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STRAIN-INDUCED STRUCTURAL CHANGES AND CHEMICAL REACTIONS—I. THERMOMECHANICAL AND KINETIC MODELS

V. I. LEVITAS[1]†, V. F. NESTERENKO[2] and M. A. MEYERS[2]

[1]University of Hannover, Institute for Structural and Computational Mechanics, Appelstraße 9A, 30167 Hannover, Germany and [2]Department of Applied Mechanics and Engineering Sciences, University of California, San Diego, La Jolla, CA 92093, U.S.A.

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Abstract—Strain-induced chemical reactions were observed recently (Nesterenko *et al.*, *Appl. Phys. Lett.*, 1994, **65**(24), 3069; *Metall. Met. Trans. A*, 1995, **26**, 2511) in experiments in the shear band in both Ti–Si and Nb–Si mixtures. Reactions can start in the solid state or after melting of at least one component. One of the aims is to find theoretically, whether there are possible macroscopic mechanisms of mechanical intensification of the above and other chemical reactions due to plastic shear in the solid state. Continuum thermodynamical theory of structural changes with an athermal kinetics, which includes martensitic phase transformations, plastic strain-induced chemical reactions and polymorphic transformations, is developed at finite strains. The theory includes kinematics, criterion of structural change and extremum principle for determination of all unknown variable parameters for the case with neglected elastic strains. Thermodynamically consistent kinetic theory of thermally activated structural changes is suggested. The concept of the effective temperature is introduced which takes into account that temperature can vary significantly (on 1000 K) during the chemical reactions under consideration. The theory will be applied in Part II of the paper for the description of chemical reactions in the shear band. © *1998 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.*

1. INTRODUCTION

It is known after classic experiments by Bridgman [1–4], that phase transitions (PTs) and chemical reactions exhibit a very strong influence of large shear plastic strains. This effect can be tentatively divided into thermodynamical and kinetic ones. The thermodynamical effect of plastic shear results in a significant reduction in PT pressure and (or) temperature; it is possible to obtain fundamentally new materials which cannot be produced without additional plastic strains [1–9]. The kinetic effect is related to the acceleration in several orders of magnitude of the rate of various chemical reactions (e.g. in polymers [10, 11], oxide decomposition [12], organic and inorganic reactions [13–15]) due to intense plastic shear.

All the above experimental results are obtained under compression and shear of materials in Bridgman anvils. It has recently been observed that intense plastic deformation inside the shear band can initiate chemical reactions in powder mixtures [16, 17]. This occurs in the absence of shock-wave loading, in high-strain-rate deformation which ensures adiabatic or quasi-adiabatic conditions in the narrow deformation bands. This regime is intermediary between thermal combustion synthesis and shock-induced reactions [18–20]. The mechanical flow of constituents and associated temperature rise are sufficient to initiate the chemical reaction within these regions. The critical shear conditions for initiation and propagation of reactions in two systems with widely varying heats of reaction, ΔH, namely Nb–Si ($\Delta H = -138$ kJ/mol) and Ti–Si ($\Delta H = -580$ kJ/mol) were experimentally established [16, 17, 21, 22], but a rigorous mechanochemical analysis of shear-induced chemical reactions is absent; likewise, the extent to which plastic flow can affect chemical reactions is not established. This paper is a first attempt to clarify, using a macroscopical approach, the possible coupling of plastic flow and chemical reactions in the shear band. The new term "reaction-induced plasticity" (RIP) is introduced to emphasize the principle importance of strong coupling between plasticity and reaction.

Due to the above experiments plastic strain is considered as a factor, producing new physical mechanisms of PT and chemical reactions. There is, for example, a quantum mechanical approach based on the assumption that large plastic shears produce a so-called highly excited atom–ion state, which allows qualitative interpretation of material behaviour under such conditions [23]. Gilman [24, 25] suggests, that elastic shear strain can accelerate

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†To whom all correspondence should be addressed.

chemical reactions by lowering the HOMO (highest occupied bonding molecular orbital)–LUMO (lowest unoccupied anti-bonding molecular orbital) energy gap.

Shock wave initiation of the Ti_5Si_3 reaction in porous mixture 5:3 Ti:Si atomic ratio was considered by Vreeland *et al.* [26]. It was experimentally found that critical shock energy for complete reaction depends upon powder particle size and the initial porosity of powder. Thadhani *et al.* [27] emphasized that "the initiation of chemical reactions in shock compression of powders is controlled by solid-state mechanochemical processes, and cannot be qualitatively or quantitatively described by thermochemical models".

A continuum thermomechanical theory for the description of martensitic PT in elastoplastic materials was developed by Levitas [28–31]. Based on this theory, the effect of shear stresses or plastic shear on martensitic PT was analysed for two typical experimental procedures: first, for PT under compression of materials in Bridgman anvils and additional plastic shear due to rotation of one anvil [30]; second, for PT in a thin layer in a half-space under the action of normal and shear stresses [30, 31]. The solutions illustrate the fundamental difference in PT conditions for strongly non-homogeneous pressure distribution in the first problem and for the homogeneously distributed pressure and shear stresses in the second problem. In particular, in the first problem rotation of an anvil works much more effectively for the synthesis of high strength phases than low strength ones. In the second problem additional shearing significantly improves the condition of appearance of soft materials and weakly affects the appearance of strong materials. A number of experimental results are explained, and some of the interpretations are completely unexpected.

One of the limitations of the above solutions is a small strain consideration. Continuum theory of martensitic PT at finite strains is developed in Refs [28, 31], but there is no application of the theory for the solution of boundary-value problems.

The aims of the present two papers are as follows:

- to extend the thermodynamic theory of martensitic PT developed by Levitas [28–31] to a wide class of strain-induced athermal structural changes (SC), including some chemical reactions, diffusive PT and so on; to make it consistent with chemical thermodynamics and to analyse which new effects exhibit the theory in comparison with classical chemical thermodynamics;
- to suggest a local (at the level of local transformed particle instead of in terms of volume fraction of new phase) kinetic description of the thermally activated reactions, consistent with the above thermodynamic theory;
- to derive simple finite strain theory of SC in rigid-plastic materials, based on the general theory of martensitic PT [28, 31];
- to find an analytical solution of the problem of SC in a shear band;
- to derive and analyse the reaction-induced plasticity phenomenon, similar to transformation-induced plasticity for martensitic and diffusive PT.
- to analyse the effect of shear stress and plastic shear on the thermodynamic condition of athermal SC and kinetics of thermally activated SC, based on the theory and solution obtained.

Direct tensor notations are used throughout this and the companion paper. Vectors and tensors are denoted in boldface type; **mn** is the dyadic product of vectors **m** and **n**; $\mathbf{A}\cdot\mathbf{B}$ and $\mathbf{A}:\mathbf{B}$ are the contraction of tensors over one and two indices. Let superscripts t and −1 denote transposition and inverse operation, subscript s symmetrization of the tensors, $\Delta\mathbf{a} = \mathbf{a}_2 - \mathbf{a}_1$ the differences in **a** after and before the SC, **I** the unit tensor second order, **i** the two-dimensional unit tensor second order, dev **A** is a deviatoric part of **A**, $|\mathbf{A}| := (\mathbf{A}:\mathbf{A})^{1/2}$ the modulus (amplitude) of tensor **A**, ∇ the gradient operator, and $:=$ means equal per definition.

2. EXPERIMENTAL TECHNIQUE AND RESULTS

Ti–Si (74 wt%–26 wt%) and Nb–Si (68 wt%–32 wt%) powder mixtures close to their stoichiometric compositions of intermetallic compounds, Ti_5Si_3 and $NbSi_2$, respectively, were used in this research. The powders (from CERAC) had sizes of −325 mesh ($< 44\ \mu$m), high purity ($> 99.5\%$) and irregular shape. These compounds had been investigated in earlier shock experiments and therefore these are good compositions for comparison with previous works. These systems have quite different enthalpies of reaction, ΔH [32]:

$$5\mathrm{Ti} + 3\mathrm{Si} \longrightarrow \mathrm{Ti_5Si_3},\ \Delta H = -580\ \mathrm{kJ/mol};$$
$$\mathrm{Nb} + 2\mathrm{Si} \longrightarrow \mathrm{NbSi_2},\ \Delta H = -138\ \mathrm{kJ/mol}. \qquad (1)$$

These differences in heat of reaction can result in widely different sensitivities to the initiation and propagation of reaction. Meyers [33] and Yu [34] calculated threshold pressures for reaction at 65% initial density and obtained values of 1.5 and 9 GPa for Ti_5Si_3 and $NbSi_2$, respectively. These calculations are based on the Krueger–Vreeland criterion [35] and are consistent with experimental results of Yu [34], Vecchio *et al.* [36] and Vreeland *et al.* [26].

The thick-walled cylinder method was developed by Nesterenko *et al.* [37, 38] for the investigation of high-strain, high-strain-rate deformation of solid materials (such as metals, ceramics and polymers), and modified for the study of inert and reactive porous powder mixtures [16, 17]. The schematic of the set-up is described by Nesterenko *et al.* [37, 38] and Chen *et al.* [21, 22] and is presented in Fig. 1(a). Detonation is initiated at the top of the charge and propagates along the cylinder axis. The powder is first consolidated by a low amplitude explosive charge, which produces weak shock loading with pressures less than 1 GPa without any chemical reactions. An orifice is then drilled along the cylinder axis and a second explosive event is carried out. This second explosive produces significant plastic deformation in the densified powder layer which results in shear localization [Fig. 1(d)]. The initial velocity of the inner cylinder surface and the collapse time were measured by the noncontact electromagnetic method [37] and are approximately 200 m/s and 8×10^{-6} s.

The porous powder was initially placed in a tubular cavity between a central copper rod and an outer copper tube. Explosive 1 [Fig. 1(a)] with low detonation velocity was used to densify the powder. No significant shear localization was observed after this stage because the global deformation is sufficiently small. This stage produced mainly the densification of the powder. The following densifications were accomplished by the first explosive event [Fig. 1(a)]: Ti–Si mixture from ~35 to 65% of theoretical density; and Nb–Si mixture from ~50 to ~75% of theoretical density. The explosive event 2 produced significant plastic deformation in the densified porous layer which was highly localized in shear bands and not homogeneously distributed [Fig. 1(d)]. The critical initiation and propagation conditions for shear localization and chemical reaction were obtained by varying the global strain in explosive event 2. Experiments with explosive event 2 for Ti–Si mixtures were also conducted without

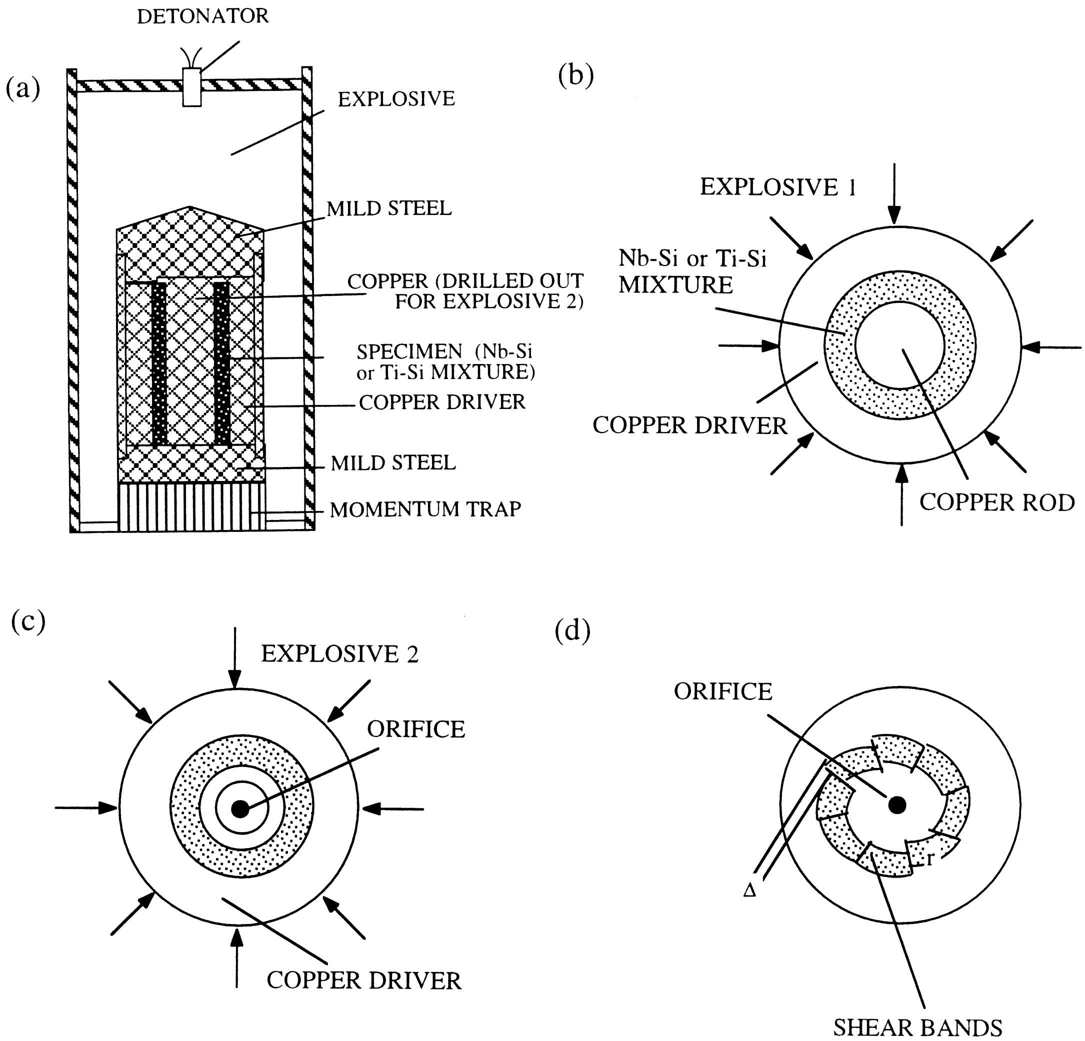


Fig. 1. Geometry and sequence of deformation events in thick-walled cylinder method: (a) experimental setup with explosive charge; (b) initial geometry, densified by explosive; (c) hole drilled into copper rod for deformation stage; (d) densified and deformed powder by explosive 2; notice formation of shear bands.

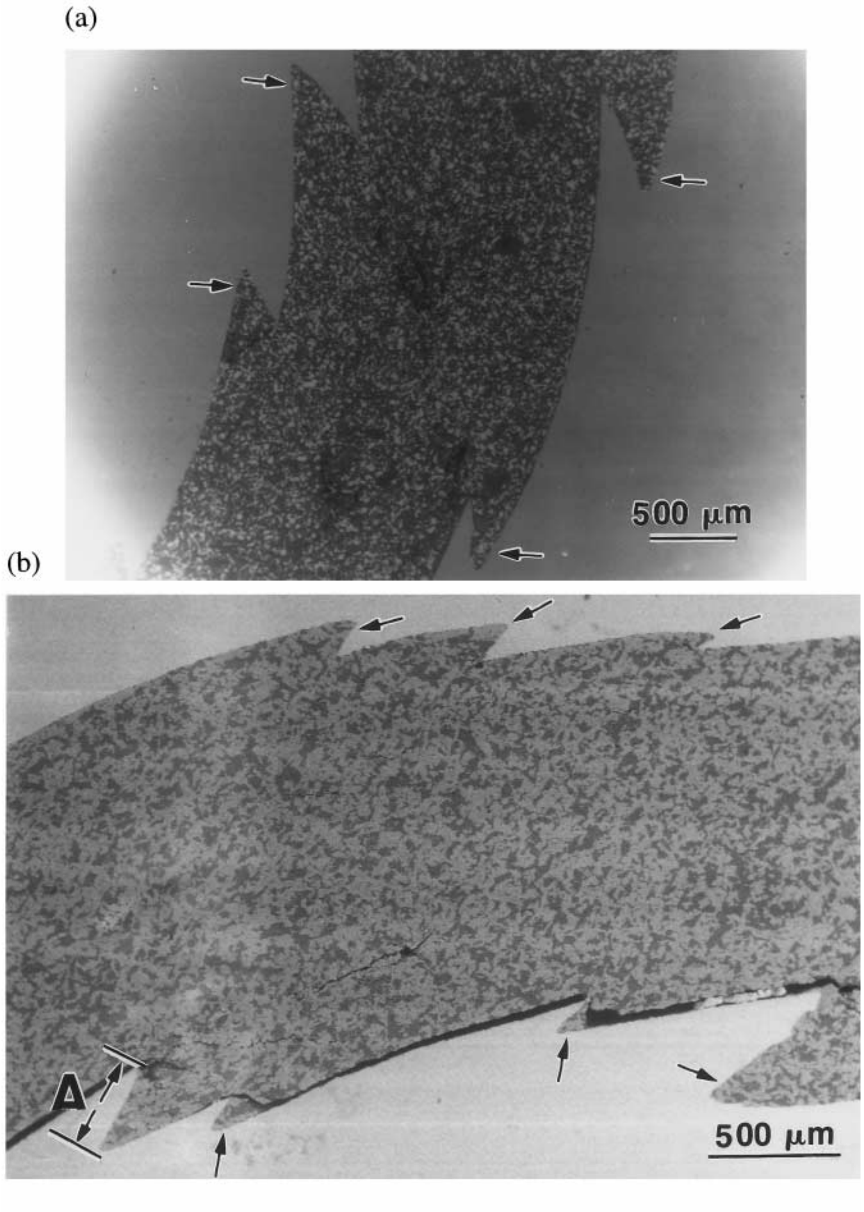


Fig. 2. Overall view of shear bands in: (a) Nb–Si mixture; (b) Ti–Si mixture.

creating a central orifice. After this shock loading without the collapse process, no shear localization or chemical reaction was observed. This confirms that the chemical reactions are truly strain controlled in the present experiments.

Figure 2 shows overall views of shear bands in both Nb–Si and Ti–Si mixtures. The ends of the bands are clearly visible by the formation of steps at the inner and outer surfaces of the thick-walled cylinder. They are marked by arrows in Fig. 2. The dark particles in the mixture are silicon, whereas the light particles are Nb or Ti. The particle size is approximately 50 μm. These bands started forming at a global effective strain, $\varepsilon_{\mathrm{eff}}\sim 0.25$, for both mixtures. The spacing between the bands was on the order of $\sim$600–1000 μm and was unaffected by the scale of the experimental setup, i.e. the number of shear bands increased linearly with the diameter of the cylinder [21, 22].

Closer views of the shear bands for the Nb–Si and Ti–Si are shown in Figs 3 and 4, respectively. It was possible to estimate the shear strain inside the band from the displacements, Δ, at the surfaces [see Fig. 1(d)] divided by the thickness of the bands,

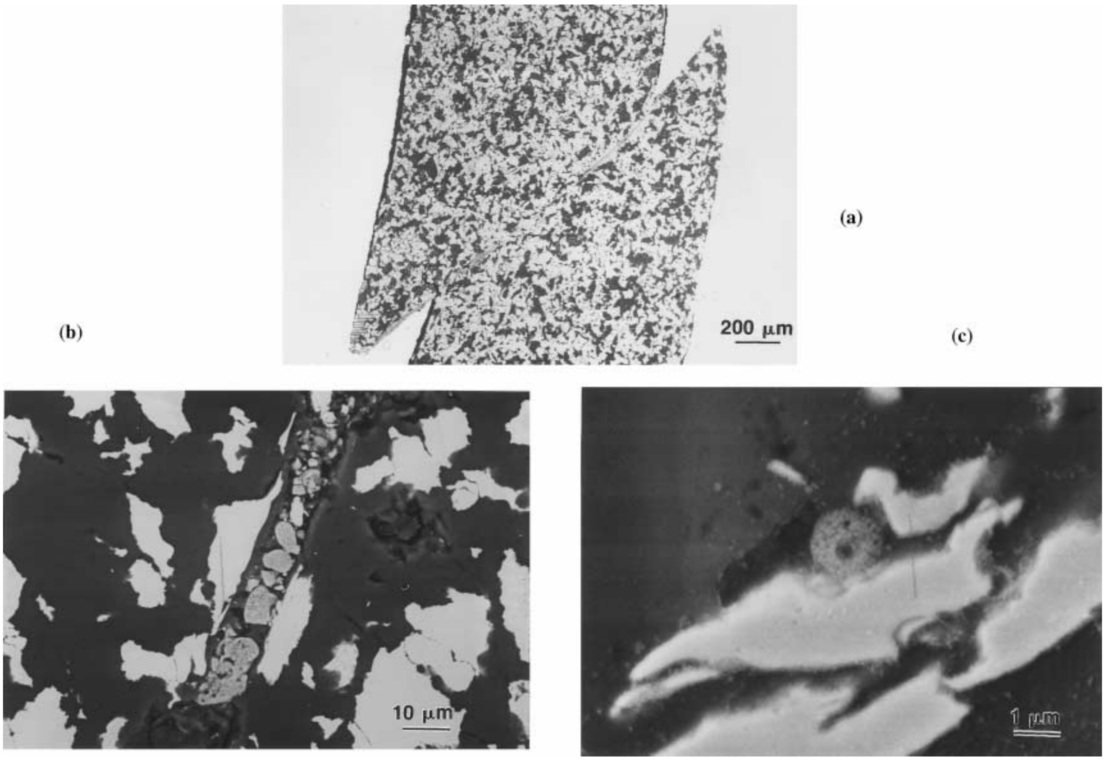


Fig. 3. Shear localization region in Nb–Si mixture: (a) deformed particles; (b) initiation of reaction inside shear band; (c) detail of reacted region.

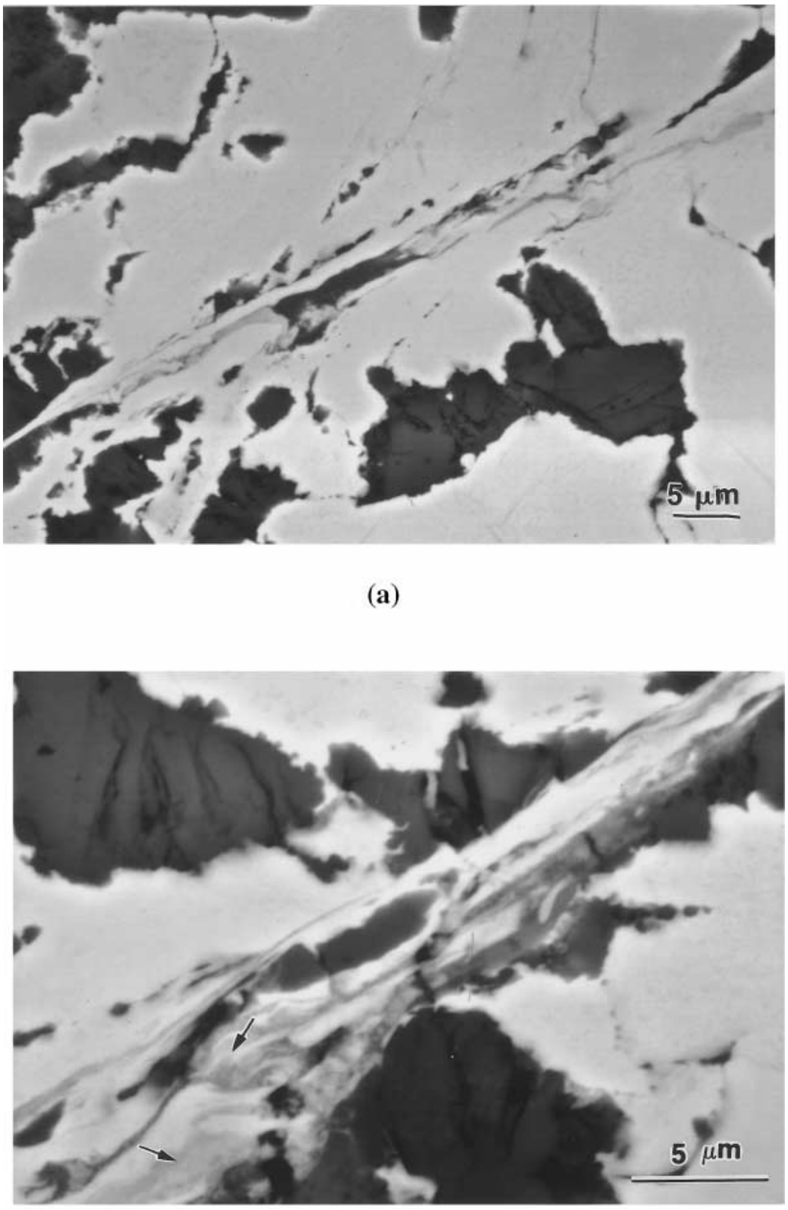
δ. The thickness of the shear bands, δ, was approximately 10–15 μm. Engineering shear strains as high as 60 were obtained in the experiments. As the displacement, Δ, and engineering shear strain, γ, increase, the microstructure within the band evolves. At lower strains, one observes primarily elongated Nb and Ti particles. These particles also fracture, creating fresh surfaces. The shear bands in these regimes, for the Nb–Si and Ti–Si mixtures, are shown in Fig. 3(a) and Fig. 4(a), respectively. For the Nb–Si mixture only partial reaction was observed, even at the highest shear strains. Figure 3(b) shows these regions, where the gray constituent is the reaction product. Figure 3(c) shows details of the reacted region. The mechanism of reaction, of the particle level, is discussed by Nesterenko *et al.* [16, 17] and Meyers *et al.* [32, 39]. Small Nb_5Si_3 spherules form at the interface between Si and Nb. For the Ti–Si mixture, on the other hand, complete reaction within the band could be obtained, at a sufficiently high shear strain. For $\gamma \sim 10$, the reaction occurred along the entire band, and for higher strains ($\gamma \sim 20$–40) the reaction actually propagated throughout the entire specimen [21, 22]. This sequence is shown in Figs 4(a)–(d). Figure 4(a) shows the unreacted shear bands, whereas Figs 4(b)–(d) show increasing extents of reaction, which are produced by increasing shear strains.

Both observations and temperature calculations [21, 22] show that initial materials and products are melted during the heating due to plastic deformation and reaction heating. It is very difficult to determine experimentally whether reactions start in the solid state or after melting of at least one component. In the second case the role of plastic shearing is reduced to heating the mixture up to the melting temperature of Si. One of the aims of this work is to establish analytically, whether there are possible macroscopic mechanisms of intensification of the above chemical reactions due to plastic shear in the solid state. In the sections that follow a number of simplifying assumptions will be made (e.g. temperature dependence of thermochemical properties is neglected) in order to formulate the simplest model and to obtain an analytical solution.

3. THERMODYNAMICS OF STRUCTURAL CHANGES WITHOUT STABLE LOCAL INTERMEDIATE STATE

3.1. Model for structural changes without stable local intermediate state

Let us consider a uniformly deformed infinitesimal volume in a process of SC. The volume can belong to the new nucleus or interface. The following features are important for the model under consideration.

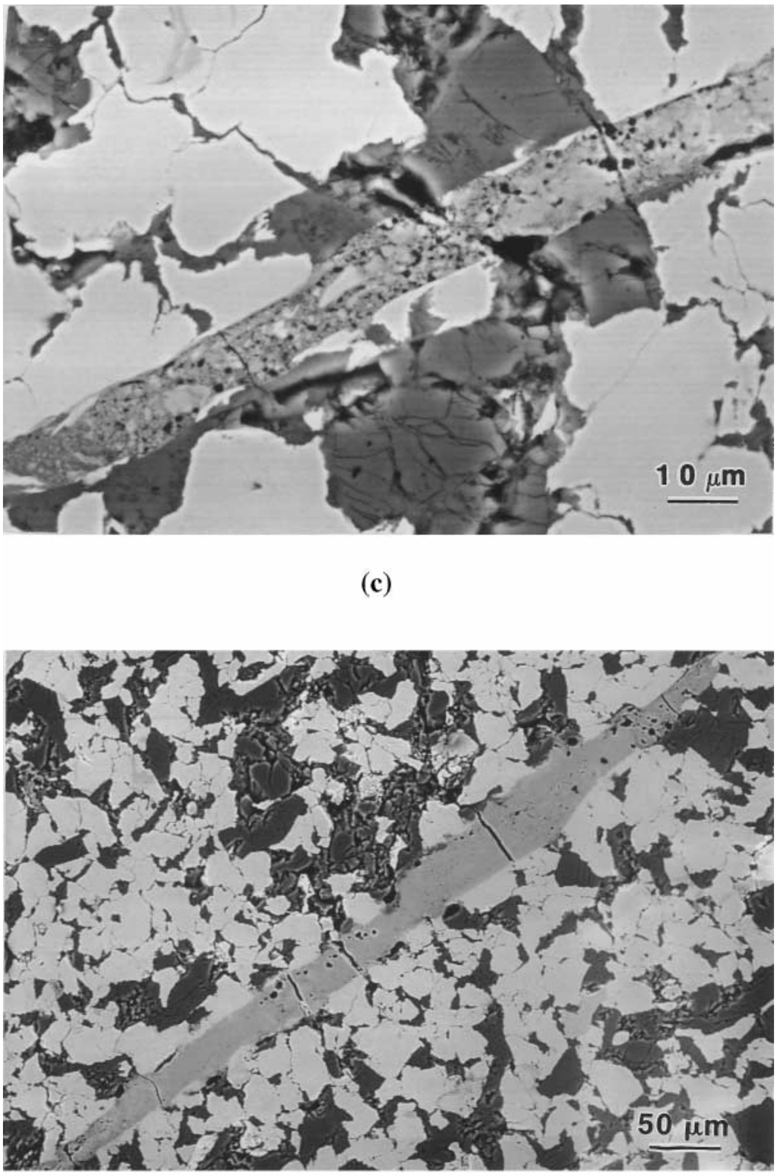


(a)

(b)

Figure 4(a) and (b).

1. As a main geometrical characteristic of SC under consideration we consider the transformation deformation gradient $\mathbf{F}_t$, which relates the geometry of infinitesimal material volume in the stress free state and some reference temperature θ_0 before and after SC. For martensitic PT the transformation deformation gradient $\mathbf{F}_t$ transforms the crystal lattice of the parent phase into the crystal lattice of the product phase. For twinning there is also correspondence between the crystal lattice before and after SC. For displacive–diffusive, diffusive PT and chemical reactions it is possible to determine for some macroscopic volume the deformation gradient related to SC. Using the polar decomposition theorem we obtain $\mathbf{F}_t = \mathbf{R}_t \cdot \mathbf{U}_t$, where $\mathbf{R}_t$ is the orthogonal rotation tensor and $\mathbf{U}_t$ the symmetric right stretch transformation tensor. The determinant $\det \mathbf{F}_t$ characterizes the volume change due to SC. We will further assume that for chemical reactions the transformation deformation gradient describes the change of volume only without change of shape, i.e. it is a spherical tensor $\mathbf{F}_t = a\mathbf{I}$.
2. For martensitic PT the transformation deformation gradient cannot be arbitrary (as elastic or



(c)

(d)

Fig. 4. Shear localization and chemical reaction in Ti–Si mixture: (a) deformed and fractured Ti particles; (b) initiation of reaction within shear band (grey area—see arrows); (c) partial reaction; (d) complete reaction.

plastic strain). For each PT the right stretch transformation tensor $\mathbf{U}_t$ is some fixed tensor to within symmetry operations. All intermediate values of the transformation right stretch tensor are unstable and cannot exist in an equilibrium. Due to the symmetry there is a finite number (e.g. 12 for the PT from cubic to monoclinic lattices) of crystallographically equivalent variants of martensite with the same (to within symmetry operations) $\mathbf{U}_t$.

For the structural changes discussed here, a similar approach will be used. The transformation process in an infinitesimal volume *cannot be stopped in an intermediate stage*. Consequently, material in the state before SC, which we will call phase 1, and in the state after SC, which is called phase 2, is stable only in each infinitesimal volume. We will call such SC *a SC without stable local intermediate state*. It is possible to consider a representative volume consisting of a mixture of phases 1 and 2 with a volume fraction c of the second phase, i.e. a global (for finite volume) intermediate stable state exists, but for each material point of this volume either $c = 0$ or 1.

Then during the SC at the given material point the transformation deformation gradient must reach the final value corresponding to phase 2 and cannot be fixed at any intermediate state. These features are similar to those for martensitic PT. Limitations for the set of final values of the transformation deformation gradient have to be formulated for each type of SC separately. For chemical reactions, only one final value of transformation deformation gradient exists which corresponds to the final value of parameter a.

Such a definition cannot be applied to the continuous transformation of the crystal lattice of one component by atoms of another substance or to spinodal decomposition. On the other hand, it allows direct application of the theory developed by Levitas [28–31].

3. The very short time $t_c = 55$–80 ns of the appearance of the martensitic nucleus [33, 40] enables, for quasi-static loading, instantaneous or so-called athermal kinetics of PT to be assumed. This means that, if under prescribed boundary conditions and temperature distribution, the martensitic PT could occur, it will occur instantaneously. Additionally, if after finishing the PT all the fields (stress, temperature, strain) are stationary, the PT will not proceed. For the continuation of the PT some fields should be changed due to a change of boundary conditions or internal processes (temperature variation, creep, stress relaxation and so on). Consequently, actual time does not play any role; stress, strain, temperature or their combination are parameters controlling transformation. The assumption of athermal kinetics enables application of the theory [28–30] without any changes.

As known from numerous experiments, plastic shearing accelerates the kinetics of various chemical reactions (e.g. in polymers [10, 11], for organic and inorganic reactions [13–15]) by several orders, making it practically instantaneous (like for martensitic PT), because the volume fraction of the product depends not on the time, but on the value of shear. At the stopping of shearing the chemical reaction or PT are interrupted. This means, that for such strain-induced SC with athermal kinetics the theory of martensitic PT [28–31] can be applied.

For diffusive, displacive–diffusive PT and chemical reactions or for dynamic loading real time is an essential parameter. The SC can proceed at fixed stress, strain and temperature for a rather long time. For such a situation the above theory has to be extended. This is done in Section 4 using the relation between dissipative force and rate as well as the concept of effective temperature.

Summarizing, let us give a definition of *SC without a stable local intermediate state*.

The SC will be considered as a process of variation of the transformation deformation gradient in infinitesimal or finite volume from the initial to final value which is accompanied by a jump in all thermomechanical properties. This process cannot be stopped at an intermediate state. Thermodynamical equilibrium for the intermediate value of the transformation deformation gradient is impossible.

3.2. Local thermodynamic description of structural changes

3.2.1. Kinematics and thermodynamics. We will consider simple materials only, i.e. a material's response at a given point is independent of the thermomechanical parameters at other points. Let the motion of the uniformly deformed infinitesimal volume in a process of structural change be described by the function $\mathbf{r} = \mathbf{r}(\mathbf{r}_0, t)$, where $\mathbf{r}$ and $\mathbf{r}_0$ are the positions of points in the actual V and reference V_0 configurations. The reference configuration coincides with the undeformable stress-free configuration of the first phase. We will neglect for simplicity the elastic and thermal strains in comparison with the plastic and transformation deformations. We assume [28, 31] for the finite strains a multiplicative decomposition of a total deformation gradient $\mathbf{F} = \partial\mathbf{r}/\partial\mathbf{r}_0$ into a transformational $\mathbf{F}_t$ part and a plastic deformation gradient in phase 1 $\mathbf{F}_{p1}$ (before SC), during SC $\mathbf{F}_p$ and after SC $\mathbf{F}_{p2}$ (in phase 2), i.e.

$$\mathbf{F} = \mathbf{F}_{p2} \cdot \mathbf{F}_t \cdot \mathbf{F}_p \cdot \mathbf{F}_{p1}. \qquad (2)$$

Here and later indices 1 and 2 denote the values before and after finishing SC. General kinematic relations with account for elastic and thermal deformation gradients are considered in Ref. [31] and can be used here as well. As in our concrete problems elastic and thermal strains are significantly smaller than plastic shear ($\gamma_p \gg 10$) as well as volumetric transformation strain and plastic normal strain which are of the order of 0.1, neglecting them does not change any conclusion, but simplifies equations significantly. In the case with elastic strain the inelastic strains which consist of transformational and plastic parts are eigenstrains and they have not to be consistent. This is important, if residual stresses after SC are of interest, which is not the case here. Neglecting elastic strains the total inelastic strains have to be consistent. If the distribution of transformation strain in the transforming region or at the interface between transforming and nontransforming region is not consistent, then transformation has to be accompanied by plastic strains even without external stresses in order to guarantee compatibility of total strains. This pure kinematic consideration leads in Part II to the revealing of the phenomenon of reaction-induced plasticity, which is very important for acceleration of chemical reactions.

The sequence of each contribution to the total deformation gradient in equation (2) and possible experimental methods of their separation are analysed in Section 8.3 of Ref. [31]. For martensitic PT $\mathbf{F}_t$ is a deformation of the crystal lattice which can be measured for instance by X-rays, and $\mathbf{F}_p$ is a deformation at the invariant crystal lattice which can be determined at known $\mathbf{F}$ and $\mathbf{F}_t$. For chemical reactions and other SC with pure volumetric transformation strain $F_t = a\mathbf{I}$, separation of transformation strain from plastic strain $\mathbf{F}_p$ is much easier than for martensitic PT, because transformation volume change can be determined through the measured densities of compact phases 1 and 2. The deformation process at each material point according to decomposition (2) is presented schematically in Fig. 5. Before the start of SC the total deformation is equal to the plastic deformation in phase 1. During transformation the deformation process occurs at some intermediate unstable state of material. Remember that this is not a mixture of phases 1 and 2, phases 1 and 2 or their mixture do not exist in the given material point during SC. That is why $\mathbf{F}_{p1}$ is fixed, as well as $\mathbf{F}_{p2}=\mathbf{I}$ and $\mathbf{F}_t$ and $\mathbf{F}_p$ describe simultaneously proceeding transformational and plastic strains in the intermediate unstable state of material. After finishing the SC at the given point tensors $\mathbf{F}_t$ and $\mathbf{F}_p$ are fixed (because the intermediate state does not exist in the given point) and total deformation is related to the change of plastic strain $\mathbf{F}_{2p}$ in phase 2. Figure 5 describes the sequences of deformation processes only and of course does not mean parallel connection or connection in sequences of rheological elements and that $\mathbf{F}_t=\mathbf{F}_p$.

We will concentrate now on the derivation of the governing equations for the material point during the SC. Since the strain $\mathbf{F}_{p2}$ after the SC does not affect the SC at the given point, assume without loss of generality $\mathbf{F}_{p2}=\mathbf{I}$, i.e.

$$\mathbf{F} = \mathbf{F}_t \cdot \mathbf{F}_p \cdot \mathbf{F}_{p1}. \tag{3}$$

Decomposition of the velocity gradient and deformation rate during the SC into transformation and plastic parts gives

$$\mathbf{l}:=\dot{\mathbf{F}} \cdot \mathbf{F}^{-1} = \dot{\mathbf{F}}_t \cdot \mathbf{F}_t^{-1} + \mathbf{F}_t \cdot \dot{\mathbf{F}}_p \cdot \mathbf{F}_p^{-1} \cdot \mathbf{F}_t^{-1} \tag{4}$$

$$\begin{aligned}\mathbf{d}&:=(\dot{\mathbf{F}} \cdot \mathbf{F}^{-1})_s = (\dot{\mathbf{F}}_t \cdot \mathbf{F}_t^{-1})_s \\ &\quad + (\mathbf{F}_t \cdot \dot{\mathbf{F}}_p \cdot \mathbf{F}_p^{-1} \cdot \mathbf{F}_t^{-1})_s = \mathbf{d}_t + \mathbf{d}_p; \\ \mathbf{d}_t&:=(\dot{\mathbf{F}}_t \cdot \mathbf{F}_t^{-1})_s;\ \mathbf{d}_p:=(\mathbf{F}_t \cdot \dot{\mathbf{F}}_p \cdot \mathbf{F}_p^{-1} \cdot \mathbf{F}_t^{-1})_s,\end{aligned} \tag{5}$$

where $\mathbf{d}_t$ and $\mathbf{d}_p$ are the transformational and plastic parts of the deformation rate. It is taken into account in equations (4) and (5) that during the SC $\dot{\mathbf{F}}_{p1} = 0$. In the present paper we will consider perfectly plastic materials and $\mathbf{F}_{p1}$ does not affect the constitutive equations. Consequently, without loss of generality we can omit $\mathbf{F}_{p1}$ in kinematic decomposition (2) as well, considering the configuration at the *beginning of SC* as the reference configuration.

Plastic deformation after the SC can be described in a standard way. Decomposition (2) and the equation $\mathbf{d} = (\dot{\mathbf{F}} \cdot \mathbf{F}^{-1})_s = \mathbf{d}_{p2} = (\dot{\mathbf{F}}_{p2} \cdot \mathbf{F}_{p2}^{-1})_s$ have to be used.

We introduce the dimensionless order parameter ξ $(0 \le \xi \le 1)$ which is related to $\mathbf{F}_t$ and has the following properties: SC starts at $\xi = 0$ and finishes at $\xi = 1$; when ξ varies between 0 and 1, the transformation deformation gradient grows from $\mathbf{I}$ to $\mathbf{F}_{t\,\max}$. During this process all the thermodynamic properties of phase 1 change into the properties of phase 2. It is possible to define the order parameter ξ, e.g. as

$$\xi:=\frac{|\mathbf{F}_t - \mathbf{I}|}{|\mathbf{F}_{t\,\max} - \mathbf{I}|} \quad \text{or} \quad \xi:=\frac{|\mathbf{F}_t - \mathbf{I}|^2}{|\mathbf{F}_{t\,\max} - \mathbf{I}|^2} \tag{6}$$

a lot of other definitions are acceptable. It is important to take into account, that all variable components of the transformation deformation gradient must participate in the definition of ξ. In the oppo-

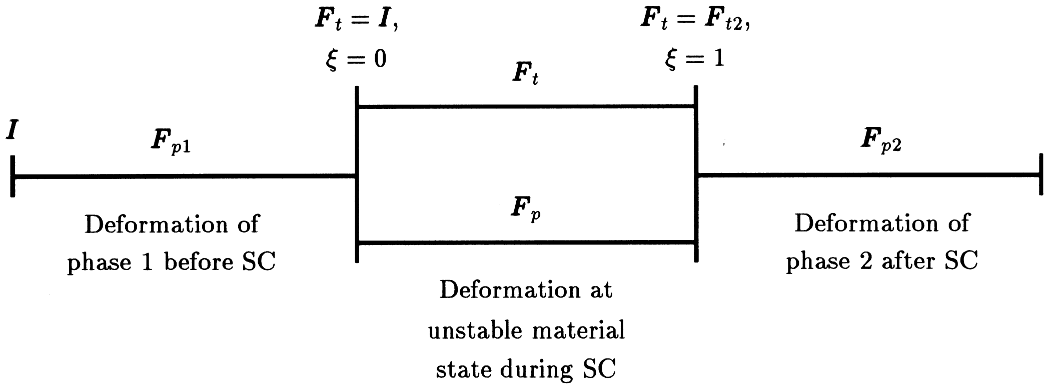


Fig. 5. Sequence of deformation processes in a material point before, during and after structural change.

site case ξ can reach 1 before $\mathbf{F}_t$ reaches $\mathbf{F}_{t\,\max}$ and SC finishes. The order parameter ξ plays a similar role in the consideration of the uniformly deformed material point, as a volume fraction of a new phase for the averaged description of SC. Let us define the specific (per unit mass) Helmholtz free energy $\psi = \psi(\theta,\xi)$, where θ is the temperature, i.e. due to neglecting the elastic energy the free energy coincides with the thermal part of the free energy determined in chemical thermodynamics. We admit the second law of thermodynamics in the form of the Planck inequality [41]

$$\rho\mathscr{D} = \mathbf{T}{:}\mathbf{d} - \rho\dot{\psi} - \rho s\dot{\theta} \geq 0. \tag{7}$$

Here $\mathscr{D}$ is the rate of dissipation per unit mass, ρ the current variable mass density in the course of SC, $\mathbf{T}$ the true Cauchy stress tensor and s the specific entropy. The substitution of the rate of free energy

$$\dot{\psi} = \frac{\partial\psi}{\partial\theta}\dot{\theta} + \frac{\partial\psi}{\partial\xi}\dot{\xi} \tag{8}$$

and decomposition of deformation rate (5) in equation (7) yields

$$\rho\mathscr{D} = \left(\mathbf{T}{:}\left(\frac{\partial\mathbf{F}_t}{\partial\xi}\cdot\mathbf{F}_t^{-1}\right)_s - \rho\frac{\partial\psi}{\partial\xi}\right)\times\dot{\xi} - \rho\left(\frac{\partial\xi}{\partial\theta} + s\right)\dot{\theta} + \mathbf{T}{:}\mathbf{d}_p \geq 0. \tag{9}$$

Generally $\dot{\theta}$ is independent of $\mathbf{d}_p$ and $\dot{\xi}$, because heating can be produced by some heat sources independent of plastic and transformation heats. The assumption that the rate of dissipation is independent of $\dot{\theta}$ results in the expression for entropy, as well as in the reduced dissipative inequality:

$$s = -\frac{\partial\psi}{\partial\theta},\ \mathscr{D} = \frac{1}{\rho}\mathbf{T}{:}\mathbf{d}_p + X_\xi\dot{\xi} \geq 0 \tag{10}$$

where

$$X_\xi := \frac{1}{\rho}\mathbf{T}{:}\left(\frac{\partial\mathbf{F}_t}{\partial\xi}\cdot\mathbf{F}_t^{-1}\right)_s - \frac{\partial\psi}{\partial\xi} \tag{11}$$

is the dissipative force conjugated with dissipative rate $\dot{\xi}$. The simplest assumption that each rate depends on the conjugate force only leads to evolution equations

$$\mathbf{d}_p = \mathbf{f}_p\left(\frac{1}{\rho}\mathbf{T},\xi\right),\ \dot{\xi} = f_\xi(X_\xi,\xi). \tag{12}$$

equation $(12)_1$ is the flow rule and equation $(12)_2$ represents the kinetic equation for SC. The allowance for the mutual influence of all thermomechanical processes can be made in a standard way.

3.2.2. Inapplicability of the standard thermodynamic approach. We assume that the condition $\dot{\xi} = 0$ is valid at $X_\xi = 0$ only. Then it is possible to describe the equilibrium SC, ($\dot{\xi} \longrightarrow 0$) with the equation $X_\xi = 0$, i.e.

$$X_\xi = \frac{1}{\rho}\mathbf{T}{:}\left(\frac{\partial\mathbf{F}_t}{\partial\xi}\cdot\mathbf{F}_t^{-1}\right)_s - \frac{\partial\psi}{\partial\xi} = 0. \tag{13}$$

equation (13) is a scalar equation which is always possible to satisfy for each ξ and $\theta(\xi)$ by choosing in various ways six components of the stress tensor $\mathbf{T}(\xi,\theta(\xi))$. Consequently, phase equilibrium is possible for arbitrary ξ. According to the assumption accepted in Section 3.1, phase equilibrium is impossible at $0 < \xi < 1$. The stable equilibrium exists only at $\xi = 0$ and 1. We received a contradiction with the standard thermodynamics. At $0 < \xi < 1$ a nonequilibrium process takes place, which requires energy and stress fluctuations. In this case a standard thermodynamic approach cannot be applied. It is necessary to average the thermodynamic parameters, related to SC, over the duration of structural changes t_c in order to filter these fluctuations [31]. We introduce the averaged dissipation rate due to SC

$$\mathscr{D}_\xi := \frac{1}{t_c}\int_0^{t_c} X_\xi\dot{\xi}\,\mathrm{d}t = \frac{1}{t_c}\int_0^1 X_\xi\,\mathrm{d}\xi = \frac{X}{t_c} = X\dot{\chi},$$

$$\text{where } X := \int_0^1 X_\xi\,\mathrm{d}\xi,\ \dot{\chi} := \frac{1}{t_c} \tag{14}$$

are the averaged dissipative force and rate. The definition of dissipative rate is natural, because a variation of the parameter ξ during the time t_c is one. The dissipative force is defined as a conjugate variable in the expression for the rate of dissipation.

3.2.3. Local criterion of SC. If the dissipation increment due to the direct SC $X < 0$, then SC is impossible, because this contradicts the second law of thermodynamics. The same is valid for the reverse SC at $X > 0$. For the macroscopically equilibrium direct or reverse SC the following equation is valid:

$$X = \int_{\mathbf{F}_{t1}}^{\mathbf{F}_{t2}} \frac{1}{\rho}\mathbf{T}{:}(\dot{\mathbf{F}}_t\cdot\mathbf{F}_t^{-1})_s\,\mathrm{d}t - \int_0^1 \frac{\partial\psi}{\partial\xi}\mathrm{d}\xi = 0. \tag{15}$$

equation (15) is the criterion for SC without dissipation. Let $X \neq 0$ and $\dot{\chi} = f(X,\ldots)$. There are only two possibilities for the behaviour of function f at $\dot{\chi} \longrightarrow 0$.

1. Let the condition $\dot{\chi} = 0$ be valid at $X = 0$ only; then the macroscopically equilibrium SC ($\dot{\chi} \longrightarrow 0$) can be described by $X = 0$ (Fig. 6, curve 1).
2. Let (Fig. 6, curves 2 and 2′)

$$\begin{aligned} &\text{at } \dot{\chi} = 0\ k_{2\to1} \leq X \leq k_{1\to2};\\ &\text{at } \dot{\chi} > 0\ X = k_{1\to2} > 0;\\ &\text{at } \dot{\chi} < 0\ X = k_{2\to1} < 0, \end{aligned} \tag{16}$$

where $k_{1\to2}$ and $k_{2\to1}$ are the threshold values of X in the direct and the reverse SC, which can depend on θ, $\dot{\chi}$, plastic strain and so on. In this

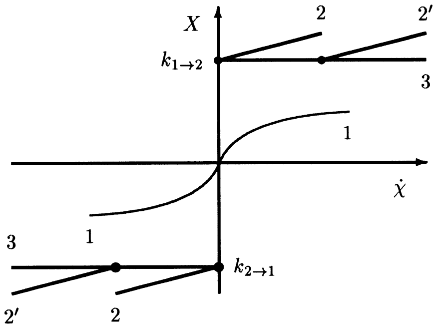


Fig. 6. Possible relationships between the dissipative force X and rate $\dot{\chi}$ (inverse of structural change time t_c).

case there is a *thermodynamic hysteresis*, i.e. direct and reverse SC begin at different values of X and between these values SC is impossible. In the first case there is no thermodynamic hysteresis. We adopt the second variant, since many transformations (for example, martensitic transformations) exhibit hysteresis. Equation (16) means that the calculated value of the dissipation increment per unit mass due to SC reaches its experimentally determined value. In dynamical experiments [33, 40] t_c is estimated as 55–80 ns. Consequently, when X reaches k the rate $\dot{\chi}$ has a jump of the order of $10^7/\text{s}^{-1}$. For some SC $k = 0$, for example, for melting, some diffusive PTs and chemical reactions, which will be considered as a particular case of equation (16).

We will distinguish two types of SC kinetics:

- Athermal kinetics, for which k is independent of rate $\dot{\chi}$ (or SC duration t_c) (Fig. 6, curve 3). In this case real time and rate play no role and the thermodynamic theory of martensitic PT [28–30] can be applied. The relation $k(\dot{\chi})$ for athermal kinetics is similar to the relation between yield stress and plastic deformation rate for rate independent plastic materials.
- Time dependent (true) kinetics, for which k is a function of rate $\dot{\chi}$ and this function has to be specified. We will consider time dependent kinetics in Section 4.

Idealization of athermal kinetics means that SC occurs instantaneously and formally all time derivatives ($\dot{\mathbf{F}}$,$\dot{\mathbf{F}}_p$,$\dot{\mathbf{F}}_t$,$\dot{\theta}$) tend to infinity. The same situation takes place for rate-independent plastic materials without SC. As real time is not important, the time-like parameters or internal time are usually introduced and all time derivatives are replaced by derivatives with respect to internal time. For plastic materials without SC the accumulated plastic strain q ($\dot{q} = (2/3\mathbf{d}_p{:}\mathbf{d}_p)^{1/2}$) is the most popular time-like parameter. For materials with SC ξ is a natural internal time. Then all time derivatives, e.g. $\dot{\theta}$, have to be expressed as $\dot{\theta} = (\partial\theta/\partial\xi)\dot{\xi}$. Despite the fact that $\dot{\xi} \longrightarrow \infty$ (the derivative $\partial\theta/\partial\xi$ is finite), it disappears from all final equations, because actual time and rate do not play any part. Due to this reason we can use usual time derivatives in all formulae, real time and infinities will not appear in the final results. This is known in plasticity theory and the theory of martensitic PT and the problem solved in Part II of the paper illustrates the same for chemical reactions. For time dependent kinetics, which is the most important for our applications, such a problem does not arise at all.

For martensitic PT the following equation for the dissipative threshold k is obtained [30]:

$$k = \rho^{-1} L \sigma_y \varepsilon_o \tag{17}$$

where σ_y is the yield stress, ε_o the volumetric transformation strain and L a coefficient. The values of L for some materials are enumerated in Table 1.

3.2.4. Alternative expression for X. Determining $(\partial\psi/\partial\xi)\mathrm{d}\xi$ from equation (8) and substituting in equation (15) with allowance for equation $(10)_1$ and equation (16) we obtain

$$X = \int_{\mathbf{F}_{t1}}^{\mathbf{F}_{t2}} \frac{1}{\rho}\mathbf{T}{:}(\mathrm{d}\mathbf{F}_t\cdot\mathbf{F}_t^{-1})_s - (\psi_2(\theta_2) - \psi_1(\theta_1)) - \int_{\theta_1}^{\theta_2} s\,\mathrm{d}\theta = k. \tag{18}$$

Introduction in equation (18) of the internal energy U by the expression $\psi = U - \theta s$ results in

$$X = \int_{\mathbf{F}_{t1}}^{\mathbf{F}_{t2}} \frac{1}{\rho}\mathbf{T}{:}(\mathrm{d}\mathbf{F}_t\cdot\mathbf{F}_t^{-1})_s - (U_2(\theta_2) - U_1(\theta_1)) + \int_{s_1}^{s_2} \theta\,\mathrm{d}s = k. \tag{19}$$

As we neglect the thermoelastic strains, the internal energy of each phase coincides (to within an unimportant constant) with the enthalpy. This equation is more convenient for applications due to the usage of tabulated functions.

3.2.5. Small strains and rotations. In this case reference and actual configurations coincide, $\mathbf{F} = \mathbf{I} + \boldsymbol{\varepsilon}$, $\mathbf{F}_t = \mathbf{I} + \boldsymbol{\varepsilon}_t$, $\mathbf{F}_p = \mathbf{I} + \boldsymbol{\varepsilon}_p$, $\mathbf{F}_{p1} = \mathbf{I} + \boldsymbol{\varepsilon}_{p1}$, $\mathbf{F}_{p2} = \mathbf{I} + \boldsymbol{\varepsilon}_{p2}$, where $\boldsymbol{\varepsilon}$, $\boldsymbol{\varepsilon}_t$, $\boldsymbol{\varepsilon}_p$, $\boldsymbol{\varepsilon}_{p1}$, $\boldsymbol{\varepsilon}_{p2} \ll \mathbf{I}$ are the tensors of the total, transformation and plastic strains during, before and after the SC, $\rho \simeq \rho_1 = \text{const}$.

$$\mathbf{d} = \dot{\boldsymbol{\varepsilon}};\ \mathbf{d}_t = \dot{\boldsymbol{\varepsilon}}_t;\ \mathbf{d}_p = \dot{\boldsymbol{\varepsilon}}_p \tag{20}$$

Table 1. Values of parameter L for different materials

Materials	L
RbCl, KCl, KBr	5.89
CdS, CdSe	1.39
Ce, InSb, Bi	0.11
Steel Fe + 30% Ni	7.5
Graphite–diamond	~3

and equations (2), (5)–(7) and (10)$_2$–(12), (15), (18) and (19) read

$$\boldsymbol{\varepsilon}=\boldsymbol{\varepsilon}_{p2}+\boldsymbol{\varepsilon}_t+\boldsymbol{\varepsilon}_p+\boldsymbol{\varepsilon}_{p1};\ \dot{\boldsymbol{\varepsilon}}=\dot{\boldsymbol{\varepsilon}}_t+\dot{\boldsymbol{\varepsilon}}_p \tag{21}$$

$$\xi:=\frac{|\boldsymbol{\varepsilon}_t|}{|\boldsymbol{\varepsilon}_{t\,\max}|};\ \xi:=\frac{|\boldsymbol{\varepsilon}_t|^2}{|\boldsymbol{\varepsilon}_{t\,\max}|^2} \tag{22}$$

$$\rho_1\mathscr{D}=\mathbf{T}{:}\dot{\boldsymbol{\varepsilon}}-\rho\dot{\psi}-\rho s\dot{\theta}\geq 0;\ \mathscr{D}=\frac{1}{\rho_1}\mathbf{T}{:}\dot{\boldsymbol{\varepsilon}}_p+X_\xi\dot{\xi}\geq 0 \tag{23}$$

$$X_\xi=\frac{1}{\rho_1}\mathbf{T}{:}\frac{\partial\boldsymbol{\varepsilon}_t}{\partial\xi}-\frac{\partial\psi}{\partial\xi} \tag{24}$$

$$\dot{\boldsymbol{\varepsilon}}_p=\mathbf{f}_p\left(\frac{1}{\rho_1}\mathbf{T},\xi\right);\ \dot{\xi}=f_\xi(X_\xi,\xi) \tag{25}$$

$$X=\int_{\boldsymbol{\varepsilon}_{t1}}^{\boldsymbol{\varepsilon}_{t2}}\frac{1}{\rho_1}\mathbf{T}{:}d\boldsymbol{\varepsilon}_t-\int_0^1\frac{\partial\psi}{\partial\xi}d\xi=0 \tag{26}$$

$$X=\int_{\boldsymbol{\varepsilon}_{t1}}^{\boldsymbol{\varepsilon}_{t2}}\frac{1}{\rho_1}\mathbf{T}{:}d\boldsymbol{\varepsilon}_t-(\psi_2-\psi_1)-\int_{\theta_1}^{\theta_2}s\,d\theta=k \tag{27}$$

$$X=\int_{\boldsymbol{\varepsilon}_{t1}}^{\boldsymbol{\varepsilon}_{t2}}\frac{1}{\rho_1}\mathbf{T}{:}d\boldsymbol{\varepsilon}_t-(U_2(\theta)-U_1(\theta))+\int_{s_1}^{s_2}\theta\,ds=k. \tag{28}$$

3.3. Determination of temperature variation

3.3.1. Energy balance. For the determination of a temperature variation before and in the course of SC we can use an energy balance equation (the first law of thermodynamics) [41]

$$\mathbf{T}{:}\mathbf{d}-\rho\dot{U}-\operatorname{div}\mathbf{h}=0, \tag{29}$$

where **h** is the heat flux and div the divergence operator. Using two definitions of specific heat capacity of each phase at constant volume [42]

$$\nu_1=\frac{\partial U_1}{\partial\theta}=\theta\frac{\partial s_1}{\partial\theta};\ \nu_2=\frac{\partial U_2}{\partial\theta}=\theta\frac{\partial s_2}{\partial\theta} \tag{30}$$

we obtain explicit expressions for the free energy and entropy

$$U_1=U_{10}+\int_{\theta_0}^{\theta}\nu_1(\theta)\,d\theta;\ U_2=U_{20}+\int_{\theta_0}^{\theta}\nu_2(\theta)\,d\theta \tag{31}$$

$$s_1=s_{10}+\int_{\theta_0}^{\theta}\frac{\nu_1(\theta)}{\theta}d\theta;\ s_2=s_{20}+\int_{\theta_0}^{\theta}\frac{\nu_2(\theta)}{\theta}d\theta \tag{32}$$

where s_{0i} and U_{0i} are the reference entropy and internal energy at some reference temperature θ_0. Functions $U_0(\xi)$, $s_0(\xi)$ and $\nu(\xi)$ are usually unknown and we assume a linear approximation

$$U_0=(1-\xi)U_{01}+\xi U_{02},\ s_0=(1-\xi)s_{01}+\xi s_{02},\\ \nu=(1-\xi)\nu_1+\xi\nu_2 \tag{33}$$

whence

$$U(\xi,\theta)=(1-\xi)U_1+\xi U_2,\ s(\xi,\theta)=(1-\xi)s_1+\xi s_2. \tag{34}$$

Then substitution of the expression $\dot{U}=\nu(\xi,\theta)\dot{\theta}+(U_2(\theta)-U_1(\theta))\dot{\xi}$ into equation (29) leads to the temperature evolution equation

$$\nu(\xi,\theta)\dot{\theta}=-\frac{1}{\rho}\operatorname{div}\mathbf{h}+\frac{1}{\rho}\mathbf{T}{:}\mathbf{d}-(U_2(\theta)-U_1(\theta))\dot{\xi}. \tag{35}$$

3.3.2. Adiabatic approximation. The temperature in the given point can be defined after formulation and solution of a boundary value problem due to the divergence term. Taking into account a very short duration of some SC and to derive simple analytical expressions, the *adiabatic* process can be assumed. In this case $\operatorname{div}\mathbf{h}=0$ and equation (35) determines the temperature evolution in each material point independently, i.e. without the solution of a boundary value problem. Then allowing for the expression

$$\Delta U(\theta):=U_2(\theta)-U_1(\theta)=\Delta U_0+\int_{\theta_0}^{\theta}\Delta\nu(\theta)\,d\theta \tag{36}$$

we obtain for temperature evolution

$$\nu(\xi,\theta)\dot{\theta}=\frac{1}{\rho}\mathbf{T}{:}\mathbf{d}-\left(\Delta U_0+\int_{\theta_0}^{\theta}\Delta\nu(\theta)\,d\theta\right)\dot{\xi}. \tag{37}$$

The linear relation between $\dot{\theta}$, **d** and $\dot{\xi}$ does not contradict the assumption made after equation (9) that $\dot{\theta}$ is an independent rate. Equation (35) proves that this is really the case. Equation (37) is a consequence of assumptions that all terms which make $\dot{\theta}$ independent of other rates are zero. As $s=(1-\xi)s_1+\xi s_2$, then

$$\begin{aligned}\theta\,ds&=\theta(\xi\,ds_2+(1-\xi)\,ds_1+(s_2-s_1)\,d\xi)\\&=(\xi\nu_2+(1-\xi)\nu_1)\,d\theta+\theta\Delta s\,d\xi\\&=\nu(\xi,\theta)\,d\theta+\theta\Delta s\,d\xi\end{aligned} \tag{38}$$

and the SC criterion can be transformed in the following form:

$$\begin{aligned}X=&\int_{\mathbf{F}_{t1}}^{\mathbf{F}_{t2}}\frac{1}{\rho}\mathbf{T}{:}(d\mathbf{F}_t\cdot\mathbf{F}_t^{-1})_s-(U_2(\theta_2)-U_1(\theta_1))\\&+\int_{\theta_1}^{\theta_2}\nu(\xi,\theta)\,d\theta+\int_0^1\theta\Delta s\,d\xi=k.\end{aligned} \tag{39}$$

3.3.3. Some specifications and simplifications of equations (37) and (39). If the specific heat of each phase is temperature independent during the SC, then

$$U_1 = U_{10} + \nu_1(\theta - \theta_0);\ U_2 = U_{20} + \nu_2(\theta - \theta_0) \quad (40)$$

$$s_1 = s_{10} + \nu_1 \ln\frac{\theta}{\theta_0};\ s_2 = s_{20} + \nu_2 \ln\frac{\theta}{\theta_0} \quad (41)$$

$$\nu(\xi)\dot{\theta} = \frac{1}{\rho}\mathbf{T}{:}\mathbf{d} - (\Delta U_0 + \Delta\nu(\theta - \theta_0))\dot{\xi} \quad (42)$$

$$X = \int_{\mathbf{F}_{t1}}^{\mathbf{F}_{t2}} \frac{1}{\rho}\mathbf{T}{:}(\mathrm{d}\mathbf{F}_t \cdot \mathbf{F}_t^{-1})_s - (\Delta U_0 - \Delta\nu\theta_0 + \nu_2\theta_2 - \nu_1\theta_1) + \int_{\theta_1}^{\theta_2} \nu(\xi)\,\mathrm{d}\theta + \Delta s_0\int_0^1 \theta\,\mathrm{d}\xi + \Delta\nu\int_0^1 \theta\ln\frac{\theta}{\theta_0}\mathrm{d}\xi = k. \quad (43)$$

Using the expression $\nu(\xi)\ \mathrm{d}\theta = \mathrm{d}(\nu(\xi)\theta) - \theta\ \mathrm{d}\nu(\xi) = \mathrm{d}(\nu(\xi)\theta) - \theta\Delta\nu\,\mathrm{d}\xi$, the SC criterion can be transformed into the form

$$\int_{\mathbf{F}_{t1}}^{\mathbf{F}_{t2}} \frac{1}{\rho}\mathbf{T}{:}(\mathrm{d}\mathbf{F}_t \cdot \mathbf{F}_t^{-1})_s + (\Delta s_0 - \Delta\nu)\int_0^1 \theta\,\mathrm{d}\xi + \Delta\nu\int_0^1 \theta\ln\frac{\theta}{\theta_0}\mathrm{d}\xi = k + \Delta U_0 - \Delta\nu\theta_0. \quad (44)$$

To obtain later a simple analytical solution we assume $\Delta\nu = 0$ and get

$$\nu\dot{\theta} = \frac{1}{\rho}\mathbf{T}{:}\mathbf{d} - \Delta U_0\dot{\xi} \quad (45)$$

$$\int_{\mathbf{F}_{t1}}^{\mathbf{F}_{t2}} \frac{1}{\rho}\mathbf{T}{:}(\mathrm{d}\mathbf{F}_t \cdot \mathbf{F}_t^{-1})_s + \Delta s_0\int_0^1 \theta\,\mathrm{d}\xi = k + \Delta U_0. \quad (46)$$

There are two heat sources in the temperature evolution equation, namely transformation heat and mechanical power, which consists of plastic dissipation and transformation power.

In the isothermal approximation θ = const. it follows from equation (18)

$$\int_{\mathbf{F}_{t1}}^{\mathbf{F}_{t2}} \frac{1}{\rho}\mathbf{T}{:}(\mathrm{d}\mathbf{F}_t \cdot \mathbf{F}_t^{-1})_s = k + \Delta\psi(\theta). \quad (47)$$

3.4. Nucleation and interface propagation criteria

PT or SC cannot occur at a single material point, because the surface energy per unit transforming volume will be infinite. In reality SC takes place in some finite volume (Fig. 7). That is why it is necessary to average the SC criterion over the transforming volume V_n (mass m_n) and to take into account the surface energy. Consequently, we arrive at the following condition of *nucleation*:

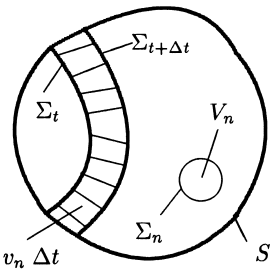


Fig. 7. Volume with structural changes.

$$\int_{m_n} X\,\mathrm{d}m_n = \int_{\Sigma_n} E\,\mathrm{d}\Sigma_n + \int_{m_n} k\,\mathrm{d}m_n \quad (48)$$

where Σ_n is the surface of the nucleus after the end of SC and E is the surface energy per unit area after the SC. We take the integrals over the mass and not over the volume of the nuclei, because the values X and k are defined per unit mass. Using equation (18) for X we obtain

$$\int_{m_n}\int_{\mathbf{F}_1}^{\mathbf{F}_2} \frac{1}{\rho}\mathbf{T}{:}(\mathrm{d}\mathbf{F}_t \cdot \mathbf{F}_t^{-1})_s\,\mathrm{d}m_n - \int_{m_n} (\psi_2 - \psi_1)\,\mathrm{d}m_n - \int_{m_n} s\,\mathrm{d}\theta\,\mathrm{d}m_n = \int_{\Sigma_n} E\,\mathrm{d}\Sigma_n + \int_{m_n} k\,\mathrm{d}m_n. \quad (49)$$

Based on the more concrete equation (46), we get

$$\int_{m_n}\int_{\mathbf{F}_1}^{\mathbf{F}_2} \frac{1}{\rho}\mathbf{T}{:}(\mathrm{d}\mathbf{F}_t \cdot \mathbf{F}_t^{-1})_s\,\mathrm{d}m_n - \int_{m_n} \left(\Delta U_0 - \Delta s_0\int_0^1 \theta\,\mathrm{d}\xi\right)\mathrm{d}m_n = \int_{\Sigma_n} E\,\mathrm{d}\Sigma_n + \int_{m_n} k\,\mathrm{d}m_n. \quad (50)$$

At small strain the transformation work in the first integral reads $(1/\rho_1)\mathbf{T}{:}\mathrm{d}\boldsymbol{\varepsilon}_t$.

The interface propagation criterion can be derived in the following way [28, 29, 31]. Assume that the volume V_n is obtained by the *interface* Σ propagation with a normal velocity v_n in time Δt, i.e. it is bounded by surfaces Σ_t and $\Sigma_{t+\Delta t}$ at the time t and $t + \Delta t$, respectively, as well as by two lateral infinitesimal surfaces with the heights $v_n\Delta t$ (Fig. 7). Using the Hadamard compatibility condition and traction continuity it is possible to simplify the stress work integral in equation (49) and to avoid the integration over the deformation process. For our problem it is more convenient to use the same transformation criterion (49) directly for the volume described.

3.5. Extremum principle for determination of unknown parameters

The SC criterion (48) [or its explicit forms (49) and (50)] is only one scalar equation which is not sufficient for the determination of all essential parameters influencing the process, for example position, shape and orientation of nucleus, plastic deformation $\mathbf{F}_p$ gradient, related to $\mathbf{F}_p$ temperature evolution and so on. To determine all unknown parameters which we will designate as **b**, let us use as suggested in Ref. [43] the postulate of realizability. In our problem the unknown parameter is the thickness of the transformed layer (nucleus). Let for the given boundary conditions

$$\int_{m_n^*} X(\mathbf{b}^*)\,\mathrm{d}m_n - \int_{\Sigma_n^*} E^*\,\mathrm{d}\Sigma_n - \int_{m_n^*} k_{1\to2}(\mathbf{b}^*)\,\mathrm{d}m_n < 0 \qquad (51)$$

for all admissible SC parameters **b***, i.e. the SC criterion is not fulfilled and SC does not occur. If in the course of continuous variation of boundary conditions and, for each boundary condition, continuous variation of all admissible parameters **b*** the criterion (48) is fulfilled for the *first* time for some of parameters **b**, then SC will occur with these **b**.

If, in the course of variation of boundary conditions and, for each boundary condition, variation of all admissible parameters **b*** the equality (48) is met the first time for one or several **b**, then for arbitrary other **b*** inequality (51) should hold, as in the opposite case this **b*** criterion (48) had to be met before it was satisfied for **b**. Consequently, we obtain the extremum principle

$$\int_{m_n} X(\mathbf{b})\,\mathrm{d}m_n - \int_{\Sigma_n} E\,\mathrm{d}\Sigma_n - \int_{m_n} k_{1\to2}(\mathbf{b})\,\mathrm{d}m_n = 0 >$$
$$\int_{m_n^*} X(\mathbf{b}^*)\,\mathrm{d}m_n - \int_{\Sigma_n^*} E^*\,\mathrm{d}\Sigma_n - \int_{m_n^*} k_{1\to2}(\mathbf{b}^*)\,\mathrm{d}m_n \qquad (52)$$

for determination of all unknown parameters **b**. The explicit form of principle (52) based on SC criterion (49) has the form of

$$\int_{m_n}\int_{\mathbf{F}_1}^{\mathbf{F}_2} \frac{1}{\rho}\mathbf{T}{:}(\mathrm{d}\mathbf{F}_t\cdot\mathbf{F}_t^{-1})_s\,\mathrm{d}m_n - \int_{m_n}(\psi_2-\psi_1)\,\mathrm{d}m_n$$
$$-\int_{m_n} s\,\mathrm{d}\theta\,\mathrm{d}m_n - \int_{\Sigma_n} E\,\mathrm{d}\Sigma_n - \int_{m_n} k_{1\to2}\,\mathrm{d}m_n = 0$$
$$> \int_{m_n^*}\int_{\mathbf{F}_1^*}^{\mathbf{F}_2^*} \frac{1}{\rho^*}\mathbf{T}^*{:}(\mathrm{d}\mathbf{F}_t^*\cdot\mathbf{F}_t^{-1*})_s\,\mathrm{d}m_n$$
$$-\int_{m_n^*}(\psi_2^*-\psi_1)\,\mathrm{d}m_n - \int_{m_n^*} s^*\,\mathrm{d}\theta^*\,\mathrm{d}m_n$$
$$-\int_{\Sigma_n^*} E^*\,\mathrm{d}\Sigma_n - \int_{m_n^*} k_{1\to2}^*\,\mathrm{d}m_n. \qquad (53)$$

The essence of the postulate of realizability is very simple: as soon as some dissipative process (plastic flow, SC) could occur from the viewpoint of thermodynamics, it will occur (or be realized), i.e. the first fulfilment of the necessary energetic condition is sufficient for the beginning of the dissipative process. A number of applications of the postulate [30, 31, 43, 44] give the impression that such an essence is a property of dissipative systems.

4. THERMODYNAMICALLY CONSISTENT KINETICS OF STRUCTURAL CHANGES: THE CONCEPT OF EFFECTIVE TEMPERATURE

Let us consider the situation when time plays an important role and a description of real kinetics is necessary. For example for reactions in Ti–Si and Nb–Si mixtures thermodynamically equilibrium temperature is negative and the driving force X is very high at each temperature, but reaction can be detected at some high temperature and the rate of reaction grows with increasing temperature. To derive a kinetic equation, we will use the following explicit dependence of $k_{1\to2}$ on $\dot{\chi}{:=}1/t_c$ in equation (16):

$$X - E\frac{S_n}{m_n} = k_{1\to2} = k + E_a + R\theta_{ef}\ln\frac{t_{c0}}{t_c}$$
$$= k + E_a + R\theta_{ef}\ln\frac{\dot{\chi}}{\dot{\chi}_0} \qquad (54)$$

which leads to threshold-type generalization of Arrhenius-type kinetics

$$\dot{\chi} = \frac{1}{t_c}$$
$$= \dot{\chi}_0\exp\frac{X - k - E\dfrac{S_n}{m_n} - E_a}{R\theta_{ef}} \quad \text{at}$$
$$0 \le X - E\frac{S_n}{m_n} - k \le E_a; \qquad (55)$$
$$\dot{\chi} = 0 \ \text{ at } \ X - E\frac{S_n}{m_n} - k < 0.$$

Here E_a is the activation energy at

$X - E(S_n/m_n) - k = 0$, $R = 8.314$ J/K mol the gas constant, θ_{ef} the effective temperature, $\dot{\chi}_0 := 1/t_{c0}$ with t_{c0} for some characteristic time and a homogeneous distribution of parameters in the transforming volume is assumed for simplicity. In equation (55) the actual activation energy includes the difference $k + E(S_n/m_n) - X$ to take into account the effect of the driving force, dissipative threshold and surface energy on kinetics. The lower bound for $X - E(S_n/m_n) - k$ in equation (55) is related to fulfilment of the SC criterion; the upper bound is due to the requirement of positivity of an actual activation energy, otherwise the process does not need thermal activation and equation (55) loses it sense. In the limit case $E_a = 0$ and $\dot{\chi} = \dot{\chi}_0$ equation (54) reduces to the thermodynamic SC criterion, i.e. it describes thermodynamically consistent kinetics. In contrast to known approaches describing kinetics in terms of the rate of product phase volume fraction change, in our local approach we determine the time of SC in some transforming volume. This is consistent with the standard method of nonequilibrium thermodynamics which relates conjugate force and rate in the expression for dissipation rate, in our case see equation (14).

Of course, other types of kinetic relations between X and $\dot{\chi}$ can be considered, see for example the paper by Ghosh and Olson [45] devoted to martensitic PT.

By introducing the effective temperature we take into account that temperature can vary significantly during the SC. In the standard approach describing kinetics in terms of the rate of product phase volume fraction change, we can use ordinary temperature, averaged over some representative volume, because a small change of volume fraction causes a small temperature variation and this can be taken into account by solution of the coupled kinetic and temperature evolution equation (see, e.g. Refs [21, 22]). In the local description we must take into account the local temperature variation in the transforming region during the whole SC, which, e.g. for reactions in Ti–Si and Nb–Si exceeds 1000 K.

We assume that during the SC (growth of ξ from 0 to 1) multiple thermal activations are necessary for each small increment $\Delta\xi$. Then as the simplest variant we define

$$\theta_{ef} = \int_0^1 \theta \, d\xi. \tag{57}$$

It is clear that alternative definitions and descriptions are possible. In this paper we will consider the initiation of chemical reaction only. For this purpose it is sufficient to be sure that the duration of SC t_c is smaller than the time of deformation in the shear band at $\theta > \theta_1$.

To describe the progress of SC we have to introduce some characteristic mass m of the transforming material during time t_c (which can depend on $X - k$), and transform the material step by step choosing the next transforming volume in the region which gives the minimum transformation time. As a simplified averaged approach we can use the following one. After multiplication of equation (55) by a characteristic volume fraction c_0 of the transforming material during time t_{c0}, we obtain the kinetic equation for the volume fraction of a product phase c

$$\dot{c} = \dot{c}_0 \exp \frac{X - k - E\dfrac{S_n}{m_n} - E_a}{R\theta_{ef}},$$

$$0 \le X - E\frac{S_n}{m_n} - k \le E_a; \; \dot{c}_0 := \frac{c_0}{t_{c0}}. \tag{58}$$

5. CONCLUSIONS

1. Strain-induced chemical reactions are experimentally observed in shear bands for both Ti–Si and Nb–Si mixtures. It is very difficult to determine, experimentally, whether reactions start in the solid state or after melting of at least one component. This is indeed a difficult problem that has been studied intensively, under shock conditions (e.g. Thadhani *et al.* [27]). For solid–liquid reactions the role of plastic shearing is reduced to heating the mixture up to the melting temperature of Si. One of the aims of this paper and its companion is to find, theoretically, whether there are possible macroscopic mechanisms of intensification of the above chemical reactions due to plastic shear in the solid state. In order to address this, a theoretical framework was developed whose principal features are outlined below. In Part II the framework is applied to structural changes in a shear localization region.
2. The class of *SC without stable local intermediate state* is treated. SCs are considered as a process of variation of the transformation deformation gradient in infinitesimal or final volume from the initial to final value which is accompanied by a jump in all thermomechanical properties. This process *cannot be stopped at an intermediate state*. Thermodynamic equilibrium for intermediate values of the transformation deformation gradient is impossible. Martensitic and displacive–diffusive PT as well as chemical reactions belong to this class; spinodal decomposition and continuous saturation of the crystal lattice of one component by atoms of another substance are excluded.
3. The continuum thermodynamic theory of SC with athermal kinetics, which include martensitic PT, plastic strain-induced chemical reactions and polymorphic transformations, is developed for finite strains. Intense plastic shear accelerates the

kinetics of the above SC by several orders making it very similar to kinetics of athermal martensitic PT. The kinetics of athermal SC can be described in terms of applied stresses, displacements (deformations), temperature or their combination, rather than real time. For a class of SCs with athermal kinetics the thermodynamic theory of martensitic PT [28–31] is applied after making it completely consistent with chemical thermodynamics. The theory includes kinematics, SC criterion and extremum principle for the determination of all unknown variable parameters for the case where elastic strains can be neglected.

4. A thermodynamically consistent kinetic theory of thermally activated SC is suggested. In contrast to known approaches describing kinetics in terms of rate of phase volume fraction change, in our local approach we determine the time of structural change in some transforming volume. This is consistent with the standard method of nonequilibrium thermodynamics which relates conjugate force and rate in the expression for dissipation rate. The kinetic theory is based on specification of dependence between $k_{1\rightarrow 2}$ and $\dot{\chi}:=1/t_c$, as well as on the concept of effective temperature introduced. The chosen dependence of $k_{1\rightarrow 2}$ on $\dot{\chi}$ leads to the threshold-type generalization of Arrhenius-type kinetics in which the actual activation energy includes the driving force, dissipative threshold and surface energy. By introducing the effective temperature we take into account that temperature can vary significantly during the SC.

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