

## SHS Joining Via Combustion of Ti-Containing Systems

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### Abstract

The joining of intermetallic parts to the metals (Ti, Al, Cu, Ni) or different intermetallics (e.g. NiAl, TiAl) is important for high-temperature applications. Traditional fusion welding is difficult to apply due to the large thermal expansion mismatch between the intermetallics to be joined and the filler material. Brazing and diffusion bonding are also inefficient, energy-consuming, and must be carried out in vacuum or protective atmosphere. Meanwhile, Self-propagating High-temperature Synthesis (SHS) that is widely used for production of powders, compact materials and parts holds considerable promise as a method of joining various component parts.

We report on a new SHS-based approach to joining TiAl and NiAl intermetallics with metal substrates Ti and Ni. The adiabatic combustion temperatures for the systems under study and stoichiometric ratios of green mixtures were determined by thermodynamic calculations. Experiments were performed in the modes of pressure-assisted thermal explosion and combustion wave propagation, with the samples placed between the punches of experimental set up.

Investigated were the processes taking place in thermally treated Ti or Ni plates mechanically impregnated (by Mechanically Activation or Vibration Milling) with a mixture of metallic particles. Vibratory treatment of an Al and Ti surfaces in a powder mixture of metals was found to result in destruction of the surface oxide film and formation of extensive physical contacts between the Ni or Ti matrix and the metallic particles mechanically impregnated into the near surface layer of Ni or Ti.

Subsequent thermal treatment was then used to launch chemical reaction yielding intermetallides within the impregnated layer. Performing SHS reactions yielding melted intermetallides in the coatings (or pellets) deposited (or placed) onto the surface of thus treated Ti or Ni plates, one can obtain strong weld joining between solidified SHS products and substrates. This approach can also be used for deposition of coatings with a desired composition onto substrates.

### Introduction

A great amount of the heat releasing during SHS process can be used not only for further treatment of the produced material or formation its structure but also as a source of additional heat for joining (welding) of heterogeneous materials [1, 2]. Production of permanent connection of different ceramic materials is of practical application. Owing to high cost and technical complexity of known methods (hot isostatic pressing [3] and pulse discharge sintering (PSD) [4]), the search of new techniques is of great importance. The special selected compositions

allowed us to join dissimilar materials which cannot be done by traditional methods. Thus, using graded compositions we can obtain the continuous transition between various materials through several layers in the mode of SHS. To control the process, we studied the rate and mechanism of atom displacement at the interface as well as influence of external factors.

### Experimental

In experiments, we used the commercially available powders of Ti ( $d = 80\text{-}120\ \mu\text{m}$ , 99.0% pure), Si ( $d < 10\ \mu\text{m}$ , 99.4% pure), and C ( $d < 55\ \mu\text{m}$ , 99.75%

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pure). The above powders were then used to prepare 5Ti + 3Si, Ti + Si, Ti + 0.5C, and Ti + 0.65C mixtures. In a cylindrical mould 12 mm in diameter, we fabricated compacts with a relative density ( $\rho$ ) of  $\rho(\text{Ti} + y\text{Si}) = 0.69$  and  $\rho(\text{Ti} + x\text{C}) = 0.66$ . In order to diminish the amount of impurity gases, some samples were thermally treated at 400 °C for 3 h under reduced pressure.

The schematic of the experimental setup is given in Fig. 1a. Two tablets of different green composition were placed on a BN stage. SHS reaction was ignited with a rapidly burning Ti + 2B tape in order to provide uniform inflammation over the entire surface of the Ti + xC pellet. Temperature was monitored with WRe5/WRe20 thermocouples  $T_1$ – $T_3$ . Ta and W wires (60–100  $\mu\text{m}$ ) were placed in between

the pellets as probes for getting information about interaction of these metals with SHS products.

In order to determine a direction and depth of penetration of the elements through the interface, some experiments were performed with Ti + Si + 10 wt.% Hf mixtures. High-contrast Hf particles (see Fig. 1b) afforded more distinct control over the depth of the diffusion of the elements from the Ti + ySi pellet into the Ti + xC one. A Ta disk (foil) placed between the pellets (Fig. 1b) was used to pinpoint a starting interface position. During combustion, the samples were loaded with some certain pressure  $F$  (0.22–26.0 kPa). The reaction chamber was filled with Ar to a pressure  $P = 1$  atm.

Combustion products were characterized by SEM, XRD, and optical microscopy.

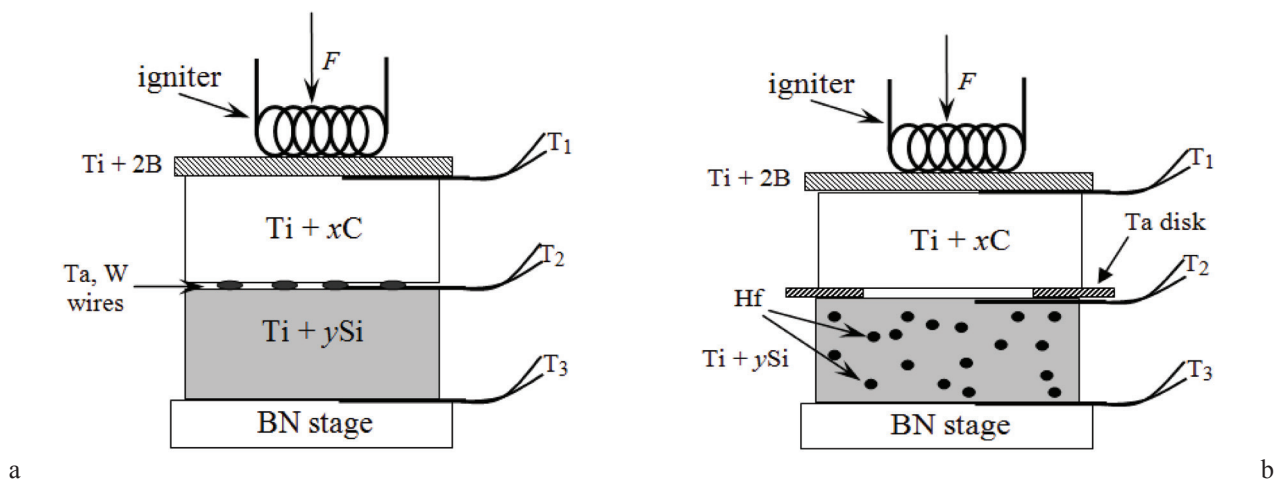


Fig. 1. Scheme of experiments (a) and (b).

## Results and Discussion

SHS reaction could propagate over the entire sandwich only when ignited from the side of the Ti + xC pellet. Figure 2 shows typical thermograms of combustion at low and high values of  $F$ . At high  $F$  (Fig. 2b), combustion proceeds faster (in 0.49 s instead of 1.12 s) due to better conditions for heat transfer.

The readings of thermocouple  $T_1$  are somewhat higher due to the influence of the highly caloric Ti + 2B igniting tape. Time period  $t_{in1}$  corresponds to the induction period for ignition of the Ti + xC tablet while  $t_{in2}$ , to that of the Ti + ySi pellet. With increasing  $F$ , transient peaks accompanying transition of combustion front from layer to layer are seen to smoothen (curves 1 and 2 in Fig. 2a, b). Time period between the responses of thermocouples 1 and 3 gives the overall duration of combustion  $t_{tot}$ .

The presence of a sufficient amount of liquid phase is a prerequisite for interpenetration of the elements and formation of permanent joint. An increase in  $F$  improves contact at the interface but shortens the reaction time and hence the lifetime of the melt (0.33 s against 0.79 s). This implies that the loading conditions should be optimized for each pair of green compacts.

Phase relations in the Ti–Si–C system [5] suggest that, on going from 5Ti + 3Si to Ti + Si, the temperature of product crystallization decreases from 2130 down to 1900 °C; while on going from Ti + 0.5C to Ti + 0.65C, it increases from 2800 to 3050 °C. Therefore, on going from (5Ti + 3Si)/(Ti + 0.5C) sandwiches to (Ti + Si)/(Ti + 0.65C) ones, the lifetime of the melt can be expected to grow, thus promoting mutual interdiffusion and probably formation of ternary compounds at the interface.

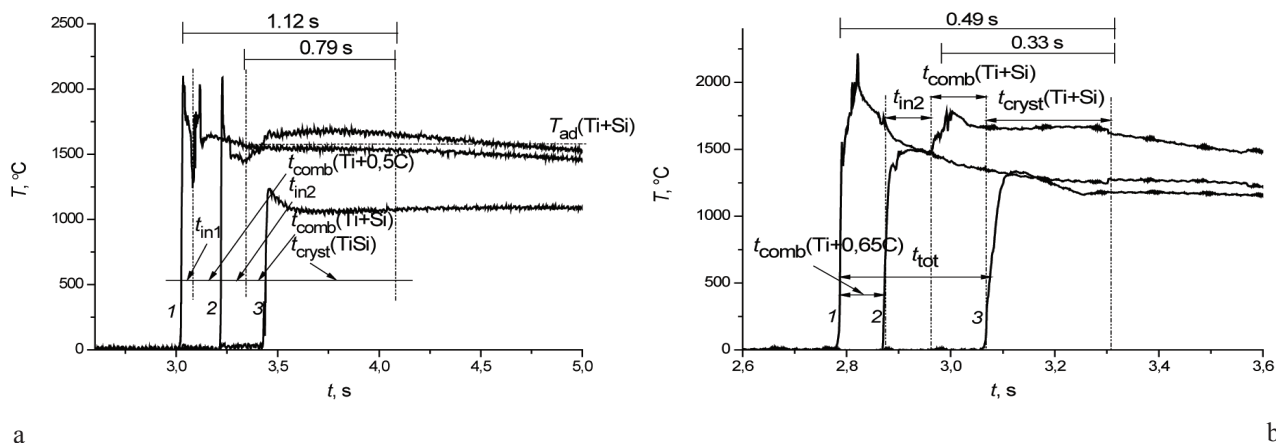
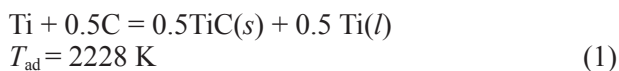


Fig. 2. Thermograms of combustion for: (a) (Ti + 0.5C)/(Ti + Si + 10 wt.% Hf) system,  $F = 0.22$  kPa; and (b) (Ti + 0.65C)/(Ti + Si) system,  $F = 26.0$  kPa. Curves 1, 2, and 3 are the readings of thermocouples  $T_1$ ,  $T_2$ , and  $T_3$ , respectively (Fig. 1).

### Thermodynamic Considerations

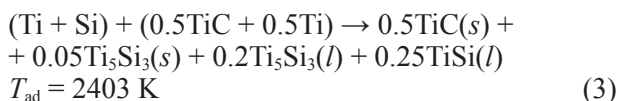
Using software THERMO [6], we could roughly estimate the values of  $T_{ad}$  and equilibrium product compositions that can be expected to develop within the above thin layer, that is, at the interface between two green compositions with different initial temperatures.

At  $T = 298$  K and  $P = 1$  atm, combustion in individual pellets can be described by the schemes:

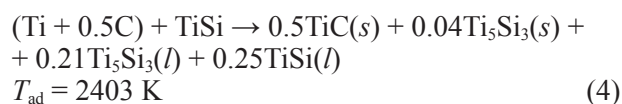


where (l) and (s) denote the liquid and solid state, respectively.

When ignition comes from the Ti + C pellet, the initial conditions are as follows:  $T(\text{Ti} + \text{Si}) = 298$  K,  $T(0.5\text{TiC}(s) + 0.5\text{Ti}) = 2228$  K,  $P = 1$  atm. In this case, the reaction scheme can be represented as

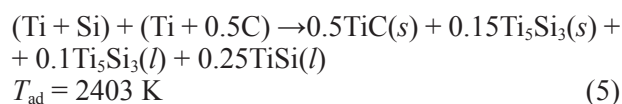


Accordingly, initiation from the side of the Ti + 0.5C pellet gives rise to the following initial conditions:  $T(\text{Ti} + 0.5\text{C}) = 298$  K,  $T(\text{TiSi}) = 1843$  K,  $P = 1$  atm. Appropriate reaction scheme acquires the form:

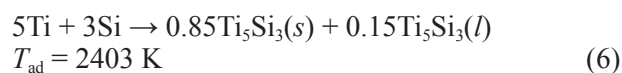


Combustion of Ti + Si + C mixture at  $T = 298$  K and  $P = 1$  atm would proceed as shown below:

Combustion of (Ti + Si) + (Ti + 0.5C) mixture (at  $T = 298$  K) can be expected to proceed as shown below:



The performed calculations prove that irrespectively which layer initiates combustion, the  $T_c$  for three-component system (Ti + Si + C) is higher than for initial (Ti + C) and (Ti + Si) mixtures. It is related with production of high caloric (enthalpy)  $\text{Ti}_5\text{Si}_3$  in reactions (3) – (5) and therefore the higher temperature at the interface.



Elevated temperatures developed at the (Ti–C)/(Ti–Si) interface may presumably provide favorable conditions for formation of a strong transition layer due to its possible strengthening with  $\text{Ti}_m\text{Si}_n$  phases.

### Effect of Dense Skin Layer

Figure 3 shows photos of welded joints obtained at different  $F$ . An increase in  $F$  is seen to smoothen the interlayer boundary. However, further increase in  $F$  led to sample deformation and melt squeezing.



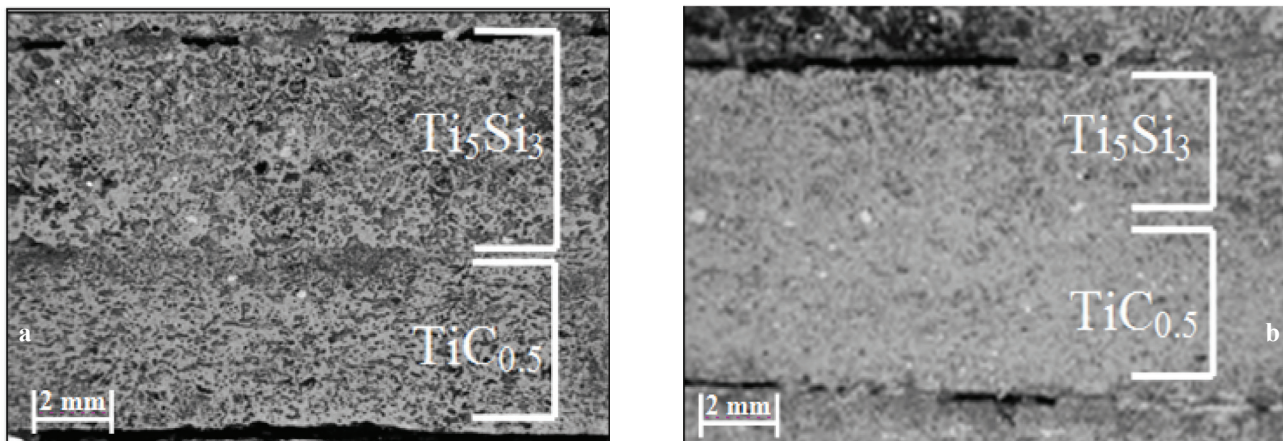


Fig. 3. Weld joints obtained at  $F = 0.22$  (a) and  $26.0$  kPa (b).

Compression of green mixtures (down to  $\rho = 0.66-0.69$ ) was found to form a denser skin layer (up to  $50 \mu\text{m}$  thick) on resultant pellets, thus creating an additional obstacle for mutual interdiffusion. To provide better conditions for joining, it seemed reasonable to remove this layer from the surface of green compacts (Fig. 4).

For the samples with uncut surface of the pellets (Fig. 4a) we failed to identify unambiguously the transition zone containing phases on the base of Ti–Si–C.

After the initial pellets of  $(\text{Ti} + 0.5\text{C})$  and  $(5\text{Ti} + 3\text{Si})$  composition were pre-polished to re-

move the compact surface layer and to provide the better contact between the layers, some dark-grey spots were revealed in the contact zone (Fig. 4b). The spots correspond to the triple phase on the Ti–C–Si base formed as a result of mutual melt penetration and element diffusion between  $(\text{Ti} + 0.5\text{C})$  and  $(5\text{Ti} + 3\text{Si})$  layers.

The XRD analysis showed presence of  $\text{Ti}_5\text{Si}_3$  and TiC phases in the interface both from the side of  $(\text{Ti} + x\text{C})$  and  $(\text{Ti} + y\text{Si})$  layers (Fig. 5). It proves formation of a weld seam as a result of mutual melt penetration and element diffusion between the layers.

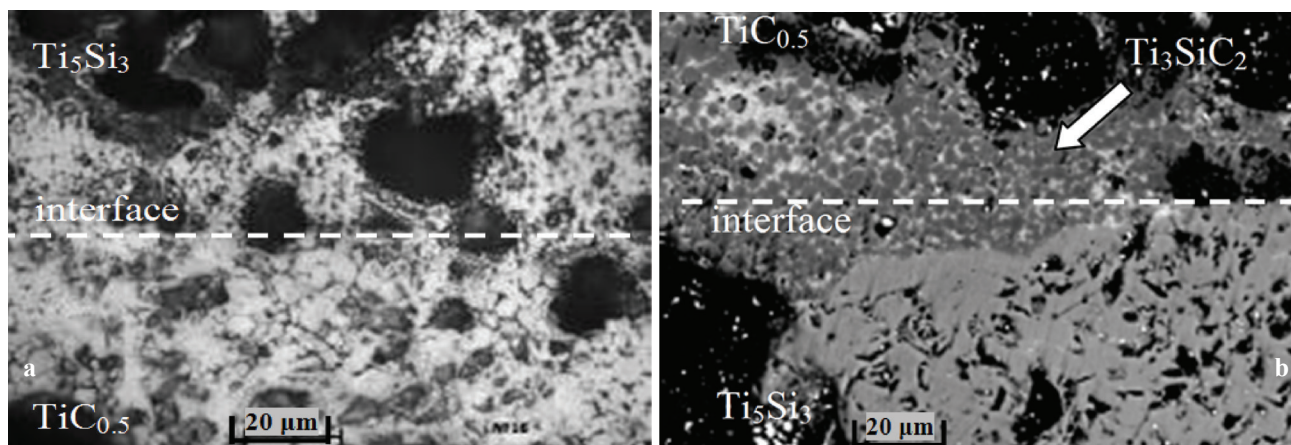


Fig. 4. Burned  $5\text{Ti} + 3\text{Si}/(\text{Ti} + 0.5\text{C})$  samples with (a) uncut surface of the pellets and (b) removed skin layer ( $50 \mu\text{m}$ ):  $F = 1.02$  kPa.

Figure 5 also shows the formation of ternary compound with a composition (18.57 C, 7.47 Si, and 74.11 wt.% Ti) close to  $\text{Ti}_3\text{SiC}_2$ . MAX compounds of the  $\text{Ti}_3\text{SiC}_2$  type are known for their unique properties in coating applications [8-10]. The crystal structure of  $\text{Ti}_3\text{SiC}_2$  exhibits weak bonding between the carbide layers  $[\text{Ti}_3\text{C}_2]_x$  and silicon layers  $[\text{Si}]_y$ . Such a nano-laminate structure

admits high strain of the material without its macroscopic destruction [11].

XRD analysis of separated burned  $(\text{Ti} + 0.5\text{C})/ (5\text{Ti} + 3\text{Si})$  sandwiches showed the presence of  $\text{TiC}_{0.5}$  in the burned  $\text{Ti} + 0.5\text{C}$  layer and of  $\text{Ti}_5\text{Si}_3$  in the burned  $5\text{Ti} + 3\text{Si}$  pellet. The absence of a ternary phase is indicative of low mutual interdiffusion during combustion.

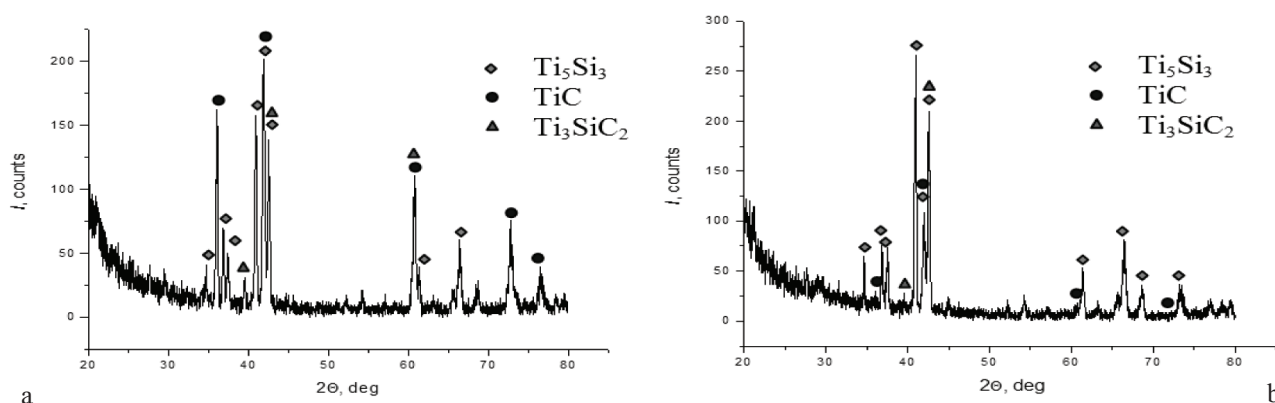


Fig. 5. Diffraction patterns of the cleft  $\text{Ti}_5\text{Si}_3/\text{TiC}_{0.5}$  interface as taken from the side of  $\text{TiC}_{0.5}$  (a) and  $\text{Ti}_5\text{Si}_3$  (b).

### Model of Transition Zone Formation

According to SEM data, the concentration profile of element distribution in the interface of  $\text{Ti} + 0.5\text{C}$  and  $5\text{Ti} + 3\text{Si}$  (10 wt.% Hf) was built. The dotted line (Fig. 6a) is in the area of a thermocouple 2 (two white regions) and corresponds to the initial position of the interface.

Figure 6 shows the SEM image of transition layer and concentration profiles of the elements in the vicinity of interface for the  $(\text{Ti} + 0.5\text{C})/(\text{Ti} + \text{Si} + 10 \text{ wt.}\% \text{ Hf})$  sandwich.

Far from the interface ( $x = 0$ ), concentrations of the elements are close to the initial ones. But upon

approaching to  $x = 0$ , the values of  $[\text{Ti}]$  and  $[\text{C}]$  gradually decrease within the  $\text{TiC}_{0.5}$  layer just as the values of  $[\text{Si}]$  within the  $\text{Ti}_5\text{Si}_3$  layer. Si and Hf are seen (Fig. 6b) to penetrate into  $\text{TiC}_{0.5}$  to a depth of up to  $1000 \mu\text{m}$ . A general trend was a slight shift of a transition layer toward  $\text{TiC}_{0.5}$ . This can be explained by the fact that crystallization of  $\text{TiC}_{0.5}$  takes place first. This is followed by impregnation of solid  $\text{TiC}_{0.5}$  with  $\text{Ti}_5\text{Si}_3$  melt due to capillary spreading. As a result, the weld seam is formed within the rapidly solidifying  $\text{TiC}_{0.5}$  layer. This is supported by the behavior of  $[\text{Hf}]$  (see Fig. 6b): it remains practically unchanged within the  $\text{Ti}_5\text{Si}_3$  layer but gradually decreases within the  $\text{TiC}_{0.5}$  layer.

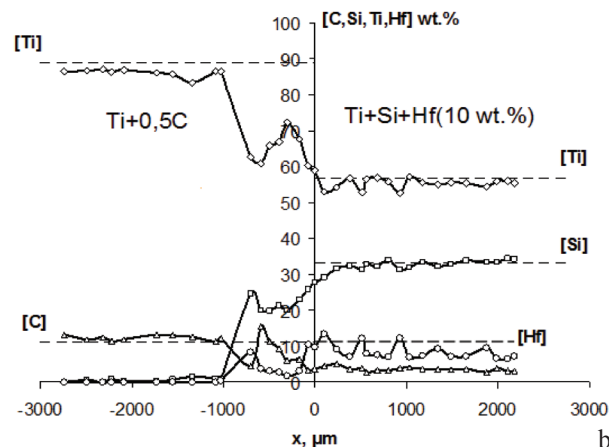
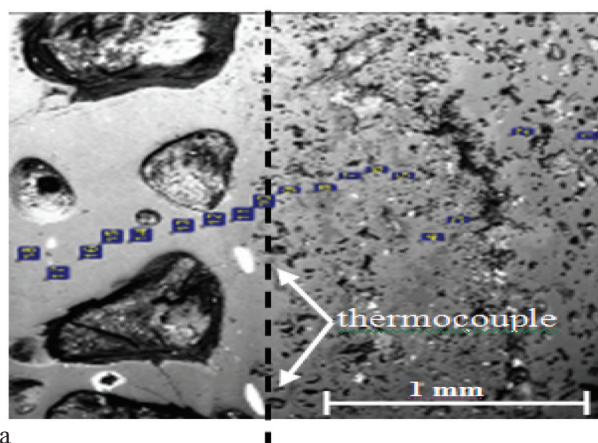


Fig. 6. (a) SEM image of transition layer and (b) concentration profiles of the elements in the vicinity of interface:  $(\text{Ti} + 0.5\text{C})/(\text{Ti} + \text{Si} + 10 \text{ wt.}\% \text{ Hf})$  sandwich.

### Diffusivity Estimates

Using the temporal data of Fig. 2 and our SEM data, we could roughly estimate diffusion coefficient  $D$  from the Einstein-Smoluchowski relationship

$$D \approx \bar{x}^2/t,$$

where  $\bar{x}$  is the mean-square displacement and  $t$  the diffusion time.

For  $5\text{Ti} + 3\text{Si} - \text{Ti} + 0.65\text{C}$  mixtures,  $t = 0.5$  s (Fig. 2b) and  $x \approx 0.03$  cm, so that

$$D \approx 2 \cdot 10^{-3} \text{ cm}^2/\text{s}$$

The titanium and silicon concentration change in  $\text{Ti}_3\text{Si}_3$  layer is watched from the surface to  $x \approx 0.02$  cm. Therefore,

$$D \approx 8 \cdot 10^{-4} \text{ cm}^2/\text{s}$$

For  $(\text{Ti} + \text{Si}) - (\text{Ti} + 0.5\text{C})$  system,  $t = 1$  s (Fig. 2a) while  $x \approx 0.09$  cm. Then we obtain:

$$D \approx 8 \cdot 10^{-4} \text{ cm}^2/\text{s}$$

The silicon penetration into the  $\text{TiSi}$  layer,  $x \approx 0.02$  cm (Fig. 7b). Then

$$D \approx 4 \cdot 10^{-4} \text{ cm}^2/\text{s}$$

The calculated values of diffusivity  $D$  significantly exceed the reported values for the elements in the melt which as a rule have a value of  $D = 10^{-4}$ - $10^{-5}$   $\text{cm}^2/\text{s}$  [12]. In other words, the above calculations indirectly confirm the key role played by convection mass transfer in formation of the transition layer.

## Conclusions

A local temperature rise in the transition zone formed between the mixtures SHS-producing carbides and silicides was explored. The effect was confirmed by thermodynamic calculations. Besides, the ternary MAX-phase  $\text{Ti}_3\text{SiC}_2$  was detected in the transition zone. The results set up good conditions for production of all-in-one joints between dissimilar materials. The estimated diffusivities provide indirect evidence for a key role of convection mass transfer in formation of weld seams.

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