ULTRAFINE GRAINED COPPER BY EQUAL CHANNEL ANGULAR EXTRUSION (ECAE) PROCESSING

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JEMNOZRNNÁ STRUKTURA MĚDI PO APLIKACI ECAE PROCESU

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Abstrakt

Měď o vysoké čistotě (99,99%) byla metodou ECAE protlačována při pokojové teplotě matrici s úhlem kanálů 105º. Vzorky byly analyzovány transmisní elektronovou mikroskopii (TEM). Analýza byla provedena po prvním, čtvrtém a 12 průchodu matricí. Mezi jednotlivými průchody bylo vzorky otáčeno o 90º ve stejném směru (cesta Bc). Po prvním protlačení, TEM ukázala subzrnitou strukturu, která byla protažená smykovou deformací. Výsledky získané optickou mikroskopií (OIM) zobrazují nehomogenní mikrostrukturu, kde jednotlivé vrstvy jsou rovněž seřazeny ve směru smykové deformace. Orientace mřížky se v materiálu cyklicky měnila. Dezorientace na hranicích zrn byla určena pomocí OIM a pohybovala se v rozmezí od 2 do 5º, v mikrostruktuře se nacházel i velký podíl subzrn. Po čtvrtém průchodu byla zjištěna jak TEM, tak i OIM shodná mikrostruktura. Podíl dezorientace hranic od 2 do 5º se snížil a byl doprovázen větším přesunem v distribuci. Nejčastější pozorovanou orientací byla typu ⟨111⟩ a inklinovala se směrem smyku. Následujícími průchody (až 12 ECAE) se velikost zrna snížela na hodnotu kolem 1,0 μm. Množství hranic s dezorientací (≥ 15 º) se zvýšilo. Charakteristika struktury Cu získaná smykovou deformací odpovídá kovům s KPC mřížkou, avšak orientace a jednotlivé složky se měnily s polohou. Zjemnění mikrostruktury vlivem velké plastické deformace je doprovázeno rozsáhlou frakmentací velkoúhlových hranic zrn.

Abstract

High-purity cooper (99.99 pct) was processed by equal channel angular pressing (ECAE) at room temperature through a die with a 105 deg angle between the die channels. Samples were examined by transmission electron microscopy (TEM) and orientation imaging microscopy (OIM) methods after one, four, and 12 passes through the die. Respetitively pressed samples were rotated by 90 deg in the same sense between successive pressing operations (route Bc). After one pressing, TEM showed a subgrain structure which was elongated in the shearing direction. Corresponding OIM data illustrated an inhomogeneous microstructure in which bandlike features were also aligned with the shearing direction. The lattice orientation varied

from location to location in the material. The boundary disorientation distribution determined from the OIM data exhibited a peak at 2 to 5 deg, in agreement with a predominance of subgrains in the microstructure. After four pressings, the microstructure data obtained by TEM and OIM were mutually consistent. The disorientation data revealed a decrease in the population of 2 to 5 deg boundaries accompanied by an overall upward shift in the distribution. Two orientations were generally apparent in the texture, although specific orientations varied with location. Often, ⟨111⟩ orientation tended to align with the shear direction. Following 12 ECA passes, the grain size was reduced further to about 1.0 μm. The populations of high-angle boundaries (≥ 15 deg) increased in the disorientation distribution. A texture characteristic of shear deformation of fcc metals became apparent, although the orientations and particular components varied with location. Microstructural refinement during severe straining includes the development of large fractions of high-angle boundaries.

Keywords: equal channel angular pressing, evolution structure Cu

1. Introduction

New forming technologies, to which the ECAE technology (Fig. 1) belongs as well, are focused on refining of grains by intensive plastic deformations. The objective consists in fabrication of structural metallic materials with ultra-fine grain with higher mechanical properties. These structures promise achievement higher mechanical properties in comparison with their coarse-grain equivalents. These concepts are based in particular on notion of validity of the Hall-Petch relationship $\sigma_f = \sigma_{o+} k.d^{-1/2}$ till the sphere of grains of nanometric dimensions. There were developed various methods for preparation of these materials, the principal issues consist in internal homogeneity of raw products, size of raw product, deformation behaviour and structure stability after deformations.

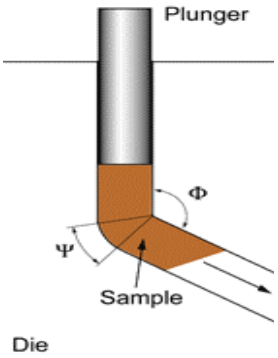


Fig.1 Diagram of ECAE processes

Another serious problem consists in increasing of resistance of fine-grain materials to growth of grain during its treatment at higher temperature or at re-heating to higher temperature, which is in many cases imperative for forming processes and for achievement of the required functional properties of products.

Fine-grain materials are the materials, the structure of which consists of components, which have at least one dimension within the range between 100 – 500 nm (these materials are

also called ultrafine-grain materials). From the viewpoint of strength properties these components can be represented by sub-grains,, grains, lamellas, layers, fibres, etc. For example lamellar pearlite can be considered as nano-composite material, which is formed by ferrite and cementite lamellas with width mostly below 100 nm. The value 100 nm does not have a physical meaning. The term ultrafine-grain material is used also for materials composed of particles below 1 micrometer.

Research of preparation of ultrafine-grain materials, investigation of their properties and possibilities of their practical application is oriented on large number of metals and their alloys. Research of technology of preparation and properties of steels with ultrafine-grain structure is of great importance. From the viewpoint of practical realisation the biggest attention is at present paid to alloys of aluminium, magnesium, copper and titanium. Our paper also deals with the issue of deformation behaviour and development of structure at the ECAE process.

2. Grain size and mechanical properties of ultrafine-grain materials

The fact that strength (hardness) of material increases with decreasing grain size in its structure was known from the early fifties of the last century, when famous Hall-Petch relationship was formulated

$$Re = \sigma_o + k.d^{-1/2} \tag{1}$$

where Re is yield value, σ_o is the stress necessary for overcoming of Peierls-Nabarr friction stress, resistance of dissolved foreign atoms, resistance of precipitates from solid solution and lattice defects, k is the constant, the measure of which is the value of shearing stress necessary for release of accumulated dislocations, d is the grain size.

It follows from the equation (1) that material yield value increases with decreasing grain size. This phenomenon is a driving force for research and development of high-strength structural materials, particularly of steels. It turns out that refining of grain can lead to increased drawability of metallic materials. On condition of identical strengthening mechanism refining of grains down to the level of nanometers can bring enormous increase in material strength.

It can be calculated that for grain sizes between 10 – 20 nm the yield value approaches the theoretical material strength.

Validity of the relationship (1) has been proved experimentally, with the exception of its validity for large grains and for very fine grains (approx. below 10 nm).

Fine-grain materials are characterised by high density of grain boundaries and other interfaces, which leads to a notion of validity of functioning of high-temperature deformation mechanisms respecting the role of grain boundaries into the zone of lower temperatures. For example at significantly lower homological temperatures the ultrafine-grain materials („nano-crystalline“) materials will be deformed by processes, which are controlled by diffusion along grain boundaries. There appears a possibility of production of plastic ceramics, super-plastic behaviour of metals at low temperatures, diffusion creep of pure copper at room temperature, etc. In the following part we discuss the most important mechanical properties of metals with ultrafine-grain and nano-crystalline structure, as well as mechanisms of processes, which determine them.

3. Strength properties

The basis of every deformation behaviour is kinetics of defects generation, their movement and annihilation. Micro-mechanisms, which respect lattice dislocations, dislocation at grain boundaries and vacancies, are of the utmost importance.

These defects can contribute to overall strength and plasticity independently or in a combined manner. Dominant mechanism can be identified by evaluation with use of strain rate, grain size and temperature dependence.

These three basic notions can be used for description of mechanical behaviour of ultrafine-grain materials:

- Hall-Petch relationship, in which dependence of flow stress on grain size at low temperatures comes from the manner of blocking of dislocations movement at grain boundaries.
- Mechanism of diffusion creep, which comprises movement of vacancies at gradient of applied stress.
- Mechanism of slips at grain boundaries, which comprises movement of all three defects mentioned above in dependence on specific micro- mechanisms.

In Hall-Petch relationship the values σ_o and k change in dependence on chemical composition of material, structure and technological processing. The constant k is temperature-independent, while σ_o increases significantly with decreasing temperature.

It was established that the Hall-Petch relationship is valid for various materials with the grain size of approximately down to 30 nm, after that the strength ceases to increase or it even drops. This is schematically shown in Fig. 2. In the area below the critical grain size d_c (G.B.Sliding) dislocation mechanism of deformation ceases to function. Several theories were developed for explanation of this phenomenon.

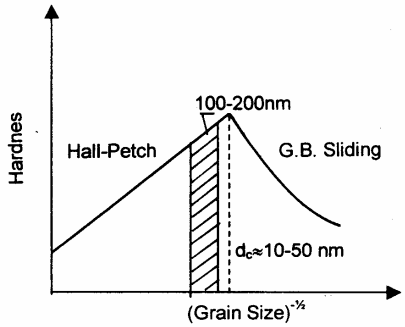


Fig.2 Dependence of strength on grain size in the area of nanometers [1]

If we summarise the findings mentioned above obtained from the Fig. 2, it means that material strength (hardness, yield value) increases with decreasing grain-size – till the area of nano-crystalline materials. Course of the curve in the area (Hall-Petch) in the Fig. 2 describes sufficiently well the Hall and Petch relationship. This fact is a driving force for research of technologies of production of massive nano-crystalline materials for structural purposes. In the area of critical grain size d_c (below approx. 10-50 nm) dislocation activity disappears and yield value (which is very high) becomes independent on grain size, and in some materials it even drops down. Mechanism of this phenomenon has not yet been unequivocally formulated.

4. Plastic and strength properties of ultrafine-grain materials

Plastic deformation at conventional forming methods can significantly increase strength of metals. This increase is usually accompanied by loss of ductility. This 3

phenomenon is illustrated in Fig. 3 as dependence of yield value on elongation at rupture for many coarse-grain pure metals.

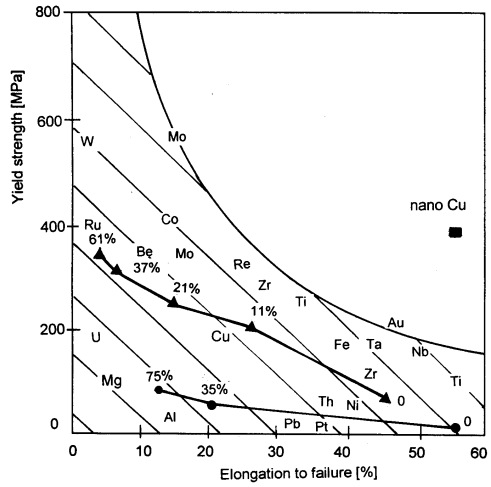


Fig.3 Dependence of strength on ductility for various metals processed by classical forming technologies and for Cu formed by the ECAE technology [2]

The figure shows two curves obtained by cold forming of samples made of Cu and Al. The data in percent values at individual points give the size of relative deformation of samples. The figure contains also the values for Cu samples with structure in nanometric dimensions. Cu sample was formed with use of the ECAE method, Fig. 3. Forming was made at room temperature. Grain size was approx. 150 nm [3]. When pressing Cu the established dependence was obtained after 12 passes [4]. Use of severe plastic deformation resulted in increased strength as well as drawability. This phenomenon was observed for the first time. It indicates change of deformation mechanism at forming with use of methods of severe plastic deformation (SPD).

5. Grain growth and temperature stability of structure

Nano-crystalline materials have due to small size of grains and large surface area a tendency to grain growth. Knowledge of temperature stability of nano-crystalline materials is important from theoretical and technological reasons. From technological point of view temperature stability is important as it eliminates coarsening of structure at super-plastic processing of metals and ceramics, or at compacting of nano-powders . From theoretical point of view it will be interesting to compare mechanism of grain growth in nano-crystalline materials and in coarse grain (conventional) materials.

Grain growth in conventional materials is described by the equation

$$\Delta D \ = D^n - D_o^n = K_o \exp\left(-\frac{Q}{RT}\right) \cdot \tau \qquad (2)$$

where D is grain size after annealing of sample at the temperature T during the time τ. D_o is the initial size of grain, n is exponent of grain growth, K_o is constant, Q jis activation energy of

grain growth and R is gas constant. Q and n are important parameters characterising kinetics and mechanism of grain growth. Exponent n is in an ideal case equal to 2, which presumes a parabolic course of grain growth. In nano-crystalline materials there were, however, observed the values from 2 to 10 [5, 6].

The value 2 is achieved only when annealing is made at comparatively high homological temperatures T/T_m (T_m is temperature of melting of investigated material). The factors, that could explain higher values of the exponent n, comprise segregation of dissolved substances at grain boundaries and blocking of grain boundaries.

Activation energy for grain growth in nano-crystalline materials (Q_n) is usually compared with activation energy either for voluminal diffusion (Q_v), or for pro diffusion at grain boundaries (Q_{gb}) of coarse grain materials.

It is usually more appropriate to compare Q_n rather with Q_{gb}, than with Q_v, although several exception were observed. It was also observed that the value Q_n of nano-crystalline Fe at the temperature exceeding 500 ^{o} C approached Q_v for coarse grain Fe, and at temperatures below 500^o C it approached more Q_{gb}, which indicates different mechanisms of grain growth. Big grain growth was found at annealing of nano-crystalline materials prepared with use of high plastic deformation or prepared by condensation of clusters and their consolidations.

6. Experimental verification of the ECAE technology on copper

Achievement of ultrafine-grain or nano-crystalline structure requires true (logarithmical) deformation of approx 6 – 8, and forming carried out at low homological temperatures [7]. The paper focuses only on preparation of ultrafine-grain Cu with use of severe plastic deformation, particularly with use of the ECAE technology, Fig. 1.

Magnitude of shearing strain after one pass can be determined from the relation:

$$\gamma = 2ctg\left(\frac{\Phi}{2}\right) \tag{3}$$

Total accumulated true deformation can be then calculated from the relation:

$$\varepsilon = \frac{2n}{\sqrt{3}} \cdot ctg\left(\frac{\Phi}{2}\right) \tag{4}$$

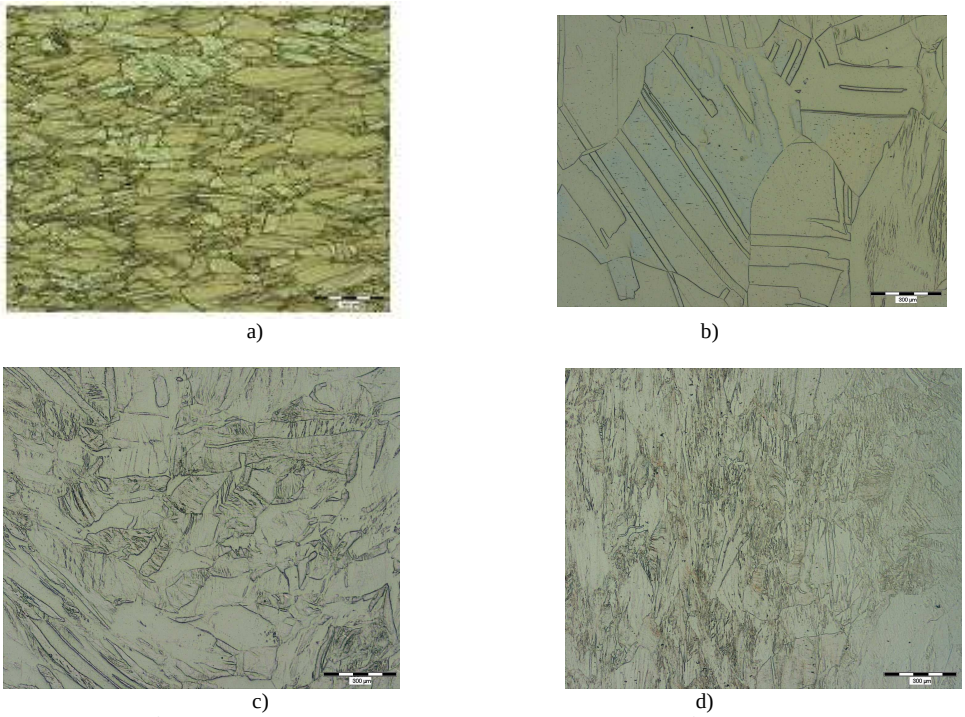
where *n* is number of passes.

The experiments were aimed at determination of extrusion force, pressure necessary in individual stages of extrusion, change of strength properties in dependence on number of extrusions and change of structure. Experiments were made on equipment, the possibilities of which were already presented [8, 9]. We have used for extrusion the copper grade in accordance with the Czech standard ČSN 42 3003. Original samples were processed by cold forming and they were afterwards annealed at temperature of 870 ^{o}C/3h [10]. Initial shape of the samples and shapes of samples after individual stages of extrusion are shown in Fig. 4.

Quadratic section of original samples was 8 x 8 mm. The samples were extruded at temperature of approx. 20 ^{o}C. In order to increase concentration of deformation in volume of the sample the samples were after individual passes turned around their longitudinal axis by 90^o and they were extruded again. The samples are ordered from the left to the right according to number of passes.

Fig.4 Copper samples after individual passes with use of the ECAE technology

We have measured at extrusion the deformation forces and we have also calculated the pressure needed for extrusion. We have approximately determined the strain rate, which was approx. 2,3 $.10^{-2}$ s^{-1} [11, 12]. Structure analysis was made by optical microscopy. Structure of original samples and that of samples after individual stages of extrusion is shown in Fig. 5.



a) b)

c) d)

Fig.5 Development of structure (in longitudinal direction) at ECAE processing of copper: a – initial structure , b – structure after the 1st extrusion, c – structure after the 2nd extrusion, d) structure after the 4th extrusion

Individual grains were elongated by main deformation in longitudinal direction. Average grain size in transverse direction was determined by quantitative metallographic methods and it varied around 50 μm at the beginning of extrusion, and around 15 μm at the end of extrusion, i.e. after the 4th pass [13-15]. HV hardness changed in dependence on number of passes through a die – see Fig. 6.

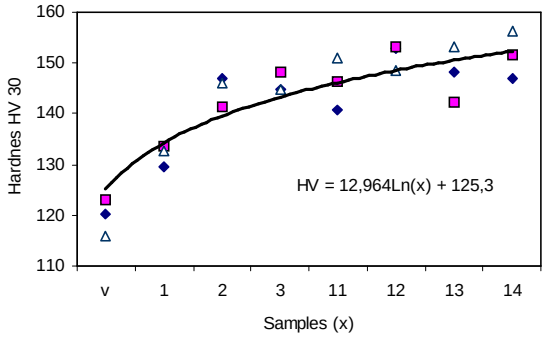


Fig.6 Hardness of individual samples after extrusion

7. Obtained results and their analysis

After individual passes there an accumulation of deformation strengthening has occurred, e.g. at extrusion with radius of rounding of inside cants (R = 0,5) the extrusion pressure at the beginning varied around τ_1 = 658 MPa. At the second extrusion it increased to τ_2 = 965 MPa, and at the third extrusion it increased to τ_3= 1188 MPa. Senderski established similar intensity of increase of pressure in dependence on number of extrusion when extruding aluminium alloys [16]. Increase in pressure at constant dimensions of samples corresponds to the increase if deformation resistance. Distinctively higher values of resistance to deformation and also strengthening at extrusion are related to high absolute value of octahedral stress [17].

8. Conclusion

1) Experiments made on poly-crystalline copper of the grade 42 3003 have confirmed that the ECAE method is efficient tool for refining of grain. This process enabled obtaining of grain size of matrix of approx. 15 μm.
2) Microstructure depends of experimental conditions, particularly on number of passes and on rotation of the sample between individual passes.
3) Convenient angle between horizontal and vertical part of extrusive channel is around 90°. Radii of rounding of working parts of extrusive channel must correspond to conditions for laminar flow of metal.

Acknowledgements

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