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ULTRAFINE GRAINED MATERIALS

Synergic effects of grain refinement and precipitation strengthening

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Abstract The article describes the combined effects of grain size and second phase particles on mechanical properties of CuCrZr alloy subjected to SPD processing and ageing in two sequences: (i) SPD processing followed by ageing and (ii) SPD processing of samples aged prior to deformation. It was revealed that each of these strengthening mechanisms acting alone gives a significant increase in mechanical strength (5 and 10 times in the case of ageing and SPD processing, respectively). However, it has been found in the present study that the strength of samples subjected to grain refinement and precipitation hardening is not a direct sum of the strengthening brought about by these two strengthening mechanisms acting alone. This finding is discussed in terms of the inter-dependence of grain size–particle strengthening in SPD nano-metals.

Introduction

Properties of metals and alloys are strongly influenced by the density of grain boundaries, dislocations and second phase particles. The strengthening effects of these elements have been utilized for already a long time to improve properties of metals by cold working combined with a low-temperature recrystallization and precipitation annealing. Such a treatment has been particularly successful in the case of aluminium alloys, which may attain the grain size in the range of a few microns and high density of precipitates. A new research direction, which has emerged recently in this field, is based on the application of severe plastic deformation (SPD). Deformation realized in such processes as equal channel angular pressing (ECAP), high-pressure torsion (HPT), cyclic extrusion compression (CEC), accumulative roll bonding (ARB) or hydrostatic extrusion (HE) reduces grain size of metals and alloys well below 1 μm and frequently below 100 nm [1–10]. Such a reduction brings about a remarkable increase in the yield and flow stress, however, an important question, which remains not fully answered is to what degree the resistance to plastic deformation of SPD nano-alloys can be further improved via combined strengthening with second phase particles, in particular precipitates. It should be noted in this context that initially, SPD methods have been applied to technically single phase metals and alloys. Much less attention has been paid on two-phase materials.

Among a few articles on precipitation strengthening of SPD metals, Zhao et al. [11] reported that ultrafine grained (UFG) 7075 aluminium alloy processed by ECAP and naturally aged exhibits 103% higher yield strength when compared to coarse grained sample after the same natural ageing. This finding has been explained in terms of a higher density of GP zones and dislocations in UFG samples. It has been shown that ECAP only accelerates the phase precipitation not changing its sequence during post-processing natural ageing. In other reports, conclusion has been also drawn that nano-precipitation may effectively improve both the ductility and strength of nanostructured aluminium alloys (AA7075 [12] and AA2024 [13]) obtained by cryo-rolling at liquid nitrogen.

The subject of this study was CuCrZr alloy which, due to an attractive combination of high mechanical strength with good thermal conductivity, is a candidate for heat removing applications. Traditionally, good mechanical properties of this alloy are obtained via precipitation strengthening taking

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place during ageing of supersaturated polycrystalline materials with the grain size in the range of tens of micrometres [14, 15]. Recently, SPD techniques have been successfully employed to refine the grain size in CuCrZr well below 1 μm [16, 17]. This paves the way for studying the effect of combined nano-grain size and second phase particles strengthening of CuCrZr, which is described in this article. The results obtained for the CuCrZr alloy are also discussed in more general context of synergy in strengthening by grain refinement and second phase particles.

Experimental

A CuCrZr alloy (available commercially as MHY) with the chemical composition given in Table 1 was used in this study. The material was delivered in the form of extruded rods with a diameter of 20 mm. The rods were solution annealed at a temperature of 1,000 °C for 1 h and water quenched. The microstructure of as-quenched sample consists of equiaxed grains (Fig. 1a) with an average equivalent diameter of ~50 μm. SEM observations revealed also particles of sub-micron size (0.5 μm in diameter) located at grain boundaries and in grain interiors (Fig. 1b). Analysis of their chemical composition indicates that they are primary particles of chromium.

In order to determine the strengthening effect induced by precipitates in coarse grained structure, as-quenched samples were aged at temperatures ranging from 350 to 650 °C. The as-quenched material was also subjected to the SPD processing using two deformation routes.

(1) HE to a total cumulative true strain of 3.77,
(2) ECAP ($\varepsilon = \sim 8$) + HE to a total true strain of 11.5.

In both cases, the final product has a form of 3 mm wire. After HE processing, the samples were water cooled at the die exit. Both ECAP and HE were conducted at ambient temperature.

Combined effect of grain size refinement and precipitation hardening was obtained by the following sequences of SPD processing and heat treatment:

(1) solution annealing (1,000 °C for 1 h), water quenching, SPD processing and ageing at 480 °C,
(2) solution annealing, ageing at 480 °C for 2 h, SPD processing.

Mechanical properties of the samples subjected to various treatments were evaluated by microhardness HV0.2 measurements and in tensile tests. Their microstructures were studied using light and electron microscopy (transmission (TEM) and scanning (SEM)) equipped with EDX detectors for local chemical analyses.

Table 1 Chemical composition of the CuCrZr alloy

Cr	Zr	Sb	Zn	Fe	P	Others	Cu
0.7	0.08	0.01	0.01	0.03	0.01	0.09	Balance

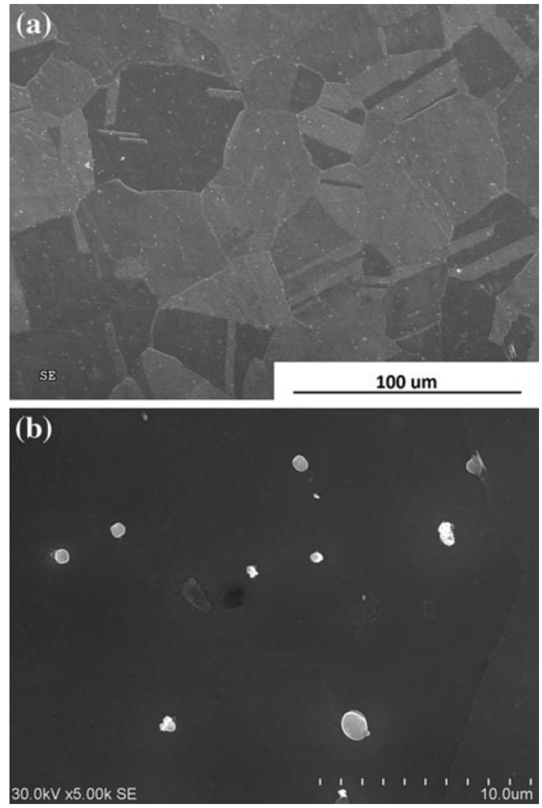

Fig. 1 Microstructure of as-quenched sample: grains (**a**) and primary precipitates (**b**)

The microstructures revealed by microscopic observations were described quantitatively in terms of the grain size and shape. The grain size was measured in terms of the equivalent diameter of grains, d, defined as the diameter of a circle, which has the surface area equal to the surface area of a given grain. The average equivalent diameter $E(d)$ and variation coefficient $CV(d)$, defined as the ratio of the standard deviation to the mean value, were determined. The grain shape was described by shape parameter defined as the ratio of the maximum diameter to the equivalent diameter of a given grain, d_{max}/d, which quantifies its elongation.

Results

Contribution of individual strengthening mechanisms

Precipitation hardening

A series of heat treatments (solution annealing at 1,000 °C followed by water quenching and ageing at various

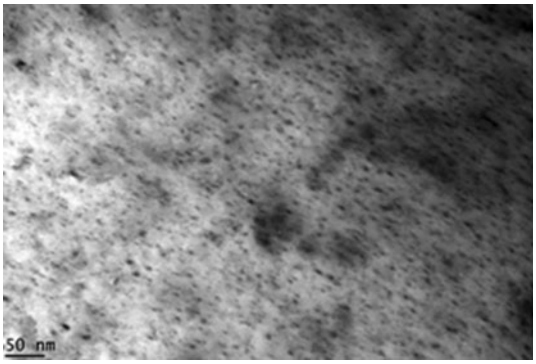

Fig. 2 Precipitates formed during ageing at 480 °C for 2 h observed in TEM

Table 2 Comparison of mechanical properties of as-quenched and peak-aged samples

Sample	HV0.2	YS (MPa)	UTS (MPa)	ε_u (%)	ε_t (%)
As-quenched	59	54	226	27.2	38.6
Aged at 480 °C for 2 h	136	277	388	12.3	23.5

ε_u—uniform deformation in tensile test

ε_t—total deformation in tensile test

temperatures for various times) allowed to establish that the maximum precipitation hardening is obtained via ageing at 480 °C for 2 h (for details see [17]). This hardening is due to the formation of small (about ten nanometres in size) GP zones evenly spaced in the matrix (Fig. 2).

The influence of heat treatment on mechanical properties of a micro-grained CuCrZr alloy is quantified by the data listed in Table 2. The as-quenched material exhibits low strength (YS = 54 MPa) and good plasticity (38% in tensile elongation). The precipitation hardening increases the yield strength by 223 MPa ($\sim$5 times) and hardness by 77 HV0.2 ($\sim$2 times).

The microscopic observations revealed that the ageing at temperatures in the range of 350–650 °C does changes the grain size, which remains at the level of 50 μm.

Grain boundary strengthening

The microstructure of the as-quenched samples processed by SPD, for both deformation routes employed in this study, results in a significant microstructure refinement. However, the microstructures after these two SPD processes differ considerably, as evidenced in Fig. 3. The microstructure of the material processed by HE features elongated dislocation cells (Fig. 3a) typical of Cu alloys subjected to plastic deformation.

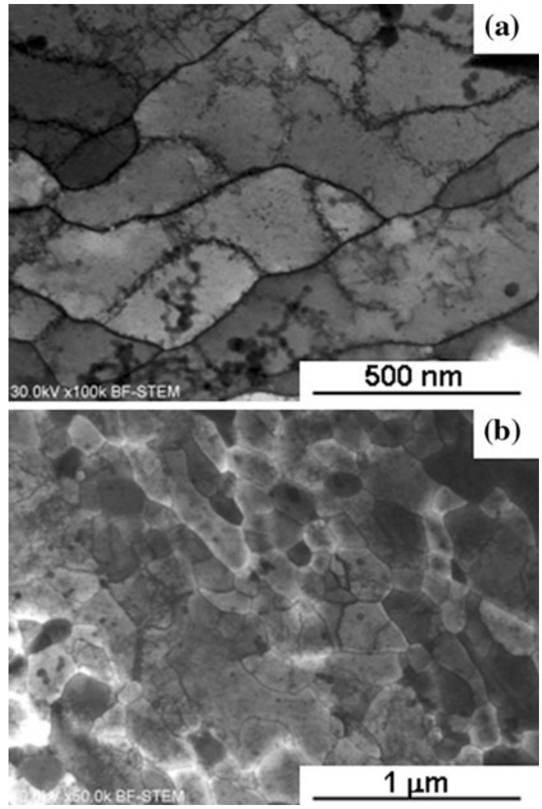

Fig. 3 Microstructures of SPD processed samples: (**a**) hydrostatic extrusion and (**b**) ECAP followed by HE

Table 3 Microstructural parameters of SPD processed samples in as-quenched state

Sample	$E(d)$	CV(d)	d_{max}/d
HE	200 nm	0.50	1.65
ECAP + HE	140 nm	0.36	1.32

In the case of ECAP/HE processing (Fig. 3b), a well-developed grain structure is observed with clearly outlined grain boundaries. The equiaxial grains are significantly smaller than dislocation cells formed as a result of HE—see Table 3, which lists the values of equivalent diameters of grain/cells, $E(d)$, their elongation factors for both HE and ECAP/HE microstructures.

It should be noted at this point that although during HE processing adiabatic heating takes place, in the case of CuCrZr alloy, the resulting temperature rise is estimated as being smaller than 250 °C, which is less than the temperature needed to induce precipitation phenomena in this alloy. It implies that strengthening effect of SPD processing is arising purely from grain refinement. This is supported by the microstructure observations, which give no evidence of precipitates in the SPD processed samples.

The results of microhardness measurements and tensile tests are shown in Table 4. Grain refinement, by SPD, leads

Table 4 Mechanical properties of SPD processed samples in as-quenched state

Sample	HV0.2	YS (MPa)	UTS (MPa)	ε_u (%)	ε_t (%)
HE	134	510	527	0.4	8.1
ECAP + HE	162	636	655	1.2	7.7

to a significant increase in the mechanical strength. Although the increase in strength is at the expense of ductility, the samples processed by ECAP/HE exhibit uniform elongation in tension of 1.2%, much higher than the ones processed only by HE (0.4%).

Synergy of grain size and precipitation strengthening

Ageing of SPD samples

The changes in microhardness as a function of ageing time at 480 °C for as-quenched sample and samples processed by HE and ECAP/HE are shown in Fig. 4. It can be concluded from the data presented in Fig. 4 that ageing of the HE processed samples results in a significant increase in microhardness with the maximum value of HV0.2 obtained after 1 h ageing. For longer ageing times, the microhardness decreases. This ageing characteristic is quite different from the one for un-deformed samples, in the case of which the maximum hardness is achieved after 2 h and the increase in microhardness is much higher than in the case of HE processed samples. The results also show that, quite surprisingly, in the case of ECAP/HE processed material post-processing ageing does not increase the microhardness.

The precipitates in HE and ECAP/HE processed samples subjected to 1 h ageing at 480 °C are illustrated in Fig. 5. In comparison to the precipitates in the coarse grained sample (see Fig. 2), their density in SPD samples is significantly lower and one should note formation of precipitation-free zones along the grain boundaries. These findings indicate that the precipitation in fine-grained structure proceeds along a different route, in particular, precipitating along the high density of the grain boundaries, which act as sinks for alloying elements and area of heterogeneous nucleation, is observed. It should be also noted that high density of the grain boundaries accelerates diffusion and in turn increases the growth of the precipitates.

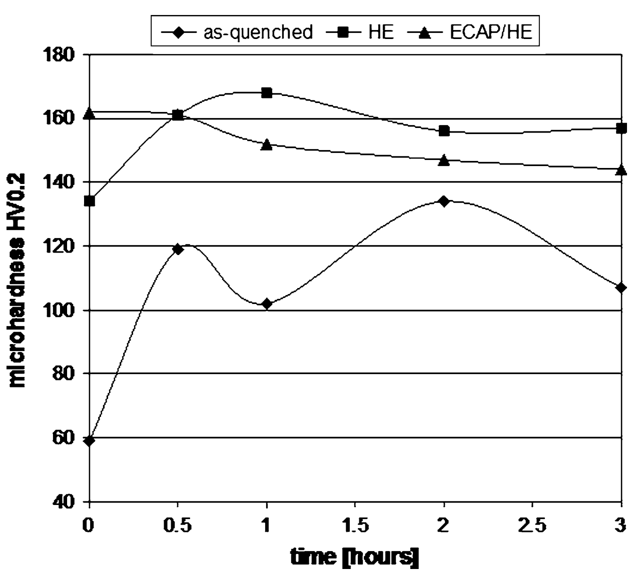

Fig. 4 Microhardness changes as a function of ageing time at a temperature of 480 °C

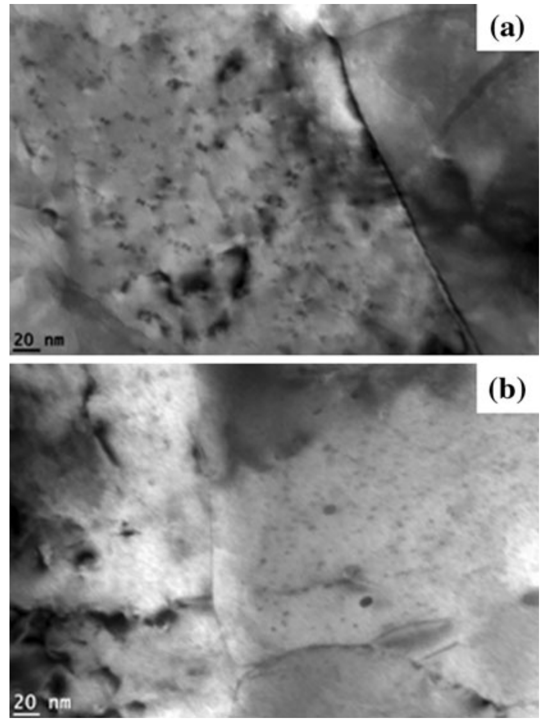

Fig. 5 Precipitates formed during ageing at 480 °C for 2 h in HE (**a**) and ECAP/HE (**b**) processed samples

The changes in the mechanical properties induced by post-SPD ageing result from two possible processes taking place concurrently: (i) formation of precipitates and (ii) grain growth. The results shown in Fig. 6 illustrate the changes in the grain size induced by the ageing of the SPD treated samples. For both SPD routes employed in this study, the grain size increases by ca. 100%, from nearly 200 to less than 400 nm. These values are still well below 1 µm and far below the initial grain size of 50 µm. Nevertheless, they cannot be neglected in the analysis of the mechanical properties.

SPD processing of samples aged prior to deformation

The microstructure of a sample aged at 480 °C for 2 h prior to HE is similar to that extruded immediately after quenching. It consists of elongated dislocation cells

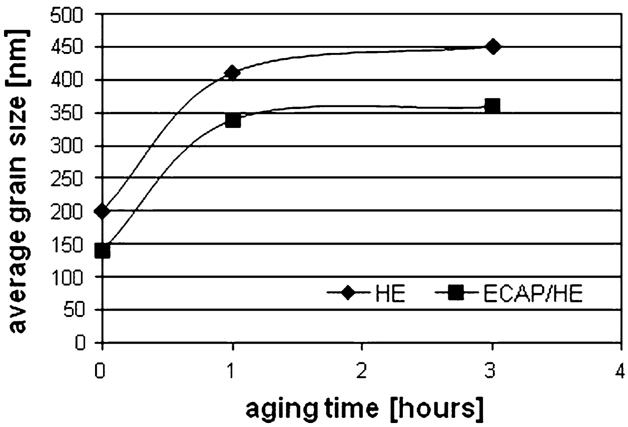

Fig. 6 Effect of ageing at 480 °C on the grain size of SPD processed samples

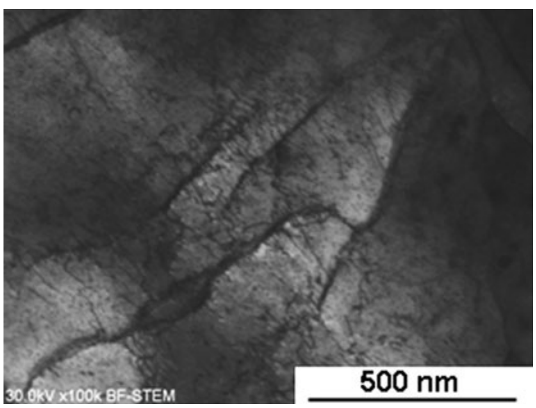

Fig. 7 Microstructure of a sample hydrostatically extruded after ageing at 480 °C for 2 h

(Fig. 7), which average size is 170 nm and elongation factor equals to 1.65. No significant changes in the size of the precipitates are observed before and after HE processing. The mechanical properties of the sample aged prior to HE are slightly better than those of samples extruded in as-quenched state (Table 5).

Discussion

The results obtained in the present study demonstrate that the mechanical properties of CuCrZr alloy can be effectively improved via both heat treatment (ageing) and SPD processing. The major strengthening factor in the former case is precipitation, whereas in the latter grain refinement plays a dominant role.

The major effort in this work was to combine these two strengthening mechanisms and discuss the possible synergic effects of grain refinement and precipitation. To this end, grain refinement and precipitation strengthening were combined in a series of experiments, which included SPD processing followed by ageing and SPD processing of samples aged prior to deformation. It should be noted that in both cases similar mechanical properties have been obtained. The microhardness of 165 HV0.2 was measured for the SPD processed sample after ageing, whereas 168 HV0.2 in the case of the samples aged after SPD processing. However, the samples differed significantly in terms of grain size, grain boundary character and distribution of precipitates. This suggests that the two strengthening mechanisms employed here are not additive and the reasons for that are given below.

In general, any two strengthening mechanisms are additive if, for a given deformation mechanism, they are fully independent. This also means that they take place at different locations in the microstructure of the material in question. An example of such a situation is the combination of solution strengthening, which increases the friction stress against the slip of dislocations in the grain interiors and grain boundary strengthening, related to the transfer of slip across the grain boundaries.

Under the assumption of additive character, the combined strengthening by grain size refinement and second phase particles could be described by adding the term accounting for the strengthening by particles to the friction stress in the well-known Hall–Petch relationship:

$$\sigma = \sigma_o + \sigma_p + k(d)^{-1/2}, \quad (1)$$

where σ_p stands for the strengthening by precipitation, σ_o the friction stress, d the average grain size, and k the constant.

However, the results obtained in the present study revealed that the strength of samples subjected to grain refinement and precipitation hardening is not a direct sum of the strengthening brought about by these two strengthening mechanisms acting alone. This suggests that the assumptions essential for additive character of the strengthening mechanisms are not fulfilled in the case of fine grained structures and the reasons for that are discussed below.

Table 5 Mechanical properties of SPD processed samples in aged state

Sample	HV0.2	YS (MPa)	UTS (MPa)	ε_u (%)	ε_t (%)
Ageing at 480 °C for 2 h + HE	165	611	691	0.7	8.5

Analysing the synergy of strengthening by the grain refinement and second phase particles, one should distinguish two locations of the latter: (a) at the grain boundaries and (b) in the grain interiors. Equation 1 is valid only under assumption that particles are uniformly distributed in the grain interiors. This is fully fulfilled for coarse grained precipitation hardened alloys [18]. However, this assumption is certainly not true in the case of CuCrZr aged after the SPD. The results obtained in the present study have shown that precipitation in SPD processed alloys proceeds in a different way comparing with their coarse grained counterparts. In particular, the grain boundaries act as sinks for alloying elements, accelerate the diffusion and stimulate heterogeneous precipitation. As a result, the distribution of precipitates is heterogeneous with precipitation-free zones being formed in the vicinity of the grain boundaries.

The precipitation-free zones at the grain boundaries significantly influence the mechanical properties of the material, which should be considered as a special type of composite with hard—precipitation strengthened—grain interiors enveloped by the relatively softer—precipitation-free—grain boundary phase. The macroscopic strain, in the early stages of plastic deformation, is likely to be predominantly accommodated in the precipitation-free phase. As a result, the effect of precipitation hardening is greatly reduced and in some cases σ_p term in the modified Hall–Petch relationship can be neglected.

It should be also noted that the strengthening due to the precipitates at the grain boundaries is far different from the one induced by the particles in the grain interiors. The influence of the grain boundary precipitates on plastic deformation is generally small, unless the grain boundary sliding makes a significant contribution to the accommodation of the applied strain (this matter is a subject of separate study). Such a situation does not take place in the case of samples investigated in the present study, however, should not be ruled for low-melting temperature nanometals [19].

It should be also noted that there is a reciprocal effect of the precipitates on the grain refinement. Small precipitates coherent with the matrix make the process of grain refinement more difficult, as reported for aluminium alloys [20–22]. On the other hand, large particles (usually primary inclusions) stimulate size reduction [22, 23], at least within the deformation zones around them.

The results obtained in the present study show that in the case of CuCrZr alloy, SPD processing after ageing brings about less developed grain structure and larger grain size. As a result, the strengthening by grain refinement is much smaller than in the case of SPD processing of as-quenched material. On the other hand, the SPD processing does not influence significantly the pre-existing precipitates and they significantly contribute to strengthening giving similar value of microhardness, as for the samples aged after SPD processing. It should be noted that there are literature reports revealing that such precipitates may dissolve during SPD [20] or are fragmented, with their shape becoming more equi-axed [24].

Conclusions

The synergic effects of precipitation hardening and grain refinement on mechanical properties of a CuCrZr alloy were investigated using samples subjected to SPD processing and ageing in various sequences. It has been revealed that ageing of micro-grained structure increases the yield strength of the alloy by 500%, whereas SPD processing by up to 1200%. It has been also shown that the strength of samples subjected to grain refinement and precipitation hardening is not a direct sum of the strengthening brought about by these two strengthening mechanisms acting alone. This is due to the fact that strengthening by grain boundaries and precipitates are inter-dependent at the processing stage.

The results presented in this article show that in analysing the prospects for combined grain size and precipitation strengthening in SPD alloys one should take into account such phenomena as formation of precipitation-free zones and different contributions of precipitates in grain interiors and at grain boundaries. This may imply the need for optimizing ageing conditions of SPD processed alloys. However, even for such optimized ageing, the assumption about additive nature of these two strengthening mechanisms is very likely to be incorrect.

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