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The potential for achieving superplasticity in high-entropy alloys processed by severe plastic deformation

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Abstract. High-entropy alloys (HEAs) are now becoming important because they offer unique combinations of solid solution strengthening and good ductility at low temperatures. Only limited information is at present available on the high temperature mechanical properties of these materials. Nevertheless, it is evident that, as in conventional metallic alloys, processing through the application of severe plastic deformation can reduce the grain size to the nanometer range and this provides a potential for achieving good superplastic elongations. The superplastic data available to date are examined in this review and a comparison is made between the behaviour of HEAs and conventional superplastic alloys.

1. Introduction

High-entropy alloys (HEAs) are a new class of material containing five or more principal elements with each elemental concentration between 5 at.% and 35 at.% but producing a relatively simple structure based on solid solution phases [1-3]. Besides the principal elements, HEAs can also contain minor elements with each below 5 at.%. These alloys are designated HEAs because their liquid or random solid solution states have significantly higher mixing entropies than those in conventional alloys [4]. Generally, when the number of alloying elements increases beyond five, the contribution of configurational entropy to the total free energy becomes sufficiently significant that it can overcome the enthalpies of compound formation and phase separation, thereby stabilizing the solid solution state relative to the multi-phase microstructure [1-3]. In practice, there is an opportunity for achieving a combination of high solid solution strengthening and good ductility if the solid solution phase possesses a simple crystal structure such as a face-centred cubic (fcc) lattice where there are a large number of slip systems [1-4]. In practice, HEAs are very attractive materials due to their potential beneficial mechanical, magnetic, and electrochemical characteristics, such as high strength, high thermal stability and oxidation resistance. Thus, these promising properties offer many potential applications in various fields, such as tools, molds and in magnetic films [5–7].

2. The significance of superplasticity in tensile testing

When metals are pulled in tension under a constant rate of straining, they generally break after only a limited amount of strain. But in some circumstances the material may pull out essentially uniformly and exhibit exceptionally high strains prior to failure. This process is known as superplasticity and it is the major feature of materials that are used for industrial superplastic forming where complex curved shapes are fabricated for use in a range of applications in the aerospace, automotive and commercial product sectors [8]. It is now well established that there are two essential requirements for attaining superplasticity in bulk metals [9]. First, the grain size of the material must be very small and typically <10 µm. Second, since superplastic flow is a diffusion-controlled process, it requires a temperature of the order of at least ~0.5T_m where T_m is the absolute melting temperature. In the superplastic forming industry these very small grains are achieved through thermo-mechanical treatments which are generally capable of reducing the grain sizes to ~2-5 µm.

Over the last 25 years it has become clear that even smaller grains, typically within the submicrometer or even the nanometer range, may be attained by processing metals through the application of severe plastic deformation (SPD). The first demonstration of the potential for achieving superplasticity in these ultrafine-grained (UFG) materials was in 1988 [10] but subsequently the approach of processing through SPD has been adopted in many research institutes around the world and it is now recognized as a viable and useful procedure for achieving exceptional grain refinement [11-15]. Although there are several different SPD processing techniques, most attention to date has focussed on the two different procedures of equal-channel angular pressing (ECAP) [16] where a rod or bar is pressed through a special die containing a channel bent through a sharp angle and high-pressure torsion (HPT) [17] where a disk is subjected to a high applied pressure and concurrent torsional straining.

In order to provide a definitive criterion for the occurrence of superplastic flow, the advent of superplasticity is now defined as a measured tensile elongation of at least 400% [18]. In superplastic flow it has been shown that the strain arises from the occurrence of grain boundary sliding [19] and this sliding must be accommodated by the glide of intragranular dislocations that cross the grains, pile up at the opposite grain boundaries and then climb into the boundaries [20,21]. A theoretical model based on grain boundary sliding accommodated by intragranular glide and climb leads to a superplastic strain rate, $\dot{\varepsilon}_{sp}$, which is given by a relationship of the form [22]

$$\dot{\varepsilon}_{sp} = \frac{AD_{gb}G\mathbf{b}}{kT}\left(\frac{\mathbf{b}}{d}\right)^2\left(\frac{\sigma}{G}\right)^2 \quad (1)$$

where A is a dimensionless constant having a value of ~10, D_{gb} is the coefficient for grain boundary diffusion, G is the shear modulus, $\mathbf{b}$ is the Burgers vector, k is Boltzmann's constant, T is the absolute temperature, d is the grain size and σ is the applied stress. Equation (1) provides an excellent description of the superplastic flow of conventional metals with grain sizes of a few micrometers but recently it was shown by analyses that the equation applies equally well to bulk ultrafine-grained materials with submicrometer grain sizes produced by either ECAP or HPT [23-25]. Specifically, it was shown that there is very good agreement between published data and the predictions of equation (1) for both aluminum-based and magnesium-based alloys. Thus, it is interesting to determine whether the same agreement between theory and experiment applies also to superplastic flow in HEAs.

3. An examination of superplasticity in HEAs

Some limited results are now available documenting the occurrence of superplasticity in a number of HEAs. For convenience, these results are summarized in Table 1 where information is provided on the composition of the HEA, the processing procedure used to attain a superplastic grain size, the gauge dimensions of the tensile specimens, the temperature and strain rate of the tensile testing and the measured elongations to failure. Data are presented for AlCoCrCuFeNi processed by multiaxial foging [26-28], CoCrFeNiMn [29] and $CoCrFeNiMnTi_{0.1}$ [30] processed by HPT and CoCrFeNiMn processed by rolling [31].

Table 1. Experimental results for superplasticity in high-entropy alloys [26-31].

Composition	Processing	Gauge dimensions (mm^3)	Temperature (K)	Strain rate (s^{-1})	Elongation (%)	Reference
AlCoCrCuFeNi	Multiaxial forging	16 × 3 × 1.5	1073	1.0×10^{-3}	160	Shaysultanov *et al.* [26] and Stepanov *et al.* [27]
			1073	1.0×10^{-4}	325	
			1173	1.0×10^{-2}	350	
			1173	1.0×10^{-3}	585	
			1173	1.0×10^{-4}	490	
			1273	1.0×10^{-1}	600	
			1273	1.0×10^{-2}	1240	
			1273	1.0×10^{-3}	850	
AlCoCrCuFeNi	Multiaxial forging	16 × 3 × 1.5	1073	1.0×10^{-3}	604	Kuznetsov *et al.* [28]
			1173	1.0×10^{-3}	405	
			1273	1.0×10^{-1}	442	
			1273	1.0×10^{-2}	858	
			1273	1.0×10^{-3}	864	
			1273	1.0×10^{-4}	753	
CoCrFeNiMn	HPT	1.1 × 1.0 × 0.6	773	1.0×10^{-3}	160	Shahmir *et al.* [29]
			873	1.0×10^{-1}	330	
			873	1.0×10^{-2}	400	
			873	1.0×10^{-3}	520	
			973	1.0×10^{-1}	410	
			973	1.0×10^{-2}	500	
			973	1.0×10^{-3}	570	
			1073	1.0×10^{-1}	310	
			1073	1.0×10^{-2}	360	
			1073	1.0×10^{-3}	390	
$CoCrFeNiMnTi_{0.1}$	HPT	1.1 × 1.0 × 0.6	873	1.0×10^{-2}	460	Shahmir *et al.* [30]
			973	1.0×10^{-1}	630	
			973	1.0×10^{-2}	830	
			973	1.0×10^{-3}	650	
			1073	1.0×10^{-2}	570	
CoCrFeNiMn	Rolling	3 × 1 × 0.3	1023	1.0×10^{-1}	160	Reddy *et al.* [31]¶
			1023	1.0×10^{-3}	290	
			1023	1.0×10^{-4}	320	

¶Superplasticity is defined formally as a tensile elongation of at least 400% and therefore the results for this CoCrFeNiMn HEA are strictly outside of the range required for true superplastic flow. Nevertheless, the experimental results were interpreted by Reddy *et al.* [31] as evidence for "superplastic-like flow" with additional evidence that the ductility may be limited due to the occurrence of cavitation. Accordingly, based on this interpretation and in view of the rather limited results available to date for superplasticity in HEAs, these results are included in this tabulation and in the subsequent analysis.

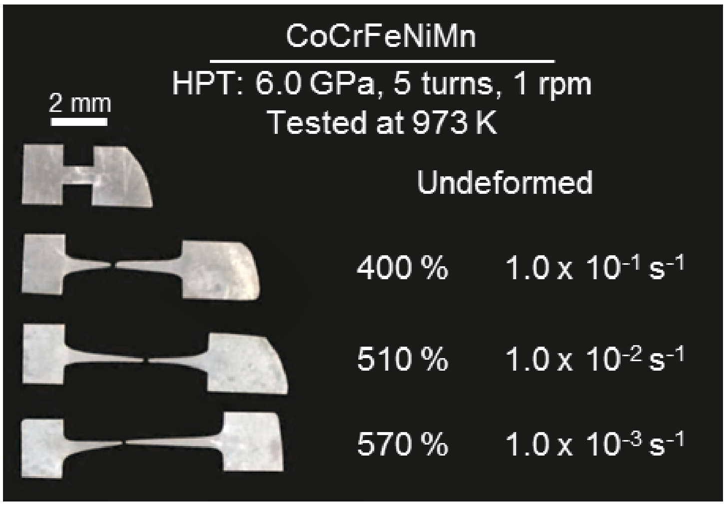

Figure 1. Examples of superplasticity in a CoCrFeNiMn HEA after processing by HPT and then testing in tension at a temperature of 973 K.

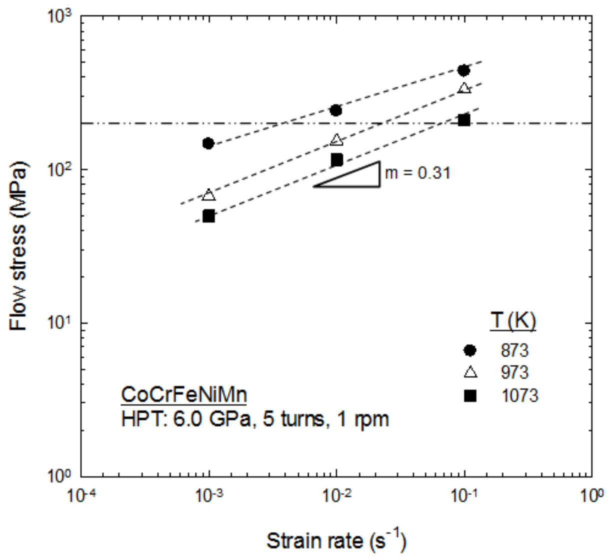

Figure 2. Flow stress versus strain rate for the superplastic CoCrFeNiMn HEA showing a strain rate sensitivity of $m \approx 0.31$ [29].

Inspection of Table 1 shows several excellent results for superplasticity in HEAs. It is necessary to also mention two important features of the data in Table 1. First, the results were obtained using different processing conditions including multiaxial forging [26-28] and HPT [29,30] which are SPD processing methods and rolling [31] which is not an SPD method. Second, noting that superplasticity requires an elongation of at least 400% [18], the results from rolling give elongations of up to only 320% which are not within the true superplastic range. Nevertheless, these results are included in Table 1 because the data were interpreted as indicative of superplastic-like flow but with the overall elongations limited by the development of cavitation.

Examples of true superplasticity are shown in Figure 1 where results are recorded for a CoCrFeNiMn HEA tested in tension at 973 K and exhibiting elongations up to 570% in samples where, as required for true superplasticity, there is no evidence for necking within the gauge length [32]. Figure 2 shows a plot of flow stress against initial strain rate for these samples where the results fall along reasonably straight lines for three different temperatures giving an average strain rate sensitivity of $m \approx 0.31$. This value of m is not consistent with equation (1) where m corresponds to the inverse of the stress exponent so that the anticipated strain rate sensitivity is $m = 0.5$. A value of $m \approx 0.3$ suggests control by an intragranular dislocation glide process [33] but samples deforming by dislocation glide are not capable of achieving elongations up to 500%. Accordingly, the data were interpreted in a different way by noting that an anomalously low strain rate sensitivity may be attained due to the occurrence of massive grain growth during tensile testing where the grains in the CoCrFeNiMn alloy grew from ~10 nm after HPT processing to ~1.0 µm after tensile testing at 973 K [29].

4. An analysis of the flow mechanism in superplastic HEAs

To evaluate the flow mechanism in these superplastic HEAs, equation (1) was re-arranged and experimental data from each set of results were plotted in the form of the temperature and grain size compensated strain rate against the normalized stress. The results are shown in Figure 3 with $D_{gb} = D_o \exp(-Q_{gb}/RT)$ where D_o is a frequency factor (19.4×10^{-4} m^2 s^{-1} for pure Ni [34]), Q_{gb} is the activation energy for grain boundary diffusion (113 kJ mol^{-1} for superplastic deformation of UFG HEA [29]), R is the gas constant, $\mathbf{b} = 2.55 \times 10^{-10}$ m [34] and $G = 85-\{16/[\exp(448/T)-1]\}$ GPa [35]. The plot was constructed taking grain sizes of d = 2.1 µm [26,27], 1.5 µm [28], 1.0 µm [29], 0.5-3.0 µm [30] and 1.4 µm [31]. The solid line labelled $\dot{\varepsilon}_{sp}$ shows the theoretically predicted rate for superplasticity occurring by grain boundary sliding. Thus, the experimental data for HEAs are in excellent agreement with the theoretical prediction and this is consistent with conventional alloys processed by SPD.

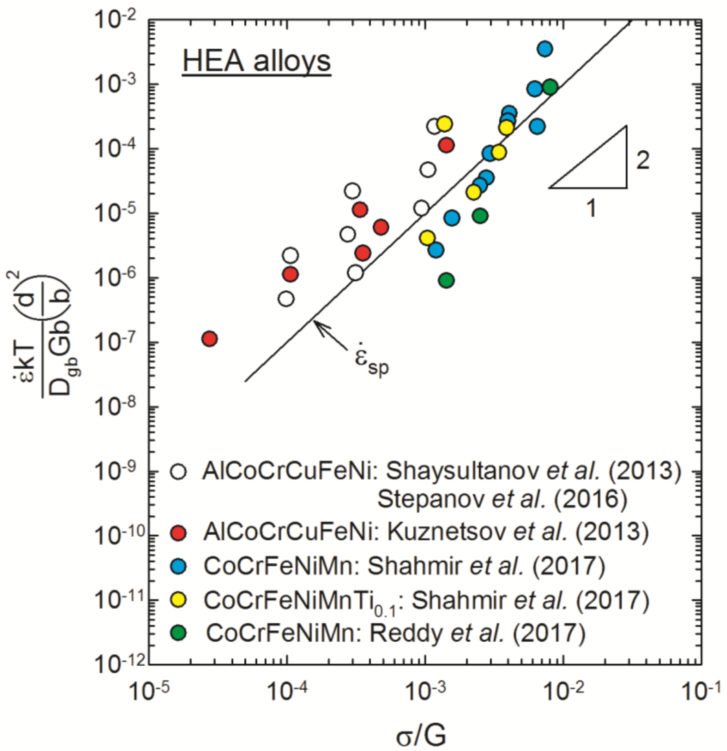

Figure 3. Temperature and grain size compensated strain rate versus normalized stress showing excellent agreement with the theoretical prediction for conventional superplasticity.

5. Summary and conclusions

1. Superplastic data are now available for several HEAs with tensile elongations up to >1000%.
2. An analysis of the experimental data shows good agreement between the measured strain rates and the predictions for conventional superplastic alloys and superplastic alloys processed by SPD.

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