The Malleability of Gold

AN EXPLANATION OF ITS UNIQUE MODE OF DEFORMATION

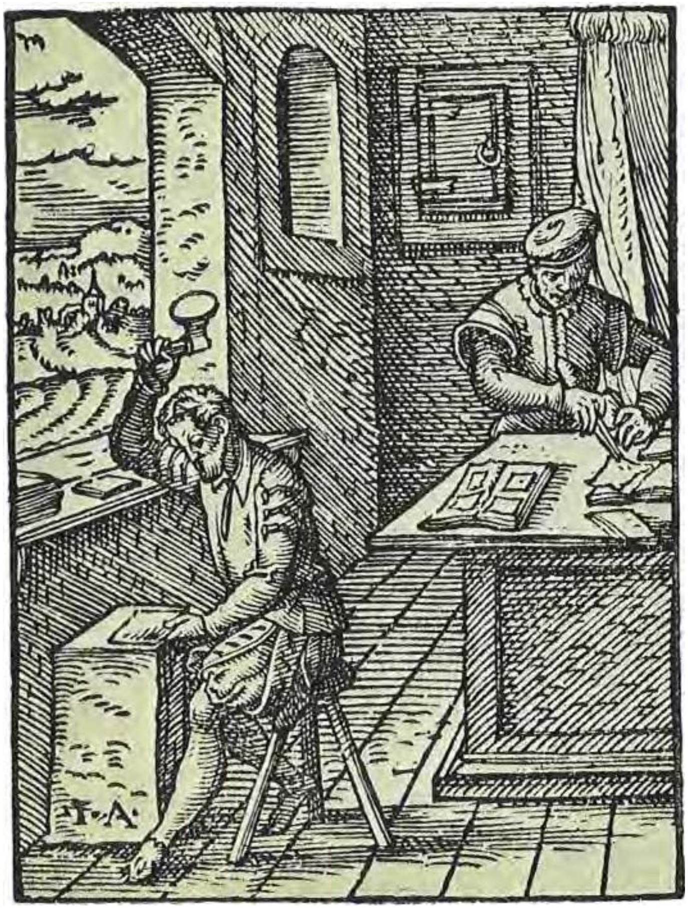
Professor J. Nutting and J. L. Nuttall
Department of Metallurgy, University of Leeds, England

Alone among the metals, gold can be rolled and beaten to a thinness less than the wave-length of visible light, but so far there has been no scientific explanation of this unique property. In this paper the authors show that gold can accommodate plastic deformation even when the thickness is less than the size of the sub-grains formed, whereas with other metals fragmentation occurs when the foil thickness reaches the sub-grain diameter. This unusual behaviour of gold is attributed to the absence of an oxide film, which enables dislocations to escape from the surface of the metal.

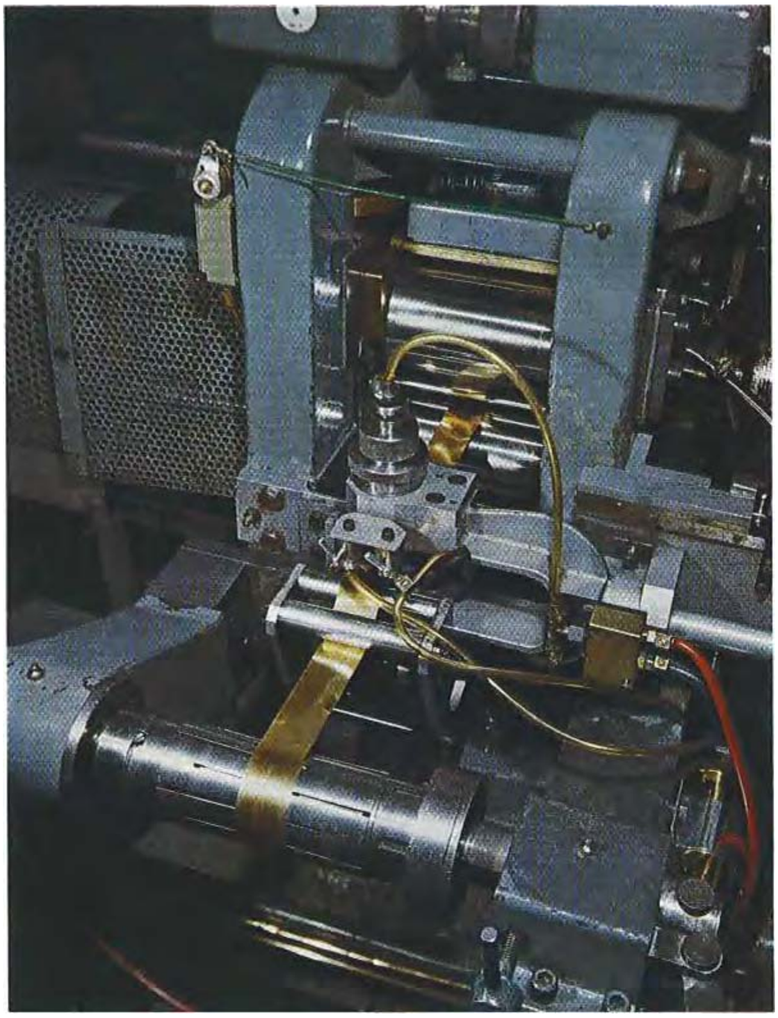
The term "malleability" is seldom used these days for describing the properties of metals. It originates from the Latin *malleus*—a hammer, and hence the meaning of malleability—capable of being hammered or pressed out of form without a tendency to return to the original shape and without fracture. Gold seems to be the most malleable of metals, for by a combination of cold rolling and hammering without any intermediate annealing it can be reduced to a foil some 50 to 100 nm, about 250 to 500 atoms, in thickness.

The ability of gold to deform plastically in this way has been known for many hundreds of years, but few attempts have been made to account for the behaviour, although it is known that thinner foils cannot be produced by further beating. It is also known that comparably thin foils cannot be produced in other metals, for during rolling or beating they fragment at a thickness of about 1μm.

The starting material for the production of gold foil is a strip 2 mm in thickness, and after rolling and beating the equivalent elongation is equal to about 186,000, or to 99.9996 per cent reduction of thickness, that is to say an equivalent logarithmic strain of 10. In other metal forming operations copper tube may undergo a logarithmic strain of 5 between the as-extruded billet and its



For many centuries craftsmen have beaten gold into leaf so thin that there can be only a few hundred atoms in its cross-section. This woodcut, showing a gold beater at work, with his assistant arranging the gold leaf in "books", the usual form in which it is supplied to users, is from the *Panoplia Omnium*, written by Hartman Schopper and published in Frankfurt in 1568



For some of the many applications of gold in industry modern precision rolling equipment is capable of producing strip down to 0.0005 inch in thickness without intermediate annealing

Photograph by courtesy of Johnson Matthey & Co Limited

finished form, while in the production of copper and iron wires logarithmic strains of 7 may be achieved without intermediate annealing.

The achievement of these high strains involves a number of physical changes which are not often considered during theoretical or experimental studies of the plastic deformation of metals. First there is an enormous increase of the surface area of the gold, and energy must be absorbed during the deformation process in creating this surface; secondly there must be a similar increase in the internal interfacial energy associated with changing the shape of the grains.

During the cold forming of metals it is usual to assume that a change in shape of the grains occurs which corresponds to the imposed macroscopic strain. Thus if a grain has an initial volume V, then after a plastic deformation the grain will have the same volume but because of the change of shape the interfacial area will increase. If it is assumed that the initial starting material is cross rolled and isotropically beaten to the final foil (an assumption which is not strictly correct), an equiaxed grain in the starting material will end up as a very thin pancake. With a starting material 2 mm thick and an assumed grain size of 50μm the thickness of a deformed grain in producing a foil 50 nm thick would be about 1 nm and the diameter would be about 10 mm; this would imply an increase in the grain boundary interfacial area of 8000. It seems very unlikely that this model of macroscopically homogeneous plastic deformation is physically feasible, and consequently the present experiments have been undertaken as part of general study of the modes by which large plastic strains are accommodated in face-centred cubic metals.

Experimental

The analysis of the gold used in the present investigation is given below in per cent:

Analysis of Gold

Pd	0.0020
Ag	0.0010
Fe	0.0004
Cu	0.0003
Si	0.0001

Balance Au

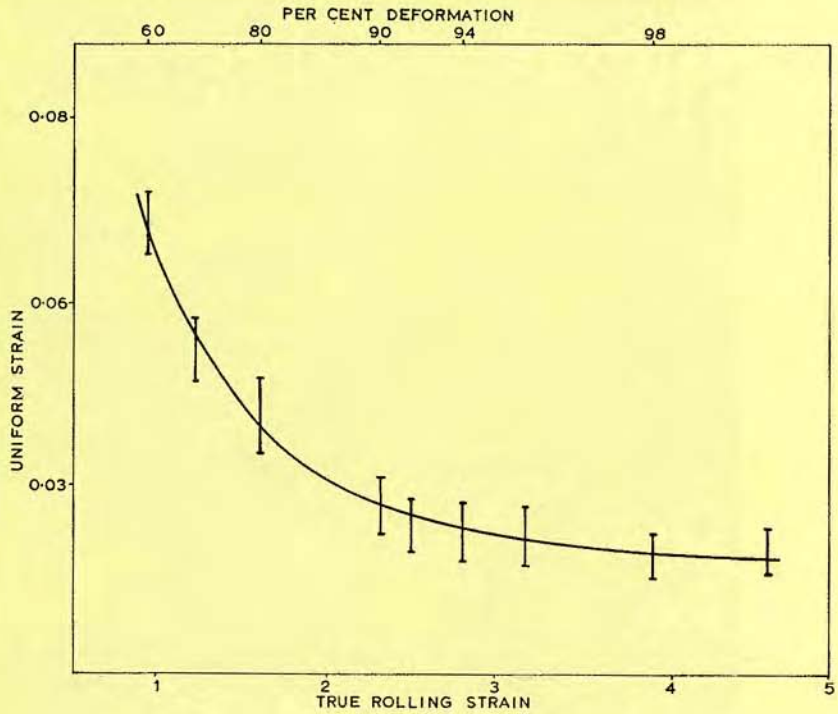


Fig. 1 The true stress-rolling strain curve for gold

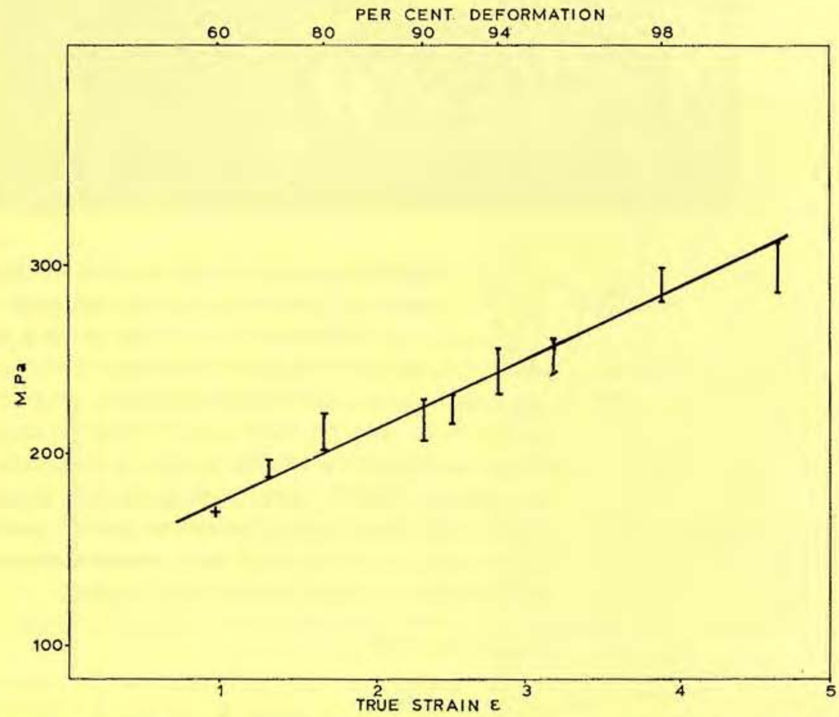


Fig. 2 The uniform strain in the tensile test versus rolling strain for gold

It was supplied in the form of a machined ingot having a cross-section size 13 mm $\times$ 25 mm and length 150 mm. The grain size was 10^3μm. The gold bar was cold rolled to strips without any cross rolling, and specimens were taken for further testing at appropriate stages during deformation. The reduction in thickness per roll pass was kept small and low roll speeds were used so that the temperature rise during rolling never exceeded 5 to 10°C above ambient. Tensile specimens were taken from the deformed strips and pulled to failure at a strain rate of 0.5×10^{-3}/s while the load extension curves were being recorded.

With the starting material used the maximum reduction in area which could be achieved while still obtaining specimens suitable for mechanical testing was 99 per cent, which is equivalent to a true strain (log strain) $\simeq 5$.

Mechanical Test Results

From the load extension results it was possible to determine the maximum engineering stress at each roll reduction and by plotting these values against the rolling strain a linear relationship was found, as shown in Figure 1. This curve corresponds to the true stress/true strain curve and it can be seen that over the rolling strain range 1 to 5 the relationship corresponds to:

$$\sigma = m'\varepsilon_t$$

or more correctly

$$\frac{d\sigma}{d\varepsilon} = m'$$

where m′ may be defined as the high strain work hardening modulus. In relation to the low strain elastic shear modulus (G) for gold:

$$m' = {}^{G}/_{750}$$

A somewhat similar result has been obtained by Clough (2) for copper.

After cold rolling the gold still showed a characteristic form of stress strain curve in tension with a 0.2 per cent proof stress value significantly below the maximum engineering stress and then a region of uniform elongation prior to the development of an unstable neck. The extent of the uniform strain as a function of prior rolling strain is shown in Figure 2.

The exact significance of these results is difficult to appreciate. Although the specimen width remained constant, the thickness decreased with prior strain and it is known that the extent of uniform elongation in a tensile test is somewhat dependent upon specimen geometry and tends to decrease as the thickness to width ratio decreases in a strip specimen for tensile testing.

However, it must be concluded that the earlier concepts involving the reduction of work hardening rates and the consequent exhaustion of tensile ductility with increasing prior plastic strain does not seem to be borne out with gold, even after 99 per cent deformation.

Metallographic Examination

The structural changes associated with the plastic deformation of annealed polycrystalline face-centred cubic metals at strains up to 30 per cent have been well documented, and consequently the low strain work on gold will not be described further. At higher strains copper and aluminium have been studied in detail by Clough et al (1), and Clough (2) and Nutting (3), who have reported the development initially of cells 1 to 2 μm in diameter outlined by dense tangles of dislocations, which at higher strains seem to collapse to give well defined sub-grains free from dislocations and having boundary structures similar to those observed at high angular misorientations. With further strain, even more clearly defined grains are formed and the over-all process has been described as strain induced recovery and recrystallisation.

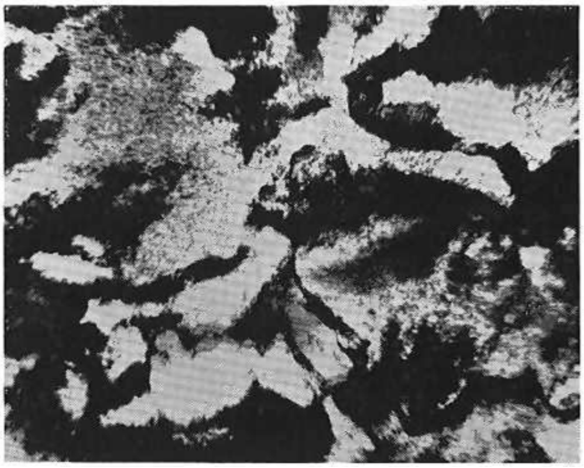


Fig. 3 Gold deformed 60 per cent by rolling. Typical deformation structure showing a high dislocation density with a few low angle boundaries ×10,000

The results obtained with gold at deformations between 60 and 96 per cent are somewhat different from those found with copper. After 60 per cent deformation the dislocation density is high and reasonably homogeneous; when cells are formed the angular misorientation across the cell walls as determined from selected area electron diffraction patterns is small, about 2° as shown in Figure 3. With increasing rolling strain to 96 per cent cells outlined by dislocations still remain, but some sub-grains are now formed having a diameter of 1 μm and an angular misorientation of 4 to 5°. An example of the microstructures observed is given in Figure 4. With copper deformed to an equivalent strain, sub-grain formation occurs much more readily than with gold, as can be seen by comparing Figure 4 with that found in copper, Figure 5.

When gold is deformed further to produce foil, the microstructure remains basically the same as that found after 96 per cent deformation with regions of high dislocation density, cell formation and higher angle sub-boundaries as shown in Figure 6. The sub-grain size is about ¼ to ½ μm as compared with that found after 96 per cent deformation, but this difference could be attributed to the fact that the gold for producing foil is usually alloyed with 1 to 2 per cent

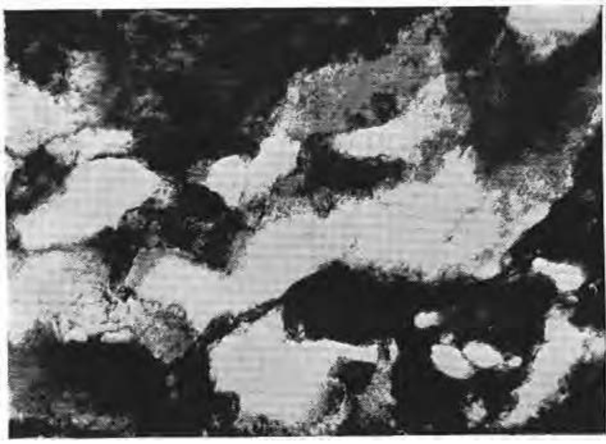


Fig. 4 Gold deformed 96 per cent by rolling. Clearly formed sub-grains have been produced but there is also a high dislocation density ×20,000

Fig. 5 Copper deformed 96 per cent by rolling. Sub-grains are clearly formed, but few regions of high dislocation density remain ×20,000

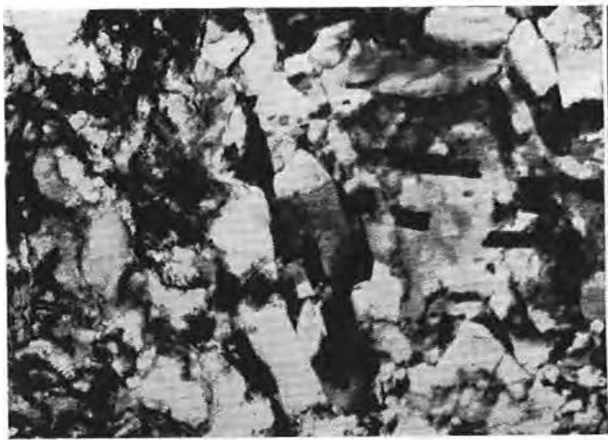


Fig. 6 Gold leaf showing distinct dislocation-free sub-grains and parallel bands believed to be stacking faults. In other regions a high dislocation density is still present ×40,000

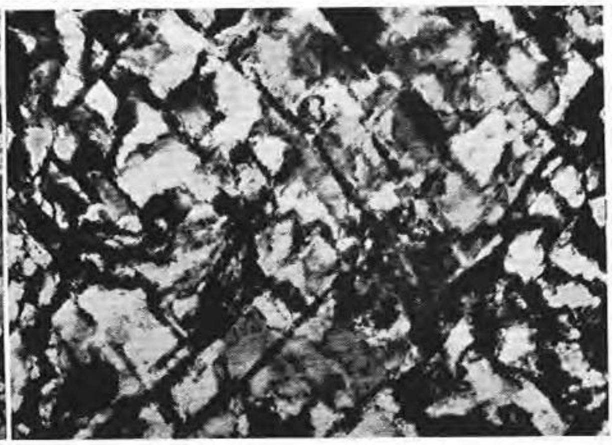


Fig. 7 Gold leaf showing relatively dislocation-free material bounded by a band like structure composed partly of dislocations and partly of stacking faults ×40,000

of copper, and it is generally felt that alloying elements can reduce the sub-grain during deformation. Within the sub-grains narrow bands are found having a width of 0.1μm arranged at right angles. In some regions these bands form a network, as shown in Figure 7. From the microstructural and diffraction evidence it is thought that these bands are stacking faults.

Discussion

As reported by Clough (2) in the case of copper, no evidence of the original grain boundaries could be found in gold after 60 per cent deformation. It must be concluded, therefore, that the grain boundaries become incorporated within the general sub-boundary structure.

It is also significant that increasing the deformation, even up to a log strain 10, is seen to result in only a slight change in the maximum sub-grain diameter. This implies that the strain is accommodated either by highly localised strains occurring at the region of the sub-grain boundaries, or by the continuous breakdown and reformation of the sub-grains as dislocations pass through the material under the action of the applied stress. The former mechanism could apply when the sub-grain size is smaller than the specimen thickness. In this case a model system would be that of hard spheres held together by a viscous liquid. When a shear stress is applied flow occurs in the liquid and a general reduction in thickness is accommodated by the hard spheres rolling over each other. A limit to deformation of this type occurs when the specimen thickness becomes equal to the diameter of the hard sphere, as further shear in the liquid phase would lead to fracture of the specimen.

However, in the production of gold foil at log strains between 5 and 10 the maximum sub-grain size diameter becomes greater than the specimen thickness. Thus after the final beating the sub-grains have an idealised shape of hexagonal prisms 2 to 5,000Å in diameter and 500 to 1,000Å in thickness.

Once the sub-grain size becomes equal to the foil thickness a mode of deformation could be conceived whereby dislocations were generated at the foil surface and then passed through the foil to emerge at the other surface. This is the classical picture of slip in the easy glide region of deformation in a single crystal and is the basis of the model of the deformation process proposed for producing gold foil by Hirsch, Kelly and Menter (4). If this were the mode of deformation then the shape of the sub-grains should conform to the imposed strain and this would imply that the maximum sub-grain diameter would increase with strain. From the microstructural observations there is no evidence for this increase; if anything there is a decrease in the sub-grain size as the total strain is increased. It must be concluded, therefore, that even when the foil thickness becomes less than the maximum sub-grain diameter, new sub-grains can be formed by dislocation movements and interactions totally within the volume of the foil.

Thus the question now arises, does grain boundary sliding play a significant role as a deformation mode when the foil thickness is greater than the sub-grain size? The evidence is not yet conclusive, but some observations support the argument that it occurs.

From the results shown in Figure 1, and assuming that the flow stress continues to vary linearly with the logarithmic rolling strain, it is possible to determine the flow stress of the beaten foil. The extrapolated value obtained is about 500 mp/mm^2 (32 tons f/sq. in.), a relatively modest value which could be achieved during the beating process.

The question that now remains to be answered is, why can gold be beaten to such a thin foil whereas other metals tend to fragment? The modes of deformation of gold up to log strains ± 5 are not abnormal, sub-grains do not form as readily as with copper or silver, and comparison of the load extension curves at these strains with other face-centred cubic metals and alloys would indicate, as shown in Figure 8, that gold is, in fact, considerably less ductile in tension than silver.

Gold has a relatively low stacking fault energy, but it is intermediate between that of copper and silver, while metals with low stacking fault energies are never looked upon as being particularly ductile. The presence of the networks of stacking faults in the gold foil shown in Figure 7, would be expected to provide barriers to dislocation movement and consequently lower the ductility. While there are many criticisms that could be made of extrapolating the flow stress from a log strain 5 to log strain 10, the results of this extrapolation indicate that the log strain 10 flow stresses are 450 to 500 mp/mm^2 for copper, gold and silver.

The really significant difference between gold and

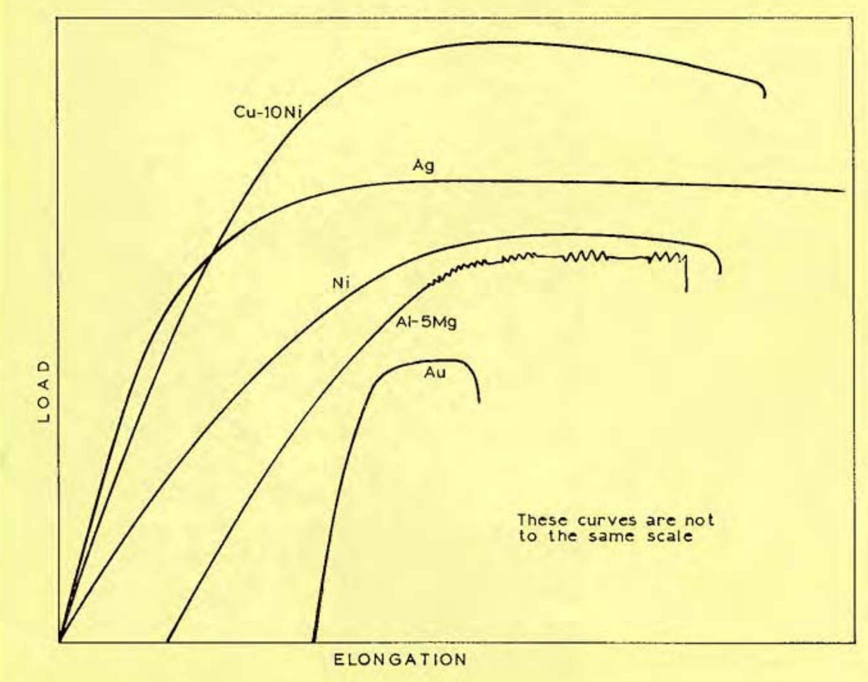


Fig. 8 Load-Elongation curves for five metals and solid solution alloys after they have been deformed 98 per cent by rolling

the other metals studied is the fact that gold, being a noble metal, does not have an oxide film on its surface. Thus dislocations formed within the gold will be able to escape easily from the metal at the surface. With metals having an oxide film on their surfaces the dislocations could well be held within the metal and this effect would become more noticeable as the total foil thickness decreased; thus the flow stress would be increased. In these conditions further strain may be accommodated by sub-grain boundary shearing, so giving rise to fragmentation at a foil thickness of $\simeq 1\mu m$, that is when the foil thickness becomes equal to the sub-grain diameter.

Conclusions

The experimental results would indicate that gold is not inherently more ductile than other face-centred cubic metals. Gold is, however, unusual in that it can accommodate plastic strain when the beaten foil thickness is less than the sub-grain size produced by plastic straining.

The reasons for this unusual behaviour of gold are probably linked with the fact that as it is a noble metal there is no oxide film on the surface and thus dislocations are able readily to escape from the foil. This accommodates the imposed strain without preferential deformation occurring at the sub-grain boundaries.

Acknowledgements

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