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# Spin combustion in the nickel–silicon system

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The combustion synthesis of five Ni–Si phases was investigated. Without preheating, samples corresponding to the initial stoichiometries $Ni_3Si$, $Ni_5Si_2$, $Ni_3Si_2$, and NiSi sustained a self-propagating combustion mode which advanced in a spin mode. With preheating ( > 500 °C), the sample combusted in a steady-state mode. Average combustion wave velocities and frequencies of spin showed maxima at a composition of 33 at% Si. The combustion temperature showed a maximum at a composition in the range of 33–40 at%. In contrast, the ignition temperature showed a minimum at a composition of 33 at%. X-ray analyses showed that in all cases, the product of combustion was multi-phase with the primary phase corresponding to the initial stoichiometry of the reactant.

## 1. Introduction

Interest in intermetallic compounds and those between metals and metal-like elements has been largely motivated by their attractive high-temperature mechanical properties and oxidation and corrosion resistance. Although these materials are still primarily prepared by conventional methods, numerous investigations have been made to assess the feasibility of preparing such compounds by the self-propagating high-temperature synthesis method [1–4]. In this method, materials are synthesized in a reaction (combustion) wave as it propagates through the reactant powder mixtures. The characteristics, advantages, and limitations of this method of synthesis are detailed in two recent review articles [5, 6]. The propagation of the combustion wave depends on the exothermicity of the reaction; highly exothermic reactions give rise to fast moving waves with constant velocities. In contrast, weakly exothermic reactions are generally not capable of sustaining themselves in the form of a combustion wave. Between these two extreme cases, i.e. for reactions with intermediate enthalpies, the propagation of the wave can assume a non-steady state mode where the front propagates in a pulsating fashion or along a spin path [6]. Reactions between nickel and silicon are examples of the spin mode of combustion. The present study focuses on the effect of stoichiometry (Ni/Si ratio) on the nature of the combustion process in the Ni–Si system.

Interactions between nickel and silicon lead to the formation of six compounds as seen in Fig. 1. These compounds, their enthalpies of formation [7], and melting temperatures are listed in Table I.

## 2. Experimental methods

Nickel powders, with a reported purity of 99.9% and a particle size in range of 3–7 μm, and silicon powders with a 99.5% purity and a particle size classification of − 325 mesh ($\leqslant$ 44 μm), were used in this study. Powders, in weight proportions corresponding to the compounds $Ni_3Si$, $Ni_5Si_2$, $Ni_2Si$, $Ni_3Si_2$, and NiSi, were mixed and pressed into cylindrical compacts of 20 mm diameters and 30 mm heights. By varying the applied hydrostatic pressures, compacts with relative densities ranging from about 50 to 59% were prepared. Small holes were drilled in the sides of the compacts to accommodate W-5%Re/W-26%Re thermocouples used to determine the combustion temperature.

Combustion of the Ni–Si samples was carried out inside a glass apparatus under a one atmosphere (~ 100 MPa) pressure of flowing 99.98% pure argon. The rate of propagation of the wave was determined by measuring the time of travel between two locations along the side of the compacts. Auxiliary experiments using a differential thermal analyser (DTA) were made to determine the effect of stoichiometry on the onset of the reaction (ignition temperature). A Du Pont, model 1600, DTA system was used at a heating rate of $100\,^{\circ}C\ min^{-1}$.

## 3. Results and discussion

When ignited, combustion in the Ni–Si systems propagated in the spin mode. In such a mode, which has been observed in other investigations [8, 9], the combustion front propagates in the form of a relatively small spot as it moves in a helical fashion around the sample. Evidence for spin combustion can be seen in the form of retained grooves on the surface of a combusted $Ni_3Si$ sample, Fig. 2. Spin combustion for gas–solid reactions is confined to a thin surface layer [9], but in contrast, spin combustion in solid–solid reactions occurs throughout the sample, as can be

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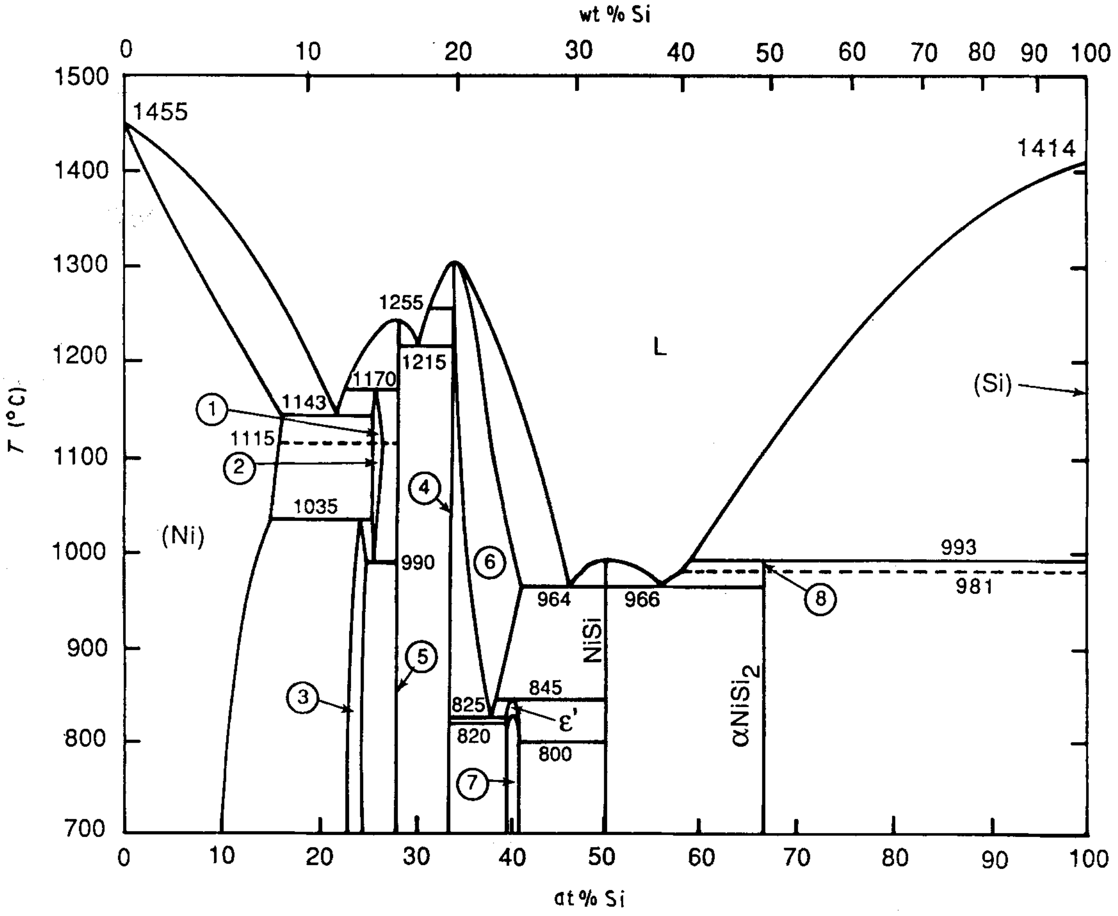

*Figure 1* The Ni–Si phase diagram. (1) $Ni_3Si\beta_3$; (2) $Ni_3Si\beta_2$; (3) $Ni_3Si\beta_1$; (4) $Ni_2Si\delta$; (5) $Ni_5Si_2\gamma$; (6) $Ni_2Si\theta$; (7) $Ni_3Si_2\varepsilon$; (8) $\beta NiSi_2$.

TABLE I Nickel silicides

| Phase | % Si | Designation | $-\Delta H_f$ (J mol$^{-1}$) | $T_m$ (PC) |
|---|---|---|---|---|
| $Ni_3Si$ | 25.0 | β | 141 | 1143 |
| $Ni_5Si_2$ | 28.6 | γ | 144[a] | 1215 |
| $Ni_2Si$ | 33.3 | δ | 144 | 1215 |
| $Ni_3Si_2$ | 40.0 | ε | 134[a] | –[b] |
| NiSi | 50.0 | – | 86 | 964 |
| $NiSi_2$ | 67.7 | – | 88 | 993 |

[a] Estimated values of enthalpies of formation.

[b] $Ni_3Si_2$ undergoes a solid state transformation before melting occurs.

clearly seen from a cross-section of a $Ni_3Si$ sample, Fig. 3.

The dependence of the spin combustion process on the initial stoichiometry of the nickel–silicon mixtures is shown by the results listed in Table II. Also indicated in Table II is the influence of initial density on the measured parameters of combustion temperature, average velocity, and frequency of the spin. The dependence of the average wave velocity and spin frequency on stoichiometry for samples with initial densities of 51 ± 1% is shown in Fig. 4. As stated above, the velocity represents an average value over a distance which is large compared with the pitch of the spin track. The frequency is calculated from this average velocity and the pitch values were measured on the surfaces of combusted samples. In both cases, velocity and spin frequency, the values are at a maximum level for samples containing 33 at % Si. The dependence of the measured combustion temperature, $T_c$, on stoichiometry is shown in Fig. 5. Also shown in this figure is the variation of the ignition temperature with powder composition. Ignition temperatures, $T_{ig}$, were obtained from DTA experiments in which loose samples were heated at a rate of 100 °C min$^{-1}$. Typical DTA traces showing the variation of $T_{ig}$ are depicted in Fig. 6. With reference to Fig. 5, it is seen that lower ignition temperatures are associated with higher combustion temperatures and that the highest $T_c$ values are at or near the stoichiometric value of 33 at %. The latter observation is in agreement with the trend in combustion velocity and spin frequency, shown in Fig. 4.

The lowest values for the combustion temperature and average velocity of combustion, and the highest ignition temperature, were observed for samples having the equiatomic composition, NiSi. Samples with this composition, which were not heated before ignition, did not sustain a combustion process to the other end of the sample. This is shown by Fig. 7 for samples with different initial densities. In all cases, the front became extinguished but the degree of its propagation increased for samples with higher initial densities. In Fig. 7 the density varied from 51.8% (left-most sample) to 57.0% (right-most sample). The other composition which had a relatively low $T_c$ and $v$ values was 25 at % Si. The propagation of the spin combustion for this composition was also near the limit of extinction, as can be seen from Fig. 8. In this sample,

*Figure 2* Spin combustion on $Ni_3Si$ sample.

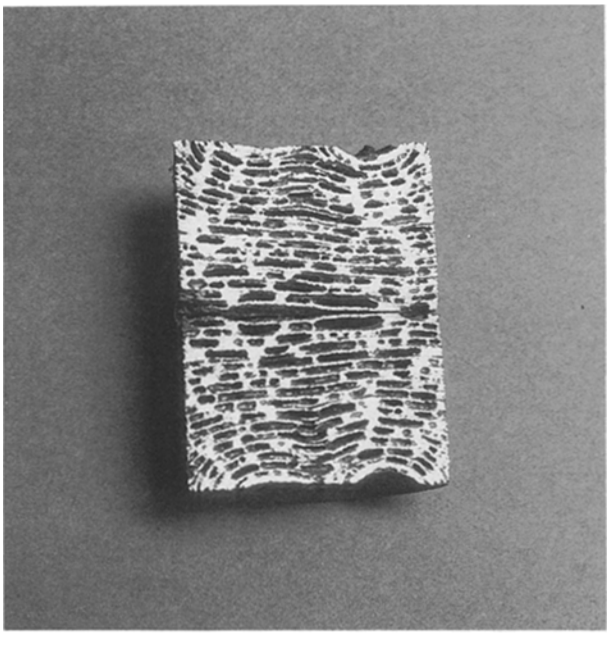

*Figure 3* Cross-section of $Ni_3Si$ sample.

the presence of a thermocouple hole led to the extinction of the combustion front, presumably due to the increased heat loss arising from the additional surface area created by the presence of the hole.

Results of X-ray analysis of the product of the spin combustion of Ni + Si powder mixtures are shown in Table III. In all cases, the product was not a single phase, although the phase corresponding to the stoichiometry of the mixed powders was the major one. Electron microscope (backscattered electron) images of the products of the samples whose initial composition corresponded to 25, 28.6, 33, and 40 at % Si are

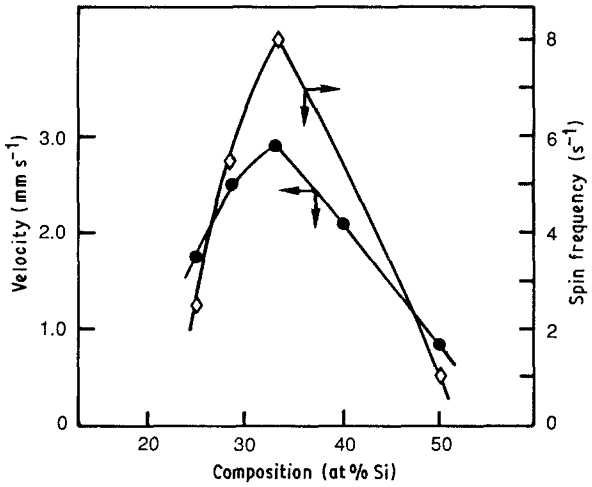

*Figure 4* The effect of stoichiometry on the average velocity and spin frequency of spin combustion of Ni–Si samples.

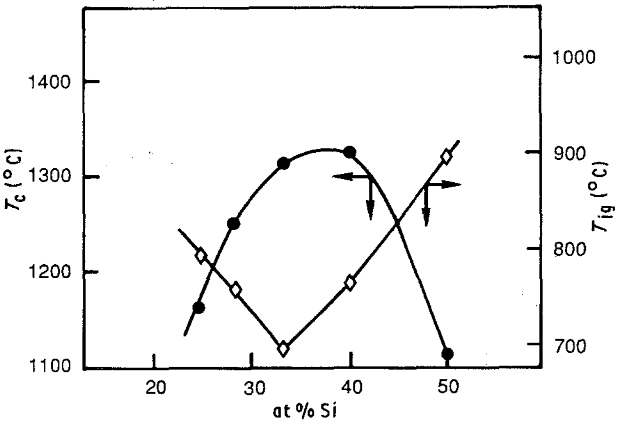

*Figure 5* The effect of stoichiometry on the combustion and ignition temperatures in the Ni–Si system.

TABLE II Spin combustion parameters in the Ni–Si system

| Composition | Relative density (%) | $T_c$ (°C) | $v$ (mm s$^{-1}$) | Pitch (mm) | Frequency (s$^{-1}$) |
|---|---|---|---|---|---|
| 3Ni + Si | 50.6 | 1160 | 1.75 | 0.7 | 2.5 |
| | 51.2 | – | 2.54 | 0.6 | 4.2 |
| | 51.6 | – | 2.54 | 0.7 | 3.6 |
| | 58.1 | – | 2.80 | 1.5 | 1.9 |
| 5Ni + 2Si | 50.3 | 1250 | 2.49 | 0.45 | 5.5 |
| | 51.9 | 1313 | 2.95 | 0.48 | 6.1 |
| | 53.3 | 1341 | 3.15 | 0.60 | 5.3 |
| | 55.5 | 1285 | 4.27 | 0.55 | 7.8 |
| 2Ni + Si | 50.7 | 1313 | 2.89 | – | – |
| | 53.7 | 1339 | 3.93 | 0.40 | 9.8 |
| | 55.8 | 1314 | | 0.33 | |
| | 57.4 | 1343 | 5.05 | 0.35 | 14.4 |
| 3Ni + 2Si | 50.8 | 1325 | 2.07 | – | – |
| | 53.8 | 1343 | 2.80 | – | – |
| | 54.5 | 1320 | 2.84 | – | – |
| | 56.5 | 1375 | 3.44 | – | – |
| | 58.5 | 1400 | 4.02 | – | – |
| Ni + Si | 51.8 | 1105 | 0.78 | 0.75 | 1.0 |
| | 52.6 | – | 1.33 | 0.67 | 2.0 |
| | 53.5 | 1163 | 1.36 | 0.65 | 2.1 |
| | 56.2 | 1155 | 1.38 | 0.63 | 2.2 |
| | 57.0 | 1170 | 1.43 | 0.62 | 2.7 |

TABLE III Product phase analysis in the Ni–Si system

| Initial composition | Phases in product |
|---|---|
| 3Ni + Si | $\beta_1$(Ni$_3$Si), $\gamma$(Ni$_5$Si$_2$), $\delta$(Ni$_2$Si) |
| 5Ni + 2Si | $\gamma$(Ni$_5$Si$_2$), $\delta$(Ni$_2$Si) |
| 2Ni + Si | $\delta$(Ni$_2$Si), $\theta$(Ni$_2$Si), $E$(Ni$_3$Si$_2$) |
| 3Ni + 2Si | $E'$(Ni$_3$Si$_2$), $\varepsilon$(Ni$_3$Si$_2$), $\mu$(NiSi) |
| Ni + Si | $\mu$(NiSi), $\varepsilon$(Ni$_3$Si$_2$) |

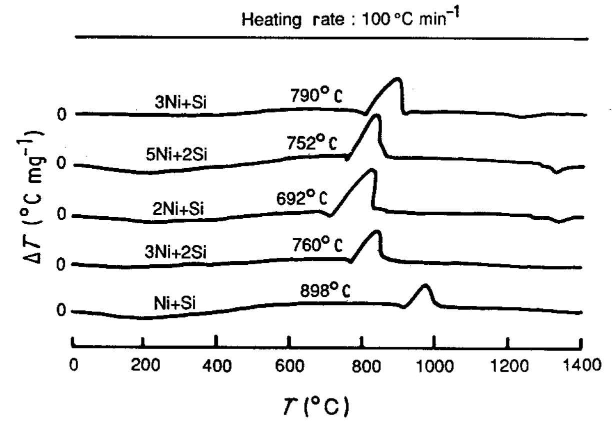

*Figure 6* DTA traces for Ni–Si samples heated at 100 °C min$^{-1}$.

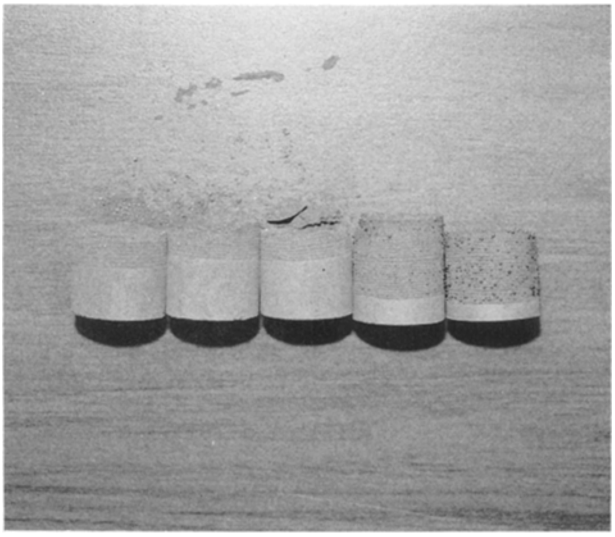

*Figure 7* Extinction of the spin combustion wave in NiSi samples. Sample density ranges from 51.8% (left-most sample) to 57.0% (right-most sample).

shown in Fig. 9a–d. The microstructure of the 25 at % Si sample (Fig. 9a) suggests a process in which the $\gamma$ phase (Ni$_5$Si$_2$) solidifies first and is followed by the solidification of the $\beta$ (Ni$_3$Si) phase and the subsequent formation of a eutectic-like Ni$_3$Si$_2$ + Ni$_2$Si microstructure. This interpretation would require that the combustion temperature be at least 1170 °C, corresponding to the peritectic isotherm of the Ni–Si phase diagram. No temperature measurements were made on higher density samples for this composition (25 at % Si); however, from the general trends observed for other compositions, higher combustion temperatures are expected for the higher density samples from which the microstructural analysis of Fig. 9a was obtained. Furthermore, the presence of Ni$_2$Si in the eutectic-like microstructure requires the existence of regions in the sample in which the local concentration exceeds 28.6 at % Si. In all other samples investigated, Fig. 9b–d, phases were identified whose silicon content was higher than that of the starting mixture, indicating departure from equilibrium conditions during the spin combustion of these samples.

As shown earlier, the combusted samples showed evidence of the spin mode of combustion on the surface and in their cross-sections. In the latter, the samples appear as layers of the product separated by cavities, see Fig. 3. Microanalyses of these layers as a function of distance along the sample are shown in Fig. 10 for samples containing 25 and 28.6 at % Si. In both cases, the overall composition of each layer (reported as at % Ni) appears to fluctuate randomly near the expected value for each of these samples.

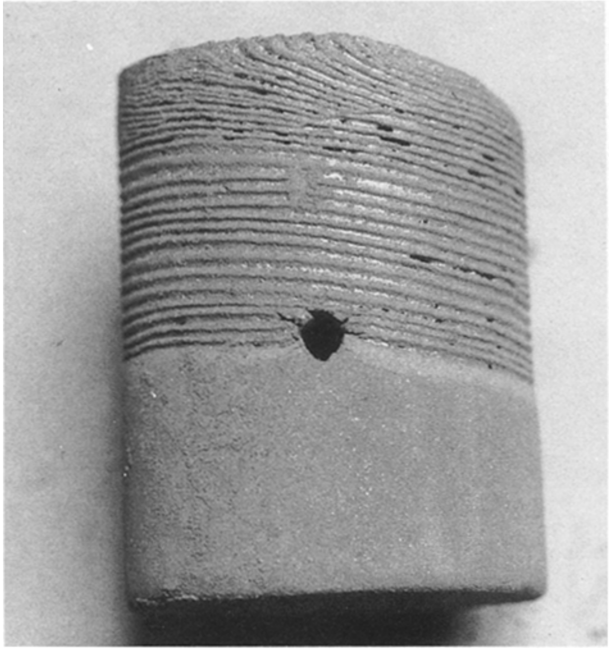

*Figure 8* Extinction of spin combustion as the wave encounters a thermocouple well. Sample composition: 25 at % Si.

When samples were preheated before ignition, the combustion process propagated in a mode that is dictated by the preheat temperature. When samples were preheated to 100 °C, combustion continued to propagate in a spin mode. However, when the preheat temperature was increased to 500 °C, the combustion wave propagated in a steady-state mode. At a preheat temperature of 800 °C, the samples ignited spontaneously, i.e. without the need for an ignition source. Since preheating results in an increase in the combustion temperature [10], more evidence of the presence of a liquid phase is expected. This is clearly seen from Fig. 11 which shows the final product of combustion of a sample with 25 at % Si nominal composition and which was preheated to 800 °C before initiating the combustion reaction. Despite the different appearance of this sample, X-ray analysis showed it to contain the same phases as other samples with the nominal composition of 3Ni + Si. In all cases the major phase identified was $Ni_3Si$ with traces of $Ni_5Si_2$ and $Ni_2Si$.

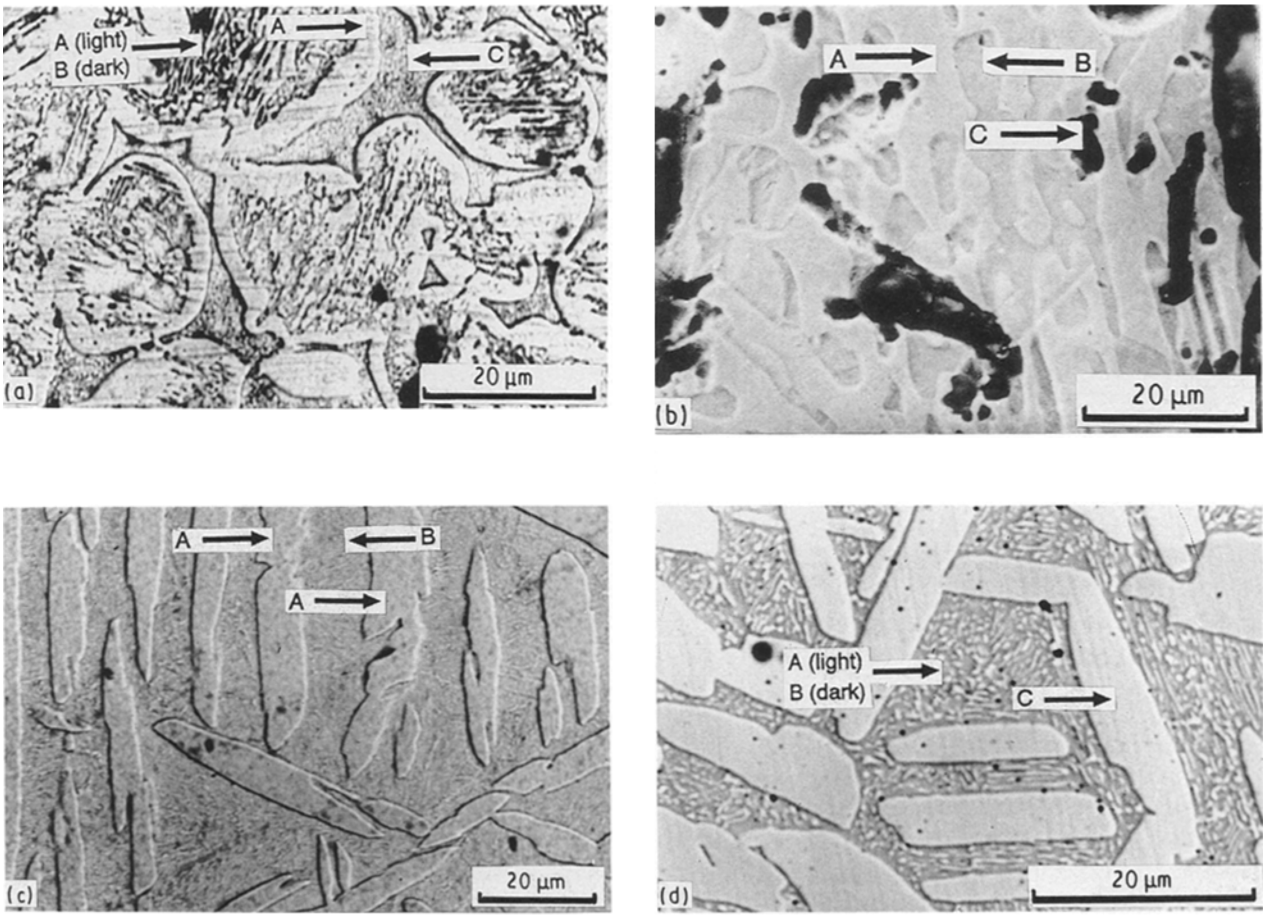

*Figure 9* SEM micrographs of products of combustion in the Ni–Si system: (a) 25 at % Si, (A) $Ni_5Si_2$, (B) $Ni_2Si$, (C) $Ni_3Si$; (b) 28.6 at % Si, (A) $Ni_5Si_2$, (B) $Ni_2Si$, (C) pore; (c) 33 at % Si, (A) $Ni_3Si_2$, (B) $Ni_2Si$; (d) 40 at % Si, (A) NiSi, (B) $Ni_3Si_2$, (C) $Ni_3Si_2$.

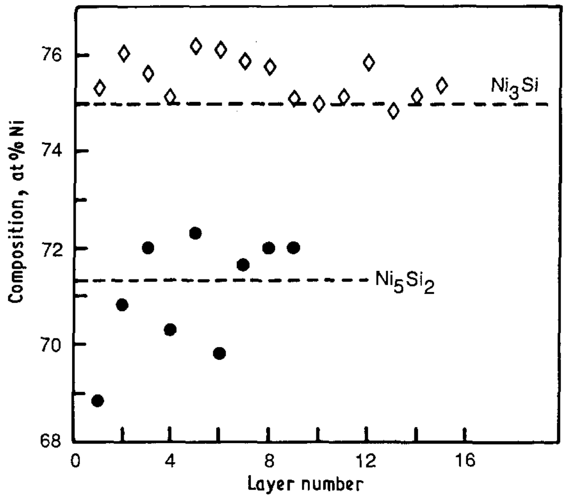

*Figure 10* Axial dependence of the composition on cross-sections of $Ni_3Si$ and $Ni_5Si_2$ samples.

*Figure 11* Cast appearance of 3Ni + Si sample ignited after preheating at 800 °C.

## Acknowledgement

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