Published paper
Kirkwood, D.H. and Ward, P.J. (2008) *Comment on the power law in rheological equations*, Materials Letters, Volume 62 (24), 3981-3983.

COMMENT ON THE POWER LAW IN RHEOLOGICAL EQUATIONS

D.H.Kirkwood and P.J Ward, Department of Engineering Materials, University of Sheffield.
d.h.kirkwood@sheffield.ac.uk
p.ward@sheffield.ac.uk

Abstract

In conformity with the principle of shear reversal, it is proposed that the power law index in the Cross equation relating steady state viscosity to shear rate in semisolid alloy slurries should have a value of 4/3, which is independent of alloy system and the fraction solid.

Keywords: Alloy slurries, Die Casting, Thixotropy.

The flow behaviour of thixotropic fluids is often described using the equation derived by Cross [1]:

$$\frac{(\eta - \eta_\infty)}{(\eta_0 - \eta_\infty)} = \frac{1}{1 + k\dot{\gamma}^m}$$

where η is the steady state viscosity, and η_∞ and η_0 are the asymptotic viscosities at high shear rate and low shear rate $\dot{\gamma}$. respectively. This equation may be expressed equivalently as:

$$\frac{(\eta_0 - \eta)}{(\eta - \eta_\infty)} = k\dot{\gamma}^m \, ,$$

so that over the intermediate shear rate range where $\eta << \eta_0$ and $\eta >> \eta_\infty$, this reduces to the power law equation [2]:

$$\eta = \frac{\eta_0}{k}\dot{\gamma}^{-m} \, ,$$

and for the power law index m>0 this means the viscosity falls with increasing shear rate $\dot{\gamma}$, which is the condition for shear thinning normally encountered in alloy semisolid slurries. This behaviour has been carefully studied in Al/7Si slurries by Quaak et al.[3] and also in the Sn/15Pb system by McLelland et al.[4], both groups obtaining similar experimental values for m = 1.3±0.1 for different fraction solids. It should be noted that a power index in these equations is dimensionless and cannot therefore be a material property of the system. Furthermore, Cross[1] has shown that

$\dot{\gamma}$ $\dot{\gamma}$

Clearly where m is an even number this condition is satisfied, but also for the fractional value m=p/q if p is even and q odd. These considerations would indicate that the power index is not exactly the decimal fraction 1.3 as derived experimentally, but using the simplest nearest fraction, 4/3. Using this value in the Cross equation and inserting experimental values for the Sn/15Pb alloy from a number of sources as illustrated in Fig.1, provides an extremely good fit and validation of the theoretical treatment and basic assumptions contained in the model. Also the proposition that the index is not dependent on the alloy system is also borne out by the above work on Al/Cu and Sn/Pb. In the light of this, it is suggested that m should be 4/3 (well within the experimental error), universal to all alloy slurry systems, and since the shear stress σ at steady state equals $\eta\dot{\gamma}^{(1\text{-m})}$, it therefore has power index of $-1/3$.

Derivation of the Cross Equation in Alloy Systems

Cross[1] originally derived his equation for particulate suspensions in aqueous and non-aqueous media, which involved the formation and rupture of structural linkages between particles during flow.

The Cross equation has been adapted by Cheng[5] to a form more appropriate to alloy slurries. He assumes a simple expression as an equation of state:

$$\eta = \eta_\infty + c\lambda \qquad (1)$$

in which the apparent viscosity η of a semisolid slurry is linearly related to its internal structure λ, whose value is zero for the fully broken down condition as $\dot{\gamma}$, the shear rate, becomes large (i.e. it consists of free discrete solid particles dispersed in a liquid matrix) and unity in the fully built up condition developed as $\dot{\gamma}$ approaches zero (i.e. large interlocking agglomerates). Under these conditions, the value of the constant, c, is given by η_0-η_∞, where η_0 is the asymptotic viscosity at low shear rates and η_∞ that at high shear rates. It should be noted that in this simple model, the structural parameter λ is defined as: $(\eta-\eta_\infty)/(\eta_0-\eta_\infty)$ and is therefore a linear function of viscosity η.

We now introduce a generalised kinetic equation for structural change:

$$d\lambda/_{dt} = a(1-\lambda) - b\lambda\dot{\gamma}^m \qquad (2)$$

where the first term on the right hand side describes the rate of structural build up being proportional to the extent of unbuilt-up structure. The second term describes the rate of breakdown proportional to the degree to which structure is already built up, *and* to the magnitude of the shear rate. Equilibrium is achieved at $d\lambda/dt=0$, leading to: $a=\lambda_e(a+b\dot{\gamma}^m)$ and $\lambda_e=1/(1+(b/a)\dot{\gamma}^m)$. Hence, $\eta_e=\eta_\infty+(\eta_0-\eta_\infty)/(1+(b/a)\dot{\gamma}^m)$, which is the Cross steady-state equation. It may also be demonstrated by substituting for a in eqn.2 and noting that $\eta\propto\lambda$ from eqn.(1), that:

$$\frac{d\eta}{dt} = (a+b\dot{\gamma}^m)(\eta_e-\eta) \qquad (3)$$

This expression has been used to calculate viscosity changes with time during the rapid compression of semisolid alloy slugs [6].

If the slurry suffers a step change in shear rate, we may integrate the above kinetic equation assuming a new constant shear rate $\dot{\gamma}$ to obtain:

$$\frac{\lambda-\lambda_e}{\lambda_i-\lambda_e} = \exp(-(a+b\dot{\gamma}^m)t \qquad (4)$$

Since λ is proportional to the viscosity, which in turn is proportional to the shear stress σ, we have:

$$\frac{\sigma-\sigma_e}{\sigma_i-\sigma_e} = \exp(-(a+b\dot{\gamma}^m)t\,,$$

showing that at constant shear rate the shear stress decays exponentially to the steady-state stress σ_e. This will provide a characteristic decay time τ, such that:

$$\tau = \frac{1}{a + b\dot{\gamma}^{m}} \qquad (5)$$

The above analysis assumes a single stage process leading to steady state conditions. However, Quaak et al.[7] have shown that at least two processes are involved in structural breakdown during shear rate increase: initially a very rapid process believed to involve the disruption of the larger agglomerates into smaller parts under the increased shear stresses, followed by a slower process involving their spheroidisation leading to the true steady state condition. This latter process, taking some minutes, has frequently been measured, but it is the former, taking place in a fraction of a second, which is of prime interest for commercial semisolid processing. We make the assumption here that the rapid breakdown, leading to a partial or pseudo steady state, can also be described by the kinetics given above, having an exponential decay to this intermediate stage in breakdown with its own characteristic relaxation time.

Experiments involving the response to step changes in shear rate in Sn/Pb alloy slurries have been carried out by Liu et al.[8] to obtain relaxation times τ for both stages in the structural breakdown. When the reciprocal of the relaxation time for the rapid breakdown $1/\tau$ is plotted against $\dot{\gamma}^{(4/3)}$, we obtain a good linear relationship consistent with eqn.(5) and m=4/3, as shown in figure [2]. This expression may be employed in equation (3) above for *dη/dt*, to determine how the viscosity changes with time during the injection of a semisolid slug into a die.

Conclusion

It is proposed that the power law index in the Cross equation, relating the steady state viscosity to the shear rate in semisolid alloy slurries, should be the simple fraction 4/3, on the principle of shear reversibility (as suggested by Cross himself), rather than the decimal fraction 1.3 previously employed. This index is dimensionless and appears to be independent of alloy system and fraction solid, and it is proposed that for alloy slurries it is a universal constant fraction. It is not understood why it has this particular value, but it should stimulate a theoretical enquiry into its origin in terms of the fundamental kinetics of the formation and breakdown of particle agglomerates that it is believed contribute to the thixotropic behaviour.

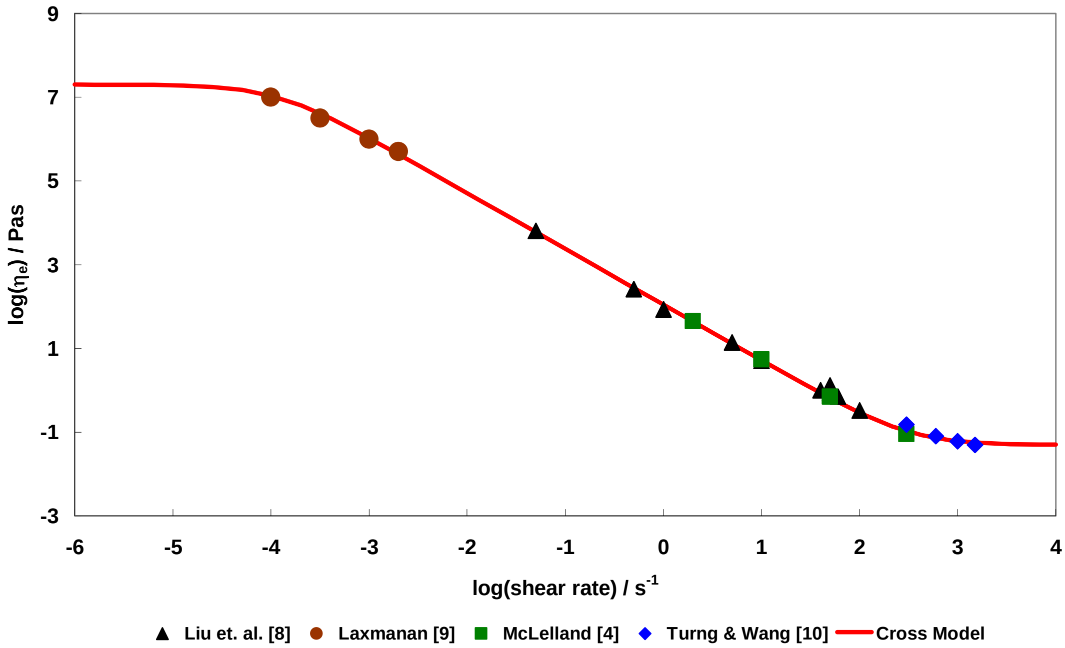

Figure 1: Cross Equation (red line) fitted to experimental equilibrium shear rate vs. viscosity data for Sn/20wt%Pb alloys at solid fraction of 0.36. Laxmanan data are compression tests on cylinders. The remainder are from concentric cylinder viscometry

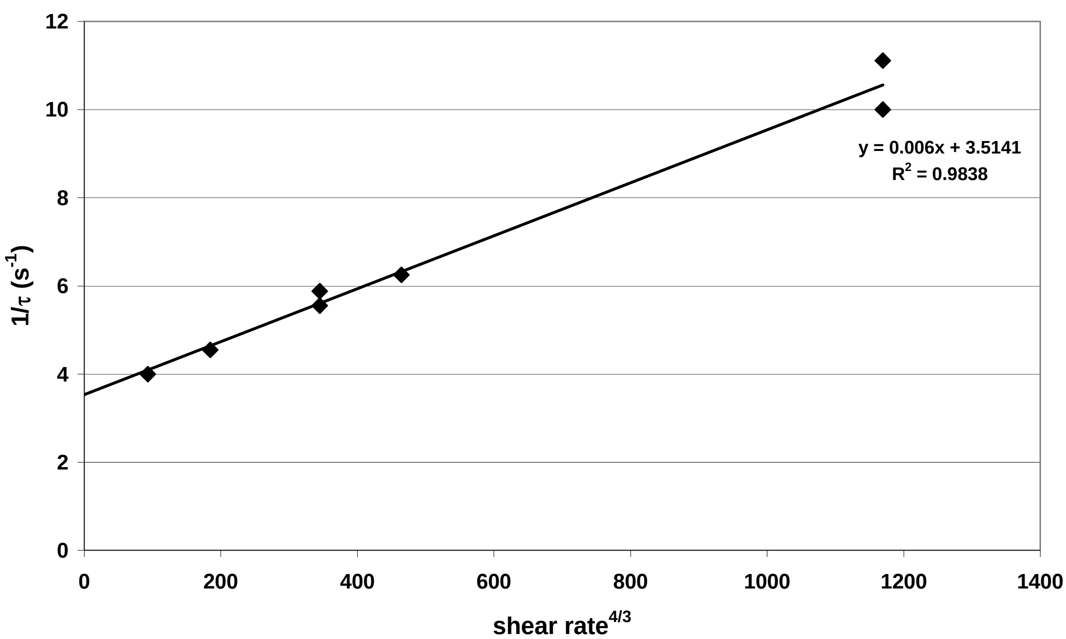

Figure 2: Structural breakdown rate for Sn/20wt%Pb alloy, with solid fraction 0.36, for rapid jumps to different shear rates. Solid line shows the dependency of breakdown rate on $\dot{\gamma}^{4/3}$.

References

1. M.Cross, J.Colloid Science: 20 (1965), 417-437.
2. H.A.Barnes,J.F.Hutton and K.Walters: An Introduction to Rheology, Elsevier, Amsterdam, 1987.
3. C.J.Quaak,M.C.Horsten and W.H.Kool: Mater.Sci.Eng.,A183,(1994),247-256.
4. A.R.A.McLelland, N.G.Henderson, H.V.Atkinson and D.H.Kirkwood: Mater.Sci.Eng.,A232,(1997),110-118.
5. D.C-H.Cheng: Int.J.Cosmetic Science:9,(1987),151-191.
6. D.H.Kirkwood and P.J.Ward: Steel Research Int.: 75,No.8/9,(2004),519-524.
7. C.J.Quaak,L.Katgerman and W.H.Kool: Proc.4th.Int.Conf.on Semisolid Processing of Alloys and Composites (1996), Sheffield, pp35-39.
8. T.Y.Liu, H.V.Atkinson, P.Kapranos, D.H.Kirkwood, S.G.Hogg: Metall.Mater.Trans. 34A(2003)1545-1554.
9. V.Laxmanan and M.C.Flemings:Metall.Trans.,11A(1980)1927-1936.
10. L.S.Turng and K.K.Wang: J.Materials Science,26,(1991),2173-2183.

<u>Figures</u>

1.Cross Equation fitted to Sn/Pb slurries

2. Plot of $1/\tau$ v. $\gamma^{\cdot 4/3}$