

Superplasticity of Metals

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Forming metals that are in a superplastic state offers the promise of obtaining large and regular deformations at reasonable levels of stress.

It is a familiar experience that a rod of soda glass, heated in the flame of a Bunsen burner and pulled by hand, will stretch out into a long, uniform fibre; the strain can be thousands per cent, without fracture. A bar of mild steel, however, when pulled in a tensile machine, will neck down locally and break after a mean strain of at most some tens per cent. The glass stretches easily and uniformly, the steel with difficulty and non-uniformly. The glass, but not the steel, behaves *superplastically*. Nevertheless, it is now possible to produce a polycrystalline alloy that will mimic hot glass in its mechanical behaviour, which has led to important industrial applications in the past few years.

Mechanics of Plastic Instability

The key to all superplastic behaviour, in glasses and crystalline materials alike, lies in the relationship between plastic strain rate, $\dot{\epsilon}$, and the stress, σ , required to sustain it. The relationships is: $\sigma = K\dot{\epsilon}^m$, where K and m (≤ 1) are functions of the material and of the temperature. The exponent m (which for hot glass is unity) is not normally constant, but varies with $\dot{\epsilon}$, as seen in Fig. 1 which shows both the stress and m as functions of strain rate for an Al-Cu alloy. Fig. 1 is, in practice, characteristic of the majority of superplastic alloys. Such plots are, by implication, standardised for a fixed strain, ϵ , as work-hardening will result in the stress required to produce a given strain rate, increasing with strain according to a relationship often adequately described by the equation: $\sigma \propto \epsilon^n$ ($n < 1$).

In most metal forming operations, deformation is performed under a constant imposed strain rate. The implications can be understood by considering a long rod stretched at fixed strain rate, $\dot{\epsilon}^*$. If a small instability (incipient neck) develops, the cross-sectional area is locally reduced and

the stress there rises. In a material which is inherently plastically stable, while deformation would tend to become concentrated in the local constriction, the local strain rate would then become much greater than the strain rate along the rest of the rod. If, however, m is fairly high, the stress required to sustain deformation in the constriction would rise to a high level and, long before this could happen, the strain would become distributed along the unnecked (and major) part of the rod. Moreover, if the strain-hardening exponent, n , is substantial, then a rapidly deforming neck requires an even higher stress to sustain continuing deformation than with a non-hardening material like glass, for which $n = 0$. A proper analysis of the triaxial stresses in a developing neck is very complex and theories abound. One theory concludes that the critical strain, ϵ^c , for a neck to develop in a sustained fashion is given by: $\epsilon^c = 2n/(1-2m)$ which implies that if m reaches 0.5, the material is plastically stable (i.e. ϵ^c is infinite) so long as $n > 0$. For the many superplastic alloys now known, m is in the range 0.4–0.7 and $n > 0$.

Conditions for Superplasticity

When a sustained neck develops, fracture quickly and necessarily follows: for any ductile material, therefore, the avoidance of neck development is a necessary condition for very large strains to be attained, although not sufficient in itself. It is also necessary to avoid, in substantial proportions, the presence of a phase, which is much harder than the matrix; if that happens, cavities develop at grain boundaries and the material breaks at small strains, especially at low strain rates, even if no neck develops. The close correlation between m and the strain to fracture in tension, valid for many alloys, is shown in Fig. 2.

We have not yet considered the influence of temperature and grain size. No practically useful superplastic alloy is superplastic at ambient temperature: superplasticity is normally restricted to the temperature range $0.4 T_m - 0.7 T_m$ (T_m = absolute melting temperature). Fig. 3 shows, for a $Zn_{78}Al_{22}$ alloy, the variation of flow stress with temperature for constant $\dot{\epsilon}$, for two quite different grain sizes illustrating a fact which has long been familiar to metallurgists, that fine-grained metals are stronger than coarse when cold, while the reverse is true when hot. When the grain-size of $Zn_{78}Al_{22}$ is kept below about $5 \mu m$ and it is strained at $\sim 0.6 T_m$ ($200^\circ C$), it can be stretched to strains exceeding 500%, at

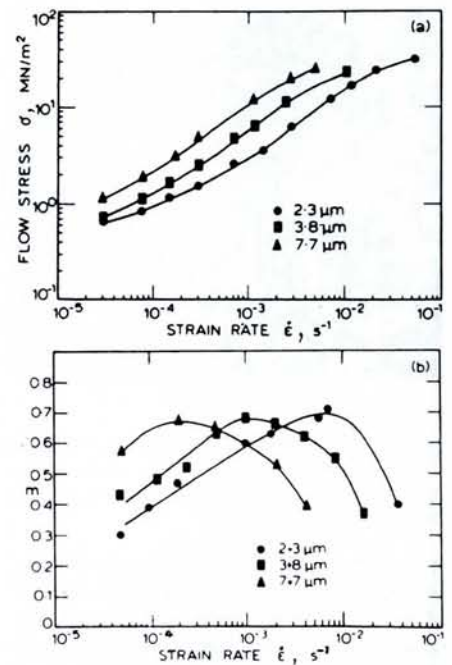


Fig. 1 — The dependence on strain rate, $\dot{\epsilon}$, of the flow stress, σ , and the exponent, m , for the eutectic Al-Cu alloy deformed at 520°C, for 3 grain sizes. (After Holt D.L. and Backofen W.A., *Trans. Quart. ASM* 59 (1966) 755.

a very low stress, whereas at 20°C ($\sim 0.36 T_m$) it is strong and its ductility is small.

We can now summarise the essential characteristics of a superplastic alloy: It must be (and remain during its deformation) very fine-grained; the index of strain-rate sensitivity, m , must exceed ~ 0.4 , which in turn is found to imply strain rates not usually exceeding 10²/s; high values of m must be restricted to temperatures well above ambient, and at such temperatures the flow stress must be very low, whereas at ambient temperature, m must be low and the flow stress high.

Mechanisms of Superplasticity

We next turn to the mechanisms which make superplastic behaviour possible. A very large amount of microstructural

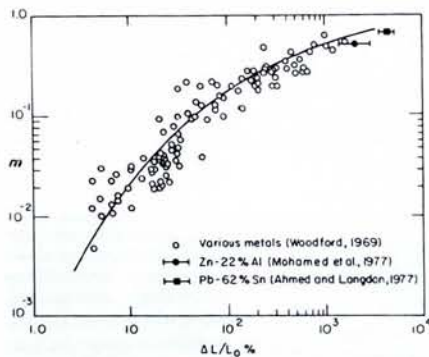


Fig. 2 — Strain rate sensitivity, m , vs. elongation to failure for various metals and two superplastic alloys. (After Langdon T.G. *Met. Trans.* 13A (1982) 698.)

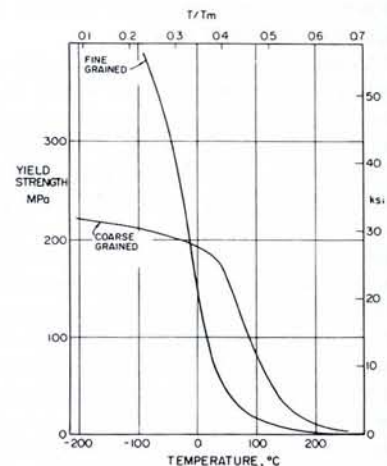


Fig. 3 — The influence of grain size on the strength of $Zn_{78}Al_{22}$ alloy as a function of temperature. (After Ball A. and Hutchison M.M. *Met. Sci. J.* 3 (1969) 1.)

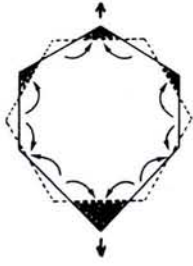


Fig. 4 — Diffusional flow in a grain under tension. (After Ashby M.F. and Verrall R.A., 1973.)

research has been done in the past decade to address this question, and even though the relative emphasis to be given to the different constituent processes is still subject to disagreement, a clear picture is beginning to emerge.

The following structural observations are generally valid:

- (1) Superplastic behaviour requires grains which are not only fine, but "equiaxed" (of roughly equal diameter in all directions); *these equiaxed grains remain equiaxed* throughout a deformation which may exceed 1000% (whereas in normal plastic deformation, initially equiaxed grains become progressively elongated, as a single crystal which is plastically stretched).
- (2) Neighbouring grains are mutually displaced by shear at grain boundaries.
- (3) Grain boundaries migrate continuously during superplastic straining.
- (4) Except at the highest stresses (right-hand side of Fig. 1), only a small proportion of the strain is accomplished by dislocation motion; the major part of the strain must therefore be due to "diffusional flow".

Diffusional flow is now a well authenticated mechanism. In Fig. 4 which outlines one version of this process for an irregularly shaped grain under tension, the arrows show, schematically, the paths of atomic self-diffusion, biased by the applied stress: vacancies move in counterflow to atoms. At higher temperatures, diffusion takes place as shown through the lattice, whereas at lower temperatures the grain boundary is the preferred diffusion path. The rate of this deformation depends on σ^2 (so that for constant conditions m should ideally be 0.5), and on $1/d^2$, where d is the grain diameter. Plainly the strain rate achievable depends crucially on the diffusion rates.

Much energy has gone into attempting to establish which property is rate-determining in superplastic flow; candidates include volume diffusion, grain-boundary diffusion, resistance to grain-boundary shear, or the rate at which local stress accumulations can be dispersed by localised dislocation motion. It is now clear that the governing factor is a function of metal, temperature, grain size and stress.

One theory which has repeatedly returned to favour is that advanced by Ashby and Verrall in 1973. The essential idea of this is a "grain-switching" mechanism where con-

stituent processes are diffusional flow (by combined lattice and grain-boundary diffusion), grain-boundary shear and grain-boundary migration; a measure of grain rotation is also involved. The version of diffusional flow in Fig. 4 differs slightly from the older models and gives faster flow. At high stresses (near the upper limit for superplastic behaviour) dislocation motion intervenes and grains begin to elongate; at low temperatures only diffusional flow operates, grains remain equiaxed and also rotate bodily (as evidenced by the gradual disappearance of any initial preferred orientation of the grains). The balance of processes, and thus also the controlling process, varies as stress is increased (and as the temperature changes).

Practical Aspects

For the metallurgist, the principal task is to provide alloys in which the grains not only are fine to begin with, but resist coarsening at the temperature of optimum superplasticity. This is done in practice either by designing a duplex microstructure in which two phases, both equiaxed in form, are present in roughly equal proportions, or else by dispersing a small fraction of second phase in very finely distributed form. In the "duplex" case, a majority of the boundaries are interphase ones, which can behave similarly to ordinary monophase grain boundaries. In the "disperse" case, the fine particles (too small to cause serious cavitation and premature fracture) pin migrating boundaries enough to prevent rapid coarsening of the grains, but not enough to prevent grain-boundary migration altogether — a delicate balancing act.

Such alloys are used industrially to manufacture highly complex shapes from

sheet; the starting sheet is pressed by gas or fluid pressure, or by isothermal forging, into a die, which can be made from inexpensive materials since the pressures involved are modest. This feature is one of the principal economic advantages of superplastic forming *vis-à-vis* such processes as high-pressure pressing of non-superplastic steel sheets. Also the accessible strains are much higher in superplastic forming than in ordinary pressing or deep drawing, so that a complex shape can be made in a single forming operation with just one die, instead of a multiple process with several dies. The technique has proved particularly useful for complex consumer goods and (using titanium alloys) for air frame components.

Practical superplastic alloys have been developed only in the past decade; serious research has been in progress for about two decades, whereas the first observation of the phenomenon dates back to 1920. Of the many alloys which have been developed, only four are in current industrial use; this is no doubt due to the demanding specifications required. The greatest possible superplastic strain rate is necessary if production times are not to be unreasonably long: $10^{-2}/s$ is probably the lower acceptable limit (and is still much lower than strain rates current in other forming processes).

A reasonably wide temperature range of superplastic working is needed, since it is not practicable to hold a large sheet within narrow temperature limits, and also a wide range of $\dot{\epsilon}$ for which $m \sim 0.5$ is desirable. To achieve these aims, it helps to have a range of (small) grain sizes, since for each grain-size component there are different optimum values of T and $\dot{\epsilon}$.



Section-K, the intermediate energy nuclear physics section Netherlands of the National Institute for Nuclear Physics and High-Energy Physics (NIKHEF), has an opening for a research associate in nuclear theoretical physics.

THEORETICAL NUCLEAR PHYSICIST

The institute has started operation of its 500 MeV high duty cycle electron linac which will be used for research in electron scattering and low energy pion/muon physics.

Applicants are expected to have experience in areas of nuclear theory which are closely related to the experimental programme.

The institute works in collaboration with the Foundation for Fundamental Research on Matter (FOM), the Catholic University at Nijmegen (KUN), the University of Amsterdam (UvA) and the Free University at Amsterdam (VU).

The appointment is for a maximum of two years.

For further information please contact Justus H. Koch (tel.: (20) - 592 21 71).

Applications including a career resume and the names of three references should be sent to:

NIKHEF, Personeelszaken, P.O. Box 41882, 1009 DB Amsterdam, before 15 February 1983.

Metallurgy and Superconductivity

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The commercial alloys today are:

- (1) $Zn_{18}Al_{22}$ (optimum $T \sim 250^\circ C$),
German F.R.;
- (2) $Al_{93.5}Cu_6Zr_{0.5}$ (optimum $T \sim 460^\circ C$),
Britain;
- (3) $Al_{90}Ca_5Zn_5$ (optimum $T \sim 475^\circ C$),
Canada;
- (4) $Ti_{90}Al_6V_4$ (optimum $T \sim 950^\circ C$), USA.

The Zn-Al monotectic alloy is an example of a duplex-phase microstructure, whereas the Al-Cu-Zr alloy is a good instance of an alloy specifically designed for stabilisation by phase dispersion. A number of duplex steels have been shown to be superplastic, but these have not yet found a use in industrial applications.

Anything which hinders dislocation creep without disturbing diffusional flow (e.g. dissolving tungsten in nickel to lower the stacking-fault energy and thereby hinder dislocation climb, needed if creep is to continue) will enhance superplastic formability. Development of an industrially usable family of superplastic steels and superalloys would be a very desirable prize, as also would, more generally, the perfection of a stably super-finegrained family of light alloys ($d \sim 0.5 \mu m$) which might offer practical superplastic strain rates approaching 1/s. For this last objective, rapid solidification processing (splat-quenching, see also Cotterill, page 8), may prove to be the key.

The above account has not touched at all upon a second form of superplasticity, which is linked with the building up of a system of microstructural internal stresses by thermally cycling an alloy during transformation, either through a phase transition or else by exploiting highly anisotropic thermal expansion in individual grains, as in α -uranium. This phenomenon has had major implications for nuclear power (less, now that metallic uranium is being phased out of use). Attempts have been made, unsuccessful up to now, to adapt this form of superplasticity for industrial use.

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Superconductivity is undoubtedly one of the most remarkable phenomena in solid state physics: an intriguing curiosity at the time of Kamerlingh Onnes' discovery, the superconducting phase transition gradually acquired fundamental importance as the signature of a possible ground state of condensed matter. According to present knowledge, the occurrence of superconductivity in electronically conducting systems is rather the rule than the exception, and the number of superconducting elements, alloys and compounds far outweighs that of, e.g., magnetically ordered substances.

The physics of superconductivity concentrates on understanding the subtle electron interactions responsible for the phenomenon, the pairing in momentum space. However, this aspect is only part of the story. The remaining, no less important part, is connected with applications and the prospecting of yet unknown alloy systems — physical metallurgy.

Superconducting materials, especially those considered for the production of high magnetic fields, are characterized by their critical surface in a three dimensional system defined by temperature, external magnetic field and transport current density. The critical temperature and critical fields are, for the most part, properties of the composition within a homogeneous phase of the material (the latter may be an equilibrium phase or a metastable one); the microstructure has not much influence because the superconducting coherence length is usually much smaller than dimensions such as grain size. On the other hand, the critical current density $J_c(H, T)$ depends — even crucially — on microstructural features such as grain size, dislocation networks, precipitates etc. There are thus at least two kinds of "metallurgy" which come into play, the first dealing with problems of phase stability and the second focussing on defect structures.

Phase Diagrams & Superconductivity

Many superconductors — particularly the most interesting, those with a high critical temperature T_c — show important variations of their properties with the method of preparation and with heat treatment, and the first step in understanding or predicting such variations is to examine the details of their alloy phase diagrams. The niobium-gallium system which exhibits an A15-type structure when the composition is near Nb_3Ga , illustrates such behaviour. If one measures T_c for one and the same specimen as a function of the annealing

temperature T_A , a complicated curve is obtained as shown in Fig. 1. T_c varies between the extremes of 9 K and 21 K and, moreover, will not exceed about 15 K unless rapidly quenched after the annealing treatment.

To attain the maximum value, the precise homogeneous phase composition is first obtained by appropriate annealing and quenching, and this is followed by a low temperature annealing (branch I b in Fig. 1), performed in a region where segregation is avoided, so ensuring an improvement in the long range order parameter.

The main reason why T_c is so dependent upon the detailed heat treatment processes is that the peritectically formed A15 compound has a strongly temperature-dependent phase limit at the Ga rich side as can be seen in Fig. 2. The stoichiometric concentration of 25% Ga, a prerequisite for a high T_c , is confined to a narrow spike near the eutectic temperature of $1740^\circ C$.

The more intriguing niobium-germanium system is governed by a topologically similar phase diagram around the superconducting A15 phase. However, the limit falls short of the composition Nb_3Ge by 2 atomic percent even at the eutectic temperature. Moreover, the tendency towards segregation below T_E is so strong that the strategy "optimum quench plus ordering anneal" does not work at all here. Yet suitably prepared, Nb_3Ge holds the record for T_c . It is then clear that the constraints of three-dimensional equilibrium thermodynamics have to be overcome right from the beginning of material synthesis. This can be done by growing films by sputtering or physical or chemical vapour deposition. The success of these techniques relies

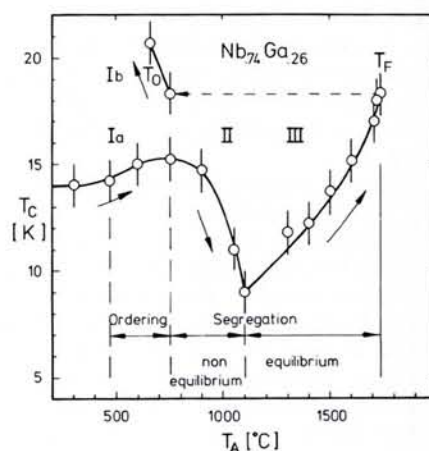


Fig. 1 — The superconducting critical temperature T_c of the niobium-gallium A15 phase vs. the annealing temperature T_A .