

SHS of NbSi₂: A Comparison Between Experiments and Simulations

Silvia Gennari*, Filippo Maglia, Umberto Anselmi-Tamburini,
and Giorgio Spinolo

INSTM, IENI/CNR, Department of Physical Chemistry,
University of Pavia, 27100 Pavia, Italy

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Summary. Computer simulation results for the Self-propagating High-temperature Synthesis (SHS) of the intermetallic compound NbSi₂ are discussed in comparison with experiments for SHS of mechanically activated powders. The variation of wave speed of the propagation front is considered while varying Nb grain size and thermal conductivity of the starting mixture. A co-operating effect of these two parameters (due to the change in morphology of reactants after milling) is outlined.

Keywords. Computer chemistry; Kinetics; Thermodynamics; SHS.

Introduction

In the last years, Nb-silicides have been extensively investigated, due to their good thermal and mechanical properties, for structural applications at high temperatures [1–3]. Among silicides, NbSi₂ has one of the highest melting points, hence suggesting non-conventional techniques of synthesis, including mechanical alloying (MA) [4], field-activated combustion synthesis (FACS) [5], and self-propagating high-temperature synthesis (SHS) [6].

The main experimental problems for a rational approach to SHS processes are related to the determination of reaction mechanism. As a matter of fact, an SHS process is mainly studied in very indirect manners, after quenching or by determining the effect of process variables (dilution, grain size . . .) on wave velocity and combustion temperature. To supplement the experimental approach, the authors have developed a computer simulation method specifically oriented to understanding reaction mechanisms [7, 8]. The method couples the heat transport equation with a detailed kinetic and thermodynamic description of the reaction steps involved. Previous results have shown that the method is indeed able to correctly predict the feasibility and to provide insights into dynamic behaviour and mech-

* Corresponding author. E-mail: silvia.gennari@unipv.it

anism of gas/solid and intermetallic SHS [8, 9]. The recent implementation of the CALPHAD approach to the thermodynamics has allowed to generalize the simulation method to a wide class of intermetallics.

The NbSi₂ system taken into consideration here has been experimentally studied [10] both in SHS and mechanical alloying (MA) conditions. The combustion characteristics have shown strong dependence on particle size: despite the high reaction heats involved, the process can be ignited only by pre-heating, by applying an electric field, or under mechanical alloying (MA) conditions. In addition, wave velocity values reported in literature are often two orders of magnitude greater for thin films than for powder pellets [11]. In a real SHS process, in fact, the compaction degree of the starting mixture is actually one of the least reproducible experimental variables, though strongly influencing the process kinetics. In this context, the simulation method is particularly helpful for ‘uncoupling’ the different effects of compaction on one side on thermal conductivity and on the other side on density and heat of reaction per unit volume.

It is the aim of the present work to use simulation results for the SHS of NbSi₂ from pure elements while varying both grain size and thermal conductivity of the system for clarifying the mechanistic aspects underlying experimental SHS results obtained under an ample range of process parameters.

Methods

The assessed thermodynamic phase diagram of the system Nb–Si [12] shows two congruently melting intermetallic compounds with 5:3 and 1:2 stoichiometry [12]. The latter behaves as a line compound and melts at 2208 K. Only this compound has been obtained by SHS without free formation of other intermediate phases, according to the general rule that the SHS of intermetallic compounds is particularly effective when applied to the compound closer in composition to the lower melting reactant. Therefore, only the 1:2 compound is considered in the present work. The underlying thermodynamic data were taken from literature [13, 14].

The computational method used has been fully described in previous papers [8, 9] and basically faces a parabolic system of partial differential equations, containing, in addition to *Fourier’s* law, one or more kinetic equations. The latter ones describe the assumed chemical or phase transformations at the level of the grains of solid phases. Briefly, at each time step of the solution of *Fourier’s* equation, a chemical routine takes care of the rate of the irreversible steps and adjusts amount and composition of the pertinent phases according to (partial or complete) thermodynamic equilibrium. The processes taken into account in the chemical routines are: a) melting of Si (the model assumes complete melting of the metal with lower melting temperature before the other starts diffusing); b) diffusion-controlled dissolution of solid Nb into the molten pool (this process is governed by the kinetic law for diffusion in a semi-infinite pool following the invariant field approximation for a spherical particle, the diffusion coefficient being obtained from isothermal experiments); c) melting of Nb (if and when pertinent); d) precipitation and melting of the compound; e) deposition of the Si + NbSi₂ eutectic mixture. Only for Nb dissolution (step b) a kinetic law is given, while steps a), c), d), and e) only enter the enthalpy balance.

Results and Discussion

Figure 1 shows simulated wave speed as a function of thermal conductivity for two different starting Nb grain sizes, r_{Nb} (continuous line). The values of thermal conductivity, χ taken into consideration span the range from $\chi = \chi_{\text{bulk}}$ (where χ_{bulk} is the amount-weighted average of thermal conductivities of the involved phases) to $\chi = \chi_{\text{bulk}}/70$ (see below). The velocity values are between 2 and 70 mm/s for $r_{\text{Nb}} = 10 \mu\text{m}$ (Fig. 1a), and between 7 and 500 mm/s for $r_{\text{Nb}} = 1 \mu\text{m}$ (Fig. 1b), in agreement with the fact that the rate determining step of the process is the dissolution of solid Nb into the molten pool. As already said, experimental evidence reports [11] how extremely different values of propagation velocity can be encountered depending on the compaction degree of the starting mixture. Quite generally, 'bulk' values of thermal conductivity mostly reproduce velocity values obtained for SHS of thin films, whereas lower values of thermal conductivity need to be used to reach a better agreement with SHS on powder compacts. Experimental values (on powder compacts) of wave speed observed for, respectively, $r_{\text{Nb}} = 1 \mu\text{m}$ and $r_{\text{Nb}} = 10 \mu\text{m}$ are 6.3 mm/s and 2 mm/s and are reported in Fig. 1 as hollow symbols. The value used here for powder compacts is the lowest one ($\chi = \chi_{\text{bulk}}/70$) which still simulates SHS ignition: as a matter of fact it also best reproduces experimental results.

Figure 2 shows values of wave speed as a function of the reciprocal of grain size r for $\chi = \chi_{\text{bulk}}/70$ (continuous line). Simulated values confirm experimental measurements (full circles) for relatively large grain sizes ($1 < r < 30 \mu\text{m}$) where the

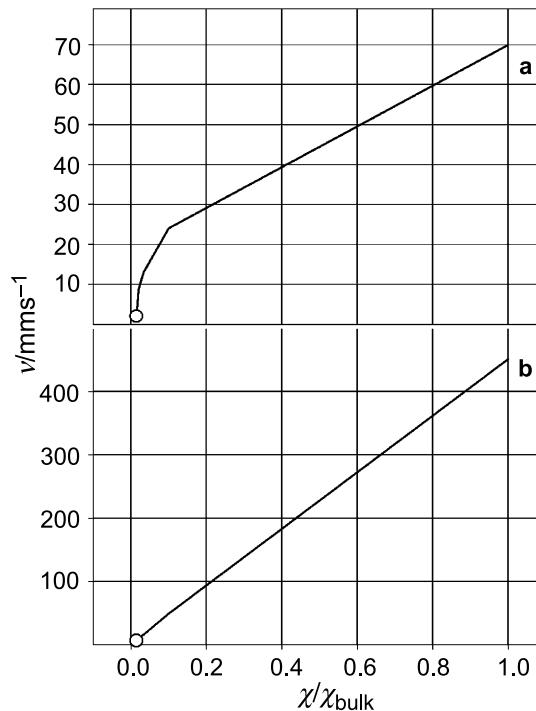


Fig. 1. Simulated wave speed as a function of thermal conductivity χ for Nb grain size r_{Nb} of $10 \mu\text{m}$ (a) and of $1 \mu\text{m}$ (b); experimental values of wave speed observed for these two different grain sizes are reported with hollow symbols

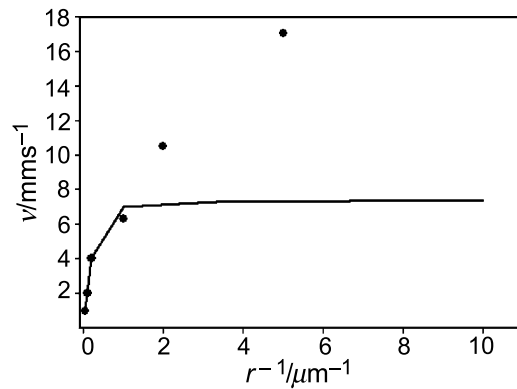


Fig. 2. Simulated wave speed as a function of Nb grain size (r) with $\chi = \chi_{\text{bulk}}/70$ (continuous line) and experimental values observed while varying grain size by ball milling (full circles)

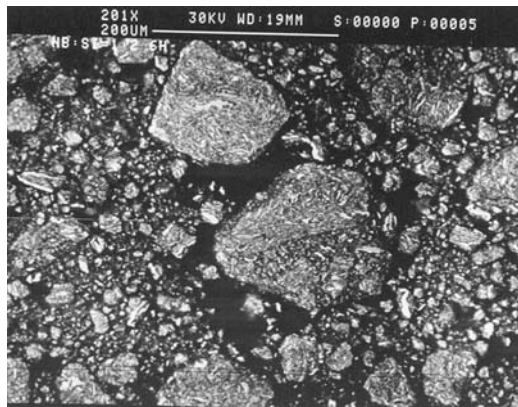


Fig. 3. Scanning electron micrograph of Nb:Si = 1:2 powder particles after 540 min of milling

wave speed shows a steep increase from 1 to 7 mm/s. Moreover, for $r = 30 \mu\text{m}$, both in simulation and in experiments, a very strong initial transient can be observed and combustion ignites with great difficulty.

For lowest values of r , the simulated ν values significantly depart from experimental ones. A closer look at samples morphology suggested, on the other side, a co-operation of the two parameters taken into consideration (thermal conductivity and grain size). Figure 3 shows a SEM image of reactant powder after a milling time of 540 min (resulting in average particle grain size $\approx 0.2 \mu\text{m}$) and clearly indicates that milling does not simply result in a reduction of spherical grains: Nb gives platelets (white) while brittle silicon fractures and packs between Nb lamellae. Then, the reactants particles arrange themselves in a morphology similar to thin multilayers.

Such a complicated situation is poorly reproducible from an experimental point of view and difficult to model. Even though our model does not presently account for any type of size distribution of the particles inhomogeneity, the above understanding can be clarified and justified by reference to Fig. 4, where the wave speed values experimentally obtained under increasing milling time (shown by full circles) are compared with the wave velocity values obtained by simulation as a function of grain size for *three different assumed values of thermal conductivity* (short dashes: $\chi = \chi_{\text{bulk}}/70$, long dashes: $\chi = \chi_{\text{bulk}}/50$, continuous line: $\chi = \chi_{\text{bulk}}/30$).

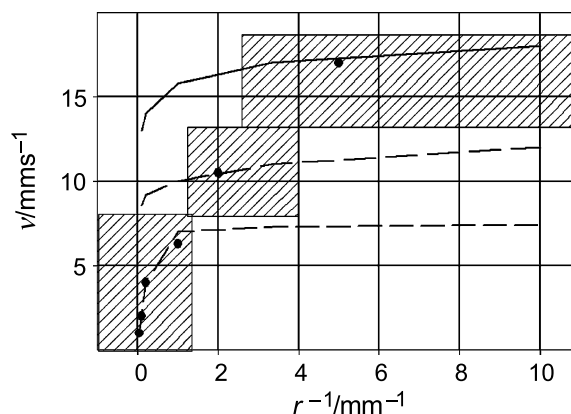


Fig. 4. Computed wave speed as a function of Nb grain size (r) for $\chi = \chi_{\text{bulk}}/70$ (short dashes), $\chi = \chi_{\text{bulk}}/50$ (long dashes), and $\chi = \chi_{\text{bulk}}/30$ (continuous line); the full circles represent experimental values obtained after different milling times; the shaded areas outline different assumed thermal conductivities required to gain best agreement with experiments

Starting from the left, for short milling times the Nb particles are expected to remain large and irregularly shaped, and to exhibit poor thermal contact: the relevant thermal conductivity of this mixture is then expected to be close to the lowest ones used in the simulation. This case is shown by the agreement between experiments and simulation (short dashes) outlined in the leftmost shaded area of the figure. With more prolonged milling, the size decreases, the microstructure of the mixture appears to be controlled by the detailed features of the milling and not only by grain size, with a better contact (and hence an increased thermal conductivity), so that the χ best reproducing experiments needs to be higher ($\chi = \chi_{\text{bulk}}/50$, long dashes) as outlined in the intermediate shaded area of the figure. For the highest milling times, a still larger χ must be used in the simulation runs to reach reasonable agreement with experiments (continuous line, right shaded area).

References

- [1] Subramanian PR, Mendiratta MG, Diminuk DM, Stucke M (1997) *Mater Sci Eng* **A239**: 1
- [2] Bewlay BP, Jackson MR, Lipsitt HA (1996) *Metall Mater Trans A* **27A**: 3801
- [3] Yamaguchi M, Inui H, Ito K (2000) *Acta Mater* **48**: 307
- [4] Lou T, Fan G, Hu Z (1997) *J Mater Res* **12**: 1172
- [5] Gedevisanishvili S, Munir ZA (1996) *Mater Sci Eng* **A211**: 1
- [6] Sarkisyan AR, Dolukhanyan SK, Borovinskaya IP (1979) *Combust Explos Shock Waves* **15**: 95
- [7] Arimondi M, Anselmi Tamburini U, Gobetti A, Munir ZA, Spinolo G (1997) *J Phys Chem B* **101**: 8059
- [8] Maglia F, Anselmi Tamburini U, Gennari S, Spinolo G (2001) *Phys Chem Chem Phys* **3**: 489
- [9] Gennari S, Maglia F, Anselmi Tamburini U, Spinolo G (2003) *J Phys Chem B* **107**: 732
- [10] Maglia F, Milanese C, Anselmi Tamburini U, Doppiu S, Cocco G (2002) *J Mater Res* **17**: 1992
- [11] Bhattacharya AK (1991) *J Am Ceram Soc* **74**: 2113
- [12] Schlesinger ME, Okamoto H, Gokhale AB, Abbaschian RJ (1993) *J Phase Equil* **14**: 502
- [13] Dinsdale AT (1991) *CALPHAD* **15**: 317
- [14] Fernandes PB, Coelho GC, Ferreira F, Nunes CA, Sundman B (2002) *Intermetallics* **10**: 993