JOURNAL OF MATERIALS SCIENCE 31 (1996) 5169–5177

Transport properties of liquid phase in capillary-like media and its application to sintering of metallic and ceramic powders

J. W. NOWOK
Materials Technologies, University of North Dakota, Energy and Environmental Research Center, P.O. Box 9018, Grand Forks, ND 58202, USA

Intergranular mass transport in materials plays an important role in successful bonding of particles, and controls the material's properties. This results from the processing conditions including the intergranular mass transport and interfacial reactions. The model of liquid mass transport of metals, molten salts, silicates, and molecular liquids, in capillary-like media is discussed. The model concentrates on the role of surface tension-to-viscosity ratio, γ/η, and volume diffusion on the liquid flow in fine pores with diameters comparable to the liquid phase above its critical thickness. We have found the following relation between two parameters: $D_{\mathrm{cap}} = (\gamma/\eta)L\alpha$, where α and L are a specific permeability and the mean diffusive jump length of atoms/ions/molecules, respectively. The specific permeability is related to the hydraulic permeability, taken from Darcy's law, and depends on capillary radius and liquid/solid contact angle. It is demonstrated that the specific permeability depends on the interfacial reactions and heterogeneity of the system. The mass transport in liquid layers seems to be initiated by atoms with low interatomic distances (low atomic radii) in liquid metals or by the high non-bridging oxygen content in aluminosilicate melts.

1. Introduction

Many theoretical and empirical models on liquid-phase sintering have been developed since 1945 [1] that employ either viscous flow driven by capillary forces or diffusional mass transport, but none of these models attempts to discuss the interrelationship between both transport processes in capillary-like media. In our treatment we have combined both of the above mass transport phenomena and tried to emphasize that both mechanisms can be equally treated if this meniscus of the liquid phase in an inactive capillary is well-preserved, and the liquid is in thermodynamic equilibrium with the solid [2–4]. One would expect that the interfacial energy between a solid and its own liquid would be very small. The complexity of this approach may arise if (1) a chemical reaction occurs between liquid and solid particles (capillaries), (2) the liquid phase contains more than two components (e.g. silicates), and (3) intergranular space and/or capillary radius changes, giving the meniscus a non-uniform curvature. In this paper, as a contribution to the understanding of capillary mass transport in a "thick liquid layer," we suggest a general phenomenological model for the description of mass transport through a liquid phase in a capillary-like medium, based on our concept of viscous flow and diffusion flux within the framework of Darcy's law. Also, we intend to define the relationship between specific permeability and physical properties of melts as described by liquid-capillary contact angles and geometrical factors related to the capillary's radius.

In considering the intergranular flow porcess, it is important to define what is meant by a "thick liquid layer" and how this can be distinguished from a "thin liquid layer." The thermodynamic constraints on phase equilibria in thick liquid layers require a structural and dynamic continuum, and this can be achieved in liquid layers with the thickness above five to ten molecular diameters [5, 6]. The behaviour of thick intergranular liquid layers is assumed to be similar to that of liquids in capillaries, and this property can be qualitatively and even quantitatively described in terms of the liquid's bulk properties, such as viscosity and surface tension. When a liquid is confined to narrow spaces whose dimension is less than the scale of molecular diameters, the liquid phase ceases to behave as a structureless continuum, and its thickness corresponds with that of thin films. The liquid thin film experiences an oscillatory force law varying between attraction and repulsion, and its viscosity increases by several orders of magnitude [7].

Considerable experimental evidence has shown that in materials with a thin liquid layer of up to 10 μm, the film migrates as a result of diffusion and stress generation. This phenomenon is examined using either in liquid film migration (LFM) or a diffusion-induced grain-boundary migration (DIGM) approach [8–10].

0022–2461 © *1996 Chapman & Hall*

2. Intergranular mass transport with simultaneous dissolution of particles

In our model, the motion of the melt originates from the activated motion of the meniscus at the neck with simultaneous dissolution of either metal or ceramic into the liquid neck (Fig. 1). As a result of the crystal dissolving in the liquid from the neck, the liquid may move either by viscous flow or by volume diffusion; however, the dissolution of solid phase into the melt is governed by the diffusion process at the solid–melt interface. Also, the liquid phase can be provided by secondary materials with lower melting temperatures than the matrix. Generally, the migration of liquid phase can realistically be treated as the following:

dissolution of particles into the melt (diffusion)

$\rightleftharpoons$ volume transport of the melt (diffusion = viscous flow)

→ pore filling and pore shrinkage

In this model, the movement of meniscus originates from the interface atomic/ionic motion and creates a dynamic surface tension of liquid phase. According to Defay and Pétré [11], this process is comparable to the diffusion resulting from the transfer of atoms/molecules from the subsurface to the surface and from the bulk to the subsurface. Because this diffusion is a collective transport process, we will call it volume diffusion.

It is convenient to begin our discussion on liquid-phase sintering by making some assumptions.

(i) The local distribution of melt is governed by surface–interfacial tensions equilibrium [2, 12].

(ii) The melt and solid are in chemical equilibrium [12].

(iii) The only shear stress acting on the melt is associated with surface tension [2–4, 12].

(iv) The Ostwald ripening process is ignored [12].

(v) The squeezing of liquid phase between solid particles does not change the thickness of the melt below some critical level [13–15].

Crystal dissolution into the melt (metal–metal, metal–ceramic, or glass–ceramic) may include three processes: reaction at the interface in case of heterogenous systems or diffusion and convection inside a diffusive boundary resulting either from a concentration gradient [16] or temperature gradient at the interface caused by exothermic or endothermic reactions. Reaction at the interface and diffusion into the melt occur simultaneously during non-convective crystal dissolution [17]. However, all dissolution processes are controlled by the slowest process related either to the rate of interface reaction or to the diffusion of products into the melt. Generally, the diffusion of products into the melt is the limiting step of the dissolution process [18]. The conventional description of diffusion in two-component systems begins with Fick's law. In heterogenous systems with more than two components, such as ionic liquids, the electrical neutrality conditions should be constrained for the flux densities of all species. Also, the diffusion species in a melt silicate are not necessarily neutral molecules but can be ions and structural units (clusters) [19]. In these systems, the interface reaction is not the rate-determining step. Thus, crystal dissolution into melt can be described by the generalized transport equation derived from Fick's law

$$J_i = -\Sigma D_{ij}\nabla C_i \qquad (i,j = 1,2) \tag{1}$$

where D_{ij} represents the diffusion coefficients in the volume-fixed reference frame and ∇ represents the spatial gradient concentration operator.

In multicomponent systems with ionic diffusion species, we may expect coupling effects of the electrostatic fields to occur, resulting from the differing mobilities of different ions. This coupling may cause a particular arrangement of cations and anions and order–disorder problems in certain local structures, especially, in silicate systems. Thus, for silicate melts, the Nernst–Planck equation was recommended which also requires the conservation of charge.

Chakraborty *et al.* have selected the neutral species as the dependent components in calculating the multicomponent diffusion coefficients [20]. They have stated that the diffusion in multicomponent melts can be described by the effective binary diffusion coefficients, even if strong multicomponent interaction exists.

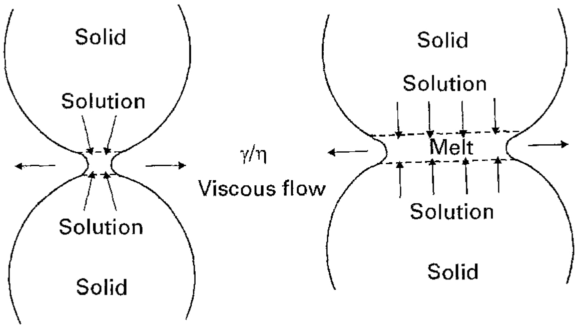

Figure 1 Schematic representation of liquid-phase transport with simultaneous particle dissolution into the melt.

3. Capillary mass transport in inactive capillaries and Darcy's law

The capillary volume transport and mechanisms of fluid flow in metals, glass–ceramics and silicates during liquid-phase sintering can be inferred from the fluid flow in porous media. One effective way to study the flow in porous media is to apply Darcy's law [21]. For a single-phase of visco-elastic fluid the flux of mass is given by

$$J_f = -k/\eta\nabla P \tag{2}$$

where k and P represent the hydraulic permeability and the pressure field that drives the flow, respectively, and η is the viscosity. The commonly used dimension for hydraulic permeability is 1 darcy, numerically equal to 1 μm^2. Both Young and Laplace recognized that the attractive forces between atoms/molecules at a curved surface would set up a pressure difference across the liquid–vapour interface, which is expressed by the capillary pressure in a capillary [22]

$$\Delta P_c = 2\gamma\cos\Theta/r \qquad (3)$$

where γ represents the surface tension, r is the capillary radius, and Θ is the characteristic contact angle of the solid–liquid interface (Fig. 2).

The total work done by surface forces on a well-preserved meniscus equals the work done in moving the surface over the distance, dx, against the outside pressure acting upon it. Generally, the outside pressure in a pore or capillary has a constant value, and only the capillary pressure is useful in causing the fluid to flow; fluid flow depends on the local structure of a fluid. Differentiation of Equation 3 gives

$$\mathrm{d}P_c/\mathrm{d}x = -2\gamma/r(\sin\Theta\,\mathrm{d}\Theta/\mathrm{d}x + \cos\Theta\,\mathrm{d}r/\mathrm{d}x) \qquad (4)$$

Equations 2 and 4 can be combined to give the flux of mass in the x direction in the following

$$J_f(x) = (2k/r)(\gamma/\eta)(\sin\Theta\,\mathrm{d}\Theta/\mathrm{d}x + \cos\Theta\,\mathrm{d}r/\mathrm{d}x) \qquad (5)$$

The transport of liquid in capillary-like media requires a reservoir of liquid that can be provided either by dissolution of solid particles into the melt (Fig. 1) or by secondary materials with lower melting temperatures. On the other hand, the dissolution process and the mass transport through a capillary may be described by the volume diffusion flux, (J_D), of atoms or structural units (in case of silicates). In silicates, the diffusion flux depends on the characteristic structural relaxation times of all constituents. The structural relaxation causes morphological changes in the silicate network, originating from structural rearrangements in the glass as a result of the complex molecular chain kinetics, such as unfolding, stretching, and cross-linking. These changes may produce non-Newtonian flow [23]. Relaxation processes equilibria are on the atomic scale (diffusion), and do not quickly follow the change of the macroscopic-state variables (viscosity). Thus, the diffusion flux of one component (ions or structural units) should include different diffusivities from initial to final Fickian behaviours [24]. So, the diffusive flux of melt formed during the dissolution process and its transport through the capillary may be expressed as the sum of the Fickian term and the flux with a finite relaxation time

$$J_D(x) = -\Sigma D_{ij}\nabla C_j - \tau\delta J/\delta t \qquad (6)$$

where τ is a characteristic structural relaxation time.

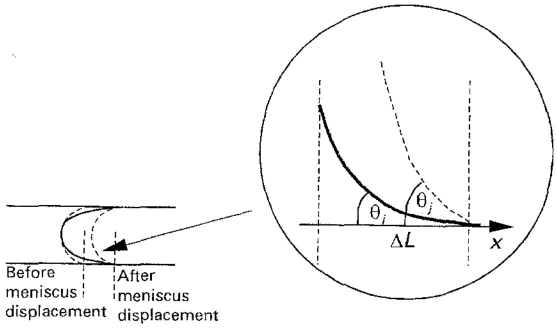

Figure 2 Schematic representation of liquid-phase transport in a capillary.

The flux of atoms/ions/structural units is always treated as a vector, and a positive sign indicates that mass flow occurs down a concentration gradient. In this particular case, the concentration gradient is the same along the diffusion path and is maintained by the motion of atoms/ions/structural units from the subsurface to the meniscus and from the bulk of capillary to the subsurface. This particular concentration gradient originates from the dynamic surface tension and does not change with time. In other words, the time scale of transport is taken to be larger than the time scale for establishing equilibrium in the local volume [20]. Under this condition, the diffusion coefficient for inflow of mass, D, must be positive, therefore, the negative sign before D must be eliminated. The negative sign before D will indicate outflow of mass.

The specific form of equilibrium between viscous and volume diffusion fluxes naturally follows from the balances of momentum, energy and mass. The momentum balances describe the flow of liquid and depend only upon the velocity gradients; the energy balance depends on the heat conduction (temperature gradient). The mass balances account for the mass balance among the liquids. With Equations 5 and 6, we can define the simple relationship between capillary volume transport of the melt described by viscosity and volume diffusion flux

$$\Sigma D_{ij}\delta C_j/\delta x - \tau\delta J/\delta t = (\gamma/\eta)(2k/r)(\sin\Theta\,\mathrm{d}\Theta/\mathrm{d}x + \cos\Theta\,\mathrm{d}r/\mathrm{d}x) \qquad (7)$$

For steady fluid motion in a capillary, with no accumulation of mass within the control volume, the excess of mass leaving the elementary volume must be compared to the mass entering this volume. This implies that the transport properties in a capillary may be considered either by the viscous flow or the volume diffusion. For steady flow, the diffusion in an unrelaxed matrix (undergoing expansion) equilibriates with the diffusion in a relaxed matrix in a very short time, so we may assume that $\delta J/\delta t = 0$. This is expected to occur in liquid metals at melting temperatures and in silicates at very high temperatures.

For steady-state conditions of directional mass flow in inactive capillaries, the liquid-phase meniscus should be well preserved; thus, Equation 7 can be simplified to

$$D = \alpha(\gamma/\eta)L \qquad (\mathrm{m}^2\,\mathrm{s}^{-1}) \qquad (8)$$

where $\alpha = (2k/r)(\sin\Theta\,\mathrm{d}\Theta/\mathrm{d}x + \cos\Theta\,\mathrm{d}r/\mathrm{d}x)$ is the specific permeability that is expressed by a non-dimensional unit ($\mu\mathrm{m}^2\,\mu\mathrm{m}^{-2}$), $\delta C_j = 1$, and δx represents the displacive movement of menisci that is comparable with the nearest distances between atoms/ions/structural units, L. In our model, the specific permeability is characterized by the specific properties of the melt described by the variation of contact angle, Θ, in direction x and the pore's structure of sintering material. The displacive movements of menisci, δx, in liquid metals are identified with the smallest distances between atoms [3] and in aluminosilicates are comparable to the bond lengths (Si–O, Al–O, etc.) [4].

With large capillary radii, the problem becomes more complicated, as the curvature of the meniscus may no longer be cylindrical.

4. Capillary mass transport and free volume model of liquid state

An important contribution to mass transport in liquids and glasses was made by Turnbull and Cohen [25, 26]. In their free volume model, liquid–state diffusive motion of atoms/molecules is caused by the redistribution of the free volume. Consequently, the potential energy of moving species changes, and this is not a thermally activated process. The free volume of an atom/molecule is defined as $v = v' - v_0$, where v' is the specific volume (the reciprocal of density), and v_0 is the volume of the atom/molecule.

The diffusive motion of atoms requires the prior opening of voids with similar dimensions. It is assumed that such voids can arise by the occasional random coalescence of the free volume of the liquid. In a capillary, atom/molecule movement from the meniscus into existing voids above the meniscus is characterized by a very narrow distribution of configurations that are completely independent of liquid structure and the formation of the transition-activated states. Thus, there is reason to assume that the diffusive motion of the entire liquid in a capillary-like medium is in the activated state. The activated state, however, depends on the potential energy of atoms stored in a meniscus, which is expressed by the surface tension. In this case, the total expansion of a liquid is proportional to the potential difference of atoms/molecules in a surface layer and sublayer, and this expansion is a relatively small value compared with the nearest distances between atoms/ions/molecules. If we assume that the shortest jump distance into an existing void above the meniscus, in the liquid state, is comparable to both the nearest distances between species and the atomic/molecular dimensions, we may further assume that atomic/molecular volumes will play a significant role in mass transport phenomena. Thus, some correlation exists between mass transport in capillaries and the free-volume model.

In Turnbull's model, the observed increase of molecular transport rate with temperature is explained by the formation of the cell potential in which the hard core radius decreases at a relatively high rate with increasing temperature [27]. In the Beukel and Sietsma model, the cell potential in Turnbull's model is equated to the local free-volume of the Wigner–Seitz cell [28]. According to Beukel and Sietsma, there are two independent contributions to the free-volume model of mass transport: chemical short-range ordering (CSRO) and topological short-range ordering (TSRO). CSRO consists of a series of processes with a broad spectrum of activation energies; TSRO is characterized by a well-defined activation energy. The spontaneous migration front of a meniscus across the channel will cause the increase of the local free volume of each Wigner–Seitz cell in the subsurface and uniformly distribute this disturbance among all the Wigner–Seitz cells in bulk liquids. Therefore, the activation energy of flowing species seems to be well defined.

5. Mass transport of liquid phase in inactive capillaries

In seeking a suitable description of mass transport of mixture systems such as silicates, in inactive capillaries, it will be instructive first to discuss the mass flow of pure systems such as liquid metals. The purpose is to define the relationship between surface tension-to-viscosity ratio, γ/η, and the atomic/molecular nature of matter. Figs 3 and 4 illustrate the variation of γ/η with the distance between atoms and with atomic radii (molar volume), respectively. The surface tension and viscosity values, for selected liquid metals near the melting temperature, are listed in Table I. It is worth noting that the mass transport through the liquid phase in a capillary can be independently analysed as a function of the distance between nearest neighbours and/or atomic radii (molar volumes). Generally, the

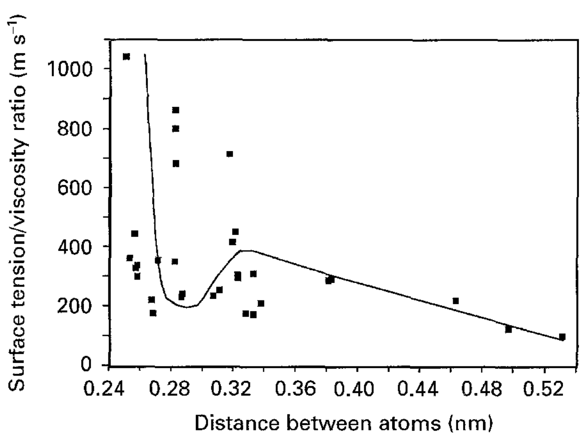

Figure 3 Surface tension-to-viscosity ratio versus the distance between nearest neighbours.

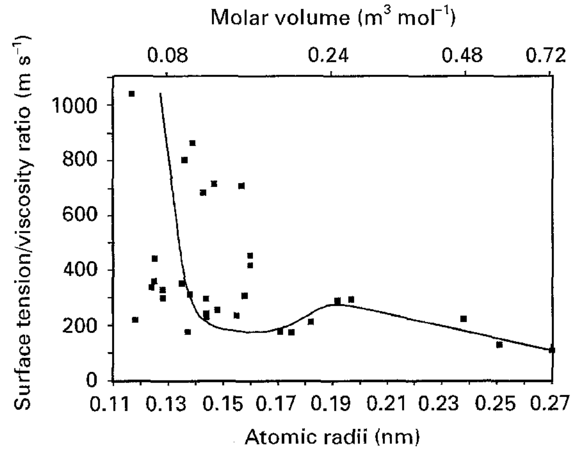

Figure 4 Surface tension-to-viscosity ratio versus the atomic radii in liquid metals [3].

TABLE I Physical properties of liquids near the melting temperature

Substance	T (K)	V_m ($10^{-6}\,m^3mol^{-1}$)	Ionic radii [30] (10^{-10} m)	γ ($10^{-3}\,J\,m^{-2}$)	η ($10^{-3}\,Ns\,m^{-2}$)	γ/η ($m\,s^{-1}$)	D ($10^{-8}\,m^2s^{-1}$)	$L\alpha$ (10^{-10} m)
Metals [2]								
Na	371	24.8	1.92	195	0.68	286	0.400	0.139
K	337	48.3	2.38	113	0.51	221	0.369	0.166
Rb	313	59.5	2.51	85	0.67	126	0.255	0.202
Mg	923	15.3	1.60	565	1.25	452	0.563	0.124
Zn	693	9.94	1.37	776	3.85	201	0.203	0.100
Cd	594	14.0	1.48	580	2.28	254	0.178	0.070
Ga	303	11.4	1.35	716	2.04	350	0.169	0.048
In	429	16.3	1.44	558	1.89	295	0.167	0.056
Sn	505	17.0	1.58	555	1.85	300	0.230	0.076
Pb	600	19.4	1.75	459	2.65	173	0.219	0.126
Sb	904	18.8	1.38	380	1.22	311	0.266	0.085
Cu	1356	7.94	1.28	1335	4.00	333	0.398	0.119
Ag	1234	11.5	1.44	906	3.88	233	0.256	0.109
Fe	1810	7.96	1.24	1095	5.00	219	0.416	0.189
Ni	1726	7.43	1.25	1855	4.90	378	0.390	0.103
Salts								
NaCl	1120	43.3 [29]	Na^+	111 [29]	1.25	88.8	0.98 [31]	1.09
			Cl^-				0.69 [31]	0.77
	1290		Na^+	98 [29]	0.774	126.6	1.56 [31]	1.23
			Cl^-				1.14 [31]	0.90
$NaNO_3$	580		Na^+	119 [32]	30.7 [32]	3.8	0.233 [33]	6.0
			NO_3^-				0.148 [33]	3.8

meniscus velocity ($m\,s^{-1}$) across the channel is larger for atoms with lower interatomic distances and/or atomic radii (molar volume). A characteristic mode, then, of this approach is that the lower interatomic distances and/or lower atomic radii (lower molar volumes) correspond with the lower values of $L\alpha$ parameters.

Also, the meniscus velocity in molten ionic salts decreases with an increase of $L\alpha$ parameter (Table I). It may seem plausible to refer to the following pair interactions when describing effects. For a metallic liquid, interactions include: (1) an array of ion cores with a Fermi gas of conduction electrons and (2) ion cores with ion cores; for molten ionic salts (1) cations with anions, (2) cations with cations and (3) anions with anions [34]. The inference seems to be that the effect of the interactions may introduce a perturbation on the motion of a liquid phase in inactive capillaries.

In silicate melts, the transport properties are strongly related to the molecular configuration and the size of structural units which is expressed by the non-bridging oxygen (NBO) content per tetrahedraly coordinated cations (T), NBO/T, where T is silicon or aluminium (Figs 5 and 6, Table II). In the aluminosilicate liquids, the larger value of NBO/T corresponds to the lower size of structural units.

The motion of atoms in liquid metals is a simple consequence of their jump to vacancies left behind a moving meniscus. The fundamental feature of a silicate melt is that its motion causes changes in local structure. The mechanisms of volume diffusion and viscous flow in polymerized silica melt require the breaking of some Si–O–Si bonds and the deforming of others during the flow [37, 38]. In molten depolymerized silicates, the volume diffusion/viscosity exchange results either from the rapid conversion of bridging oxygens to non-bridging oxygens and vice

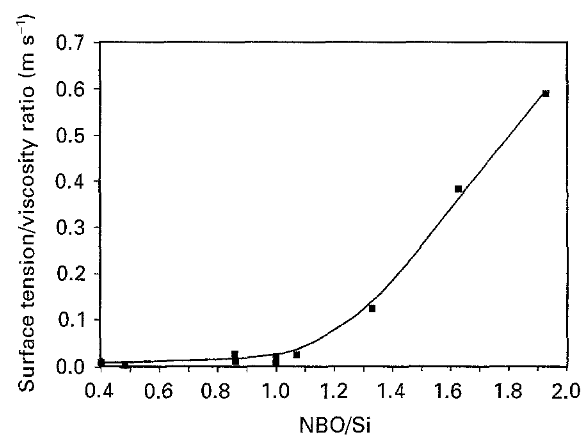

Figure 5 Surface tension-to-viscosity ratio versus the non-bridging oxygen content per tetrahedrally coordinated silicon (NBO/Si) in M_2O–SiO_2 silicates at 1200 °C where M = Li, Na [35, 36].

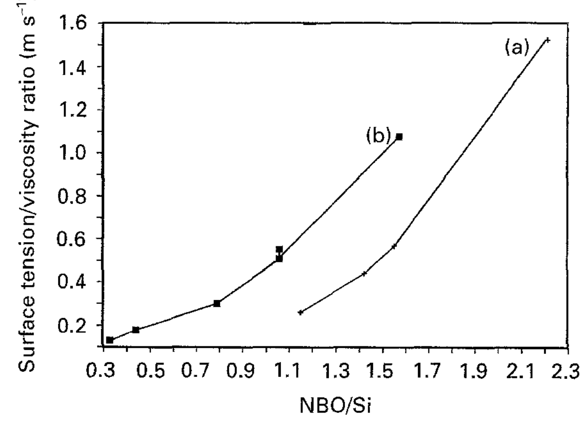

Figure 6 Surface tension-to-viscosity ratio versus the non-bridging oxygen content per tetrahedrally coordinated silicon (NBO/Si) in (a) CaO–SiO_2 and (b) CaO–Al_2O_3–SiO_2 systems at 1500 °C [35, 36].

versa [39] and/or from the transport of structural units such as SiO_4^{4-} [40, 41]. The energy required to move an atom from a tetrahedron through a diffusive jump and/or viscous flow is dependent upon the local environment of the moving species, and both processes should have similar energy values [42, 43]. In silicate systems, the diffusion in capillary-like media may be controlled by more than one component, and should be constrained by the less-mobile species such as non-bridging oxygen, silicon, aluminium and calcium atoms (see Table III) [4]. The diffusion of alkali ions such as sodium is very high, and this may change the local structure of silicate melts resulting from the appearance$\rightleftharpoons$disappearance of non-bridging oxygens [45], and cause the reduction of their viscosity that simultaneously may facilitate intergranular mass transport. We know very little of how the motion of atoms in silicate melts may impose some structural organization on nearest neighbours and effect a perturbation on the motion of silicate in inactive capillaries. It seems possible that modifying ions concentrate at the meniscus along with the non-bridging oxygens, and cause the surface tension to increase [46]. This suggests that ions in silicate liquid in capillary-like media may have the ability to be more mobile than those in bulk silicate liquids.

TABLE II Surface tensions and viscosities for selected silicates

Silicate (mol %)	NBO/T	γ [35] (10^{-3} J m^{-2})	η [36] (N s m^{-2})	γ/η (m s^{-1})
M_2O–SiO_2 $T = 1200$ °C				
Na_2O (19.5)	0.48	275.6	79.4	0.003
Li_2O (30)	0.86	316.2	11.5	0.027
Na_2O (30.1)	0.86	279.7	22.3	0.013
Na_2O (33.4)	1.00	280.9	14.1	0.020
Na_2O (35)	1.07	284.0	11.2	0.025
Li_2O (40)	1.33	331	2.69	0.123
Li_2O (45)	1.63	340	0.891	0.382
Na_2O (49.2)	1.93	294.6	0.501	0.588
CaO–Al_2O_3–SiO_2 $T = 1500$ °C				
20.8/15.3/63.9	0.33	400.3	3.11	0.129
30/29/41	0.44	459.6	2.57	0.179
35.6/20/44.4	0.79	452.8	1.5	0.302
41.5/20.9/37.6	1.06	470.7	0.92	0.512
39.7/15.5/44.8	1.06	473.5	0.854	0.554
36.5/0.0/63.5	1.15	403.1	1.54	0.262
41.6/0.0/58.4	1.42	413.2	0.935	0.442
43.7/0.0/56.3	1.55	436.3	0.765	0.570
46.9/10/43.1	1.57	484.1	0.448	1.081
52.5/0.0/47.5	2.21	462.8	0.303	1.527

The increase of αL values from a metallic liquid to a molecular one (Tables I and III) in capillary-like media suggests that the jump distance for molecular liquid must be predominantly longer than that for metallic liquid. Generally, the nearest-neighbour distances for all considered liquids are comparable to each other and range between 2.5 and 5×10^{-10} m [47–49]. Evidently, the transport coefficients depend on the local structure of an appropriate fluid.

Fig. 7 illustrates the variation of surface tension-to-viscosity ratio versus reciprocal temperature that

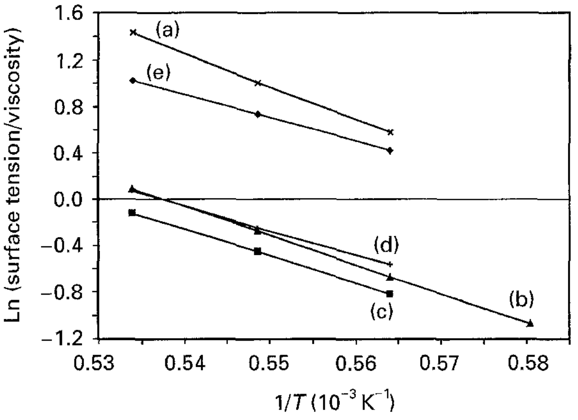

Figure 7 Ln surface tension-to-viscosity ratio versus temperature in silicates [35, 36]. CaO–Al_2O_3–SiO_2, NBO/T: (a) 0.44, (b) 1.06, (c) 1.42. CaO–SiO_2, NBO/Si: (d) 1.55, (e) 2.21.

TABLE III Physical properties of silicates and molecular liquids

Substance	T (K)	V_m (10^{-6} m^3 mol^{-1})	γ (10^{-3} J m^{-2})	η (N s m^{-2})	γ/η (m s^{-1})	D (m^2 s^{-1})	$L\alpha$ (10^{-10} m)
Silicates [4] (mol %)							
Transport of oxygen							
CaO–Al_2O_3–SiO_2	1673	~23.8[a]	453.6	1.90	0.238	1.58×10^{-10}	6.6
40/20/40	1773		460.9	0.88	0.523	3.96×10^{-10}	7.6
Transport of silicon							
K_2O–SiO_2	1473	~24.1[a]	216.9	68.0	0.031	3.21×10^{-12}	10.3
26.4/73.6	1573		213.0	25.5	0.083	7.47×10^{-12}	9.0
Transport of silica							
Na_2O–SiO_2	1373	~24.3[a]	283.8	35.5	0.079	2.58×10^{-12}	3.2
33.4/66.6	1473		280.9	14.1	0.199	4.55×10^{-12}	2.3
Molecular liquids						from [29]	
Ar	90	24.98 [29]	12.22 [29]	2.32×10^{-3} [29]	5.26	2.43×10^{-8}	46.1
CH_4	100	31.06 [29]	16.24 [29]	1.45×10^{-3} [29]	11.20	3.02×10^{-8}	26.7
C_6H_6	287	82.82 [29]	30.2 [44]	7.08×10^{-3} [29]	4.26	1.6×10^{-8}	37.5
CCl_4	289	87.1 [29]	26.9 [44]	8.88×10^{-3} [29]	3.02	1.41×10^{-8}	46.6

[a] Molar volumes were silicates were calculated from the density data using the following relationship: $V_m = \Sigma X_i M_i/\rho$, where M_i is the molecular weight of component "i" and X_i represents the mole fraction of component "i" in the glass.

suggests the mass transport in the Newtonian range is an activated process related to viscosity changes with temperature, and this change comes from topological short-range ordering (TSRO). A similar conclusion was previously derived for the mass transport in Na_2O–SiO_2 silicates [4].

6. Capillary mass transport in active capillaries with interfacial reaction

Relatively little work has been performed on reactions at solid–liquid interfaces and their effect on mass transport in capillary-like media. There are, however, several reports on rapid liquid metal penetration along grain boundaries in some solid–liquid systems such as Zn/In, Zn/Bi, Zn/Pb, Zn/Sn [50] as well as glass–metal and glass–ceramic/metal [51]. Melt migration in capillaries and/or in intergranular space may be disturbed by the interfacial chemical reactions that are driven by chemical potential differences. The contact angle, Θ, will vary with the progress of intergranular chemical reactions between the liquid phase and the capillary. Accordingly, this process may force cooperative rearrangement of all atoms/molecules in some small region of the liquid at the interface and reduce the crystal–melt interfacial tension, which decreases with increasing mutual solubility of solid–liquid phases [18]. The liquid may interface with an amorphous phase, at least in the initial stage of reaction [52], amorphous phase with nucleates of crystalline phase [53] and/or a metastable amorphous phase with a controlling selection of crystalline products [54]. This implies that the same liquid phase in contact with the different solid may form different corrosive products which may also affect the specific permeability value. Yoon and Huppmann have found that a convex shape of a nickel meniscus becomes more irregular after prolonged contact with spherical tungsten particles at 1640 °C [55]. This results from changes in chemical potentials of the equilibrium W–Ni alloy during the corrosion process.

The reduction of crystal–melt interfacial tension in homogeneous systems is due to the decrease of entropy of liquid phase near the interface. The entropy rises more slowly with distance from the crystal than the enthalpy [56]. In Spaepen's model, the interface is treated as a system characterized as between a dense random packing of hard spheres (liquid) and a close-packed crystal surface. Chemical potentials of fluid components are the same in the liquid and solid phase.

In heterogeneous systems, both the local atomic/molecular configuration and the structure-dependent energy at the interface must change as a consequence of the entropy of mixing. The entropy of mixing is dominated by the changes in local atomic environments caused by changes in the vibrational entropy, in the configurational entropy as a consequence of changing of chemical interactions, and in magnetic and electric entropies [57]. In fact, the configurational entropy is the excess entropy of a liquid over that of the crystalline phase and is directly associated with mass transport in liquid phase by Adams and Gibbs formula [58]. The changes of configurational entropy of the liquid phase at the interface will significantly affect mass transport in capillary-like media.

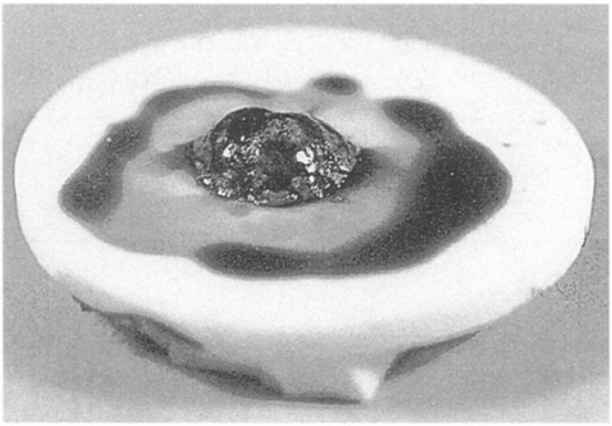

Figure 8 A sessile drop of Na_2O–CaO–Al_2O_3–Fe_2O_3–SiO_2 melt on alumina at a melting temperature near 1150 °C (unpublished result).

Assuming that both the crystal and the melts have the same composition, Cahn has indicated that atoms in the crystal–melt interface may introduce surface stress if the solid phase sustains an elastic strain [59]. This situation may create gradients of chemical potentials at the interface, and these gradients may allow the liquid to migrate on the solid surface without any influence of capillary forces. In heterogeneous systems, such as those of metal–ceramic and glass–ceramic, the inhomogeneities can create higher interfacial stresses and gradient flows that may enhance the melt motion. This effect has been notified in a glass–ceramic system, as illustrated in Fig. 8. Generally, the mass flow of silicate over alumina ceramic is non-uniform, which causes the creation of silicate rings around the sessile drop. The energy changes of a moving melt do not depend on whether the energy is isotropic or anisotropic or if the surfaces are curved or facetted and have edges or are smooth; the moving melt is dominated by interfacial stresses and surface energy effects [60]. In principle, the surface energy effects are represented by Young's equation, and the driving force for spreading a liquid over a rigid substrate can be given by the following relation: $\gamma_{SV} > \gamma_{LV}$, where γ_{SV} and γ_{LV} refer to the surface energies of solid and liquid, respectively.

7. Physical significance of specific permeability

The specific permeability has some physical significance because it is characterized by an effective capillary radius for transport and by the equilibrium contact angle of the liquid on the solid. The angle Θ is near 0° if liquid-phase migration occurs in an inactive capillary (such as that composed with its own solid) near the melting temperature, and this model corresponds to the previous one discussed on metals and silicate systems. As mentioned above, the specific permeability may be given by

$$\alpha = (2k/r)(\sin\Theta\, d\Theta/dx + \cos\Theta\, dr/dx) \quad (9)$$

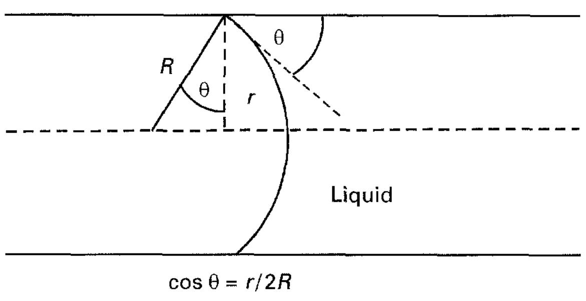

Figure 9 Cross-section of intergranular space with indication of changes of capillary radius, contact angle and curvature of the meniscus.

which includes all possible physical changes in a liquid–solid interface as expressed by the liquid–solid contact angle and geometrical changes in capillaries and/or fine pores. The specific permeability decreases as the capillary radius increases; thus the amount of melt migrating per unit time increases. Equation 9 losses its significance when the liquid wets the solid completely, and this may occur if the liquid–solid interaction occurs in a thin liquid film (below its critical thickness) or liquid is spread over the surface by pressing.

A crude quantitative analysis of Equation 9 suggests that α mostly depends on the capillary radius (or intergranular space) and less on the contact angle. Both parameters, however, affect the curvature of the interface (Fig. 9).

Tables I and III list αL parameters for liquid metals, molten salts, silicates, and molecular liquids. Generally, the αL parameters are low for all entities with structurally equivalent sites, such as in liquid metals, and high for ionic liquids such as in silicates. Such extreme examples imply that the mass transport in ionic liquids (in inactive capillaries) may undergo mixing effects resulting from the possible cooperative rearrangement of all flow entities [61] and coupling-decoupling processes of different species [62]. Practically speaking, the mixing entropy is zero if structural entities cannot be switched from one place to another and differs from zero if flowing species of different charges switch their positions, and this switching depends on structural properties of melts (molten salts, silicates) and relaxation timescales [39, 63]. The large values of αL for molecular non-associated liquids suggests that another factor may affect the mass transport, most likely, related to the dominant influence of the rotational contribution resulting from the anisotropic forces between the molecules [49].

8. Conclusion

It was found that the surface tensions and viscosities of bulk melts can be used to explain the mass transport in capillary-like media and examine liquid-phase sintering behaviour of materials when the liquid thicknesses are above some critical value. The mass transport in capillary-like media may be analysed either by the surface tension-to-viscosity ratio or by the volume capillary diffusion, and these properties depend on the distance between neighbouring atoms (in liquid metals) or bond distances (in liquid silicates). Also, either atomic radii (for metals) or non-bridging oxygen content per tetrahedrally coordinated cation (for silicate) may be employed in the consideration of mass transport in appropriate liquids. It was presented that specific permeability mostly depends on the capillary radius and less on contact angle between liquid phase and solid. In general, the surface tension of liquids is considerably higher than the solid–liquid interfacial tension, especially in inactive capillaries. Therefore, the self-diffusion coefficient for liquid metals and volume diffusion for silicate liquids, molten salts, and molecular liquids, can be estimated from the surface tension, viscosity, and nearest distances between atoms/ions/molecules data.

References

1. J. FRENKEL, *J. Phys.* **9** (1945) 385.
2. J. W. NOWOK, *Scripta Metall. Mater.* **29** (1993) 931.
3. *Idem, Acta Metall. Mater.* **42** (1994) 4025.
4. *Idem, J. Mater. Res.* **10** (1995) 401.
5. P. C. HESS, *J. Geoph. Res.* **99** (1994) 7219.
6. J. N. ISRAELACHVILI, P. McGUIGGAN, M. GEE, A. HOMOLA, M. ROBBINS and P. THOMSON, *J. Phys. Condens. Matter* **2** (1990) SA89.
7. J. N. ISRAELACHVILI, *Surf. Sci. Rep.* **14** (1992) 109.
8. T. K. CHAKI, *Philos. Mag.* **62** (1990) 465.
9. R. A. FOURNELLE, *Mater. Sci. Eng.* **A138** (1991) 133.
10. M. D. VAUDIN, J. E. BLENDELL and C. A. HANDWERKER, in "Structure and Property Relationships for Interfaces", edited by J. L. Walter, A. H. King and K. Tangri (ASM, 1991) p. 329.
11. R. DEFAY and G. PÉTRÉ, in "Surface and Colloid Science", edited by E. Matijevič (Wiley, New York, 1971) p. 28.
12. D. J. STEVENSON, *Geophys. Res. Lett.* **13** (1986) 1149.
13. F. F. LANGE, *J. Am. Ceram. Soc.* **65** (1982) C–33.
14. V. SMOLEJ, *ibid.* **66** (1983) C–33.
15. R. M. GERMAN, *ibid.* **69** (1986) C–40.
16. P. L. VITAGLIANO, L. AMBROSONE and V. VITAGLIANO, *J. Phys. Chem.* **96** (1992) 1431.
17. Y. ZHANG, D. WALKER and C. E. LESHER, *Contr. Mineral. Petrol.* **102** (1989) 492.
18. R. E. LOEHMAN and A. P. TOMSIA, *Ceram. Bull.* **67** (1988) 375.
19. H. WAKABAYASHI and Y. OISHI, *J. Chem. Phys.* **68** (1978) 2046.
20. S. CHAKRABORTY, D. B. DINGWELL and D. C. RUBIE, *Geochim. Cosmochim. Acta* **59** (1995) 255.
21. PO-ZEN WONG, *MRS Bull.* **19** (1994) 32.
22. A. W. ADAMSON, "Physical Chemistry of Surfaces" (Wiley, New York, 1967).
23. J. H. SIMMONS, R. K. MOHR and C. J. MONTROSE, *J. Appl. Phys.* **53** (1982) 4075.
24. G. CAMERA-RODA and G. C. SARTI, *AIChE J.* **36** (1990) 851.
25. D. TURNBULL and M. H. COHEN, *J. Chem. Phys.* **34** (1961) 120.
26. *Idem, ibid.* **52** (1970) 3038.
27. D. TURNBULL, in "Liquid: Structure, Properties, Solid Interactions", edited by T. J. Hughel (Elsevier, Amsterdam, 1965) p. 6.
28. A. VAN DEN BEUKEL and J. SIETSMA, *Mater. Sci. Eng.* **A179/A180** (1994) 86.
29. H. EYRING and M. S. JHON, "Significant Liquid Structures" (Wiley, New York, 1969) p. 91.
30. F. M. MILLER, "Chemistry and Dynamics" (McGraw-Hill, 1984) p. 176.
31. H. BLOOM and J. M. BOCKRIS, in "Structural Aspects of Ionic Liquids", edited by B. R. Sundheim (McGraw-Hill, New York, 1964) p. 1.

32. G. J. JANZ and R. P. T. TOMKINS, "Molten Salts", Vol. 5, Part 2, *J. Phys. Chem. Ref. Data* **12** (3) (1983).
33. B. R. SUNDHEIM, (ed.) "Fused Salts" (McGraw-Hill, New York, 1964) p. 165.
34. N. E. CUSACK, "The Physics of Structurally Disordered Matter" (Adam Hilger, Bristol, 1987).
35. N. P. BANSAL and R. H. DOREMUS, "Handbook of Glass Properties" (Academic Press, Orlando, FL, 1986) p. 101.
36. M. P. RYAN and J. Y. K. BLEVIS, "Viscosity of Synthetic and Natural Silicate Melts and Glasses at High Temperatures and 1 bar Pressure", US Geological Servey Bulletin (1987) p. 1764.
37. N. F. MOTT, *Philos. Mag.* **B56** (1987) 257.
38. L. FERRARI, N. F. MOTT and G. RUSSO, *ibid.* **59** (1989) 263.
39. S. B. LIU, J. E. STEBBINS, E. SCHNEIDER and A. PINES, *Geochim. Cosmoch. Acta* **52** (1988) 527.
40. T. DUNN, *ibid.* **46** (1982) 2293.
41. T. DUNN, in "Silicate Melts", edited by C. M. Scarfe, Short Course Handbook, Vol. 12 (Mineralogical Association of Canada, Ottawa, Ontario, 1986) p. 57.
42. H. A. SCHAFFER, *J. Non-Cryst. Solids* **67** (1984) 19.
43. S. CHAKRABORTY, *Reviews in Mineralogy* **32** (1995) 411.
44. R. C. WEAST (ed.) "CRC Handbook of Chemistry and Physics" (CRC Press Inc., Boca Raton, FL, 1987) p. F35.
45. T. UCHINO, T. SAKKA, Y. OGATA and M. WASAKI, *J. Phys. Chem.* **97** (1993) 9642.
46. J. W. NOWOK, J. P. HURLEY and J. A. BIEBER, *J. Mater. Sci.* **30** (1995) 361.
47. Y. WASEDA, in "Liquid Metals", edited by E. Evans and D. A. Greenwood (The Institute of Physics, Bristol, 1977) p. 230.
48. R. L. McGREEVY, *Solid State Phys.* **40** (1987) 247.
49. C. HONEISEL, "Theoretical Treatment of Liquids and Liquid Mixtures" (Elsevier, Amsterdam, 1993) p. 226.
50. A. PASSERONE and N. EUSTATHOPOLOUS, *Acta Metall.* **30** (1982) 1349.
51. A. P. TOMSIA and J. A. PASK, in "Ceramics and Glasses" Vol. 4, edited by S. J. Schneider (ASM International, 1991) pp. 493 and 482.
52. R. SINCLAIR, D. H. KO, T. J. KONNO and T. P. NOLAN, *Mater. Res. Soc. Symp. Proc.* **238** (1992) 269.
53. C. A. HANDWERKER, J. W. CAHN and J. R. MANNING, *Mater. Sci. Eng.* **A126** (1990) 173.
54. A. L. GREER, *ibid.* **A134** (1991) 1268.
55. D. N. YOON and W. J. HUPPMANN, *Acta Metall.* **27** (1979) 973.
56. F. SPAEPEN, *Solid State Phys.* **47** (1994) 1.
57. A. NAVROTSKY, *Rev. Mineral.* **17** (1987) 35.
58. G. ADAMS and J. H. GIBBS, *J. Phys. Chem.* **43** (1965) 139.
59. J. W. CAHN, *Acta Metall.* **28** (1980) 1333.
60. J. W. CAHN and J. E. TAYLOR, *Acta Metall. Mater.* **42** (1994) 1045.
61. P. RICHET and O. R. NEUVILLE, in "Thermodynamic Data, Systematics and Estimation", edited by S. K. Saxena (Springer, New York, 1992) p. 132.
62. S. CHAKRABORTY, D. B. DINGWELL and D. C. RUBIE, *Geochim. Cosmochim. Acta* **59** (1995) 265.
63. J. F. STEBBINS, I. FARNAN and X. XUE, *Chem. Geol.* **96** (1992) 371.

Received 22 May
and accepted 1 December 1995