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H. Chen, V. Nesterenko, J. Lasalvia, M. Meyers. Shear-Induced Exothermic Chemical Reactions. Journal de Physique IV Proceedings, 1997, 07 (C3), pp.C3-27-C3-32. 10.1051/jp4:1997307. jpa-00255380

HAL Id: jpa-00255380

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Submitted on 4 Feb 2008

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Shear-Induced Exothermic Chemical Reactions

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Abstract. The structure of controlled high-strain-rate shear bands generated in Ti-Si reactive powders has been investigated by means of the radial symmetric collapse of a thick-walled cylinder. Shear localization developed at global strains of 0.2-0.4 and a strain rate of 10^4 s^{-1} . Within the shear bands, local shear strains were up to 100 and local shear strain rates were 10^7 s^{-1} . Chemical reactions were initiated at these shear bands and propagated throughout the entire specimen under critical global strain conditions. A model for a periodic distribution of "hot spots" in reactive powders is proposed. It is possible to estimate the reaction rate from the triangular unreacted regions formed by the shear localization process.

Résumé. La structure de bandes de cisaillement créées dans des poudres réactives Ti-Si a été étudiée avec le collapsé symétrique d'un cylindre de parois épaisses. Les bandes de cisaillement se forment à des déformations globales de 0.2-0.4 à une vitesse de déformation de 10^4 s^{-1} . Dans les bandes de cisaillement les déformations de cisaillement atteignent des valeurs jusqu'à 100 et la vitesse de déformation est 10^7 s^{-1} . Les réactions chimiques sont initiées dans ces bandes de cisaillement. Leur propagation dans l'échantillon demande une déformation globale critique. La modélisation des bandes de cisaillement avec la réaction des poudres réactives est proposée. Il est possible d'estimer le taux de réaction à partir de régions triangulaires formées par les bandes de cisaillement dans lesquelles il n'y a pas eu de réaction.

1. INTRODUCTION

The importance of shear deformation on chemical reactions was first demonstrated by Bridgman [1], and this was reemphasized by Vereshchagin *et al.* [2], Teller [3] and Enikolopyan *et al.* [4]. Under shock conditions, Dremin and Breusov [5] suggested that shear can assist chemical reactions and proposed the "ROLLER" model to explain this phenomenon. Recently, shock densification experiments conducted on Mo-Si, or Nb-Si powder mixtures by Yu *et al.* [6], and Meyers *et al.* [7] and Nesterenko *et al.* [8-10] revealed the formation of localized reactions in nonuniformly deformed areas. These studies also showed that the powder mixtures intensely deformed in localized regions underwent chemical reaction even at pressures lower than the shock threshold pressure. Nesterenko *et al.* [8-10] carried out controlled shear experiments at a shock pressure lower than 1 GPa and demonstrated that intense shear deformation can initiate chemical reaction. The objectives of this research are: (a) to establish the shear-induced chemical reactions, and (b) to find the threshold global strains which can initiate shear localization and which can trigger and propagate the chemical reactions. To achieve these purposes, the controlled high-strain, high-strain-rate experiments [8-11] were conducted to generate shear localization by varying global strains. Ti-Si reactive powder mixtures were used to investigate the chemical reactions under shear localization, because of their exothermic heat which can sustain the reactions.

2. EXPERIMENTAL PROCEDURES

A Ti-Si (74 wt% - 26 wt%) powder mixture in its stoichiometric composition of the intermetallic compound Ti_3Si_3 was used in this research. The powders (from CERAC) had sizes of ~325 mesh ($< 44 \mu\text{m}$), high purity (99.5% for Ti; 99.9% for Si) and irregular shape. The thick-walled cylinder (TWC) method [8-11] was applied for this investigation. The experimental configuration was used to generate controlled and prescribed shear localization in porous samples. The porous powders were initially placed in a tubular cavity between a central copper rod (diameter ~16 mm) and an outer copper tube (inner diameter ~20 mm

and outer diameter ~ 31 mm). The first explosive (mixture of ammonite and sand in 3:1 volume ratio) with low detonation velocity (~ 2.5 km/s) was used to densify the powder. No significant shear localization was observed after this stage because the global deformation is sufficiently small (final diameter of inner surface of driving copper cylinder is equal to 18–19 mm). This stage produced mainly the densification of the powder. An orifice with diameter 11 mm was drilled along the longitudinal axis of copper rod and a cylindrical copper stopper rod was inserted in the central orifice. This composite cylinder was deformed by the detonation of a second cylindrical explosive charge (ammonite) with a detonation velocity of 4.0 km/sec, an initial density of 1 g/cm³, and an outer diameter of 60 mm. This second explosive event produced significant plastic deformation in densified porous layer which was highly localized in shear bands and not homogeneously distributed.

3. RESULTS AND DISCUSSION

Four different deformation levels were applied in the second explosive event; global strains of 0.23, 0.32, 0.35, and 0.37 were obtained. The global strains and strain rates for Ti-Si powder mixtures layers can be obtained quantitatively from the strains in compressible copper shell driving the homogeneous deformation process [8-10]. Table 1 shows the global strains of the inner layers with different sized stoppers. Profuse shear localization can be seen in samples with $\epsilon \sim 0.32, 0.35,$ and 0.37 , but not with $\epsilon \sim 0.23$. The global view of shear localization after deformation stage is shown in Figures 1. The local shear strain is the ratio of the displacement, Δ , and the thickness of the shear band, δ [8–10]. Local shear strains vary between 10 and 100, approximately.

The microstructural observations for Ti-Si system are shown in Figures 2. After the second explosive event with varying deformation conditions, the structures are quite different. Although there are no well developed shear bands at $\epsilon \sim 0.23$, small localized regions of shear concentration were observed (Fig. 2(a)). This phenomenon is probably due to material nonuniformity or fracture of Si particles. Figs. 2(b), (c) present the typical shear band structure for $\epsilon \sim 0.32$ and 0.35 , respectively. At $\epsilon \sim 0.32$ and 0.35 , partial reaction was found only inside shear localization regions (shown by arrows in Figs. 2(b), (c)). Fracturing and extensive plastic flow of Ti particles inside shear localization regions is similar to the Nb-Si system [8-10]. In some experimental results at $\epsilon \sim 0.37$, the reaction propagated throughout the whole specimen (Fig. 2(d)) except the triangular area produced by discontinuity in displacement due to shear localization (Fig. 1(b)). Only cracks were left as the main feature of shear localization, as a result of solidification and shrinkage of molten reacted products. The unreacted triangular area is due to rapid heat extraction by the copper walls at an angle of 45°. The x-ray diffraction pattern for the fully reacted specimen is shown in Figure 3 and the reacted products were confirmed as Ti₅Si₃. The melting point of Ti₅Si₃ is 2403 K; the reaction is initiated inside the shear localization regions, and the heat in the environment of shear regions must be higher than 2403 K. This high local temperature is due to the heat transferred from plastic work and released from chemical reaction. This increase in temperature from plastic work ΔT_s can be estimated by:

$$\Delta T_s = \frac{1}{\rho C_{pl}} \int_0^{\gamma} \tau d\gamma \quad (1)$$

where ρ and C_{p1} are the initial density and heat capacity of unreacted densified powder; they are equal to 3.85 g/cm³ and 0.57 J/g, respectively. The shear stress, τ , was equal to approximately 0.5 GPa [9] and thermal softening was ignored. If the local shear strain is 20, then the plastic work is equal to 1170 J/g and ΔT_s is equal to 2100 K. This temperature is higher than the melting point of silicon (1700 K). Meyers *et al.* [12] and Vecchio *et al.* [13] considered this temperature as the initiation temperature for reaction in shock compression.

Assuming that the reaction is adiabatic and the process is initiated at 1700 K:

$$-\Delta H_{1700} = \int_{1700}^{T_m} C_{p2} dT + L_m + \int_{T_m}^{T_{ad}} C_{p3} dT, \quad T_{ad} > T_m \quad (2)$$

where ΔH_{1700} (≈ -247 kJ/mole) is the heat of reaction at 1700 K, T_m (≈ 2403 K) is the melting point of product Ti₅Si₃, L_m (≈ 25.6 kJ/mole) is the latent heat of fusion for Ti₅Si₃, C_{p2} ($\approx 196.44 + 0.045T - 2 \times 10^{-6}T^2$

Table 1: Global strain for Ti-Si mixture

Diameter of copper stopper (mm)	6	3	1.5	0
Global strain ϵ	0.23	0.32	0.35	0.37

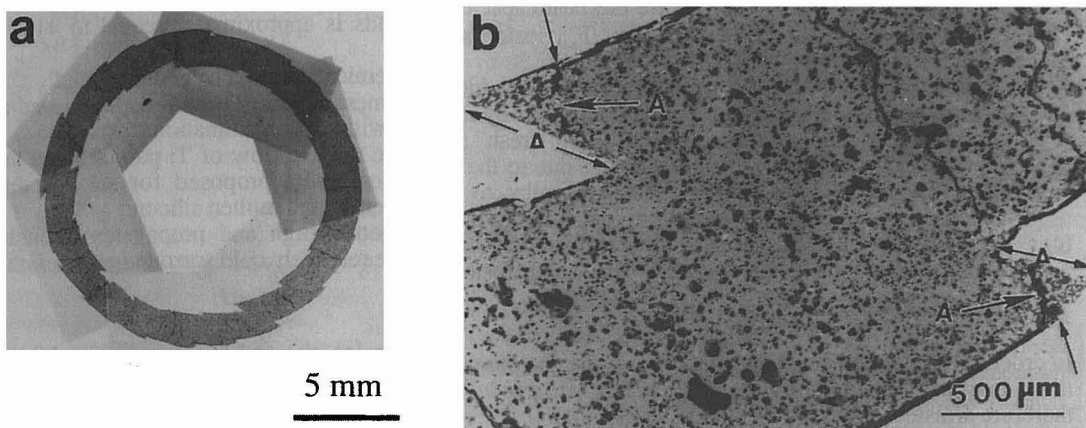


Figure 1: (a) Global view of Ti-Si mixture layer after deformation ($\epsilon \sim 0.37$); (b) close-up of shear localization region with displacement, Δ .

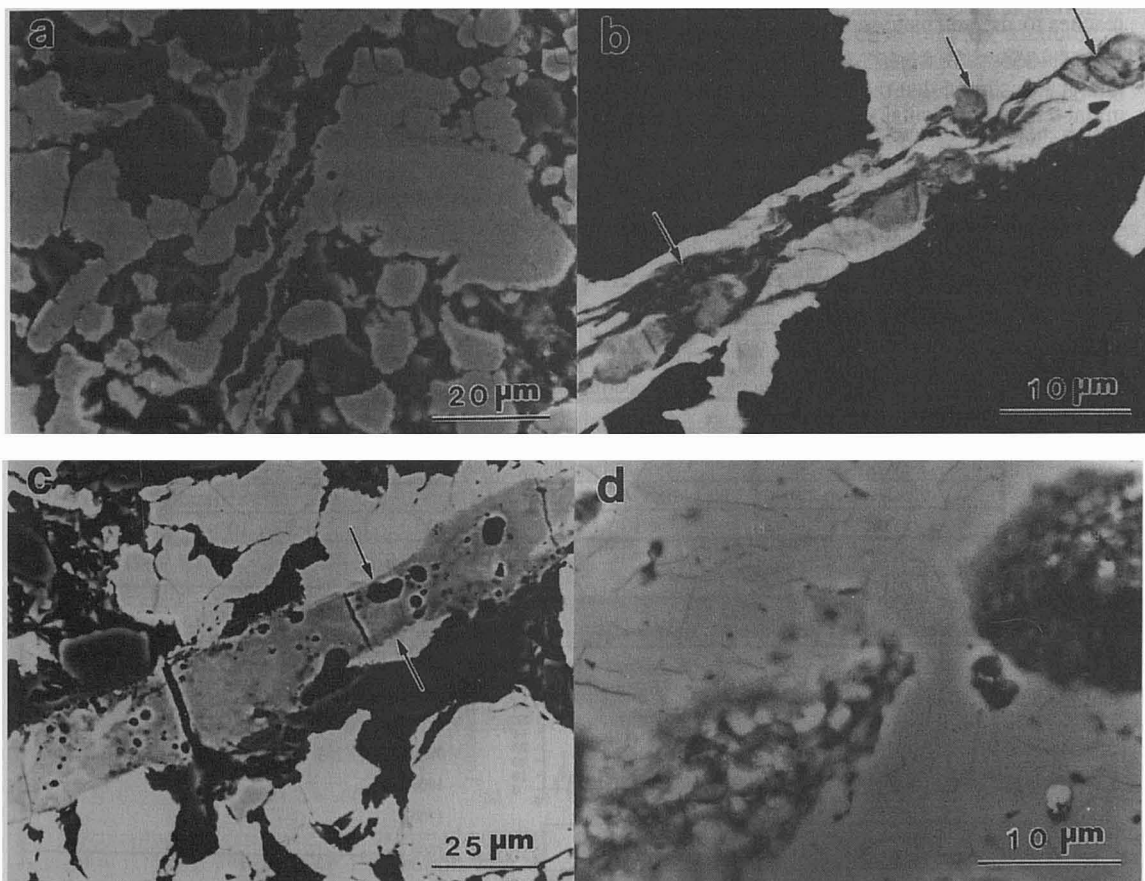


Figure 2: Deformed Ti-Si mixtures under global strain: (a) ~ 0.23 ; (b) ~ 0.32 ; (c) ~ 0.35 ; and (d) ~ 0.37 .

J/mole·K) and C_{p3} (≈ 42.2 J/mole·K) are the heat capacities of solid and liquid phase Ti_5Si_3 , respectively [14]. The calculated adiabatic temperature, T_{ad} , inside shear bands is approximately equal to 4100 K, higher than the melting point of Ti_5Si_3 .

According to the observations, a mechanism of shear-induced chemical reaction can be proposed:

- (a) Ti particles are multifractured and split into foils by localized mesoshears. These foils are heated as a result of intense shear deformation and have “fresh” surfaces without contamination by oxides.
- (b) Si particles are molten and reaction begins due to the extensive relative flow of Ti particles and those molten Si inside shear bands. This is similar to the Roller model proposed for shock-induced reactions [5]. The reaction proceeds along the interface between Ti and molten silicon.
- (c) Reaction continues in places where temperatures are sufficiently high and propagates throughout entire specimen, then is quenched by thermal diffusion into the relatively cold surrounding materials.

4. REACTION RATE ANALYSIS

In order to estimate the reaction rate, one can use the unreacted triangles, shown by arrows in Fig. 1(b). In these unreacted triangular regions, the reaction rate was lower than the rate of heat loss and the reaction was therefore arrested. Thus, $\partial T/\partial t$ should be less than 0. From the conservation of energy, one can obtain:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + \frac{Q}{C_p} \frac{\partial \eta}{\partial t} < 0, \quad \frac{Q}{C_p} \frac{\partial \eta}{\partial t} < -\alpha \frac{\partial^2 T}{\partial x^2}, \quad \dot{Q}_r = Q \frac{\partial \eta}{\partial t} < -\alpha C_p \frac{\partial^2 T}{\partial x^2} \quad (3)$$

where C_p is the heat capacity (J/kg·K), α is the thermal diffusivity (m^2/s), ($\alpha = k/\rho C_p$, k is the thermal conductivity (W/m·K)), η is the degree of conversion, \dot{Q}_r is the reaction rate. When the temperature reaches to the adiabatic temperature T_{ad} , the reaction rate \dot{Q}_r is maximum [15]. The adiabatic temperature for $5Ti+3Si \rightarrow Ti_5Si_3$ is 2403 K for the heat of reaction at 298 K [16]. Therefore, to estimate the reaction rate, it is assumed that the unreacted triangle consists of a 5Ti+3Si powder mixture at 2403 K because the initial temperature outside shear bands is 298 K; the temperature in copper is 298 K; and the fully reacted regions with Ti_5Si_3 compound is at 2403 K. In this case, only heat transfer is considered to calculate the cooling rate for this triangle region. The thermophysical properties are listed on Table 2 [16, 17]. Fig. 4 shows the calculated results at point A in this region [18]. Points A marked the boundaries between reacted and unreacted regions. From the calculated temperature-time curve (Fig. 4), one can estimate the cooling rates; this corresponds to the slope of the curve. The cooling rate varies as a function of time and is maximum at the inflection point of the curve in Fig. 4. The rate of heat loss \dot{Q}_{loss} is:

$$\dot{Q}_{loss} = C_p \frac{\partial T}{\partial t}, \quad \dot{Q}_r < -\dot{Q}_{loss} \quad (4)$$

Table 2 Thermophysical properties for Cu, 5Ti+3Si mixture, and Ti_5Si_3

Thermophysical Property	Cu	5Ti+3Si	Ti_5Si_3
ρ (kg/m ³)	8930	3850	4315
k (W/mK)	398	36.5	15.2
C_p (J/kgK)	386	570	773
α (m ² /s)	1.15×10^{-4}	1.66×10^{-5}	4.56×10^{-6}

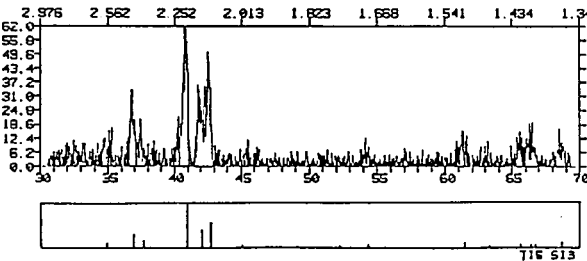


Figure 3: X-ray diffraction analysis results of products.

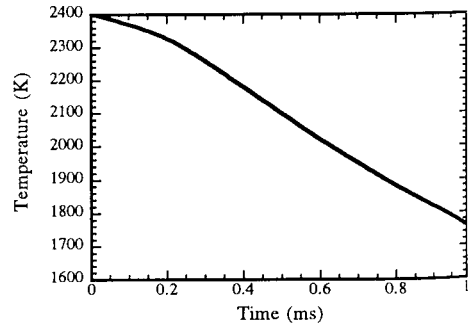


Figure 4: Predicted temperature profile inside the unreacted triangular regions (points A in Fig. 1(b)).

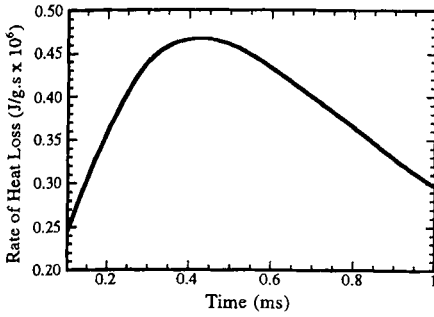


Figure 5 Predicted rate of heat loss inside the unreacted triangular region (points A in Fig. 1(b)).

Fig. 5 shows the time-dependent rate of heat loss. The maximum \dot{Q}_{loss} is equal to 4.5×10^5 J/g.s. Therefore, the reaction rate for the Ti-Si powder mixtures should be less than this value.

5. PERIODIC "HOT SPOT" MODEL

From the experimental results, it can be seen that distribution of shear localization regions is periodic. Therefore, a model for the idealized periodic distribution of "hot spots" in reactive powder mixtures is proposed. Figure 6 is a schematic illustration of the idealized model. The "hot" shear localization regions (shaded area) have a width equal to δ (10–20 μm) and a spacing d (~600 μm). The temperature inside the shear localization regions increases to T_s ($= T_0 + \Delta T_s$) during deformation. If T_s is sufficiently high, the chemical reactions between reactive powder mixtures can be initiated. At this time, the reaction heat is released and the temperature increases by some amount ΔT . Therefore, the temperature inside the shear localization regions is $T_s + \Delta T$. However, the surrounding powder mixtures are at a lower temperature ($T = T_0 \approx 300\text{K}$). The heat will be conducted to the surrounding. The conservation of energy for this model is given by:

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \rho Q \frac{\partial \eta}{\partial t} + \frac{\partial(\tau \dot{\gamma})}{\partial t}, \quad \frac{\partial \eta}{\partial t} = K_0 (1 - \eta)^n e^{-\frac{E}{RT}} \quad (5)$$

where k is the thermal conductivity (W/m.K), K_0 is the reaction-rate constant (s^{-1}), n is the order of the reaction, E (~200 kJ/mol [19]) is the activation energy for the reaction, and R is the universal gas constant. For the sake of simplicity, the following assumptions are made:

- (a) The shear localization and the chemical reaction do not occur simultaneously, i.e. they occur sequentially.
 (b) Define $t = 0$ when T_s (≈ 2400 K) is reached. Therefore, the deformation work term in Eqn. 5 can be eliminated and the initial condition defined as:

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \rho Q \frac{\partial \eta}{\partial t}, \quad (6)$$

$$\text{I.C.} \quad T(x, 0) = \begin{cases} T_s & \text{at } 0 \leq x < \delta/2, d - \delta/2 < x \leq d \\ T_0 & \text{at } \delta/2 \leq x \leq d - \delta/2 \end{cases}$$

- (c) The boundary conditions are defined as:

$$\text{B.C.} \quad \frac{\partial T(x, t)}{\partial x} = 0 \quad \text{at } x = 0, d/2, d$$

- (d) Thermophysical properties are assumed constant.

Assuming $n=1$, the temperature distribution with varying time is shown in Figs. 7. Fig 7(a) shows that at $T_s \approx 2400\text{K}$, the reaction can propagate throughout the entire specimen. The maximum temperature in shear bands is equal to approximately 4000 K. It is consistent with the calculated adiabatic temperature. At $T_s \approx$

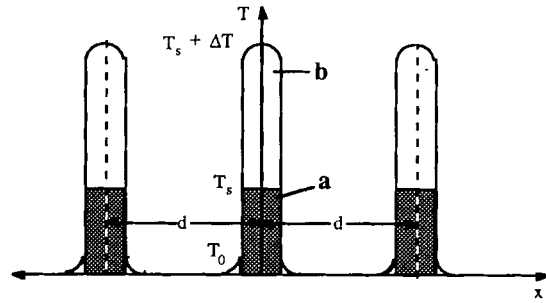


Figure 6 Schematic one-dimensional model of periodic "hot spots": (a) temperature distribution after shear localization; (b) temperature distribution after chemical reaction initiation.

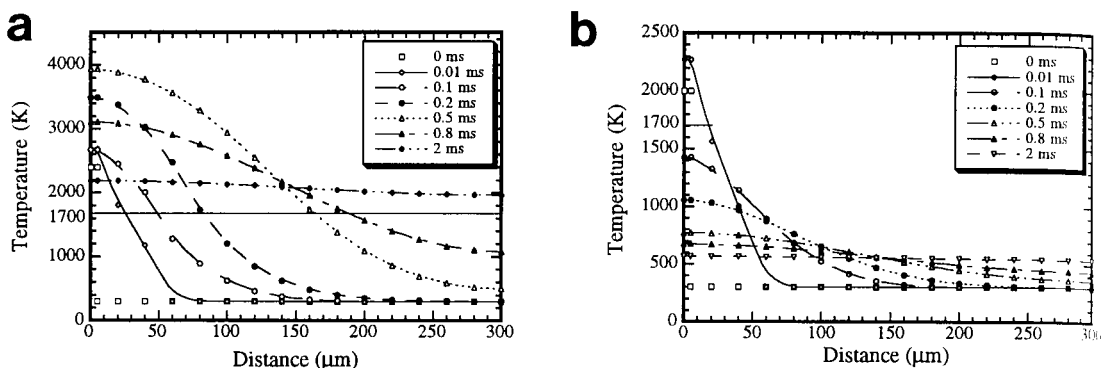


Figure 7 Temperature distribution calculated by periodic "hot spots" model: (a) $T_s \approx 2400$ K; (b) $T_s \approx 2000$ K.

2000 K, the reaction only can propagate a short distance (Fig 7(b)). Therefore, the critical temperature, T_c ($2000 \text{ K} < T_c < 2400 \text{ K}$) created by shear deformation can be predicted by this model.

ACKNOWLEDGMENTS

This research is supported by the U.S. Army Research Office, Contract DAAH-04094-G-031 and by the U.S. Office of Naval Research, Contract N00014-94-1-1040 (program officer Dr. J. Goldwasser). The help of M.P. Bondar, Y. Lukyanov (IGIL, Novosibirsk), and S.M. Usherenko (RIIP, Minsk) in conducting experiments is gratefully acknowledged. We thank Dr. E. Olevsky for help with the heat transfer and reaction computations.

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