Enhanced creep properties of copper and its alloys processed by ECAP

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Abstract. This work describes the effect of equal channel angular pressing (ECAP) on the microstructure and creep properties of pure copper and its two binary alloys with addition of small amounts of Zr or Co. The ECAP pressing was performed at room temperature by route Bc up to 12 passes using a die with an internal angle of 90° between the two parts of the channel. Ultrafine-grained (UFG) microstructure formed through ECAP process has been studied by methods of transmission electron microscopy (TEM) and scanning electron microscopy (SEM) equipped with the electron backscatter diffraction (EBSD) unit. Tensile creep tests were conducted in tension at temperature 673 K and at different applied stresses on ECAP material and, for comparison purposes, on un-pressed coarse-grained states of materials under investigation too. It was found that both alloys processed by ECAP exhibited similar character of creep behaviour. Creep resistance was markedly improved after first two ECAP passes in comparison with creep behaviour of un-pressed materials. The minimum creep rate of ECAP material may be up to two orders of magnitude lower than that of un-pressed material. However, subsequent ECAP passes lead to a decline of creep life and the difference in the minimum creep rate for the ECAP material and un-pressed state consistently decreases with increasing number of ECAP passes. Further, ECAP process led to significant improvements in fracture strain. The link between microstructural processes and creep behaviour of pressed copper and its selected alloys is examined in detail.

1. Introduction
Processing through the application of severe plastic deformation (SPD) is now accepted procedure for producing bulk ultrafine-grained sizes in submicrometer or nanometer range [1]. At the present time, equal-channel angular pressing (ECAP) is the most well developed of all potential SPD techniques for achieving ultrafine-grained (UFG) microstructure in bulk materials [1,2]. Depending upon the processing regimes, ECAP may influence the microstructure in a number of significant ways. Besides the introduction of a very high density of dislocations into the crystalline lattice, the high pressure involved in the processing may lead to the fragmentation and decohesion of precipitates. Unfortunately, UFG materials are not always stable at elevated temperature. The grain growth and recrystallization can be observed already at about 0.3Tm [3]. This is the reason why alloys are doped by precipitates which active block grain boundary movement. Our early works [4-7] carried out on pure Al and Cu proved enhancement of creep properties already after one ECAP pass only. However, the creep resistance of these materials decreases with the subsequent increasing number of ECAP passes. Nevertheless, some precipitate strengthened aluminium alloys showed the deterioration of creep resistance in comparison with their as-received states [8-10]. By contrast, recent investigation on the creep behaviour of a dispersion-strengthened Cu-0.2wt.%Zr alloy has shown [10-13] that the alloy after up to 4 ECAP passes exhibits a considerable improvement in the creep properties in comparison with the behaviour of the unprocessed alloy. Many experiments were conducted to evaluate the influence of ECAP on the magnetic properties of Cu-Co alloys [14]. Dilute alloys of the Cu–Co system are unique, since small Co precipitates are formed in the Cu matrix during aging. This system has therefore been investigated as a precipitation-hardening alloy [14,15]. In principle two microstructure forms of a Cu-2wt.%Co can be prepared: Solid solution state and precipitate hardened one [14-16]. However, in this work binary Cu-2wt.%Co alloy without precipitate
annealing was examined at first and this material was then compared with high purity Cu and precipitate strengthened Cu-0.2wt.%Zr alloy with an emphasis on the link between microstructure and creep. The temperature for the pure Cu is different from Cu alloys. The reason is that the creep behaviour of Cu is described in detail in our previous works [5-7], while this paper describes mainly the behaviour of Cu alloys.

2. Experimental materials

Materials used in this investigation were coarse-grained pure Cu, a precipitate strengthened Cu-0.2wt.%Zr alloy and a binary Cu-2wt.%Co alloy. These materials were processed by ECAP technique at the IPM AS CR Brno [17]. All of the ECAP processing was performed using billets with cross-section of 100 mm² and lengths of 70 mm. The ECAP pressing was conducted at room temperature using a die that had a 90° angle between the channels with a speed of 10 mm/min. The subsequent extrusion passes were performed by route Bc (a billet rotates by 90° in the same sense between subsequent passes) up to 12 passes. All billets were coated in MoS2 lubricant prior to pressing. Details of processing of pure Cu and precipitate strengthened Cu-0.2 wt.% Zr alloy was described earlier [7,12]. The Cu-2wt.%Co alloy was prepared by casting and subsequent heat treatment of ingot followed by hot rolling. Further heat treatment at 1273 K for 7 hours followed by water cooling was applied to obtain a homogenous structure in the state of supersaturated solid solution. Creep specimens were cut from the as-pressed billets with the gauge lengths parallel to the longitudinal axis. Flat tensile specimens had the gauge length of 10 mm and the cross-section of 12.8 mm². Constant load creep tests in tension were conducted at temperature of 573 K (Cu) and 673 K (Cu-2Co and Cu-0.2Zr alloys) under different values of the applied uniaxial stress. Creep tests were run up to the final fracture of the creep specimens. For each level of the applied stress the pressed specimens with 1, 2, 4, 8 and 12 ECAP passes and coarse-grain (CG) as-received state specimens were tested. Microstructural investigations were performed using transmission electron microscope Philips CM 12 and microscope TESCAN LYRA 3 XMU FEG/SEM/FIB scanning electron microscope equipped by EBSD unit.

3. Experimental results

3.1. Creep results

Representative creep curves for Cu-2Co alloy are shown in Fig. 1. All of these curves were obtained at temperature of 673 K (~0.5 T_M, T_M is the melting temperature) and at the applied tensile stress of 50 MPa. The creep testing was conducted on CG material and, for comparison purposes, on the same material additionally processed by ECAP method.

![Creep results](image)

Fig. 1 Different creep curves of Cu-2Co alloy for un-pressed state and various number of ECAP passes (creep in tension up to fracture): a) standard creep curves, b) creep rate dε/dt vs. time t, and c) creep strain ε vs. time t.
Standard creep curves ε vs. t show that highest creep life is achieved already after 1 ECAP pass and 2 ECAP passes and then further pressing leads to its lowering. After 4 ECAP passes, further dramatic decrease in time to fracture was observed, nevertheless, the creep resistance was still better in comparison with the CG alloy. However, after 8 and 12 ECAP passes is the time to fracture approximately similar as creep resistance of CG state. Standard ε vs. t creep curves can be easily replotted in the form of the instantaneous strain rate de/dt versus time or strain as shown in Fig. 1b,c. As demonstrated by figures, the minimum creep rate for the ECAP material is about one or two orders of magnitude less than that of CG material. The shapes of tensile creep curves for the ECAP material after high number of pressing differ considerably from the tests conducted at small number of the ECAP passes by the extent of individual stages of creep. Despite intensive straining by ECAP, the creep elongation of the pressed alloy is gradually improved with following ECAP passes.

It is important to note that with different numbers of ECAP passes there are differences in the creep results between investigated materials which is illustrated by Fig. 2. First, creep resistance is markedly improved already after 1 (Cu, Cu-Co alloy) and/or 2 ECAP passes (Cu-Zr alloy). The following passes lead to a significant reduction in creep resistance. The highest changes of creep behaviour occur during the first four (Cu, Cu-Co) or 8 (Cu-Zr) ECAP passes and the additional ECAP passes have only negligible effect on creep resistance of all studied materials. By contrast with CG state, pressed pure Cu has still much better creep life while Cu alloys having the same or even reduced creep life. Second, some differences in minimum creep rates of materials under investigation can be seen in Fig. 2b. While its value gradually increasing with increasing number of passes for Cu alloys, stationary state after four passes is achieved for pure Cu. Further, for all materials, the minimum creep rates for the pressed materials are higher after 4 ECAP passes in comparison with CG state. Finally, fracture strain is considerably increased by an application of ECAP.

![Fig. 2 Effect of number of ECAP passes on a) time to fracture, b) minimum creep rate, and c) strain for pure Cu, Cu-0.2Zr alloy and Cu-2Co alloy](image-url)

The determination of rate controlling mechanisms in high temperature creep depends on the ranges in testing temperature, stress and grain size as well as a careful assessment of the values for stress exponent and activation energy which are considered to be the important indicators of deformation mechanisms. Fig. 3 shows the logarithmic dependences of the minimum creep rate on the stress for CG materials and materials processed by 8 ECAP passes. The values of stress exponent of the creep rate n~6 determined at 573 K is approximately the same for both states of pure Cu (Fig. 3a). Similar value was determined for UFG state of Cu-Zr alloy (Fig. 3b). However, the stress exponent n for CG state is shifted towards higher values (n~9). Larger difference between exponents n was observed for Cu-2Co alloy. From Fig. 3c it is evident that minimum creep rates of CG state at lower stresses are markedly lower in comparison with UFG material. The opposite tendency can be seen at
higher stresses. Further, the slopes of both dependences are considerably different. The stress exponents for CG state \( n = 20 \) and for UFG alloy \( n = 3.3 \) were determined.

Fig. 3 Stress dependences of minimum creep rate for the CG state and UFG materials: a) Cu, b) Cu-0.2Zr alloy and c) Cu-2Co alloy

3.2. Microstructure after ECAP

Fig. 4a shows initial state of Cu-2Co alloy after solution annealing for 7 hours at 1273K. This microstructure is characterized by large equiaxed grains of no preferential orientation with an average size of structural elements above 1mm and numerous annealing twins. Both scanning and transmission electron microscopy (SEM and TEM) confirmed homogeneous coarse grained microstructure with low dislocation density and with all Co particles dissolved in the matrix. The size of structural elements is subsequently reduces down to the submicron level by application of ECAP process. A further comparison with pure Cu shows that the grain homogenization in the Cu-2Co solid solution is shifted towards higher number of ECAP passes [5,6]. First ECAP pass (Fig. 4b) leads to formation of grains but the microstructure still reflected its CG state. In this place there were measured about 6.5% of HAGBs. Significant changes in the size of structural elements as well as in the relative amount of high angle grain boundaries (HAGBs~27%) were observed after 4th ECAP passes. Orientation of structure is caused by deformation of the new equiaxed grains created on the previous ECAP pass. Microstructure is oriented to the shear plane of the last ECAP pass making an angle of approximately 30°. The final mean size of structural elements after 12 ECAP passes reached 0.5µm and population of HAGBs was about 43%. The slightly lower value of grain size was measured for Cu-0.2Zr alloy. Experiments on this alloy revealed that processing by ECAP reduced the size of structural elements from 350µm to ~ 0.4µm after only one ECAP pass and no dramatical reducing was observe with further ECAP pressing. Cu (purity 4N) processed in the same way [4] exhibited final size of structural elements about 0.6µm.

Fig. 4 Microstructure of Cu-2Co alloy: a) solid solution state, b) processed by 1 ECAP pass, c) processed by 4 ECAP passes and d) processed by 12 ECAP passes
3.3. Microstructure after creep
Creep properties of materials could be affected by microstructure instability at elevated temperatures. Fig. 5 shows the stability of size of structural elements during static annealing for Cu and its selected alloys. Low stability up to 473 K was observed for pure Cu. The growth of structure elements and the movement of the dislocations could be restricted by precipitates which stabilize the microstructure after ECAP pressing. The microstructure of Cu-0.2Zr alloy contains high number density of Zr precipitates [7,12]. In the Cu-2Co alloy precipitates were fully dissolved in the matrix. For both alloys, the average size of structural elements after 8 ECAP passes was reduced to ~ 400 nm and the microstructure was stable up to 673 K. The slight growth was revealed in Cu-2Co alloy. However, at higher temperatures the considerable growth of the structural elements was observed.

The EBSD analyses performed on the crept specimen processed by ECAP revealed scatter in the number of high angle grain boundaries (HAGBs). It was observed that with the increasing number of ECAP passes, a considerable amount of subgrain boundaries was gradually transformed to HAGBs as shown in Fig. 6. That transformation from LAGB to HAGB during ECAP and creep exposition is faster for Cu-2Co alloy, where majority fraction of HAGB is achieved already after 2 ECAP passes. For more, highest fraction of HAGB was measured already after 4 ECAP in case of Cu while for Cu alloys its value gradually growth with subsequent ECAP passes.

Fig. 5 The dependences of an average size of structural elements on the annealing temperature in Cu and its alloys.

Evolution of ECAP-ed microstructure during creep exposition is shown on Fig. 7. EBSD maps of samples processing by 2 ECAP passes and after creep at temperature 673 K and applied stress of 50 MPa revealed less homogeneous microstructure with areas of submicron grains next to areas with larger grains subdivided to LAGBs (Fig.7a). With following ECAP passes microstructure after creep becomes more homogeneous with occurrence of higher fraction of HAGBs (Fig. 7b,c). In all stages of preparation of the material was also observed the presence of large amounts of twin boundaries. The creep exposure led to an increase in grain size about one order of magnitude compared to the ECAP condition only. The same creep testing temperature did not lead to significant change in the size of structural elements for Cu-0.2Zr alloy. However, our previous work executed on pure Cu proved a significant grain growth.
after tensile creep test. The size of structural elements of about ~17 µm was evaluated after applied 8 ECAP passes and subsequent creep exposure at 573 K.

4. Discussion
The previous results showed that the creep behaviour of ECAP processed materials is influenced by thermal stability of the ultrafine-grained microstructure and strongly depends on the number of ECAP passes [3-12,18]. The resulting size of structural elements of Cu after creep exposure at temperature 573 K for 78 h is more than 4 times higher than the size of structural elements of the same material after annealing at the same temperature for 100 h (Fig. 5). Some works reported experimental evidences for the presence of high non-equilibrium grain boundaries in microstructure of UFG materials prepared by SPD [19]. Blum et al. [6] observed the dynamic coarsening of the grains in microstructure of ECAP pressed copper after creep. It was suggested that creep behaviour is controlled by storage and dynamic recovery of dislocations at HAGB [18-20]. The presence of large grains in the microstructure of UFG copper after creep test can be also the result of some kind of dynamic recrystallization. However from the present result it is not clear whether large grains observed in Cu alloys were formed by recrystallization and/or were inherited from ECAP microstructure. Static annealing and creep exposition proved a good stability precipitate strengthened Cu-0.2Zr alloy. The (sub)grain growth was effected by presence of dispersion precipitates which to some extent pinned the boundaries against their migration and restricted the movement of dislocation. Annealing of Cu-2Co alloy at the same temperature led to increasing of size of structural elements already after a short period of time and further coarsening during creep was observed as well. Dissolved precipitates probably do not require such active barrier against migration of grain boundaries which leads to static or/dynamic recrystallization. The occurrence of twin boundaries after creep may support this suggestion.

It was found, that the creep resistance of Cu and its alloys was considerably increased in comparison with the CG state already after first ECAP pass. However, successive ECAP pressing lead to a noticeable decrease in the creep properties. This softening may be related to the decrease of the spacing of HAGBs at approximately constant size of structural elements with increasing number of ECAP passes, resulting in the fraction of low-angle boundaries decreasing considerably. The softening by HAGBs may be explained in terms of the indirect effect which grain boundaries exert on the creep resistance by influencing the evolution of the dislocation microstructure in modifying the rates of generation and annihilation of
dislocations. Further, a progressively increasing contribution of GBS along HAGBs to overall creep strain can be expected as a consequence of accompanying transformation of LAGB towards an equilibrium state when the number of passes increases. Higher resistance of UFG Cu against its CG state is caused by combination larger grain size and lower fraction of HAGBs which limit GBS.

The results demonstrate that creep occurs in pure Cu after processing by ECAP by the same mechanism as in conventional CG material with intragranular dislocation glide and climb as the dominant rate-controlling deformation processes. Precipitate strengthened alloys are generally characterized by high value of stress exponent which is confirmed for Cu-0.2Zr alloy. The reduction of stress exponent n after 8 ECAP passes is probably the consequence of synergetic effect of sliding along mesoscopic shear bands created during ECAP and more intensive contribution of GBS. Some controversial result was obtained in case of Cu-2Co alloy. Stress exponent n for CG state reached the value close to 20. Latest TEM examinations proved occurrence of precipitate in materials processed by 8 ECAP passes and creep at temperature 673 K and stress of 30 MPa. This indicate that process of precipitation set in before (during heating to test temperature) or during creep exposition. However, to explain why processing by 8 ECAP passes reduced the value of stress exponent to n=3.3 is not clear so far and further creep tests and more detailed microstructure examination is needed. It should be noted that in our previous work similar value of n was obtained for binary Al-0.2Sc and Al-3Mg alloys with the similar size of structural elements [17,20]. Increasing fracturing elongation with increasing number of ECAP passes indicates that HAGB could increase the contribution of GBS to the total creep strain [10]. Our tests on Cu alloys did not prove expressive improvement of creep elongation such as in Al-0.2Sc alloy [17]. Examination of polished but un-etched surfaces of pressed and crept specimens of Cu-0.2Zr alloy revealed long mesoscopic shear bands exceeding considerably the average grain dimension [9]. Detailed observations of the mesoscopic shear plane by EBSD revealed, that the microstructure of mesoscopic shear bands is created by HAGBs. It is clear that such mesoscopic sliding can represent an important contribution to the creep strain. It is reasonable to assume that such mesoscale-banded structure may have important consequences for the fracture process in creep of Cu-2Co alloy as well. Indeed, cavities and microcracks nucleate along shear bands due to the development of the necessary high local stress concentrations after considerable amounts of mesoscopic sliding as a consequence of insufficient activity of accommodation processes.

In future work we will focus on the behaviour of Cu-2Co alloy in precipitate strengthened state preparing by static annealing at temperature in the range 773–973 K resulted in the precipitation of fine coherent Co particles. Nowadays three microstructure variant forms of this alloy were prepared (Fig. 8). This investigation could give us the answer about the role of Co precipitation in microstructure and its influence on creep behaviour of Cu-2Co alloy.

5. Summary

High purity copper and their Cu–2Co and Cu–0.2Zr alloys were processed by equal-channel angular pressing (ECAP) and then examined in terms of their microstructure and creep
properties. Creep behaviour is influenced by thermal stability of microstructure and its evolution during ECAP. The results show that highest resistance is achieved already after one ECAP pass. Subsequent ECAP passes lead to deterioration in creep life due to transformation of LAGB to HAGB one. It was found that homogenization and development of HAGBs are different for particular materials in dependence on number of ECAP passes. Microstructural investigations showed that a homogeneous microstructure together with a high fraction of high-angle grain boundaries leads to an increase in the creep ductility. The measured value of stress exponent $n \approx 6$ suggests an intragranular deformation mechanism as the rate-controlling process.

Acknowledgment: The authors acknowledge the financial support for this work provided by the Czech Science Foundation under the Grant No. P108/11/2260. This work was realized in CEITEC – Central European Institute of Technology with research infrastructure supported by the project CZ.1.05/1.1.00/02.0068 financed from European Regional Development Fund.

References
[1] Valiev R. Z. et al. Prog. Mater. Sci. 45 2000 103
[2] Furukawa M, Horita Z and Langdon T G Met. 2003 Mater. Int. 9 141
[3] Blum W, Li Y J, Durst K. 2009 57 17 Acta Materialia 5207
[4] Sklenicka V., Dvorak J., Svoboda M. Mat. Sci. Eng. A, 2004, vol. 387-389, p. 696-701.
[5] Dvorak J, et al. 2010 Rev. Adv. Mater. Sci. 25 225
[6] Blum W, Dvorak J, Kral P, Eisenlohr F, Sklenicka V 2014 Mater. Sci. Eng. A 590 423
[7] Blum W, Dvorak J, Kral P, Eisenlohr F, Sklenicka 2014 J Mater Sci. 49 2987
[8] Sklenicka V et al. Mater. Sci.Forum 2007 539-543 2904
[9] Sklenicka V et al. 2011 Mat. Sci. Forum 667-669 897
[10] Sklenicka V, Dvorak J, Kral, P, Svoboda M, Kopalova, M, Langdon T G 2012 Mat. Sci. Eng. A 558 403
[11] Kral P et al. 2012 Acta Physica Polonica A 122 457
[12] Dvorak J, Kral P, Kopalova M, Svoboda M, Sklenicka V 2011 Mat. Sci. Forum 667 821
[13] Dvorak J et al. 2013 Mat. Sci.Eng. A 584 103
[14] Fujita T, et al. 2006 Mat. Sci. Eng. A 417 149
[15] Lothian B W, Robinson A C, Sucksmith W 1958 Phil. Mag. 3 999
[16] Bursik J et al. 2014 Key Eng. Mater. 586 100
[17] Sklenicka V et al. 2012 In Zaki, Ahmad (ed.). Aluminium Alloys - New Trends in Fabrication and Applications. Rijeka : InTech. 3,
[18] Kawasaki I, Beyrlein I J, Vogel S C et al. 2008 Acta Materialia 56 2307
[19] Valiev, R Z, Ivanisenko Y V, Rauch E F, Baudelet B 1997 Acta Mater. 44 4705
[20] Dvorak J, Kral P, Kopalova M, Sklenicka V, Svoboda M Mechanical and creep behaviour of aluminium alloys processed by ECAP method 2007 In METAL. Ostrava : Tanger 96 22.05.2007-24.05.2007, CZ