



## STRAIN-INDUCED STRUCTURAL CHANGES AND CHEMICAL REACTIONS—II. MODELLING OF REACTIONS IN SHEAR BAND

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**Abstract**—The problem on strain-induced chemical reaction (SICR) and structural changes (SCs) in a thin layer inside the shear band is formulated and solved for large strains. It is analytically demonstrated that intense plastic deformation can accelerate chemical reactions. The phenomenon of reaction-induced plasticity (RIP), similar to transformation-induced plasticity at phase transitions is derived and modelled. A criterion for athermal SICR is derived and distinctive points of the approach proposed at zero shear stresses and classical chemical thermodynamics are analysed. Two mechanisms are proposed for the experimentally observed positive effect of shear stresses on SC from the low temperature phase to the high temperature phase. The first one is related to the necessity of fulfilment of the yield condition for the transforming material. The second mechanism is connected with the additional heating due to RIP. A kinetic criterion of chemical reaction is formulated. As an example, the SICR in Ti–Si and Nb–Si mixtures is considered. It is shown that the main reason for acceleration of reaction kinetics due to shear stress or strain is related to the increase of effective temperature due to RIP. The increase of driving force due to shear stresses does not affect the kinetics. © 1998 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

### 1. INTRODUCTION

It has recently been shown experimentally that shear localization in plastic deformation of a reactive mixture can initiate exothermic chemical reactions [1–3]. In Part I [4] the principal characteristics of these reactions inside shear bands are presented for Nb–Si and Ti–Si mixtures; a thermodynamic and kinetic theory of strain-induced structural changes (SCs) is developed. In Part II this theory is applied to the study of SC and strain-induced chemical reactions (SICRs) in a shear band. Our aim is not a detailed description of experiments, but the search for the main factors which are potentially responsible for the acceleration of chemical reactions. That is why the simplest model is considered and a lot of details are neglected (e.g. temperature dependence of all materials properties).

Pure volumetric transformation strain is considered in this paper. In Section 2 the problem formulation for SC in a shear band is presented. The problem is reduced to SC in a thin layer in a rigid-plastic half-space at plane strain. A complete system of equations is presented and the kinematics of the problem is analysed. In Section 3 the thermodynamics of SC in a shear band is studied. An analytical solution of the problem is found. It includes the SC criterion, the temperature evolution equation, the equation for the thickness of the transforming

region, variation of the components of total, transformation and plastic deformation gradients.

Due to special geometry some specific peculiarities of the SICR progress take place. For example, after the appearance of the nucleus the layer thickness increases by a factor of 2 at fixed stresses and temperature due to spontaneous interface propagation. The reaction-induced plasticity (RIP) phenomenon, similar to transformation-induced plasticity for PT, is revealed and analysed. The distinct aspects of the results obtained at zero shear stress are numerated in comparison with those which follow from classical chemical thermodynamics. The effect of shear stress (or plastic strain) on the driving force is studied. The kinetic description of SICR is given in Section 4. The effect of shear stress on the kinetics of reactions in Nb–Si and Ti–Si systems is analysed and is related to the increase of effective temperature due to RIP.

### 2. FORMULATION OF THE PROBLEM

Consider an infinite rigid-plastic half-space with prescribed normal  $\sigma_n$  and shear  $\tau$  stresses on the whole surface (Fig. 1) under plane strain condition. We assume the existence of a region with localized plastic shear deformation, i.e. shear band, along the whole surface. Material outside of the shear band is rigid. It is assumed that a coherent SC occurs in the

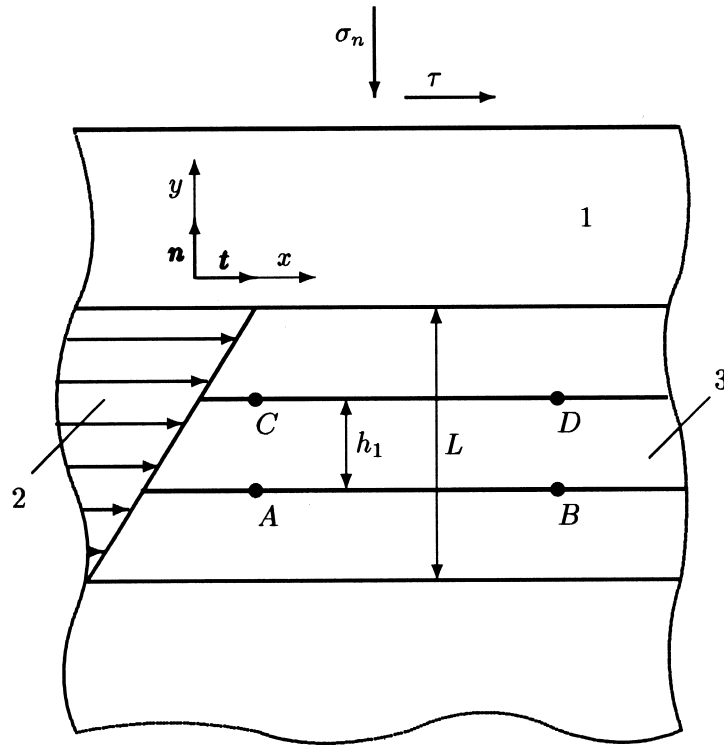


Fig. 1. Schematic illustration of structural changes in a shear band: 1, half space; 2, shear band with displacement; 3, layer with structural changes.

layer inside the shear band. For coherent SCs the displacements are continuous across the interface. In perfect plasticity, preliminary homogeneous plastic shear does not affect the stress-strain state during the SC and we can consider the state at the beginning of SC as a reference configuration. Plastic shear before SC determines the initial temperature. Consequently, we arrive at the problem formulation similar to that considered in Refs [5, 6], namely coherent SC parallel to the external surface infinite layer inside of the rigid half-space (Fig. 2). The presence of a shear band results in the condition, that shear stress is equal to yield stress in shear for the first phase,  $\tau = 0.5\sigma_{y1}$ . If the yield stress of the transforming region  $\sigma_y(\xi)$  is smaller than that of the first phase, then during the SC  $\tau = 0.5\sigma_y(\xi)$ . We will consider a more general formulation with arbitrary prescribed  $\tau$  which does not violate the yield condition.

The solution of the problem does not depend on the  $x$  coordinate. In Fig. 2, a transformed particle is shown after transformation strain. In order to satisfy displacement continuity across the interface AB and independence of the solution of  $x$ , additional plastic strain is needed [Fig. 2(b)]. We assume that total, transformation and plastic deformation gradients are homogeneous in a layer and

that the stress field is homogeneous and time independent. A complete system of equations is given in the Box. Due to the homogeneity of all fields the equilibrium equation and compatibility condition are satisfied automatically. The Tresca yield condition (3) is assumed [7], where  $\sigma_t$  is the tangential stress,  $\sigma_y$  the yield limit at simple compression (tension), and  $\mathbf{S}$  the stress deviator.

For the complete solution of a problem it is necessary to know how the yield stress in the transforming particle varies during the SC, i.e. a function  $\sigma_y(\xi)$  with  $\sigma_y(0) = \sigma_{y1}$  and  $\sigma_y(1) = \sigma_{y2}$ . For simplicity we assume constant yield stress, i.e. at the beginning of the SC the yield stress makes an instantaneous jump to some effective value, which we will designate as  $\sigma_{y2}$ . Various alternative assumptions are possible, e.g.  $\sigma_y(\xi) = (1 - \xi)\sigma_{y1} + \xi\sigma_{y2}$ , but for variable  $\sigma_y(\xi)$  it is difficult to find an analytical solution.

The SC criterion for the given problem can be presented in the form of equation (8). We use the expression  $m_n = \rho_1 V_1 = \rho_1 h_1 \Sigma_1$ , where  $\rho_1$  is the mass density of phase 1, i.e. in the reference configuration (before SC),  $V_1$  and  $h_1$  are the volume and the thickness of the transforming layer in the reference configuration.

Decomposition of deformation gradient

$$\mathbf{F} = \mathbf{F}_t \cdot \mathbf{F}_p \tag{1}$$

Decomposition of deformation rate

$$\mathbf{d} := (\dot{\mathbf{F}} \cdot \mathbf{F}^{-1})_s = (\dot{\mathbf{F}}_t \cdot \mathbf{F}_t^{-1})_s + \mathbf{d}_p; \quad \mathbf{d}_p := (\mathbf{F}_t \cdot \dot{\mathbf{F}}_p \cdot \mathbf{F}_p^{-1} \cdot \mathbf{F}_t^{-1})_s \tag{2}$$

Tresca yield condition for the transforming layer

$$\varphi(\mathbf{T}) = 2(\mathbf{S}:\mathbf{S}) - \sigma_y^2 = (\sigma_n - \sigma_t)^2 + 4\tau^2 - \sigma_y^2 = 0; \tag{3}$$

$$\mathbf{S} := \text{dev } \mathbf{T} = 0.5(\sigma_n - \sigma_t)(\mathbf{nn} - \mathbf{tt}) + 2\tau(\mathbf{tn})_s \tag{4}$$

Associated flow rule

$$\mathbf{d}_p = 0.5h \frac{\partial \varphi}{\partial \mathbf{S}} = 2h\mathbf{S}; \quad \mathbf{d}_p = d_{pn}(\mathbf{nn} - \mathbf{tt}) + \hat{\gamma}_p(\mathbf{tn})_s; \tag{5}$$

$$d_{pn} = h(\sigma_n - \sigma_t); \quad \hat{\gamma}_p = 4h\tau \tag{6}$$

Yield condition for the nontransforming phase

$$|\tau| \leq 0.5\sigma_{y1} \tag{7}$$

Criterion of structural change

$$\begin{aligned} &(X - k)\rho_1 h_1 - 2E = \\ &= \int_I^{\mathbf{F}_{t2}} \frac{\rho_1}{\rho} \mathbf{T} : (d\mathbf{F}_t \cdot \mathbf{F}_t^{-1}) h_1 + \rho_1 \Delta s_0 \int_0^1 \theta d\xi h_1 - \rho_1(k + \Delta U_0) h_1 - 2E = 0 \end{aligned} \tag{8}$$

Extremum principle for thickness of layer

$$\int_I^{\mathbf{F}_{t2}} \frac{\rho_1}{\rho} \mathbf{T} : (d\mathbf{F}_t \cdot \mathbf{F}_t^{-1}) h_1^* + \rho_1 \Delta s_0 \int_0^1 \theta d\xi h_1^* - \rho_1(k^* + \Delta U_0) h_1^* - 2E \rightarrow \max \tag{9}$$

Temperature evolution equation

$$\nu(\xi, \theta) \dot{\theta} = \frac{1}{\rho} \mathbf{T} : \mathbf{d} - (U_2(\theta) - U_1(\theta)) \dot{\xi} \tag{10}$$

Kinetic equation

$$\dot{\chi} = \dot{\chi}_0 \exp \frac{X - k - 2E/(\rho_1 h_1) - E_a}{R\theta_{ef}} \quad \text{at} \quad 0 \leq X - 2E/(\rho_1 h_1) - k \leq E_a; \tag{11}$$

$$\dot{\chi} = 0 \quad \text{at} \quad X - 2E/(\rho_1 h_1) - k < 0. \tag{12}$$

Let us consider the kinematics of the problem. As displacements across the interface are continuous and material outside of the layer is rigid, then normal  $F_{tt}$  and shear  $F_{nt}$  components of the deformation gradient are one and zero, respectively, and the deformation gradient in the layer has the following form:

$$\mathbf{F} = \mathbf{i} + \gamma\mathbf{tn} + \delta\mathbf{nn} = \begin{pmatrix} 1 & \gamma \\ 0 & 1 + \delta \end{pmatrix} \tag{13}$$

where  $\delta$  and  $\gamma$  are the normal and shear strains,  $\mathbf{i}$  the two-dimensional unit tensor, and  $\mathbf{n}$  and  $\mathbf{t}$  the unit vectors in the directions  $x$  and  $y$ , respectively [see Fig. 2(a)]. The tensor  $\mathbf{F}$  describes simple shear along the interface and tension (compression) along the normal  $\mathbf{n}$ ; the interface is nondeformable. It is clear that the tensor  $\mathbf{F}$  has the same structure as the transformation deformation gradient  $\mathbf{F}_t$  in the crystallographic theory of PT, because both describe

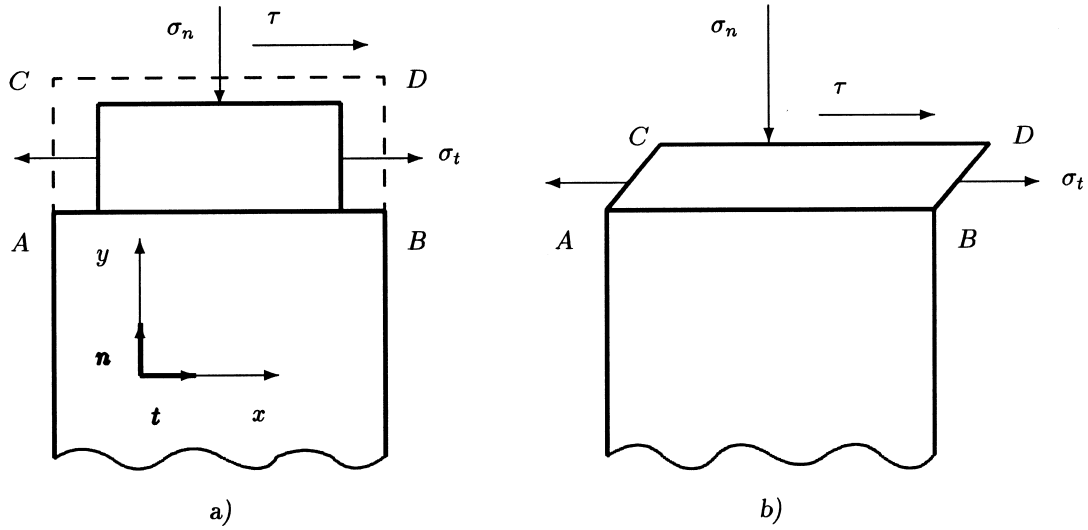


Fig. 2. Scheme of coherent SC in a thin layer.

transformation with an invariant (nondeformable and nonrotating) plane [8]. Direct calculations of the rate of deformation gradient, inverse deformation gradient, velocity gradient and deformation rate result in

$$\dot{\mathbf{F}} = \dot{\gamma}\mathbf{tn} + \dot{\delta}\mathbf{nn}; \quad \mathbf{F}^{-1} = \mathbf{i} - \frac{\gamma}{1+\delta}\mathbf{tn} - \frac{\delta}{1+\delta}\mathbf{nn} \quad (14)$$

$$\mathbf{l} := \dot{\mathbf{F}} \cdot \mathbf{F}^{-1} = (\dot{\gamma}\mathbf{tn} + \dot{\delta}\mathbf{nn}) \left( \mathbf{i} - \frac{\gamma}{1+\delta}\mathbf{tn} - \frac{\delta}{1+\delta}\mathbf{nn} \right) \\ = (\dot{\gamma}\mathbf{tn} + \dot{\delta}\mathbf{nn}) \frac{1}{1+\delta} \quad (15)$$

i.e.

$$\mathbf{l} = \dot{\mathbf{F}} \frac{1}{1+\delta}; \quad \mathbf{d} := (\dot{\mathbf{F}} \cdot \mathbf{F}^{-1})_s = (\dot{\gamma}(\mathbf{tn})_s + \dot{\delta}\mathbf{nn}) \frac{1}{1+\delta} \\ = (\dot{\mathbf{F}})_s \frac{1}{1+\delta}. \quad (16)$$

Expression (14)<sub>2</sub> can be proven by checking that  $\mathbf{F} \cdot \mathbf{F}^{-1} = \mathbf{i}$ .

Further, we will consider chemical reactions only. We assume that the transformation deformation gradient describes pure volumetric compression (or dilatation)

$$\mathbf{F}_t = a\mathbf{i} = \begin{pmatrix} a & 0 \\ 0 & a \end{pmatrix}; \quad a := 1 + \epsilon \quad (17)$$

where  $\epsilon$  is the normal transformation strain. The expressions for the inverse transformation deformation gradient, rate of transformation deformation gradient and deformation rate are

$$\mathbf{F}_t^{-1} = \frac{1}{a}\mathbf{i}; \quad \dot{\mathbf{F}}_t = \dot{a}\mathbf{i}; \quad \dot{\mathbf{F}}_t \cdot \mathbf{F}_t^{-1} = \mathbf{d}_t = \frac{\dot{a}}{a}\mathbf{i}. \quad (18)$$

At small strains and rotations

$$\mathbf{F} = \mathbf{i} + \boldsymbol{\epsilon}; \quad \boldsymbol{\epsilon} = \delta\mathbf{nn} + \gamma(\mathbf{tn})_s; \quad \mathbf{d} = \dot{\boldsymbol{\epsilon}} = \dot{\delta}\mathbf{nn} + \dot{\gamma}(\mathbf{tn})_s \quad (19)$$

$$\mathbf{F}_t = \mathbf{i} + \boldsymbol{\epsilon}_t; \quad \boldsymbol{\epsilon}_t = \epsilon\mathbf{i}; \quad \mathbf{d}_t = \dot{\boldsymbol{\epsilon}}_t = \dot{\epsilon}\mathbf{i}. \quad (20)$$

### 3. THERMODYNAMICS OF STRUCTURAL CHANGES IN A SHEAR BAND

#### 3.1. Transformation work

Let us calculate the work integral in SC criterion (8). As

$$\mathbf{T} = \sigma_n\mathbf{nn} + \sigma_t\mathbf{tt} + 2\tau(\mathbf{tn})_s = \begin{pmatrix} \sigma_t & \tau \\ \tau & \sigma_n \end{pmatrix} \quad (21)$$

then using equation (8) we calculate

$$\mathbf{T} : \mathbf{d}_t = \mathbf{T} : \dot{\mathbf{F}}_t \cdot \mathbf{F}_t^{-1} = (\sigma_n + \sigma_t) \frac{\dot{a}}{a}. \quad (22)$$

For the factor  $1/\rho$  we derive

$$\frac{1}{\rho} = \frac{1}{\rho_1} \frac{\rho_1}{\rho} = \frac{1}{\rho_1} \frac{dV}{dV_1} = \frac{1}{\rho_1} \det \mathbf{F} = \frac{1}{\rho_1} \det \mathbf{F}_t \det \mathbf{F}_p = \frac{a^2}{\rho_1}. \quad (23)$$

Here  $dV$  is the infinitesimal volume in the actual configuration (i.e. during the SICR) and plastic incompressibility  $\det \mathbf{F}_p = 1$  as well as mass conservation  $dm = \rho_1 dV_1 = \rho dV$  are taken into account. As  $\det \mathbf{F} = 1 + \delta$  [see equation (13)], then from equation (23) it follows

$$\delta = a^2 - 1 = \frac{dV}{dV_1} - 1; \quad a = \sqrt{1 + \delta} \quad (24)$$

i.e. the normal component of the deformation gradient is completely determined by the normal component of  $\mathbf{F}_t$  and  $\delta$  is the relative volume change. Then for the velocity gradient we obtain

$$\dot{\mathbf{F}} \cdot \mathbf{F}^{-1} = \frac{\dot{\mathbf{F}}}{a^2} = (\dot{\gamma} \mathbf{tn} + \dot{\delta} \mathbf{nn}) \frac{1}{a^2}; \quad \dot{\delta} = 2a\dot{a}. \quad (25)$$

$$d_{\text{pn}} = \frac{\dot{a}}{a} \quad \text{and} \quad \hat{\gamma}_p = \frac{\dot{\gamma}}{a^2} \quad (33)$$

It follows from equations (22) and (23)

$$\frac{1}{\rho} \mathbf{T} : \dot{\mathbf{F}}_t \cdot \mathbf{F}_t^{-1} = \frac{1}{\rho_1} (\sigma_n + \sigma_t) a \dot{a}. \quad (26)$$

Integrating equation (26) over the transformation process with account for  $\mathbf{T} = \text{const.}$ , we obtain for the specific transformation work

$$A_t := \int_{\mathbf{i}}^{\mathbf{F}_t} \frac{1}{\rho} \mathbf{T} : d\mathbf{F}_t \cdot \mathbf{F}_t^{-1} = \frac{1}{2\rho_1} (\sigma_n + \sigma_t) (a^2 - 1)$$

$$= \frac{1}{\rho_1} p \delta_2; \quad p := 0.5(\sigma_n + \sigma_t). \quad (27)$$

Consequently, the transformation work per unit volume of phase 1  $\rho_1 A_t$  is the product of hydrostatic pressure (mean stress)  $p$  and relative volume change  $\delta_2$ . For small strain formulation  $A_t = (1/2\rho_1)(\sigma_n + \sigma_t)\epsilon_2$ . From the yield condition (3) it follows

$$\sigma_t = \sigma_n - \frac{\epsilon}{|\epsilon|} \sqrt{\sigma_y^2 - 4\tau^2}. \quad (28)$$

We have used the yield stress of the new phase 2 and taken into account that at  $\epsilon > 0$  plastic tension in direction  $\mathbf{n}$  is possible at  $\sigma_n > \sigma_t$  only; at  $\epsilon < 0$  plastic compression in direction  $\mathbf{n}$  is possible at  $\sigma_n < \sigma_t$  only. Using equation (28) we obtain the final expression for transformation work

$$A_t := \frac{1}{2\rho_1} \left( 2\sigma_n - \frac{\epsilon}{|\epsilon|} \sqrt{\sigma_y^2 - 4\tau^2} \right) \delta_2. \quad (29)$$

### 3.2. Reaction-induced plasticity

To determine all kinematic characteristics (plastic and total deformation gradient, deformation rate) and total stress power it is necessary to integrate the associated flow rule (6). The plastic deformation gradient can be calculated as

$$\mathbf{F}_p = \mathbf{F}_t^{-1} \cdot \mathbf{F} = \frac{1}{a} (\mathbf{i} + \gamma \mathbf{tn} + \delta \mathbf{nn}). \quad (30)$$

It is convenient to derive the expression for the plastic deformation rate as the difference between the total and transformation deformation rates [see equation (2)]

$$\mathbf{d}_p = (\dot{\mathbf{F}} \cdot \mathbf{F}^{-1})_s - (\dot{\mathbf{F}}_t \cdot \mathbf{F}_t^{-1})_s = -\frac{\dot{a}}{a} \mathbf{i} + 2\frac{\dot{a}}{a} \mathbf{nn} + \frac{\dot{\gamma}}{a^2} (\mathbf{tn})_s. \quad (31)$$

Using the expression  $\mathbf{i} = \mathbf{nn} + \mathbf{tt}$  for the unit tensor we obtain

$$\mathbf{d}_p = \frac{\dot{a}}{a} (\mathbf{nn} - \mathbf{tt}) + \frac{\dot{\gamma}}{a^2} (\mathbf{tn})_s = d_{\text{pn}} (\mathbf{nn} - \mathbf{tt}) + \hat{\gamma}_p (\mathbf{tn})_s \quad (32)$$

with

for the normal and shear components of plastic deformation rate. For small strains and rotations

$$\mathbf{F}_p = \mathbf{i} + \epsilon_p; \quad \delta = \epsilon; \quad \frac{1}{a} = \frac{1}{1+\epsilon} = \frac{1-\epsilon}{1-\epsilon^2} \simeq 1 - \epsilon \quad (34)$$

$$\epsilon_p = \mathbf{F}_p - \mathbf{i} = -\epsilon \mathbf{i} + \epsilon \mathbf{nn} + \gamma (\mathbf{tn})_s = \epsilon (\mathbf{nn} - \mathbf{tt}) + \gamma_p (\mathbf{tn})_s \quad (35)$$

$$\gamma_p := \gamma; \quad \mathbf{d}_p = \dot{\epsilon}_p = \dot{\epsilon} (\mathbf{nn} - \mathbf{tt}) + \dot{\gamma}_p (\mathbf{tn})_s.$$

Combining equations (6) and (33)<sub>1</sub> we obtain

$$\hat{\gamma}_p = 4h\tau = 4 \frac{\dot{a}}{a} \frac{\tau}{(\sigma_n - \sigma_t)}. \quad (37)$$

Using equations (28) and (33)<sub>2</sub> we obtain the final expression for the shear deformation rate in terms of known parameters

$$\dot{\gamma} = 4a\dot{a} \frac{\tau}{\sqrt{\sigma_y^2 - 4\tau^2} |\epsilon|}. \quad (38)$$

Integrating equation (38) we obtain

$$\gamma = 2(a^2 - 1) \frac{\tau}{\sqrt{\sigma_y^2 - 4\tau^2} |\epsilon|} = 2 |a^2 - 1| \frac{\tau}{\sqrt{\sigma_y^2 - 4\tau^2}}$$

$$= |a^2 - 1| \frac{b}{\sqrt{1 - b^2}}; \quad b := \frac{2\tau}{\sigma_y}. \quad (39)$$

We took into account in equation (39) that the terms  $(a^2 - 1)$  and  $\epsilon$  have the same sign. It is evident from equation (30) that plastic shear  $\gamma_p = \gamma/a$ .

Relationship (39) is shown in Fig. 3. It is easy to see from equation (39) that plastic shear strain (as well as total shear strain) is proportional to the transformation volume change and is independent of normal stresses. Plastic flow occurs at arbitrary (even at infinitesimal) shear stresses, external stress  $\tau$  and  $\sigma_n$  must not satisfy the yield condition. Plastic straining takes place due to variation of volumetric transformation strain. Such a phenomenon for martensitic and diffusive PT is called transformation-induced plasticity or TRIP [9–11]. This problem models the mechanism of TRIP similar to the Greenwood–Johnson effect [12] when at relatively small external stresses (much less than the yield stresses) it is possible to obtain very large values of macroscopic plastic strain due to martensitic or diffusive PT. The distinctive point of our consideration is related to the fact, that in the Greenwood–Johnson mechanism plastic flow occurs outside the transforming region, but in our problem the transforming particles deform plastically. This effect is independent of the concrete nature of SC, it is caused by volumetric transformation strain only and takes place for chemical reactions as well. In analogy with TRIP we will call this phenomenon

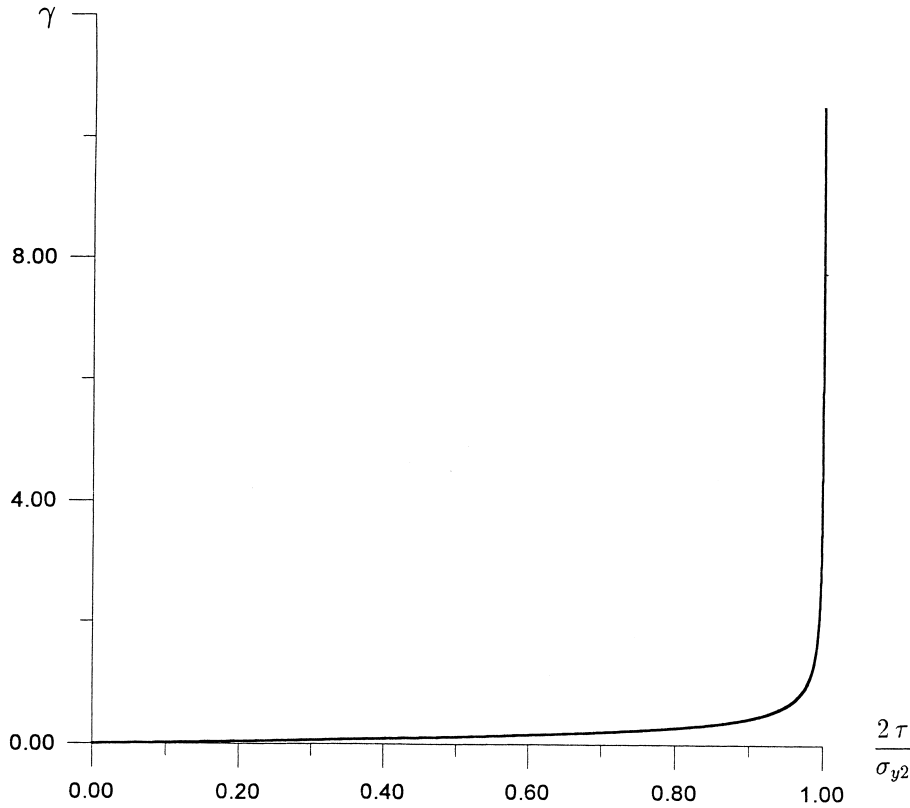


Fig. 3. Relation between shear strain  $\gamma$  and shear stress  $\tau$  for  $a = 1.1$ .

reaction-induced plasticity (RIP) for chemical reactions.

At small  $\tau$  equation (39) results in a linear relation between shear stress and total shear strain (Fig. 3). When shear stress tends to the yield stress in shear  $0.5\sigma_{y2}$ , then the total (and plastic) shear strain tends to infinity. Equation (39) shows qualitatively good agreement with known experimental relationships between the external stresses and plastic strain [9–11] and can be used as a starting point for the formulation of the equation for the description of RIP or TRIP in the three-dimensional case.

3.3. Temperature evolution

The total specific stress power can be calculated as

$$\begin{aligned} \frac{1}{\rho} \mathbf{T} : \mathbf{d} &= \frac{a^2}{\rho_1} \mathbf{T} : \mathbf{d} = \frac{a^2}{\rho_1} \mathbf{T} : (\dot{\mathbf{F}} \cdot \mathbf{F}^{-1}) = \frac{1}{\rho_1} \mathbf{T} : \dot{\mathbf{F}} \\ &= \frac{1}{\rho_1} \mathbf{T} : (2a\dot{a}\mathbf{m}\mathbf{n} + \dot{\gamma}\mathbf{t}\mathbf{n}) \\ &= \frac{2}{\rho_1} \sigma_n a \dot{a} + \frac{4}{\rho_1} a \dot{a} \frac{\tau^2}{\sqrt{\sigma_y^2 - 4\tau^2}} \frac{\epsilon}{|\epsilon|} \\ &= \frac{\dot{\delta}}{\rho_1} \left( \sigma_n + \frac{2\tau^2}{\sqrt{\sigma_y^2 - 4\tau^2}} \frac{\epsilon}{|\epsilon|} \right). \end{aligned} \tag{40}$$

Equations (25) and (38) are taken into account. Substitution of equation (40) into equation (10) leads to

$$\begin{aligned} v(\xi, \theta) \dot{\theta} &= \frac{\dot{\delta}}{\rho_1} \left( \sigma_n + \frac{2\tau^2}{\sqrt{\sigma_y^2 - 4\tau^2}} \frac{\epsilon}{|\epsilon|} \right) \\ &\quad - \left( \Delta U_0 + \int_{\theta_0}^{\theta} \Delta v(\theta) d\theta \right) \dot{\xi}. \end{aligned} \tag{41}$$

The parameter  $\xi$  up to now has not been fixed. It was explicitly in equations (33) and (34) of Part I, and the results are sensitive to the definition of  $\xi$ . Since there is no theoretical or experimental rationale for the choice of  $\xi$ , it will be defined based on convenience of solution of the temperature evolution equation. If we choose

$$\xi := \frac{\delta}{\delta_2} \tag{42}$$

then equation (41) will be linear in  $\xi$  (in case, e.g.  $\xi = (a - 1)/(a_2 - 1)$  equation (41) is nonlinear in  $\xi$  and the solution is unnecessarily complicated). Designating

$$A := \frac{\delta_2}{\rho_1} \left( \sigma_n + \frac{2\tau^2}{\sqrt{\sigma_y^2 - 4\tau^2}} \frac{\epsilon}{|\epsilon|} \right) - \Delta U_0 \tag{43}$$

we obtain in a compact form

$$v(\xi, \theta)\dot{\theta} = \left( A + \int_{\theta_0}^{\theta} \Delta v(\theta) d\theta \right) \dot{\xi}. \quad (44)$$

Assuming temperature independent specific heats, we obtain a linear differential equation

$$(v_1 + \Delta v \xi)\dot{\theta} = (A - \Delta v(\theta - \theta_0))\dot{\xi} \quad (45)$$

with the following solution:

$$\theta = \theta_0 + A \frac{\xi}{v_1 + \Delta v \xi} + \frac{v_1(\theta_1 - \theta_0)}{v_1 + \Delta v \xi}. \quad (46)$$

### 3.4. Criterion for structural change

*3.4.1. General expression.* Utilization of equation (46) in SC criterion (8) leads to results which are rather complicated for analysis. That is why we assume  $\Delta v = 0$  and obtain, for temperature and SC condition

$$\theta = \theta_1 + \frac{A}{v} \xi; \quad \theta_2 := \theta(1) = \theta_1 + \frac{A}{v} \quad (47)$$

$$\left( \frac{1}{2\rho_1}(\sigma_n + \sigma_t)\delta_2 + \Delta s_0 \left( \theta_1 + \frac{A}{2v} \right) - k - \Delta U_0 \right) \times \rho_1 h_1 = 2E \quad (48)$$

or

$$\left( \frac{1}{2\rho_1}(\sigma_n + \sigma_t)\delta_2 + 0.5\Delta s_0(\theta_1 + \theta_2) - k - \Delta U_0 \right) \times \rho_1 h_1 = 2E \quad (49)$$

where  $\theta_2$  is the temperature after finishing the SC. An isothermal approximation can be obtained if the specific heat  $v$  approaches infinity in equation (48). Allowance for the temperature variation at  $\Delta v = 0$  results in substitution of  $\theta_1$  by  $0.5(\theta_1 + \theta_2)$ . Substituting equation (28) and the explicit expression for  $A$  (43) in equation (48) we derive the final expression for SC condition

$$\begin{aligned} & \frac{1}{2\rho_1} \left( 2\sigma_n - \frac{\epsilon}{|\epsilon|} \sqrt{\sigma_y^2 - 4\tau^2} \right) \delta_2 + \Delta s_0 \theta_1 \\ & + \frac{\Delta s_0 \delta_2}{2v\rho_1} \left( \sigma_n + \frac{2\tau^2}{\sqrt{\sigma_y^2 - 4\tau^2} |\epsilon|} \right) \\ & - \frac{\Delta s_0 \Delta U_0}{2v} = k + \Delta U_0 + \frac{2E}{\rho_1 h_1}. \end{aligned} \quad (50)$$

We can express shear stress through shear strain (or plastic strain) using equation (39); after substituting it in equation (50) we obtain the SC criterion in terms of shear strain. That is why it is irrelevant to ask if shear stress or strain affect the SC. In the isothermal approximation tending  $v$  to infinity we get

$$\begin{aligned} & \frac{1}{2\rho_1} \left( 2\sigma_n - \frac{\epsilon}{|\epsilon|} \sqrt{\sigma_y^2 - 4\tau^2} \right) \delta_2 + \Delta s_0 \theta_1 \\ & = k + \Delta U_0 + \frac{2E}{\rho_1 h_1}. \end{aligned} \quad (51)$$

At  $\tau = 0$  equation (50) results in

$$\begin{aligned} & \left( \frac{\sigma_n \delta_2}{\rho_1} - \Delta U_0 \right) \left( 1 + \frac{\Delta s_0}{2v} \right) - \left( \frac{\sigma_y |\delta_2|}{2\rho_1} - \Delta U_0 \right) \\ & - \frac{\sigma_y |\delta_2|}{2\rho_1} + \Delta s_0 \theta_1 = k + \frac{2E}{\rho_1 h_1}. \end{aligned} \quad (52)$$

At  $\tau = 0$  and isothermal approximation we obtain

$$\frac{\sigma_n \delta_2}{\rho_1} - \Delta U_0 - \frac{\sigma_y |\delta_2|}{2\rho_1} + \Delta s_0 \theta_1 = k + \frac{2E}{\rho_1 h_1}. \quad (53)$$

*3.4.2. Analysis of results at  $\tau = 0$ .* Classical chemical thermodynamics of solid state chemical reactions neglects dissipation due to SC and plasticity (like for liquids), as well as temperature variation in the course of SC. The equilibrium temperature for our problem is determined by

$$\frac{\sigma_n \delta_2}{\rho_1} - \Delta \psi(\theta_{\text{eq}}) = \frac{2E}{\rho_1 h_1} \quad (54)$$

or, for temperature-independent and equal specific heats

$$\frac{\sigma_n \delta_2}{\rho_1} - \Delta U_0 + \Delta s_0 \theta_{\text{eq}} = \frac{2E}{\rho_1 h_1}. \quad (55)$$

The deviation of the actual temperature of SC from the equilibrium one is usually explained by slow kinetics, i.e. a detectable quantity of the new phase during the time of experiment can be obtained at relatively large value of driving force, but the reaction in principle occurs at arbitrary small driving force. There are three distinctive points of the approach proposed and classical chemical thermodynamics.

1. Allowance for threshold type dissipation due to the SC  $k$  causes the thermodynamical (not kinetic!) shift of the actual temperature of SC away from the equilibrium temperature obtained in equation (54). This fact is recognized in the theory of martensitic PT, but was not taken into account for solid state chemical reactions. Using equations (53) and (55), the temperature difference can be estimated as

$$\theta_1 - \theta_{\text{eq}} = \frac{k}{\Delta s_0}. \quad (56)$$

If we assume validity of equation (17) of Part I  $k = \rho^{-1} L \sigma_y \epsilon_0$  for chemical reactions as well and use data for the Ti–Si mixture, then for

$$\begin{aligned} \rho &= 3.85 \times 10^3 \text{ kg/m}^3; \quad L = 5; \quad \sigma_y = 10^3 \text{ MPa}, \\ \epsilon_0 = \delta_2 &= 0.1 \quad (k = 1.3 \times 10^5 \text{ J/kg}) \quad \text{and} \\ \Delta s_0 &= 25 \text{ J/kg K} \end{aligned} \quad (57)$$

we obtain  $\theta_1 - \theta_{\text{eq}} = 5195 \text{ K}$ , i.e. temperature deviation can be very significant. Such deviation is much higher than for martensitic transformation in steel (220 K) due to the four times higher volumetric strain  $\delta_2$  and one order smaller entropy difference  $|\Delta s_0|$ . In reality for the Ti–Si mixture such a big difference is not important, because at  $E = \sigma_n = 0$  the equilibrium temperature  $\theta_{\text{eq}} = \Delta U_0 / \Delta s_0 = -70\,370 \text{ K}$ , but for other reactions it can play a crucial role. Note that negative equilibrium temperature means that the second phase is always (at arbitrary temperature) more stable, but due to some dissipative terms and activation barriers material can be in the first (metastable) phase.

2. Plastic flow to accommodate the volumetric transformation strain and necessity of the fulfilment of plasticity condition (28) causes nonhydrostatic stress state and difference between the normal and tangential stresses. This is taken into account by the term  $\sigma_y |\delta_2| / 2\rho_1$  in equation (53) which also increases deviation from the equilibrium temperature. Using the same material parameters we obtain  $\theta_1 - \theta_{\text{eq}} = 519.5 \text{ K}$ . The contribution of this term can be very important, especially at relatively small  $\Delta s_0$  and  $L$ .
3. Account for local temperature variation in the transforming region during the SC leads to an increase of the driving force at  $\Delta s_0 A > 0$  (e.g. for exothermic chemical reaction at  $\Delta s_0 > 0$ ) and to decrease of the driving force in the opposite case (e.g. for endothermic chemical reactions at  $\Delta s_0 > 0$  and martensitic PT), see equations (43) and (48). It leads to the conclusion that the SC criterion (49) determines not the fixed temperature of SC, but  $0.5(\theta_1 + \theta_2)$ . If, e.g. the temperature variation  $\theta_2 - \theta_1 = 400 \text{ K}$ , then  $\theta_1$  is smaller than  $0.5(\theta_1 + \theta_2)$  by 200 K, i.e. the reaction start temperature is 200 K lower than calculated using the isothermal approximation. If  $\theta_2$  is less than the melting temperature of phases 1 and 2, then reaction will occur in the solid state. In the opposite case to estimate the possibility of melting we should compare  $\theta(\xi)$  and  $\theta_m(\xi)$ , where  $\theta_m(\xi)$  is the melting temperature of the intermediate phase at internal time  $\xi$ .

**3.4.3. Effect of shear stress.** Let us analyse the effect of shear strains or stresses on SC. We can distinguish two macroscopic thermomechanical mechanisms.

1. Shear stress  $\tau$  contributes to the yield condition of the transforming phase (28) and SC criterion (50) in a way equivalent to the *decrease* of the

yield limit of the transforming phase, which promotes the SC. At possible maximum shear stress  $\tau = 0.5\sigma_y$  the term related to necessity of fulfilment of the yield condition disappears from the SC criterion, like in the usual equation of chemical thermodynamics.

2. Shear stress produces reaction-induced plastic shear strain and heating due to mechanical work. This makes the condition of the SC from the high temperature phase to low temperature phase (at  $\Delta s_0 < 0$ ) worse and promotes the SC from the low temperature phase to high temperature phase (at  $\Delta s_0 > 0$ ). The distinguishing feature of reaction-induced plastic shear is that it can be very large for shear stresses close to the yield stress in shear  $0.5\sigma_y$  and tends to infinity, when shear stress tends to the yield stress in shear [see equation (39)]. The correspondingly very large contribution to the driving force for the SC from the low temperature phase to high temperature phase is possible. There are two limitations for such a large temperature and driving force rise.

- (a) We should take into account inequality (7) which means that the applied stresses cannot violate the yield condition for the first phase outside the transforming region. The temperature and strain rate dependence of the yield stress and difference in the temperature and strain rate inside and outside the transforming region have to be taken into account. As it follows from Fig. 3, if  $\tau_{\text{max}} = 0.5\sigma_{y1} < 0.5 \cdot 0.9 \sigma_{y2}$ , then transformation-induced shear does not exceed 1.0 and is not very important in comparison with the values of total shear (10–60) in the experiments described in Section 2 of Part I. If the new phase is weaker than the parent one, then limitation (7) does not play any role. Consequently, in contrast to the problem of compression and shearing of substances using Bridgman anvils, plastic shear in shear bands promotes the appearance of weak phases by solid state chemical reaction.
- (b) If melting occurs, then  $\sigma_y = 0$  and heating due to RIP ceases to play any role. At the same time SICR with melting can lead to strong product phases (as for Ti–Si and Nb–Si systems), because high strength is exhibited at the end of reaction and solidification of product.

**3.4.4. Plastic shear necessary for the reaction start.** The temperature variation during the plastic flow before SC in the adiabatic approximation can be determined by integration of the evolution equation

$$\nu \dot{\theta} = \frac{1}{\rho_1} \tau \dot{\gamma} \quad (58)$$

from initial (e.g. room temperature)  $\theta_0$  to reaction



start temperature  $\theta_1$ . It is done in Refs [3, 13] for Ti–Si and Nb–Si mixtures with account for temperature and strain rate dependence of yield stress. At constant shear stress  $\tau$  the temperature increase is proportional to plastic shear  $\gamma_1$  necessary for the beginning of reaction

$$\theta_1 - \theta_0 = \frac{\tau}{\rho_1 v} \gamma_1. \quad (59)$$

For the SC from the low temperature phase to the high temperature phase, we substitute equation (59) in SC criterion (48) and obtain the value of plastic shear, necessary for the beginning of SC. For SC from the high temperature phase to the low temperature phase, SC occurs at the very beginning of plastic straining, i.e. at  $\gamma_0 = 0$ , because any temperature increase reduces the driving force.

**3.4.5. Thickness of the layer.** Let us determine the thickness of the layer, based on the extremum principle (9). We should take into account that usually  $k$  depends on the volume fraction of the new phase. For example, for shape memory alloys concrete relationships are given in Refs [14, 15]. Such a dependence should be also introduced from a formal point of view, because at constant  $k$  the SC will occur in an infinitely thick layer (see below). For an infinite long layer, the dependence on volume fraction is reduced to dependence on  $h_1/L$ .

Maximizing the expression in equation (9) with respect to  $h_1$  we obtain

$$\int_1^{F_2} \frac{1}{\rho} \mathbf{T} : (d\mathbf{F}_t \cdot \mathbf{F}_t^{-1}) + \Delta s_0 \int_0^1 \theta d\xi - (k + \Delta U_0) - \frac{\partial k}{\partial h_1} h_1 = 0 \quad (60)$$

or taking into account equation (8)

$$2E = \frac{\partial k}{\partial h_1} \rho_1 h_1^2. \quad (61)$$

For linear  $k = A + B(h_1/L)$  ( $B > 0$ ) we get

$$h_1 = \left( \frac{2EL}{\rho_1 B} \right)^{1/2}. \quad (62)$$

The thickness of layer  $h_2$  after the SC can be determined from the mass conservation, i.e.

$$h_2 = h_1 \frac{\rho_1}{\rho_2} = h_1 \frac{V_2}{V_1} = h_1 a_2^2. \quad (63)$$

It follows from equation (62), that at  $B = 0$ ,  $h_1 \rightarrow \infty$ , at  $E = 0$ ,  $h_1 = 0$ . The parameter  $h_1$  determined by equation (62) differs from the critical radius for PT liquid–vapour. For liquid and vapour the nucleus with the radius exceeding the critical one is unstable and should grow monotonously at fixed temperature and pressure. In the problem under consideration the nucleus with the thickness, determined by equation (62), is stable, to increase

the thickness it is necessary to increase the driving force  $X$  due to growing  $k$ .

**3.4.6. Interface propagation.** The interface propagation can be modelled as a subsequent nucleation in the layer contacting the existing layer of the second phase. For rigid-plastic material at adiabatic approximation stress and temperature variation in each subsequent layer is the same as in the first one. Consequently, the interface propagation criterion has the same form, as the nucleation criterion [equation (8)]. As the area of the interface does not change during the interface motion, then the increment of surface energy is zero and in equation (8) we should use  $E = 0$ . As the increment of surface energy disappears immediately after the appearance of the nucleus with the thickness determined by equation (62), then at fixed stresses and temperature the layer thickness  $h_1$  will increase to the value of  $h$  at which the threshold  $k$  will be equal to the driving force  $X$  at nucleation. This condition results in

$$X = k(h_1) + \frac{2E}{\rho_1 h_1} = k(h). \quad (64)$$

For the linear function  $k(h_1)$  we obtain with the help of equations (64) and (62)

$$h = h_1 + \frac{2EL}{\rho_1 B h_1} = 2h_1, \quad (65)$$

i.e. due to spontaneous interface propagation the thickness of the layer becomes two times higher.

If  $k$  is independent of  $h_1$ , then the interface will propagate at constant applied stresses and temperature. When  $k$  is an increasing function of  $h_1$ , then stresses and temperature should be changed in order to satisfy the SC criterion (50) at new  $h_1$ . Differentiating equation (50) at  $E = 0$  with respect to time, we obtain the evolution equation for  $h_1$ . The temperature for interface propagation has to be determined without the adiabatic assumption, i.e. by solution of the boundary-value problem.

### 3.5. Description of chemical reactions kinetics

We will consider the initiation of chemical reaction only. As an example we use threshold-type kinetic equation (11) with an expression for  $X - k$  from equation (8). To take into account melting during the SC we multiply the terms containing yield stress in the expression  $X - k$  by  $\xi_{m1}$  and take into account the latent heat of fusion in the temperature evolution equation, where  $\xi_{m1}$  is the internal time, during which yield stress is nonzero. Then substituting in equation (8) the expression for transformation work equation (29) and using  $k = \rho^{-1} L \sigma_y \sigma_0$  we obtain

$$X - k = \frac{1}{\rho_1} \sigma_n \delta_2 - \frac{\xi_{m1} \delta_2}{2\rho_1} \left( \frac{\epsilon}{|\epsilon|} \sqrt{\sigma_y^2 - 4\tau^2} + 2L\sigma_y \right) - \Delta U_0 - \frac{2E}{\rho_1 h_1} + \Delta s_0 \theta_{ef} \quad (66)$$

$$\dot{\chi} = \dot{\chi}_0 \exp\left(-\frac{E_a + \Delta U_0 + 2E/\rho_1 h_1}{R\theta_{ef}}\right) \exp\frac{\sigma_n \delta_2}{\rho_1 R\theta_{ef}} \exp\frac{\Delta S_0}{R} \cdot \exp\left(-\frac{\xi_{m1} \delta_2}{2\rho_1 R\theta_{ef}} (\sqrt{\sigma_y^2 - 4\tau^2} + 2L\sigma_y)\right). \quad (67)$$

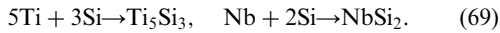
We assume that  $\sigma_n$  is small and will neglect it. At  $\tau = 0$  equation (67) reduces to the following equation:

$$\dot{\chi} = \dot{\chi}_0 \exp\left(-\frac{E_a + \Delta U_0 + 2E/\rho_1 h_1}{R\theta_{ef}^0}\right) \cdot \exp\frac{\Delta S_0}{R} \exp\left(-\frac{\xi_{m1}^0 \delta_2}{2\rho_1 R\theta_{ef}^0} (1 + 2L)\sigma_y\right), \quad (68)$$

where superscript 0 means that the parameters are determined at  $\tau = 0$ .

Fulfilment of the thermodynamic criterion of SC  $X - k - E/(\rho_1 h_1) = 0$  does not assure the initiation of SICR. As the kinetic criterion of initiation of SICR we can accept that the time of chemical reaction determined by equation (67) is less than the time of deformation in the shear band at  $\theta > \theta_1$ .

We will estimate the effect of shear stresses and associated shear strains on the rate of chemical reactions for two SICRs in the systems



These systems were experimentally investigated, see Part I. The effect of shear stress is twofold.

- Shear stress increases the driving force due to necessity of fulfilment of the plasticity condition. Comparison of equation (67) at maximum possible shear stress and equation (68) shows that the effect increases the rate  $\dot{\chi}$  by a factor

$$\frac{\dot{\chi}_{\tau=0.5\sigma_y}}{\dot{\chi}_{\tau=0}} = \exp\left(\frac{\xi_{m1}^0 \delta_2}{2\rho_1 R\theta_{ef}^0} \sigma_y\right). \quad (70)$$

Substituting the numbers, accepted for the Ti–Si mixture in equation (57) and  $\theta_{ef}^0 = 2000$ ,  $\xi_{m1}^0 = 0.175$  [such  $\xi_{m1}^0$  corresponds to  $\theta_1^0 = 1476$  K, see equation (73)], we obtain  $\xi_{\tau=0.5\sigma_y}/\xi_{\tau=0} = 1.045$ . Consequently, despite the significant influence of the above effect on equilibrium temperature, its influence on kinetics is negligible. This is due to the high effective temperature  $\theta_{ef}$  in the denominator and relatively small internal time interval  $\xi_{m1}^0 = 0.175$  when a mixture is in a solid state.

The increase in driving force caused by temperature rise due to RIP [the term  $\rho_1 \Delta S_0 \theta_{ef}$  in the criterion of SC equation (8)] does not play a role for kinetics as well, because the effective temperature  $\theta_{ef}$  disappears due to the term  $R\theta_{ef}$  in the denominator [see equation (11)].

- Heating due to RIP increases the effective temperature  $\theta_{ef}$  in the denominator of kinetic

equation (11) and accelerates the reaction. This effect will be studied below.

We assume that the melting temperature  $\theta_{m1}$  for Ti–Si and Nb–Si mixtures is a mass averaged temperature of Ti and Si, and Nb and Si, respectively. Let us consider each mixture separately.

### 3.6. Ti–Si mixture

The temperature variation in the transforming region can be described by the following equations (Fig. 4):

$$\theta = \theta_1 + \frac{A_p - \Delta U_0}{\nu} \xi; \quad \xi < \xi_{m1} (\theta < \theta_{m1});$$

$$\theta = \theta_{m1}; \quad \xi_{m1} \leq \xi \leq \xi_{m1} + \Delta \xi_1;$$

$$\theta = \theta_{m1} - \frac{\Delta U_0}{\nu} (\xi - \xi_{m1}); \quad \xi_{m1} + \Delta \xi_1 < \xi < \xi_{m2};$$

$$\theta = \theta_{m2}; \quad \xi_{m2} \leq \xi \leq \xi_{m2} + \Delta \xi_2;$$

$$\theta = \theta_{m2} - \frac{\Delta U_0}{\nu} (\xi - \xi_{m2}); \quad \xi_{m2} + \Delta \xi_2 < \xi;$$

$$\Delta \xi_1 := -\frac{L_1}{\Delta U_0} \quad \text{and} \quad \Delta \xi_2 := -\frac{L_2}{\Delta U_0}, \quad (71)$$

where  $\theta_{m1}$  and  $\theta_{m2}$  are the melting temperature of mixture and product,  $\xi_{m1}$  and  $\xi_{m2}$  the values of parameter  $\xi$  at melting temperatures  $\theta_{m1}$  and  $\theta_{m2}$ ;  $\Delta \xi_1$  and  $\Delta \xi_2$  the variation of parameter  $\xi$  during the absorption of latent heat of fusion  $L_1$  and  $L_2$  at melting of the mixture and product phase, respectively;

$$A_p = \tau \gamma_p = \frac{2\tau^2 \delta_2}{\rho_1 \sqrt{\sigma_y^2 - 4\tau^2}} \quad (72)$$

is the plastic work during the SC. The temperature at  $\tau = 0$  can be calculated by making  $A_p = 0$  in equation (71) (Fig. 4). All parameters at  $\tau = 0$  will be marked with superscript zero. Using equation (71) and Fig. 4 we obtain

$$\xi_{m1} = \frac{\nu(\theta_{m1} - \theta_1)}{A_p - \Delta U_0}; \quad \xi_{m1}^0 = -\frac{\nu(\theta_{m1} - \theta_1^0)}{\Delta U_0} \quad (73)$$

$$\Delta \xi_1 = \Delta \xi_1^0; \quad \Delta \xi_2 = \Delta \xi_2^0 \quad (74)$$

$$\xi_{m2} = \xi_{m1} + \Delta \xi_1 - \frac{\nu(\theta_{m2} - \theta_{m1})}{\Delta U_0};$$

$$\xi_{m2}^0 = \xi_{m1}^0 + \Delta \xi_1 - \frac{\nu(\theta_{m2} - \theta_{m1})}{\Delta U_0} \quad (75)$$

$$\begin{aligned} \theta(1) &= \theta_{m2} - \frac{\Delta U_0}{\nu} (1 - \Delta \xi_2 - \xi_{m2}) \\ &= -\frac{\Delta U_0}{A_p - \Delta U_0} \theta_1 + \theta_{m1} \frac{A_p}{A_p - \Delta U_0} \\ &\quad - \frac{\Delta U_0 + L_1 + L_2}{\nu} \end{aligned} \quad (76)$$

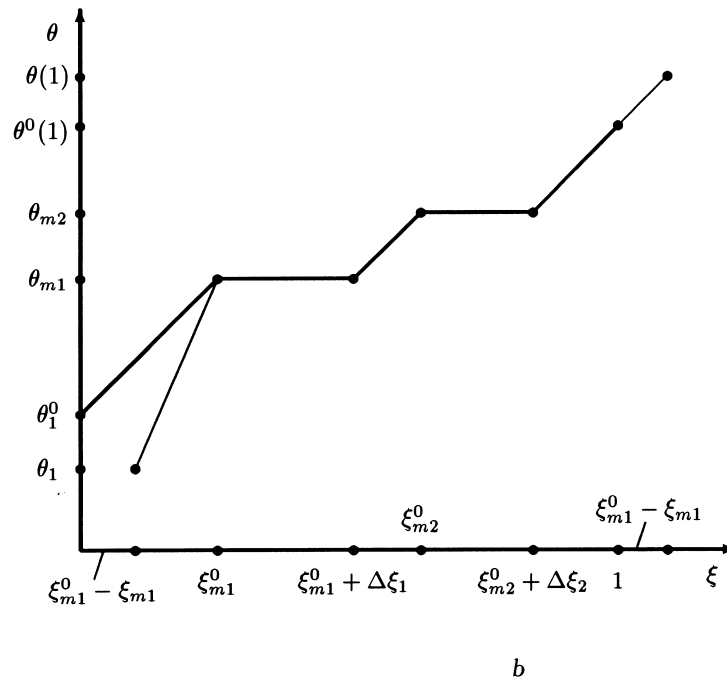
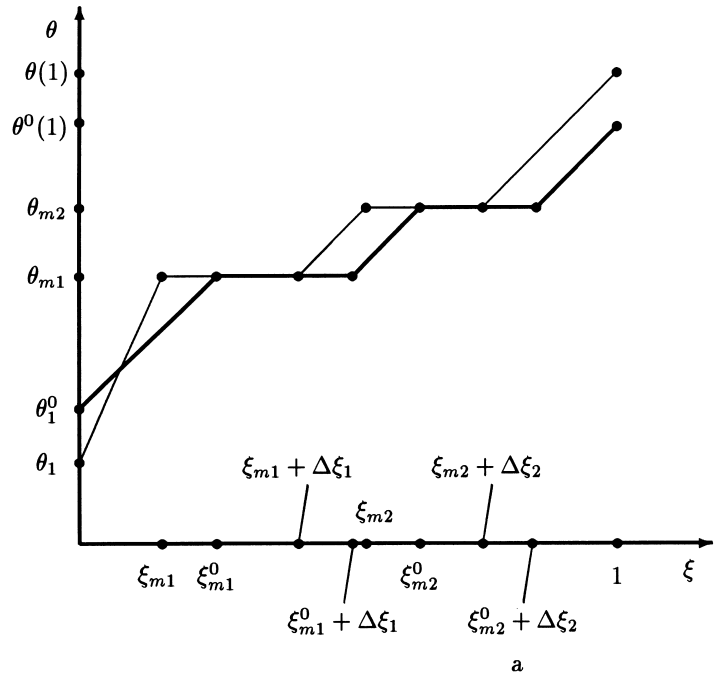


Fig. 4. (a) Temperature variation in the transforming region for a Ti-Si mixture in the case without shear stresses (thick lines) and for strain-induced chemical reaction (thin lines). (b) The same as in (a), but the curve for strain-induced chemical reaction is shifted by  $\xi_{m1}^0 - \xi_{m1}$  along the axis  $\xi$ .

$$\theta^0(1) = \theta_1^0 - \frac{\Delta U_0 + L_1 + L_2}{v}, \quad (77)$$

where  $\theta(1)$  and  $\theta^0(1)$  are the temperatures at the end of reaction (at  $\xi = 1$ ). For the effective temperature we obtain

$$\begin{aligned} \theta_{ef} = & 0.5(\theta_1 + \theta_{m1})\xi_{m1} + 0.5(\theta_{m1} + \theta_{m2}) \times \\ & (\xi_{m2} - \xi_{m1} - \Delta\xi_1) + 0.5(\theta_{m2} + \theta(1)) \times \\ & (1 - \xi_{m2} - \Delta\xi_2) + \theta_{m1}\Delta\xi_1 + \theta_{m2}\Delta\xi_2. \end{aligned} \quad (78)$$

The difference  $\theta_{ef} - \theta_{ef}^0$  can be estimated by the equation

$$\theta_{ef} - \theta_{ef}^0 = 0.5[(\theta_1 + \theta_{m1})\xi_{m1} - (\theta_1^0 + \theta_{m1})\xi_{m1}^0] + (\theta(1) + \theta^0(1))(\xi_{m1}^0 - \xi_{m1}) \quad (79)$$

which can be easily derived with the help of Fig. 4(b). The contribution to effective temperature at  $\theta \leq \theta_{m1}$  under applied shear stresses is smaller than without stresses, because due to more intense heating the melting temperature  $\theta_{m1}$  can be reached quicker ( $\xi_{m1} < \xi_{m1}^0$ ). The positive contribution to the effective temperature during the heating between temperatures  $\theta^0(1)$  and  $\theta(1)$  exceeds the negative contribution at  $\theta \leq \theta_{m1}$  and makes the difference  $\theta_{ef} - \theta_{ef}^0$  positive.

Theoretically, plastic shear and plastic work can be infinite at  $\tau = 0.5\sigma_y$  [see equation (39)].

In the limit  $A_p \rightarrow \infty$  we obtain for the possible maximum difference

$$(\theta_{ef} - \theta_{ef}^0)_{\max} = (\theta_{m1} - \theta_1^0) \left( 1 + \frac{L_1 + L_2}{\Delta U_0} \right). \quad (80)$$

Results are independent of  $\theta_1$ . After algebraic transformation of equation (79) we obtain

$$\theta_{ef} - \theta_{ef}^0 = -\frac{\nu}{2(A_p - \Delta U_0)} (\bar{a}\theta_1^2 + b\theta_1 + c) \quad (81)$$

with

$$\bar{a} := \frac{A_p}{A_p - \Delta U_0}; \quad b = q - 2\theta_{m1}\bar{a};$$

$$q := 2 \frac{\Delta U_0 + L_1 + L_2}{\nu},$$

$$c := \theta_{m1}^2 \bar{a} - q\theta_{m1} \frac{A_p}{\Delta U_0} + q \frac{A_p - \Delta U_0}{\Delta U_0} \theta_1^0. \quad (82)$$

For interpretation of the role of plastic heating on kinetics of reaction let us find how the initiation temperature can be decreased  $\theta_1^0 - \theta_1$  at the same effective temperature, i.e. at the same duration of reaction in the given transforming volume. After determination of  $\theta_1$  from equation (81) at the condition  $\theta_{ef} - \theta_{ef}^0 = 0$  we obtain

$$\theta_1^0 - \theta_1 = \theta_1^0 + \frac{b + \sqrt{b^2 - 4\bar{a}c}}{2\bar{a}}. \quad (83)$$

Results for three different ratios  $A_p/\Delta U_0 = -0.1, -1$  and  $-3$  are presented in Fig. 5. The following data are used:

$$\theta_{m1} = 1876 \text{ K}; \quad \theta_{m2} = 2403 \text{ K}$$

$$\Delta U_0 = -570 \text{ kJ/mol}; \quad \nu = 250 \text{ J/(K} \cdot \text{mol)}$$

$$L_1 = 68.8 \text{ kJ/mol}; \quad L_2 = 178.88 \text{ kJ/mol}. \quad (84)$$

If reaction without shear stresses starts at the melting temperature  $\theta_{m1}$ , then plastic heating plays no

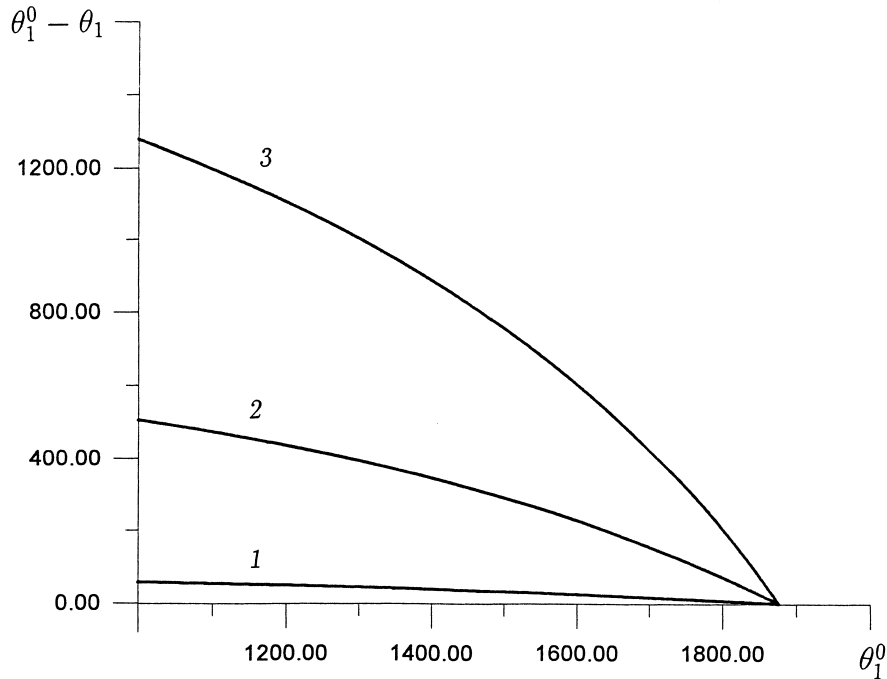


Fig. 5. Decrease in reaction start temperature due to reaction-induced plasticity vs reaction start temperature without shear stress for the Ti-Si system for different ratios between plastic work and the heat of reaction: 1,  $A_p/\Delta U_0 = -0.1$ ; 2,  $A_p/\Delta U_0 = -1$ ; 3,  $A_p/\Delta U_0 = -3$ .

role, because both  $\xi_{m1}^0 = \xi_{m1} = 0$ . With increasing plastic work and decreasing start temperature  $\theta_1^0$  in the absence of shear stress, the effect of plastic heating increases. In particular, at  $A_p/\Delta U_0 = -1$  and  $\theta_1^0 = 1000$  K the decrease of start temperature of reaction due to shear stresses is 500 K, i.e. the effect is very high.

It follows from equations (81)–(83) that results are independent of melting temperature of the product  $\theta_{m2}$ , i.e. at  $L_2 = 0$  we can apply the same equations for the case without melting of product.

The difference  $\theta_{ef} - \theta_{ef}^0$  depends on specific heat, heat of reaction and latent heats of fusion  $L_1$  and  $L_2$  (at fixed  $A_p/\Delta U_0$ ) through the parameter  $q$  only. It follows from Fig. 6, that the larger  $q$  for the different mixtures (larger heats of fusion  $L_1$  and  $L_2$ , smaller heat of reaction  $|\Delta U_0|$  and specific heat  $v$ ), the less effective shear stresses are in reducing the reaction start temperature. It is clear that  $q$  must be negative, otherwise  $\Delta \xi_1 + \Delta \xi_2 \geq 1$  and there is no possibility to heat the product to a temperature higher than its melting temperature. The opposite situation corresponds to the Nb–Si mixture and will be treated below. Estimation of some terms in equation (68) at  $\theta_{ef}^0 = 2000$  gives

$$\exp \frac{\Delta S_0}{R} = 2.65; \quad \exp \left( -\frac{\xi_{m1}^0 \delta_2}{2\rho_1 R \theta_{ef}^0} (1 + 2L)\sigma_y \right) = 0.614. \quad (85)$$

3.7. Nb–Si mixture

As for the Nb–Si mixture the heat of reaction is less than the latent heat of fusion for NbSi<sub>2</sub>, then the region  $\xi_{m2} + \Delta \xi_2 < \xi$  in equation (71) does not exist (Fig. 7) and the following equations are valid:

$$\begin{aligned} \theta &= \theta_1 + \frac{A_p - \Delta U_0}{v} \xi; & \xi < \xi_{m1} (\theta < \theta_{m1}); \\ \theta &= \theta_{m1}; & \xi_{m1} \leq \xi \leq \xi_{m1} + \Delta \xi_1; \\ \theta &= \theta_{m1} - \frac{\Delta U_0}{v} (\xi - \xi_{m1}); & \xi_{m1} + \Delta \xi_1 < \xi < \xi_{m2}; \\ \theta &= \theta_{m2}; & \xi_{m2} \leq \xi \leq 1; \end{aligned} \quad (86)$$

with the same equations (73)–(75) for  $\Delta \xi_1 = \Delta \xi_1^0$ ,  $\xi_{m1}^0$ ,  $\xi_{m2}$  and  $\xi_{m2}^0$ . For the effective temperature we obtain

$$\begin{aligned} \theta_{ef} &= 0.5(\theta_1 + \theta_{m1})\xi_{m1} + 0.5(\theta_{m1} + \theta_{m2}) \\ & \quad (\xi_{m2} - \xi_{m1} - \Delta \xi_1) + \theta_{m1} \Delta \xi_1 \\ & \quad + \theta_{m2}(1 - \xi_{m2}). \end{aligned} \quad (87)$$

The difference  $\theta_{ef} - \theta_{ef}^0$  can be estimated by the equation (see Fig. 7)

$$\begin{aligned} \theta_{ef} - \theta_{ef}^0 &= 0.5(\theta_1 + \theta_{m1})\xi_{m1} - 0.5(\theta_1^0 + \theta_{m1})\xi_{m1}^0 \\ & \quad + \theta_{m2}(\xi_{m1}^0 - \xi_{m1}) \end{aligned} \quad (88)$$

or after algebraic transformations

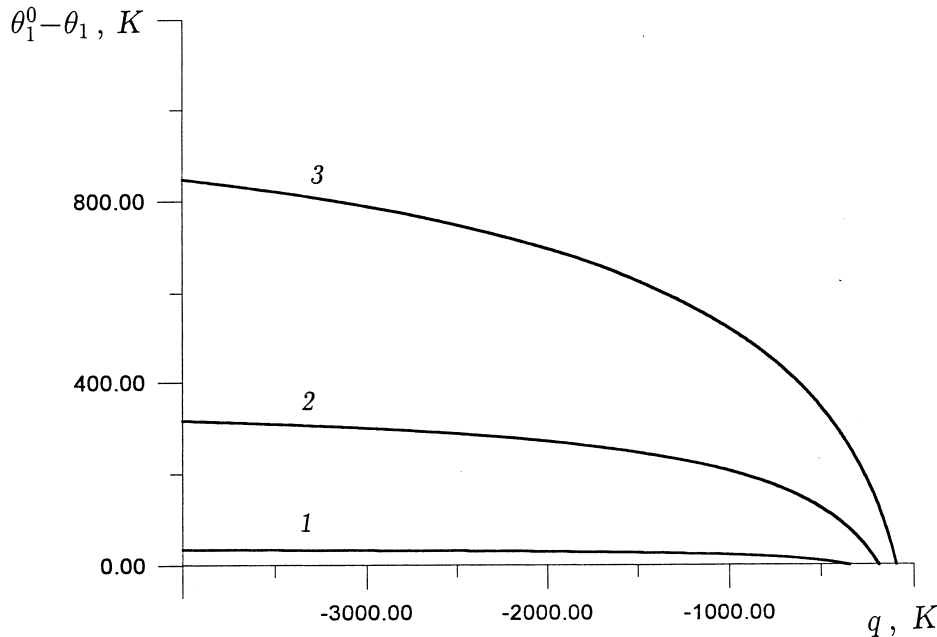


Fig. 6. Relation between decrease in reaction start temperature due to reaction-induced plasticity and parameter  $q$  at  $\theta_1^0 = 1500$  K for different ratios between plastic work and the heat of reaction: 1,  $A_p/\Delta U_0 = -0.1$ ; 2,  $A_p/\Delta U_0 = -1$ ; 3,  $A_p/\Delta U_0 = -3$ .

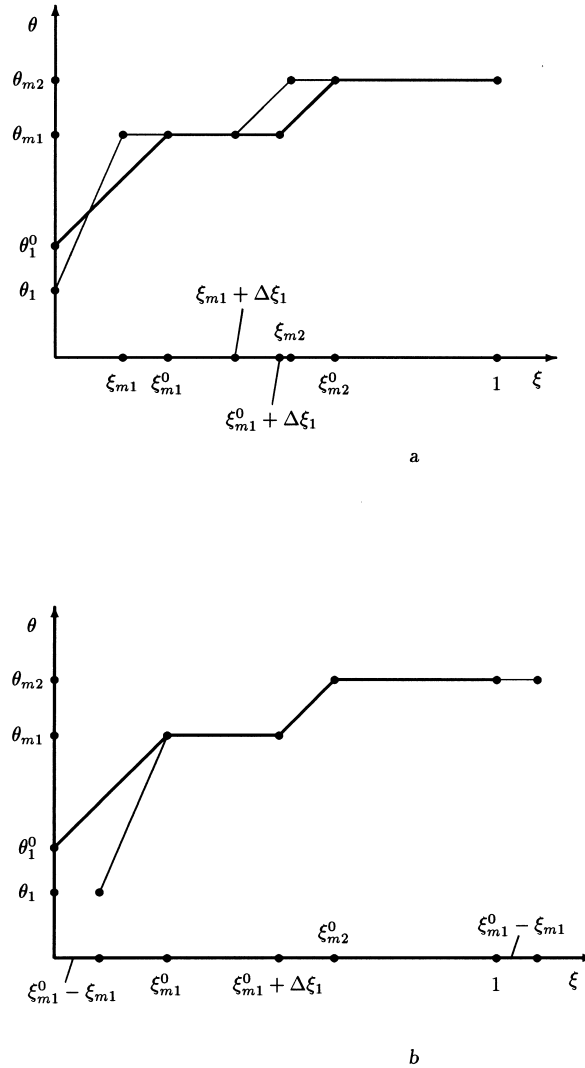


Fig. 7. (a) Temperature variation in the transforming region for a Nb-Si mixture in the case without shear stresses (thick lines) and for strain-induced chemical reaction (thin lines). (b) The same as in (a), but the curve for strain-induced chemical reaction is shifted by  $\xi_{m1}^0 - \xi_{m1}$  along the axis  $\xi$ .

$$\theta_{ef} - \theta_{ef}^0 = -\frac{\nu}{2(A_p - \Delta U_0)}(\theta_1^2 - 2\theta_{m2}\theta_1 + c); \quad \theta_1^0 - \theta_1 = \theta_1^0 - \theta_{m2} + \sqrt{\theta_{m2}^2 - c}. \quad (91)$$

$$c = ((\theta_1^0)^2 - 2\theta_{m2}\theta_1^0) \frac{A_p - \Delta U_0}{\Delta U_0} - (\theta_{m1}^2 - 2\theta_{m2}\theta_{m1}) \frac{A_p}{\Delta U_0}. \quad (89)$$

In the limit  $A_p \rightarrow \infty$  we obtain the possible maximum difference

$$(\theta_{ef} - \theta_{ef}^0)_{\max} = -\frac{\nu}{\Delta U_0} [\theta_{m2} - 0.5(\theta_1^0 + \theta_{m1})](\theta_{m1} - \theta_1^0). \quad (90)$$

Results are again independent of  $\theta_1$ . After determination of  $\theta_1$  from equation (89) at the condition  $\theta_{ef} - \theta_{ef}^0 = 0$  we obtain the expression for decrease of reaction start temperature due to shear stresses

Results for three different ratios  $A_p/\Delta U_0 = -0.1, -1$  and  $-3$  are presented in Fig. 8. The following data are used:  $\theta_{m1} = 1962$  K;  $\theta_{m2} = 2240$  K. Again, if reaction without shear stresses starts at melting temperature  $\theta_{m1}$ , then plastic heating does not affect the reaction, because both  $\xi_{m1}^0 = \xi_{m1} = 0$ . In contrast to the case for the Ti-Si mixture, the decrease in reaction start temperature due to plastic heating is independent of specific heat, latent heats of fusion and heat of reaction (at fixed  $A_p/\Delta U_0$ ), but depends on the melting temperature of the product. Despite this difference results for both mixtures are very close. This fact leads to the conclusion that  $A_p/\Delta U_0$  is the most important parameter for the decrease in reaction start temperature due to shear stresses.

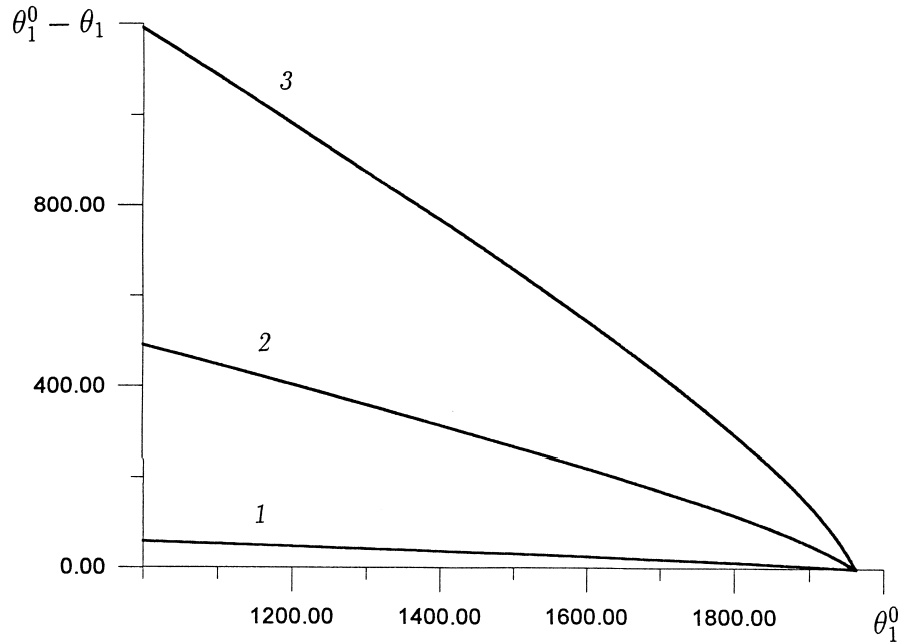


Fig. 8. Decrease in reaction start temperature due to reaction-induced plasticity vs reaction start temperature without shear stress for the Nb-Si system for different ratios between plastic work and the heat of reaction: 1,  $A_p/\Delta U_0 = -0.1$ ; 2,  $A_p/\Delta U_0 = -1$ ; 3,  $A_p/\Delta U_0 = -3$ .

Processes inside the shear band include multiple fracture of Ti particles, resulting in the creation of hot fresh surfaces. This can essentially accelerate chemical interaction. Flow instability has also been observed [1], which increases the mixing of the components as well. Both these facts can be taken into account in a more detailed model, which will be developed in the future.

#### 4. CONCLUSIONS

1. The problem of strain-induced chemical reaction (SICR) in a thin layer inside the shear band is formulated and solved analytically for large strains and adiabatic approximation.

Plastic straining takes place due to variation of volumetric transformation strain and displacements continuity across an interface. It is obtained, that plastic shear strain during the chemical reaction is proportional to transformation volumetric strain and is independent of normal stresses. Plastic flow occurs at arbitrary shear stresses, external stresses  $\tau$  and  $\sigma_n$  must not satisfy the yield condition. This phenomenon we called reaction-induced plasticity (RIP), similar to TRIP at martensitic or diffusive PT. At small  $\tau$  a linear relation between shear stress and plastic shear strain is valid. When shear stress tends to the yield stress in shear, then plastic shear tends to infinity.

2. The initial thickness of the transformed layer is determined based on the extremum principle (9). Due to independence of the surface energy of the

system of the thickness of the layer, the increment of surface energy disappears immediately after the appearance of the nucleus. Then at fixed stresses and temperature the layer thickness  $h_1$  increases by a factor of 2 due to spontaneous interface propagation. Further growth of the nucleus is stable, if  $k$  is an increasing function of  $h_1$ , i.e. to increase the thickness the stresses and (or) temperature should be changed.

3. A criterion for athermal SC is derived. There are three distinct aspects of the approach proposed for zero shear stresses and classical chemical thermodynamics.

- Allowance for threshold type dissipation due to the SC  $k$  causes the thermodynamic (not kinetic!) shift of the actual temperature of SC relative to the chemical equilibrium temperature. Deviation from equilibrium temperature due to  $k$  can be very high, e.g. in our example it exceeds 5000 K.
- Plastic flow for accommodation of the volumetric transformation strain and necessity of the fulfillment of plasticity condition result in nonhydrostatic stress state. This is taken into account by the term  $\sigma_y |\delta_2| / 2\rho_1$  in equation (53) which also increases the deviation from the equilibrium temperature (in our example it exceeds 500 K).
- Allowance for local temperature variation in the transforming region during the SC leads to an increase of the driving force at  $\Delta s_0 A > 0$  (e.g. for exothermic chemical reaction at  $\Delta s_0 > 0$ ) and to the decrease of the driving force in the opposite case (e.g. for endothermic chemical reactions at  $\Delta s_0 > 0$ ), see equation (48). In this case SC cri-

terion (49) determines not the fixed temperature of SC, but  $0.5(\theta_1 + \theta_2)$ .

4. Two macroscopic mechanisms of the experimentally observed positive effect of shear stresses on SC from the low temperature phase to the high temperature phase are found.

- Shear stress  $\tau$  contributes to the yield condition of the transforming phase (28) and SC criterion (50) in a way equivalent to the *decrease* of the yield limit of the transforming phase, which promotes the SC. At possible maximum shear stress  $\tau = 0.5\sigma_y$  the term related to necessity of fulfilment of the yield condition disappears from the SC criterion, like in the usual equation of chemical thermodynamics.
- Shear stress produces RIP and heating due to mechanical work. This fact suppresses the SC from the high temperature phase to the low temperature phase (for  $\Delta s_0 < 0$ ) and promotes the SC from the low temperature phase to the high temperature phase (for  $\Delta s_0 > 0$ ). In the second case a very large contribution to the driving force can be obtained, because shear strain is very large for shear stresses close to the yield stress in shear ( $0.5\sigma_y$ ) and tends to infinity, when shear stress tends to  $0.5\sigma_y$ . There are two limitations for such a large temperature and a driving force rise.
  - (a) Necessity of fulfilment of the yield condition for the first phase outside the transforming region. If the new phase is weaker than the parent one, then limitation (7) does not play any role. Consequently, in contrast to the problem of compression and shearing of substances in Bridgman anvils, plastic shear in shear bands promotes the appearance of weak phases by solid state chemical reaction.
  - (b) If the transforming material is melted, then heating due to RIP ceases to play any role. At the same time, SICR with melting can lead to strong product phases (as for Ti–Si and Nb–Si systems), because of the high strength exhibited at the end of reaction and solidification of product.

5. According to equation (39), shear stresses and shear strains (and shear plastic strains) are related uniquely and are in monotone relation to each other, i.e. they produce an equivalent contribution to the driving force of SC. That is why two equivalent forms of the SC criterion are possible, namely in terms of shear stress or plastic shear strain.

6. SC from the high temperature phase to the low temperature phase occurs at the very beginning of plastic straining, because heating due to plastic dissipation makes the SC condition worse. For SC from the low temperature phase to the high temperature phase the temperature rise promotes SC. That is why SC begins at some critical plastic shear,

necessary for reaching the temperature satisfying the SC condition.

7. The initiation of chemical reaction is studied. An expression for time of chemical reaction in a thin layer is derived. Fulfilment of the thermodynamics criterion of SC does not assure the initiation of SICR. As the kinetic criterion of initiation of SICR, we accept that the time of chemical reaction determined by equation (67) is less than the time of deformation in the shear band at  $\theta > \theta_1$ . As an example SICR (69) in Ti–Si and Nb–Si mixtures are considered. It is shown that the main reason for acceleration of reaction kinetics due to shear stress or strain is related to the increase of effective temperature due to RIP. The increase of driving force  $X$  due to shear stresses does not affect the kinetics because of the high effective temperature in the denominator of equation (11).

8. For interpretation of the role of plastic heating on kinetics of reaction it is found how the reaction start temperature can be decreased  $\theta_1^0 - \theta_1$  at the same effective temperature, i.e. at the same duration of reaction in the given transforming volume. Despite the difference between the two systems, the decrease in reaction start temperature due to RIP at fixed  $A_p/\Delta U_0$  and variable reaction start temperature  $\theta_1^0$  without shear stresses are very close. This means that  $A_p/\Delta U_0$  is the most important parameter for the decrease in reaction start temperature due to RIP. With increasing plastic work and decreasing start temperature without shear stress  $\theta_1^0$ , the effect of plastic heating increases.

9. The analytical treatment enables the estimation of the effect of various parameters on  $\theta_1^0 - \theta_1$  for other systems. For a system with the completely melted product it is obtained that:

- results are independent of melting temperature of product  $\theta_{m2}$ , i.e. at  $L_2 = 0$  we can apply the same equations for the case without melting of product;
- the larger (at fixed  $A_p/\Delta U_0$ ) the heats of fusion  $L_1$  and  $L_2$ , the smaller the heat of reaction  $|\Delta U_0|$  and specific heat  $v$  for the different mixtures, the less effective shear stresses are in reducing the reaction start temperature.

For systems with partially melted product, the results are independent of specific heat, latent heats of fusion and heat of reaction (at fixed  $A_p/\Delta U_0$ ), but depend on the melting temperature of product. It is necessary to mention that, due to the very simple stress–strain state found, a number of generalizations can be easily obtained. For example, elastic strain and more complicated SC kinetics can be taken into account. An averaged description of SC in terms of the volume fraction of the second phase is possible as well.

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