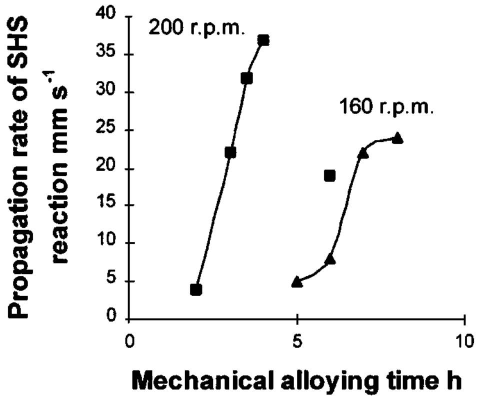


Figure 6 The propagation rate of the SHS reaction as a function of MA time in the Ni_3Si system at two milling intensities (r.p.m. of the planetary ball mill).

The enhancing influence of MA time on the SHS propagation rate was fairly linear for 200 r.p.m. alloying up to 5 h of milling. After 6 h the propagation rate started to decrease rapidly. Powders milled for 7 h or more at 200 r.p.m. did not ignite at all. When 160 r.p.m. milling was used the ignition behavior had the same tendency but the influence was much slower. A 20% decrease in milling efficiency (decrease of rotation speed from 200 to 160 r.p.m.) decreased the effect of milling on the propagation rate by about 50%. The influence of MA time on the propagation rate is presented in Fig. 6.

Mechanically alloyed powders are more reactive than unalloyed powders and, therefore, they need not be preheated, as all unalloyed powder. Even a small amount of preheating has a considerable effect on the propagation rate. The propagation rate was nearly doubled when preheating temperatures of the order of 200 °C were used. A preheating temperature of 300 °C seems to be the maximum for preheating these Ni–Si MA powders. The reaction ignites during heating, if higher temperatures are used.

The influence of MA time on the measured peak temperature of the reaction was not as drastic as on the propagation rate. The measured peak temperatures do not necessarily correspond to the adiabatic temperature of the material, because the temperature was measured on the surface of the reacting material. Inside the material the temperature can be expected to be higher than on the surface. The measured maximum temperatures were of the order of 900–1000 °C for pure Ni_3Si and 950–1050 °C for Ti-modified Ni_3Si. During these SHS powder experiments, only slight sintering took place because no pressure was applied after reaction.

The propagation mode was noticed to correlate with propagation rate and milling time. Propagation of the reaction front at a speed of 10 mm^{-1} s was quite stable. However, the slower reaction fronts did not propagate at a constant rate. They propagated at a fluctuating (oscillating) rate in intervals of 1.5–2.5 mm. This was measured by studying different layers in the reacted material. In the case of the slowest propagation, the reaction front did not proceed only in the direction of the rod. Instead it rotated around the rod and the propagation distance along the rod axis was only about 1 mm during a circle.

The powders alloyed for several hours ignited easily. The reaction started after a very short heating with a Kanthal coil. Shorter alloying times resulted in more difficult ignition: higher temperatures and longer heating times were needed. Powders that reacted during mechanical alloying, or that were alloyed only for a short time, did not ignite at all; not even when heated with a white glowing coil.

The tests performed with the non-precompacted powders resulted in about 30% lower propagation rates as compared with precompacted powders. Reaction temperatures up to 1150 °C were measured for non-compacted powders. The peak reaction temperatures for non-precompacted powders were higher than those for the compacts, because the junctions of the thermoelements were buried inside the powder where the thermal losses were smaller than on the surface.

A dense SHS material was produced using powder milled for 6 h (160 r.p.m.). The powder was packed in a cylinder-shaped steel mould ($\phi = 70$ mm) with a compaction pressure of 5.2 MPa. After reaction the material was compacted with a pressure of 52 MPa. The peak reaction temperature was about 1250 °C. The value was higher than in laboratory tests because of the larger amount of reacting material and consequently smaller thermal losses. The SHS compacted material consisted mainly of Ni_3Si and $Ni_{31}Si_{12}$ phases. Its density was about 99% of the theoretical value, except for a 5 mm thick layer on the surface that was more porous. The $Ni_{31}Si_{12}$ phase could be transformed into Ni_3Si by annealing. The XRD pattern of the SHS compacted material is presented in Fig. 7 and an optical micrograph in Fig. 8. According to chemical analysis, the composition of the compact was the same as the initial composition of the powder.

4. Discussion

During initial mechanical alloying of Ni–Si powder mixtures a fine layered composite microstructure was formed in powder particles. During mechanical alloying no compound formation occurred before 6-h milling at 200 r.p.m. Only the formation of a supersaturated solution of silicon in nickel was observed. The observed influence of mechanical alloying on the ignition and propagation rates was based on the decreasing diffusion distance between reacting elements. Less diffusion was needed to bring the components together and, therefore, the reaction zone propagated more rapidly after alloying. The increased internal energy level of the milled powders eased the ignition and had a positive effect on the propagation rate. The dissolution of silicon to nickel and the disturbance of the crystal structure resulting from MA having an opposite influence on the adiabatic temperature. Mutual dissolution of elements decreases the formation energy of the intermetallic compound. The adiabatic temperature originates mainly from the heat of formation of the compound, but dissolution itself is an exothermic reaction. Therefore, the adiabatic temperature of the partly dissolved elemental powder is lower than it would be for a purely elemental composite powder. On the other hand, the extra energy related to the high lattice defect content in the MA powder increases total enthalpy. Then the cumulative net effect is small. The maximum allowable alloying time regarding reactivity is reached when a significant part of the mechanically alloyed powder has already reacted. These reactions may include compound or solid solution formation, and the metastable energy state is hence relaxed. After this maximum MA time, reactivity starts to decrease rapidly. If milling is continued after this point the reactivity is entirely lost (the stable state is already reached during milling).

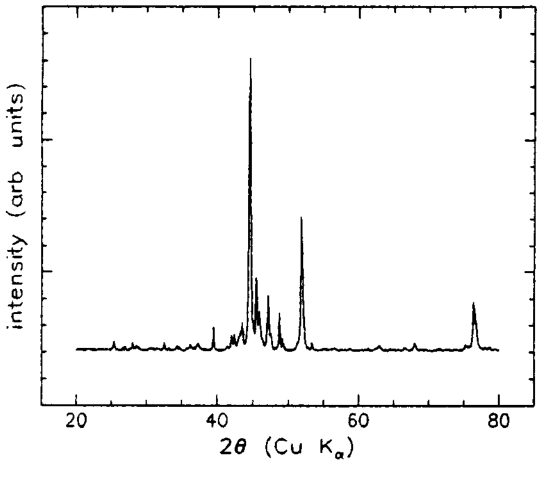


Figure 7 The XRD pattern of SHS processed Ni_3Si-type material. Major peaks correspond to the Ni_3Si phase. Minor peaks between 40 and 50 2θ values correspond to the $Ni_{31}Si_{12}$ phase.

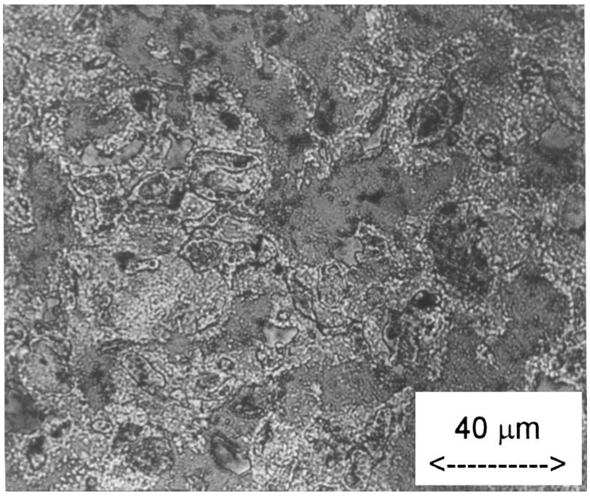


Figure 8 Optical micrograph of SHS processed Ni_3Si-type material. Darker areas correspond to Ni_3Si and lighter areas to $Ni_{31}S_{12}$ (magnification ×465).

DTA measurements indicate that reactivity decreases as a function of MA time. On the other hand, SHS experiments suggest the opposite. Only non-milled powders reacted in DTA at a specific temperature; milled powders did not give any peaks during DTA testing. This discrepancy can be explained by a difference in the reaction mechanisms. During the slow heating in DTA there is enough time for diffusion and no significant heat evolution occurs. Reaction does occur, but not at any particular temperature, and the heat is released during a long period of time. In SHS the high temperature and the rapid temperature increase make the reaction rate so high that all the material reacts practically at a constant temperature at the reaction front. DTA is not the best possible method of studing the reactivity of this kind of powder.

The effects of precompaction and preheating can easily be understood. Precompaction alters the heat conduction characteristics and decreases the relative heat losses. Therefore, reaction propagates more easily. Preheating increases the adiabatic temperature, like in the SHS of the conventionally mixed powder. MA seems to decrease the ignition temperature below the level characteristic of conventional SHS. This can be related to the metastable energy brought in by MA, hence it lowers the activation energy of the SHS reaction. The ignition temperature may also be influenced by the increase in vacancy content and dislocation density caused by mechanical alloying. These lattice defects enhance the diffusion rate and, therefore, enable ignition at lower temperatures.

After SHS reaction the structure does not consist totally of the desired Ni_3Si phase. It contains a clearly noticeable amount of $Ni_{31}Si_{12}$ phase. This originates from the higher formation temperature of the $Ni_{31}Si_{12}$ phase as compared with the Ni_3Si phase. As the temperature decreases from the reaction temperature, $Ni_{31}Si_{12}$ remains in the material as a metastable phase. The decomposition reactions of the $Ni_{31}Si_{12}$ phase and high temperature Ni_3Si phases, β_2 and β_3, may be beneficial by releasing latent heat, which enhances the densification of the material. The released latent heat may cause so-called mushy zones, which are widely considered as beneficial during sintering. This was especially noticed when the powders were thermally sprayed to form a coating.

The SHS tendency of an alloy can be enhanced by MA in cases where the adiabatic temperature is not high enough to sustain a self-propagating reaction. Thermodynamic balance and the reaction kinetics of the system can be controlled by preparing a proper mixture of already reacted stable phases and reactive material. An example is the group of functionally gradient materials. By modifying the SHS characteristics of powders by mechanical alloying the inhomogeneous propagation rates of functionally gradient materials can be balanced. Furthermore, by MA the propagation rate of the SHS reaction can be increased and more uniform compacts be produced.

5. Conclusions

Mechanical alloying of an Ni–Si powder mixture, with the composition of the intermetallic compound Ni_3Si, can be used to enhance and optimize the reactivity of the system in order to achieve better quality SHS compacts. Self-propagating high-temperature synthesis of Ni_3Si is difficult, if not totally impossible, without mechanical alloying. In the present study the propagation rate of the reaction is influenced by MA. The maximum observed propagation rate was 40 mm s^{-1}. The ignition became easier as the reactivity increased due to MA. Increasing reactivity lowered the threshold temperature where reaction starts and therefore decreased the need for preheating.

Mechanical alloying for 6–6.5 h in a planetary ball mill at 160 r.p.m. and under argon atmosphere was found to be suitable for optimizing the reactivity of the Ni_3Si powder mixture for SHS processing. The reaction propagation rate was then of the order of 15 mm s^{-1}. A 99% dense, one-piece compact with a diameter of 70 mm and thickness of 20 mm was produced by SHS and subsequent compaction of such MA powder.

The compact consisted of Ni_3Si and $Ni_{31}Si_{12}$ phases, where the $Ni_{31}Si_{12}$ phase was embedded as separate islands in the Ni_3Si matrix. By annealing, the $Ni_{31}Si_{12}$ phase could be transformed to a Ni_3Si phase.

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Received 20 April
and accepted 3 September1998