BRNO UNIVERSITY OF TECHNOLOGY

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ÚSTAV MATERIÁLOVÝCH VĚD A INŽENÝRSTVÍ

STRUCTURE AND MECHANICAL PROPERTIES BIODEGRADABLE Mg-3Zn-2Ca ALLOY PROCESSED BY ECAP

STRUKTURA A MECHANICKÉ VLASTNOSTI BIODEGRADABILNÍ HOŘČÍKOVÉ SLITINY Mg-3Zn-2Ca ZPRACOVANÉ METODOU ECAP

BACHELOR'S THESIS

BAKALÁŘSKÁ PRÁCE

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VEDOUCÍ PRÁCE

BRNO 2017

Zadání bakalářské práce

Ústav:	Ústav materiálových věd a inženýrství
Student:	**Štěpán-Adam Havlíček**
Studijní program:	Aplikované vědy v inženýrství
Studijní obor:	Materiálové inženýrství
Vedoucí práce:	**Ing. Pavel Doležal, Ph.D.**
Akademický rok:	2017/18

Ředitel ústavu Vám v souladu se zákonem č.111/1998 o vysokých školách a se Studijním a zkušebním řádem VUT v Brně určuje následující téma bakalářské práce:

Struktura a mechanické vlastnosti biodegradabilní hořčíkové slitiny Mg–3Zn–2Ca zpracované metodou ECAP

Stručná charakteristika problematiky úkolu:

Podstatou práce je návrh a zpracování nové biodegradabilní hořčíkové slitiny na bázi Mg–Zn–Ca metodou equal channel angular pressing (ECAP). Práce bude zaměřena na posouzení vlivu parametrů zpracování metodou ECAP na strukturně mechanické charakteristiky slitiny.

Cíle bakalářské práce:

Cílem práce je zpracování základního materiálu slitiny Mg–3Zn–2Ca metodou ECAP, posouzení vlivu metody a jednotlivých parametrů zpracování na dosaženou strukturu a základní napěťové a deformační charakteristiky.

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Termín odevzdání bakalářské práce je stanoven časovým plánem akademického roku 2017/18

V Brně, dne

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ABSTRACT

The present study focused on mechanical behavior and microstructure of biodegradable magnesium alloy Mg-3Zn-2Ca processed by equal channel angular pressing (ECAP). Each specimen differ by number of passes. Path of pass is Bc. Processed alloy exhibit improvement of stress and deformation characteristics, but with raising number of passes deformation characteristics starts to decrease underneath the value of unprocessed gravity cast alloy. Applied ECAP processing resulted refinement of grains, elongation in the direction of extrusion. The assessment of microstructure was performed by light microscopy and mechanical properties were determined by tensile tests.

KEYWORDS

Magnesium, biodegradable magnesium alloy, Mg-Zn-Ca, ECAP processing, mechanical properties, microstructure

ABSTRAKT

Zaměření této bakalářské práce je na mechanické vlastnosti a mikrostrukturu biodegradabilní hořčíkové slitiny Mg-3Zn-2Ca zpracované pomocí uhlového protlačování skrze shodné kanály (ECAP). Každý vzorek se liší počtem protlaku ve směru Bc. Zpracovaná hořčíková slitina ukazuje zlepšení napěťových a deformačních charakteristik, avšak s rostoucím počtem protlaků začínají klesat deformační charakteristiky. Aplikace ECAP metody způsobila v mikrostruktuře zjemnění zrn a ve směru protlačování prodloužení zrn. Ke studiu mikrostruktury bylo využito světelné mikroskopie a studium tahových vlastností bylo provedeno tahovými zkouškami.

KLIČOVÁ SLOVA

Hořčík, biodegradabilní hořčíková slitina, Mg-Zn-Ca, ECAP, mechanické vlastnosti, mikrostruktura

Havlíček, Š. STRUCTURE AND MECHANICAL PROPERTIES BIODEGRADABLE Mg-3Zn-2Ca ALLOY PROCESSED BY ECAP. Brno: Vysoké učení technické v Brně, Fakulta strojní, Ústav materiálového inženýrství, 2017. 35 s., 12 s. příloh. Bakalářská práce. Vedoucí práce: Ing. Pavel Doležal, Ph.D.

PROHLÁŠENÍ

Prohlašuji, že svou bakalářskou práci na téma Struktura a mechanické vlastnosti biodegradabilní hořčíkové slitiny Mg-3Zn-2Ca zpracované metodou ECAP jsem vypracoval samostatně pod vedením vedoucího bakalářské práce a s použitím odborné literatury a dalších informačních zdrojů, které jsou všechny citovány v práci a uvedeny v seznamu literatury na konci práce.

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V Brně dne ....

(podpis autora)

ACKNOWLEDGMENT

I would love to thanks to my supervisor Ing. Pavel Doležal, PhD for great advices in theoretical and practical field. Also great thanks belongs to my girlfriend and family.

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1. Introduction

Mg alloy has specific importance in non-metallic alloys. It's specific strength is lower than in other non-metallic alloys. Weight and good machinability makes from this alloy good opponent. Additional elements make great change in mechanical properties, microstructure and corrosion resistance, which is by the way quite bad for pure alloy. Such as Al, Zn, Cu, Ni, Th, Zr, Zn. Each doping preserves the best form Mg and ads the best from the element. Also there is number of disadvantages for application such as bad corrosion resistance as mentioned, bad formability in low temperatures, quite problem could be for this alloy classical type of welding, high reactivity with oxygen and last but not least low notched toughness [1]. The best thing is that the reaching price of pure magnesium is low. Similar alloys with less disadvantages are more expansive to harvest. This characteristics aren't good for application and one would say that applying this alloy is hazardous but we can enhance this material and apply it in fields where disadvantages turns to advantages. Mostly in areas in which isn't exposed to medium in which could lead to destruction. Noteworthy are industries: aeronautics, medicine, car and cosmic industry.

Appling ECAP means that UFG structure would undergo great deformation and this leads to improvement of mechanical properties. Also makes whole structure more homogeneous [2].

As it was mentioned before possible application could be medical application. Nowadays Ti alloys aren't as good as we would expect (don't interact well with body, have to be applied surface adjustment) and after surgical intervention need reparation or reopening of the operated person and remove implanted screws or plates or other used implanted components which were inserted in the body. This alloy offers chance for everybody to skip this reoperation and enjoy their healing process fully. This it possible because of biodegradability of this alloy [3]. Biodegradation of this alloy is good and bad in our body. For now, the speed of dissolving is too fast and the growth of bone is slower which causes exposure of naked impaired bone. And could lead to another injury. For solving this problem we have to look closely to microstructure and enhance it. Any interfaces to microstructure changes mechanical behavior. And Zhang Shaoxian presented enhanced alloy could resist longer. In spite this fact Asian scientist already experiment with Mg-3Zn-2Ca on rabbits. Results are already great [3]. But still not good enough for application to human body.

2. Thesis aims

Bachelors thesis aim is to process biodegradable Mg-3Zn-2Ca (2.5 - 3.5 wt% Zn and 1.5 – 2.5 wt% Ca, residue of Mg) and perform application of Equal channel angular pressing (ECAP). Path for repetitive extrusion was chosen Bc, even thou this path shows best transformation results for BCC crystal grid for one extrusion. Consider influence of this method and parameters of processing on the reached structure and stress and deformation characteristics.

3. Literary overview of the problem

3.1. Magnesium alloys

Magnesium as an element is silver glossy soft material with low temperature melting. One of the elements in second group in periodic table. Its high reactivity makes hard to find pure in the nature, mostly obtain in compounds for example magnezit ($MgCO3$), or see water (0,13%).

Crystal structure is tight hexagonal system. Because of its grid parameters $a = 0{,}32092\ nm$ and $c = 0{,}52105\ nm$ has its axial ratio $\frac{c}{a} = 1{,}1623\ nm$. This means that ideal axial ratio is quite near and this crystalic arrangement is the tightest one possible. Magnesium alloys are one of the construction materials. Without enhancing compounds it can be summarized as alloy with low strength, low elastic module, bad ductility in low temperatures, low corrosion endurance and high shrinkage of liquid during solidification Table 3.1. Even adding some elements wont enhance mechanical properties enough. Temperature of ignition deepens on the size of construction [4].

Table 3.1. Physical and chemical behavior of magnesium [4]:

Proton number	12
Atomic weight	24,3050
Density (in 20 °C)	1738 kg m^3
Melting temperature	650 °C
Boiling temperature	1107 °C
Volume change during solidification	4,2 %
Elasticity module	45 GPa
Heat	372 kJ kg^{-1}
Thermal conductivity (in 20 °C)	155 W m^{-1} K^{-1}

3.1.1. Effects of Zn on the microstructure and mechanical properties

Microstructure of Mg alloy after adding certain amount of Zn especially for example from the work of Zhang Shaoxian who used three types of processing for Mg-6Zn alloy [3]. Fig. 3.1.a) is showing as-cast alloy. The rood consist of α-phase matrix (gray one) and on the boundaries, there is precipitated γ-phase MgZn (Black one). However, after heat treatment the net of γ-phase MgZn is destroyed and Zn became part of α- matrix involved in grains. On Fig. 3.1.b) we can see a bit of dendrite grown through grain. In article by Zhank “Research on an Mg–Zn alloy as a degradable biomaterial,” was nothing said about cooling down process, and so we can only argue, if after heat treatment of gravity cast

Mg-6Zn was there microstructure dendrite or not [3]. Let’s have a look on the size of the grains after extrusion. Fig. 3.1.c) is a pic of heat-treated and then extruded, as it is possible to see the grain structure is much finer then as-cast and then extruded. Also, there is none bulk impurities which means that uniform microstructure was received in the sample Fig. 3.1.c). Disappearing of γ-phase MgZn enhance the mechanical properties.

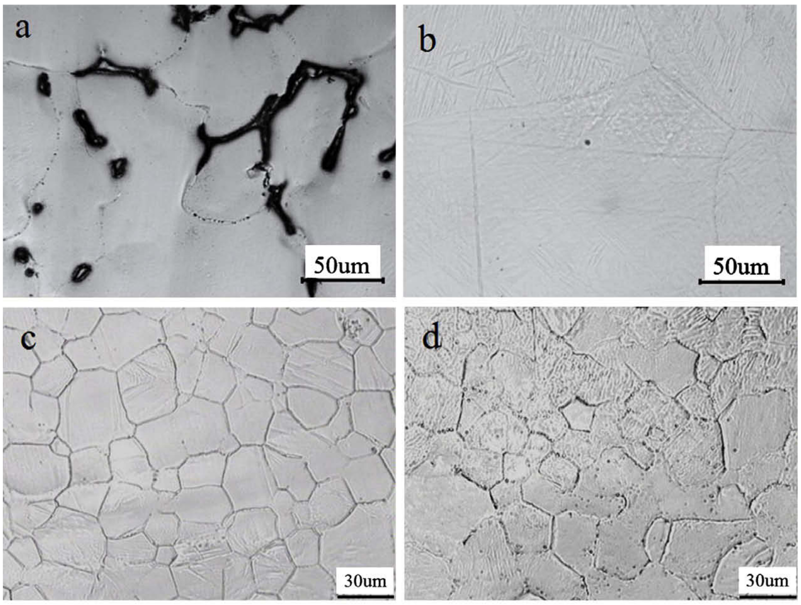

Fig. 3.1. Microstructure of a) as-cast, b) heat-treated, c) heat treated and then extruded Mg-6Zn and d) extruded pure Mg [3].

Mechanical properties of Mg alloy are enhance by adding pure Zn up to 7 %. Than the mechanical properties decrease. The tensile strength and modules, yield strength, elongation and compression strength of Mg-6Zn is shown in Table 3.2. There is also shown mechanical properties of binary alloy Mg-Ca [3,4]. If we compare them, we can notice that tensile strength is enhanced by adding of Zn. However the most rapid change of character undergoes compression strength, which is nearly doubled. Elongation of material in tensile test as it was expected is also doubled. In compare with Mg-Ca. That results shows that the size of the grain is important also as the network of the intermetallic phase. Theoretically if we dissolve the intermetallic phase network on grain boundaries and use extrusion then we can extract maximum of mechanical properties of Mg-6Zn alloy.

Table 3.2. Mechanical properties of extruded Mg-Zn alloy in compare with other possibilities:

Alloy	Module [GPa]	Yield strength [MPa]	Ultimate Tensile strength [MPa]	Elongation [%]	compression strength [MPa]
Mg-Zn [3]	42,3±0,1	169,5±3,6	279,5±2,3	18,8±0,8	433,7±1,4
Mg-3Ca [6]		110	239,63±7,21	10,63±0,64	273,2±6,1
Mg-Zn-Ca [7], 8]	36,5	89,8	101	8	269,8

3.1.2. Effects of Ca on the microstructure and mechanical properties

Microstructure of Mg-Ca alloy chiefly depend on mass percentage of calcium. Calcium form secondary phase network on grain boundaries. With higher mass ratio, grows the size of the network and primary phase α(Mg) starts form dendrite structure Fig. 3.2. This happens when Ca wt% cross 5 wt%. The reason for this is that, during solidification of the alloy α-Mg and small portion of Mg_2Ca as well is formed. With decreasing temperature, the affinity of Ca to Mg-alloy is lower and lower which leads to enriching the unsolidified melt by calcium. After the temperature of 517 °C, melt enriched by Ca undergoes eutectic reaction which produce α(Mg) and Mg_2Ca phase Fig. 3.2.

These two phases are produced around the grain boundaries. EDS results shows from work Hui Du tells us that lamellar phase formed on the grain boundaries are composed of Mg and Ca. And that confirms the theory that lamellar phase Mg_2Ca phase. The grain boundary is thick [6].

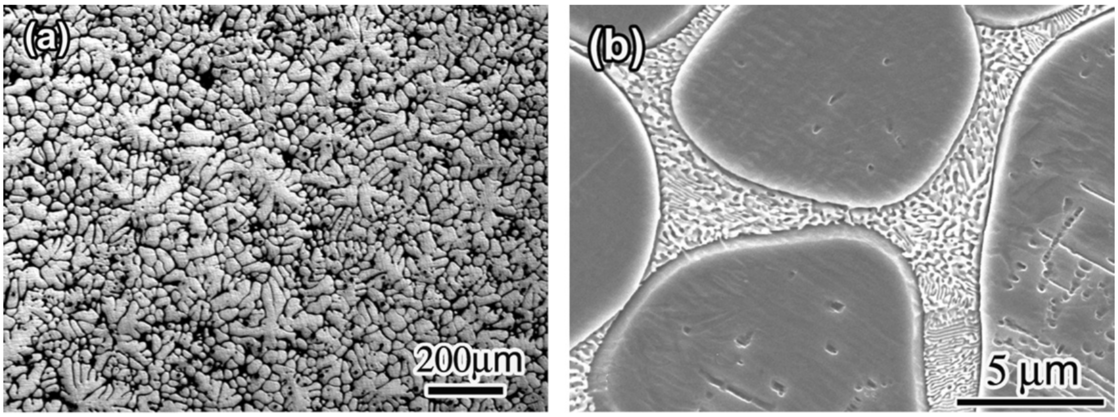

Fig. 3.2. a) Optical microscopy of Mg3Ca; b) SEM micrograph of Mg3Ca [6].

Mechanical properties won't be something wonderful shown in Fig. 3.3. The network of fragile secondary phase will be causing deterioration of yield stress and elongation. This problem is accepted because of great bioactivity of calcium. The best results were reached by with the Mg-Ca. He also applied several mechanical enhancing which lead to ameliorate of yield strength UTS and elongation. As we can see on Fig.3.3. It's obvious that as-extruded Mg-1Ca is by this graph recommended for processing.

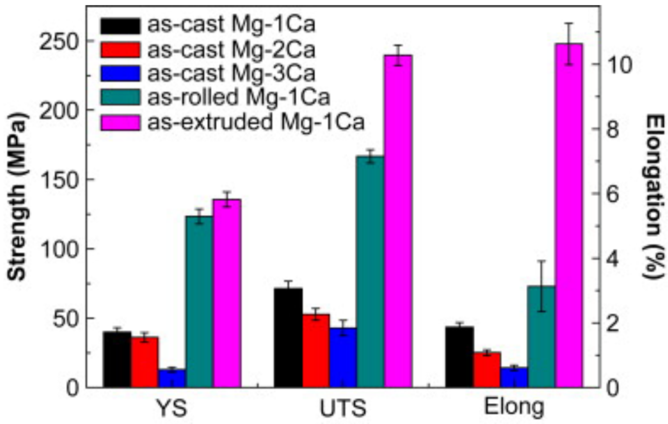

Fig. 3.3. Mechanical properties of Mg-xCa according to mass percentage of Ca and different elaboration [5].

3.1.3. Ternary alloy Mg-Zn-Ca

Microstructure of ternary alloy Mg-Zn-Ca consist of primary phase α(Mg) and two secondary phase differentiate by chemical character. First of them is Mg_2Ca and the second secondary phase $Ca_2Mg_6Zn_3$. On the Fig. 3.4. b) secondary phases are concentrated on the grain boundaries. By adding Zn to Mg-Cn alloy the only change in the microstructure is that $Ca_2Mg_6Zn_3$ is formed around the grain boundaries together with lamellar Mg_2Ca and α(Mg). Fig. 3.4. c) confirms by XRD that phases precipitated on the boundaries are really those which were mention before.

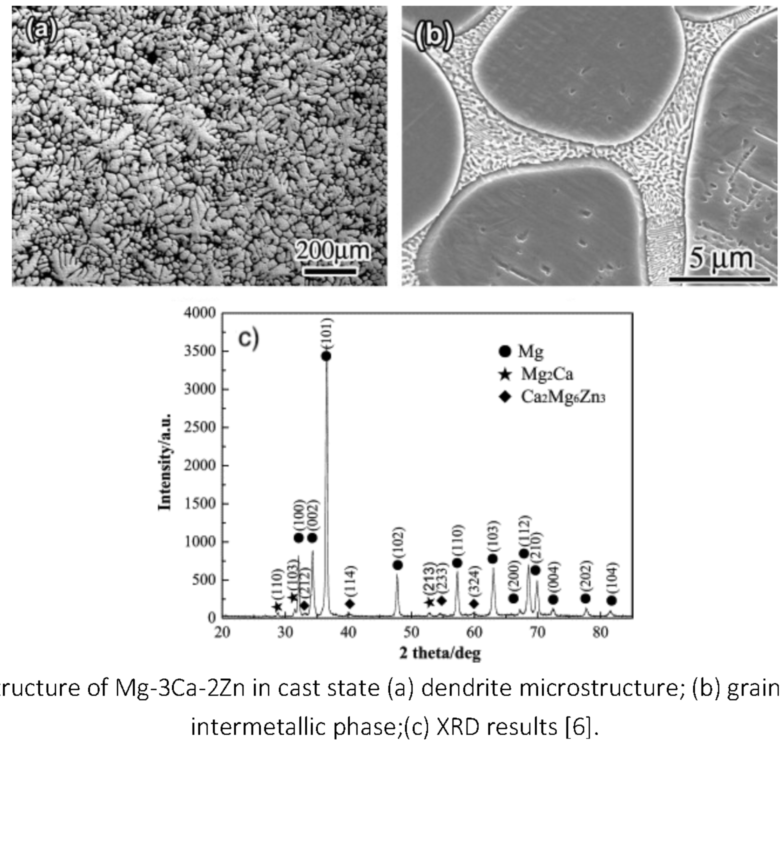

Fig. 3.4. Microstructure of Mg-3Ca-2Zn in cast state (a) dendrite microstructure; (b) grain boundaries with intermetallic phase;(c) XRD results [6].

In the Fig. 3.4. a) the typical dendrite microstructure can be observed in GC alloy. When the atomic ratio of Zn/Ca is more than 1.2 eutectic phases ($\alpha Mg+Ca_2Mg_6Zn_3$) are formed, however when the ratio is less than 1.2 eutectic ($\alpha(Mg)+Ca_2Mg_6Zn_3+Mg_2Ca$) phases precipitated. On Fig. 3.4.b) is shown eutectic phase with lower ratio than the 1.2. According to the XRD and EDS, it can determine that the deep color phase is Mg_2Ca and the bright is $Ca_2Mg_6Zn_3$ [6, 8].

The size of the primary grain is directly proportional to the amount of calcium contained in the alloy. Fig. 3.5. shows that the Mg-1Zn-0,2Ca obtain bigger grains than Mg- 1Zn- 0,5Ca. And the thermal pressing preserves that difference between sizes. However the reason for fine grain is because of dynamic recrystallization of the alloy. This means that new grains grow on the boundaries where were concentrated majority of dislocations. On Fig. 3.4. b) there is microstructure in which is basically possible to see by normal light microscope the intermetallic phase. Not like in Fig. 3.5. a) where the microstructure after thermal pressing spheroidized intermetallic phase and fine by half the grain size. Also big difference is that even electron microscopy isn't able to notch the intermetallic phases [9, 10].

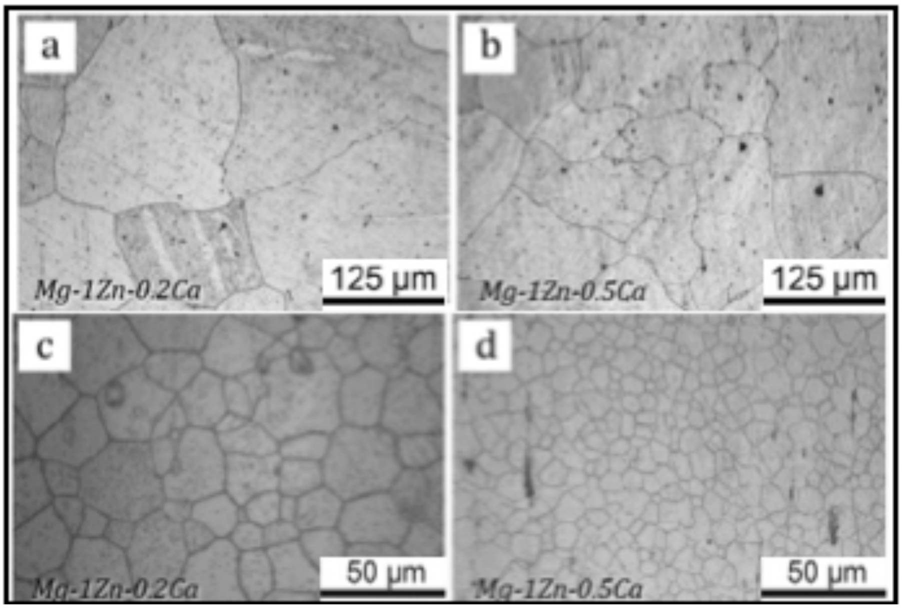

Fig. 3.5. Microstructure of Mg-1Zn-xCa (a, b)gravity cast; (c, d) gravity cast and thermal pressed [11].

Y. Wan confirmed is his article "Preparation and characterization of a new biomedical magnesium-calcium alloy," that by the XRD results in Fig. 3.6. where the peak of a) are lower than peaks of b) from Fig. 3.5. That means that XRD results for a) have corresponding value [10].

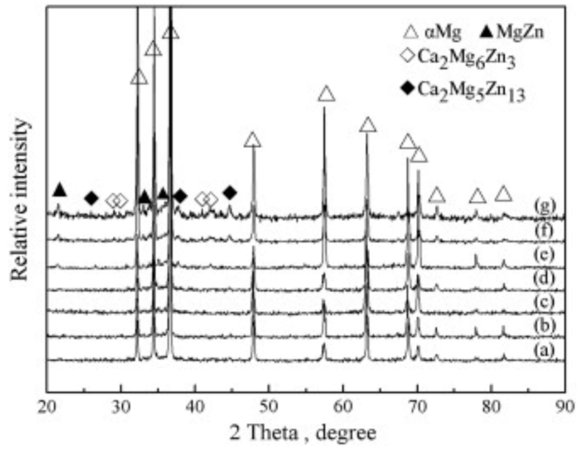

Fig. 3.6. XRD of intermetallic phase of Mg-Zn-Ca [1].

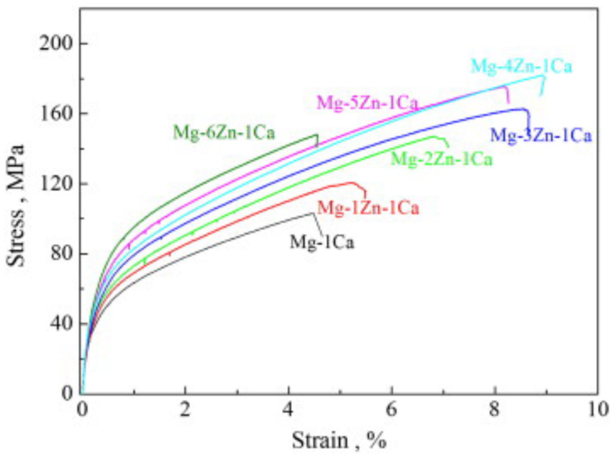

Fig. 3.7. Typical stress-strain curves of Mg-xZn-1Ca [1].

Mechanical characteristics of ternary alloy Mg-Zn-Ca is combination of characteristic of Mg-Zn and Mg-Ca. Conclusion from this means that different chemical composition could differ by different tensile curves Fig. 3.7. This means that calcium makes intermetallic phase around the boundaries and Zn enhance deformation characteristic [7]. Mechanical properties are rapidly influenced by heat treating or other type of processing. The reason why is obvious, that the network of intermetallic phase concentrated on grain boundaries is dissolved and α- Mg matrix is spheroidized and around this spheroidized matrix is concentrated intermetallic phase. This guarantee enhancing all mechanical properties. However higher amount of calcium ensures finer grains in compare with other alloys. And blocking dislocations, this event is connecting with growth of stress but leads to higher fragility [9, 10].

Fig. 3.8. shows ternary diagram of Mg-Zn-Ca. different chemical composition of material could cause formation of different phases. From this figure was confirmed that secondary phase which concentrate on the grain s boundaries were expected and could be reduced by changing of chemical composition.

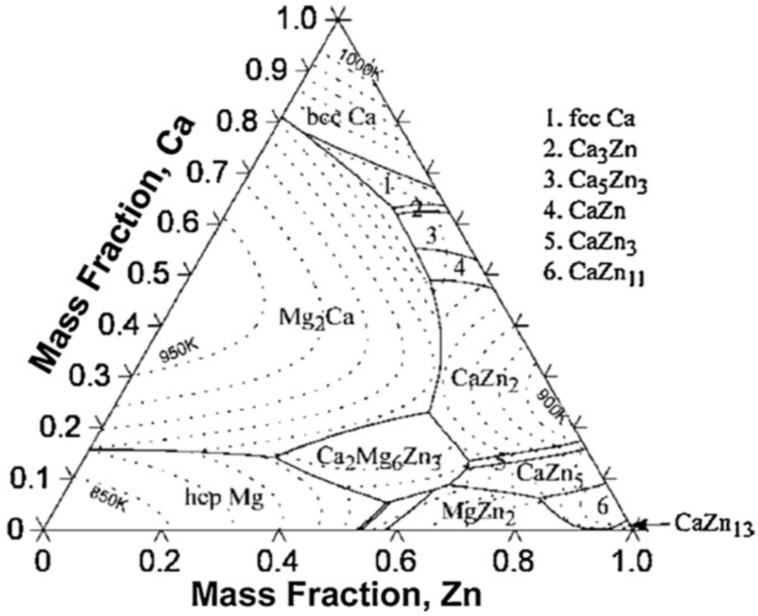

Fig. 3.8 Ternary diagram of Mg-Zn-Ca explanatory the phase concentration in Mg-3Zn-2Ca [6].

3.2. Equal channel angular pressing (ECAP)

3.2.1. Characteristics of the ECAP method

Was developed in 1960s by Russians. However, there was no use for this method. But by the improving and précising optical microscopy, scientist realized that, this method could be quite useful for processing ultrafine-grain microstructure.

This technique involves angular pressing through a die consisting of two geometrically equal channels connected in the certain angle Φ. This angle is major for shear transformation on basal planes. With the size of angle you can regulate intense of the plastic deformation. However the die is made with angel you ask for, you can't change the angel during the processing or between. For extrusion Mg-alloy is best to apply internal angle $\psi = 20°$ and external angle $\Phi = 90°$ [2].

In location of shear line occurs to slip deformation on basal planes. As it is shown on Fig. 3.9. the deformation on width of the sample will differ. Because each material path (1), (2), (3), don't flow through the shear line at the same time. This means that resulted deformation will differ in each path. That is cause by the angle and friction. Friction is really important for homogenous deformation though the width of the sample. That's why lubrication of the specimen is so important. The same goes for preheating temperatures and temperatures in the die. Which could influence importance of lubricant [2].

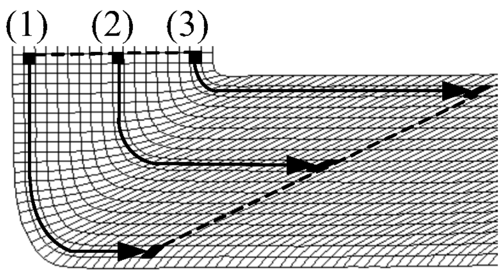

Fig. 3.9.Design of deformation in shear line [2].

ECAP as the method allows possibility of repeatable processing through die. Processed paths don't have to match with the previous one. For ECAP processing were developed four routes. Each of routes uses different slip system and strain value. Rout A is without any rotation of the billet, while rout C rotates billet after each passes for 180. B_A and B_C routes defers by opposite direction of the billet rotation for 90 ° Fig. 3.10.

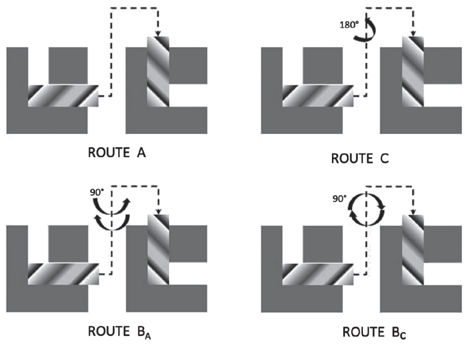

Fig. 3.10. basic routes for ECAP pressing [12].

3.2.2. Magnesium alloy processed by ECAP

Magnesium alloy as the part of grope with HCP lattice have problems with deformation in low temperatures. Before ECAP it have to be applied preheating for release more slip systems. Significant grain refinement is proving that fact that strong microstructure was changed and that's why yield stress and ductility is ameliorated. Nevertheless the processed texture depends on the deformation route. Main changes could be caused by direction and angle between each passes. ECAP leads to anisotropy in mechanical behavior and grain heterogeneous character. Twinning in whole sample is anisotropic. Final grain size depends on initial grain structure and strain imposed. The new grains of alpha Mg are formed along grain boundaries. If we continue in processing we would receive UFG structure in witch initial size of grains is much bigger than the final one as it is shown on Fig. 3.11. Also the same result could be reached by increasing of strain impose [13]. Same principle could be applied to any magnesium alloy processed by ECAP. For example AX41 processed by route Bc showed great promises in multiple passing's. Higher temperatures have to be applied. During tensile test alloys processed by Bc routes exhibits high tendency for activation basal slip systems.

Great grain refinement occurs after several passing's. The grain boundaries are concentration of deformation energy. This energy is used for nucleation of new grains and also for dissolving net of secondary intermetallic particles to smaller ones Fig. 3.11.

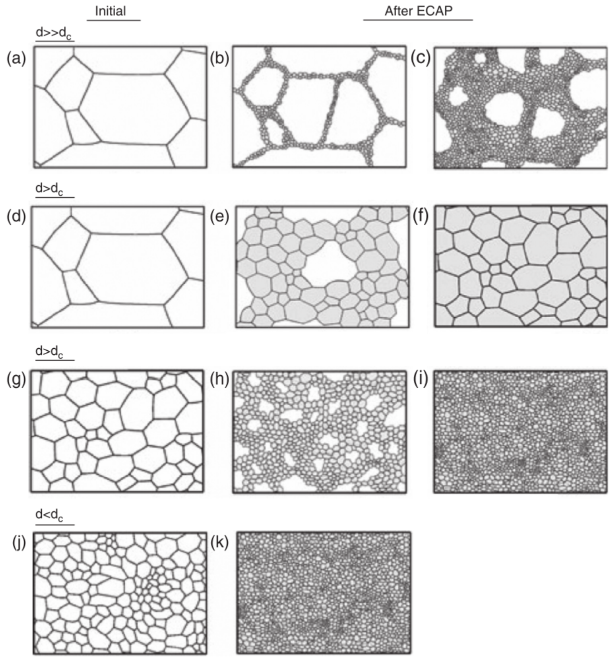

Fig. 3.11. Illustration of grain refinement mechanism of Mg alloy processed by ECAP. After applying multiple passing through ECAP die [14].

Table 3.3. Mechanical properties of Mg_6Zn alloy: yield stress, ultimate tensile strength and strain to fracture [14]:

	yield stress [MPa]	ultimate tensile strength [MPa]	strain to fracture [%]
ECAP at 200 °C [13]	58-82	152-210	8-10

Mg-Zn alloy processed by ECAP

In general the alfa-matrix of processed alloy features partial recrystallization and high deformation. Microstructure of processed Mg-Zn alloy reports that grain size is rapidly lower than in initial state and this theorem we can apply on any chemical concentration of Zn in Mg alloy. And also the quantity of $Mg_{21}Zn_{25}$ is lower than in initial state. Scientist M. Němec verified that Zn concentration is higher in proximity of $MgZn_2$ intermetallic particles and α(Mg) grain boundaries [15]. Mechanical properties after processing by ECAP reaches two times higher value than in initial state, Table 3.4. Volume of Zn in Mg alloy has influence on size of mechanical properties however ECAP approximately double the tensile strength, yield stress and ductility. But if there is need to reach best tensile test we have to keep volume of Zn under 7 wt%, that there is possibility getting maximum from this alloy, if we hold purity of alloy. Also M. Němec mentioned that multiple passes can increase corrosion resistance in Hamilton fluid and whole mechanical structure.

Table 3.4. Mechanical properties of Mg_6Zn alloy: yield stress, ultimate tensile strength and strain to fracture [15]:

	yield stress [MPa]	ultimate tensile strength [MPa]	strain to fracture [%]
GC [15]	75	290	26
ECAP [15]	302	314	19

Mg-Ca alloy processed by ECAP

Before applying equal channel angular pressing material shown great network of secondary phase with heterogeneous distribution. With the raising volume of calcium in the alloy precipitates are more stabilized. But after applying ECAP extrusion things changed. Network of secondary phase changes its character and homogenously spread through specimen. On refine grains boundaries were distributed spheroidized secondary phase. This led to enhance mechanical properties [16].

Mechanical properties were enhanced. Mostly because the size of grains was reduced, secondary phase concentrated on grain boundaries was dissolved. Deformation which was given to material by this method gives enough energy for spreading of dislocation. By the raising volume of deformation raise refinement. But behavior of magnesium under big deformation led to fragileness. It is caused by unappropriated deformation of lattice [17].

Mg-Zn-Ca ternary alloy processed by ECAP

First processing of the virgin (unprocessed) Mg-alloy by ECAP causes elongation grains surrounded by intermetallic phase (Mg_2Ca, $Ca_2Mg_6Zn_3$), before presented at the grain boundaries, which are oriented into extrusion direction Fig. 3.12. The average grain size of extruded Mg-Zn-Ca in direction of the extrusion is 84,3 ± 0,3 µm, size of grains in the perpendicular direction to the extrusion is 30,5 ± 2,6 µm. Which means that perpendicular direction, reached size of the grains is one third of grains in parallel direction [7]. Intermetallic phases are elongated in common with grains.

Table 3.5. Mechanical properties of yield stress, ultimate tensile strength and strain to fracture [7]:

	yield stress [MPa]	ultimate tensile strength [MPa]	strain to fracture [%]
GC	89,8	101,0	0,4
ECAP	166,1	206,4	1,1

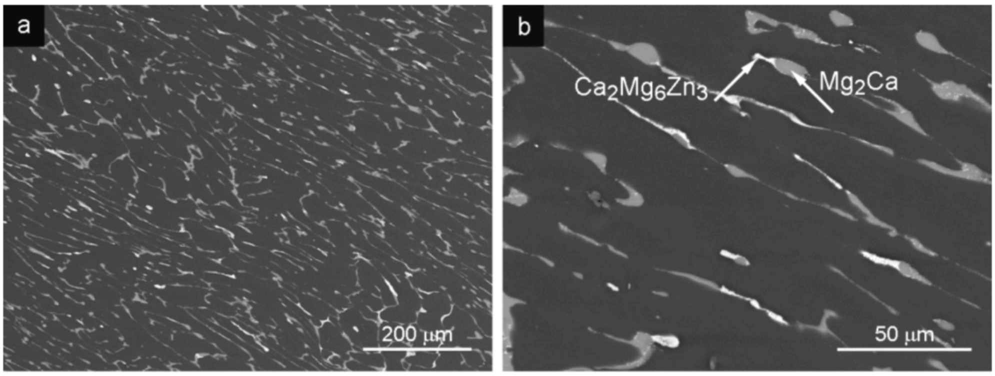

Fig. 3.12. a) Microstructure of the ECAPed alloy b) Microstructure after applying ECAP [7].

Chemical composition is not affected by pre heating of the material. Phases $Ca_2Mg_6Zn_3$ and Mg_2Ca are observed. What was there before stays there after processing. Preheating of the material has no effect on changing concentration of phases and elements dispersity.

Mechanical properties are enhanced, in result of the dissolving of intermetallic network which led to higher toughness with maintaining strength [18]. This can be observed in the Table 3.5. ECAPed alloy reported two times higher yield stress than GC (Gravity cast). The same pattern goes for ultimate tensile strength and for values of strain to fracture it's obvious that this method enhanced material three times. Values can be seen in the Table 3.5. Extruded magnesium alloy could deform by twining, because it's the only chance how to handle such mechanical force or by (0001) basal plane or other slip system if the material receive enough energy. Assuming that other option are out of table such as deformation by basal plane or material aster such deformation becomes fragile, also another possibility is to deform other direction than in basal, but it is elegiacally inefficient. In chapter about Magnesium was mentioned that the only possible plane for deformation is in (0001) plane but if the temperature raise than another plane is activated. And stress characteristics raise.

4. Experimental procedures

4.1. Default material

For experiment as a default material was used gravity cast Mg-3Zn-2Ca (2.5 - 3.5 wt% Zn and 1.5 – 2.5 wt% Ca, residue of Mg). Chemical composition of this alloy was determined by a few facts.

Calcium in small amount protects liquid from oxidation during casting and following thermal processing. Enhance rolling capacity of magnesium sheets and after exceedance of 0,3 wt% starts to make problem during welding. Added calcium to Mg-Zn refine the grains which lead to better formability and causes formation of secondary phase Mg2Ca on the grain boundaries.

Zinc one of the most added element after aluminum to magnesium alloy, enhance strength solid solution α(Mg) and up to 3wt% increase corrosion resistance. However zinc and calcium, if the circumstances are positive, ternary phase $Ca_2Mg_5Zn_{11}$ is formed. For preparation of Mg-alloy was chosen convenient method: as-cast to send form in VPCH-Kovohutě, s.r.o. v Čelakovicích. In a shape of cube 20 x 20120 mm. Surface of material wasn't modified.

4.2. *Applied experimental method*

Applied experimental method was Equal channel angular pressing. This method was done in room temperature 24 °C and in atmospheric pressure 1010,14 hPa.

The equal channel angular pressing was done on an NMT 3000 type machine (Rakovnické tvařecí stroje s.r.o., Rakovník, Czech Republic). Material was processed through a die of external angle 20 ° and internal angle 90 °, with preheating of the die up to 350 °C (temperature was changing during process) and processed with a speed of 4 mm*s^{-1}. From two up to eight passes were applied on the samples. Bc path was used for all samples. Used deformation force reached 3MN and size of the product was 20 x 20 x 120 mm from material Mg-3Zn-2Ca. For reaching optimal product it was necessary to apply back pressure in a size of 0,5 MPa. During the process did not appear problems with the method.

Preheating of samples was done on standardized laboratory furnace in Technical University of Ostrava. Pictures of microstructures were taken by light microscope OLYMPUS GX71, equipped with camera Olympus DP71. More detailed analyses was done by raster electron microscope Philips XL-30 with EDS detector EDAX. Basic mechanical characteristics were tested by machine Zwick Z250 by the norm ČSN EN ISO6892-1 [tensile (tah)]. For brushing and polishing as used standard equipment of Brno University of technology.

Mechanical properties were investigated by Zwick Z250 PC-controlled testing device (Zwick GmbH & Co.KG in Germany, Ulm, Germany) with an initial strain rate of $\varepsilon = 2.5 \times 10{-}4\ s^{-1}$ at room temperature (23 ± 2 °C). Tensile specimens were machined and tested according to the EN ISO 6892-1 standard. The gauge length and diameter of the cylindrical specimens were 25 mm and 5 mm, respectively. Tested samples were cut from the treated semi products so that the longitudinal sample axis was identical with the applied force direction in the manufacturing tool. The specimens for compression tests exhibited diameter and length of 8 mm and 12 mm.

4.3. Workflow and specimen preparation

Preheated block (20 x 20 x 120 mm) of Mg-Zn-Ca Fig. 4.1. on 120 °C for 30 minutes are put into Natrium lubricant for reduction of friction (delta forge F-578). The die is preheated for 300 – 350 °C and it is introduce in Fig. 4.2. b) 2. Than 20 cl of lubricant is put into the die. The specimen is pressed by the force of 3 MN by the thorn shown in Fig. 4.2. b) 1 and with back pressure of maximal value 5 bar. The back pressure was variable and moved in the interval of <4,8 - 5> bar. Extruded mate specimen was extruded out of channel shown in Fig 4.2. b) 3.

This process was repeated every single Equal channel angular pressing. With the small change. Bc route of processing was used for whole experiment without changes. Four specimen were prepared, each of them differ by the number of passes. Designation of specimen is in the Table 4.1. As we can see on Fig. 4.1a) processed cubes not every time coincide with dimensions of other specimen. Sometimes small part from specimen was separated. This led to material loss. With more passes , defects started to occur. The most frequent defect were laps. Peeling of the material was obvious immediately after extrusion. Peeled parts, which were possible to remove without any problems, were removed. Those parts weren't used I further processing.

Table 4.1. Specimen designation:

Specimen	Passes
F2	2 times
F4	4 times
F6	6 times
F8	8 times

From each specimen was removed lubricant by using alcoholic removal. Cutting each samples for strength test and SEM (in sizes necessary for preparing four 9 x 9 x 50 mm samples for strength test and for two smaller pieces 9 x 10 x 5 mm for SEM). Cutting was done by standardized cutter Struers 10S25 (36TRE).

After that it had to be decided if samples aren't degraded by lap, which could possibly debase tensile strength test. Laps occur immediately during cleaning from Natrium lubricant. At first, it look like it is only on the surface, but it wasn't the right idea. This laps occurred inside of the sample and show up immediately after cutting, as you can see on Fig. 4.1. c) This led to exclusion 81% of samples. On Fig. 4.1.c) we can see lap which occur on every extruded sample. Strength test were done on the Zwick Z250.

Specimen 9 x 10 x 5 mm for SEM were cut in half parallel direction of pressing Fig 4.1. Because than it can be observed more from formed structure and also be compered sizes of each formed phases. After that, each specimen, in size of 4 x 5 x 10 mm, was sealed to plastic.

Brushing of samples was done in the standard way. Abrasive papers very applied in this order 400, 1200, 4000 for 3 min. To make sure, that photos of microstructure are as sharp as possible, after each end of cycle whole machine was cleaned and then applied other abrasives. The same goes for polishing. Used polishing diamante pastas was used in this order 3, 1, ¼ um for 1 min. As a wetting agent was used DP-Lubricant Red, Struers, Depo 5320. Samples for tensile test and experimental test were prepared in a standard way.

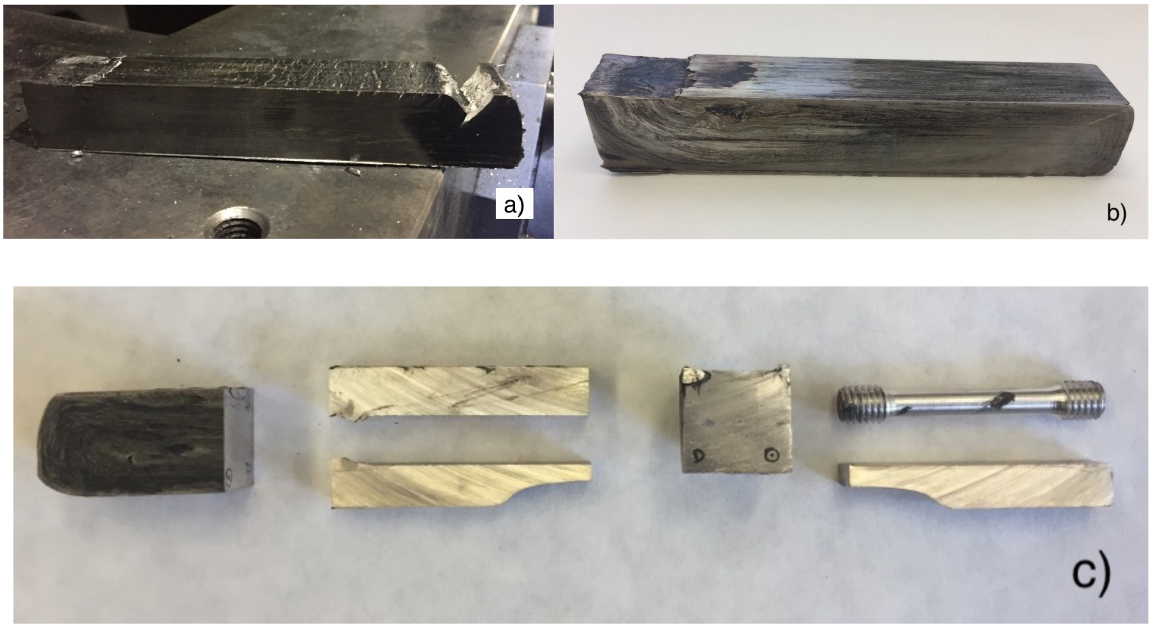

Fig. 4.1. samples: a) immediately after extrusion b) after removing lubricant c) processed, cleaned and cut 8 passes Mg-3Zn-2Ca with perceptible laps and defects.

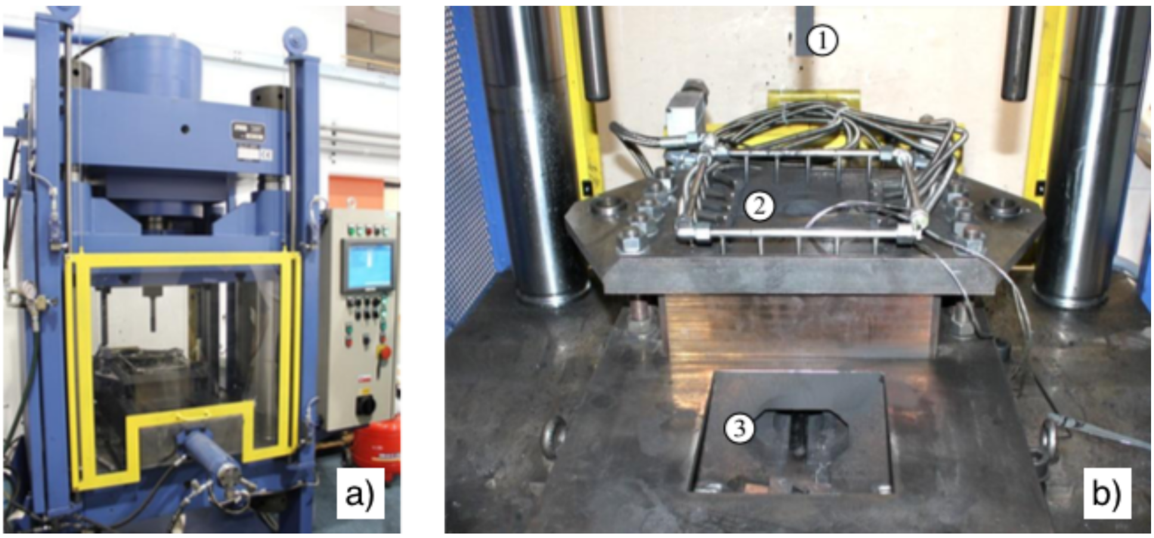

Fig. 4.2. Equal channel angular machine (ECAP) a) ECAP in starting position b) ECAP die.

4.4. Microstructure and mechanical properties of default material

Microstructure of default magnesium alloy consist of primary phase α(Mg) and two secondary intermetallic phases differentiate by chemical character and defects as microshrinkage and bubbles. In the primary phase α(Mg) and two secondary phases The first is Mg_2Ca and the second secondary intermetallic phase $Ca_2Mg_6Zn_3$. On the Fig. 4.2. Both secondary intermetallic phases are distributed on the grain boundaries. This makes from secondary intermetallic phase great net of In use of program Image J was done analytic counting of dispersity of these phases with result: 6 % of Mg_2Ca, 4 % of $Ca_2Mg_6Zn_3$, 90 % of α(Mg). As we can see in the annex 1. the typical dendrite microstructure is observed on as-cast alloy. Also this picture represents both direction of unprocessed specimen, longitudinal and transverse. Chemical composition of the specimen was determined by the work of Doležal, who in his work done XRD test. The average grain size of gravity cast magnesium alloy is 40,7 ± 5,9 μm.

Mechanical properties of unprocessed magnesium alloy were summarized in literary overview in bigger scale. Here is only summation of major characteristics. The yield strength and UTS reached under 100 MPa in reason to concentrated fragile intermetallic phase on the grain boundaries [7]. Elongation responds to ductile material [8].

4.5. Experimental results

4.5.1. Microstructure

With gaining number of passes by rout Bc shape of phases were changing rapidly. This claim confirms annex 1 and annex 2. Each extrusion caused shear deformation and every third extrusion canceled the first one. Despite that fact, there was enhancing length of the secondary phase. Also defects were affected, for us, positively. Defects size was reduced by introduced deformation. And that happened, because canceling the deformation has effect opposite then the first deformation and lead to repeated movement of shear line. If first deformation prolonged this defects, but did not break deformation as a whole in reason that have had enough energy, the third one canceling the first one brings to already prolonged defect enough energy to split one to two smaller defects. The same goes for each secondary phase Mg_2Ca and ternary phase $Ca_2Mg_5Zn_{11}$, if is it contained.

As it is possible to see in transverse direction of cut. Photos of samples shows reduction of width (Annex 2). And that has the effect on the size of secondary and ternary phases. Generally we can say that snap of F4 shows completely different structure than on the snap of F8. As suggested the team around mr. Doležal. Snap F4 contains heterogeneous structure with great differences in sizes between each grain: see Table 4.2. This could cause difference in mechanical behavior of alloy. However snap F8 shows homogeneous structure. For more imagining see annex 2. Sizes of grains are comparable to a certain extend. This rapid change of microstate could cause increasing behavior in tensile tests. Defects and secondary intermetallic phase are more globalized than in previous passes. Spheroidized phases aren't such concentrator of stress. Tensile curve grows and mechanical behavior gives alloy chance of more application Fig. 4.4.

As it can be observed in annex 1 microstructure of GC alloy Mg-3Zn-2Ca was rapidly changed even after two passes when compared with samples (annex 1). Net structure, which is so typical for gravity casted Mg- alloy (annex 1), was partially destroyed which means that secondary phase was in due to exhibition to high deformation homogenously distributed. The distribution depends on the value of deformation. Grains were prolonged as we can see on annex 1 and also we can observe created texture by creep.

Table 4.2. Grain sizes after extrusion:

	Transverse [μm]	Longitudinal [μm]
GC alloy	$40,7 \pm 5,9$	$40,7 \pm 5,9$
F2	$24,0 \pm 2,3$	$39,6 \pm 4$
F4	$14,8 \pm 3,8$	$61,5 \pm 5,1$
F6	$13,2 \pm 4,5$	$77,8 \pm 5,6$
F8	$8,1 \pm 4,1$	$18,6 \pm 7,3$

Gravity cast magnesium alloy shows promising chance to enhance the grain structure by ECAP. After two passes through die, sample shows reduction of size. The reduction happens mostly in transverse direction. The longitudinal direction is growing with the number of passes but sample F8 shows different results (Annex). Suddenly the longitudinal grain size drops to 11,4 μm. For comparison each number of passes see Table 4.2.

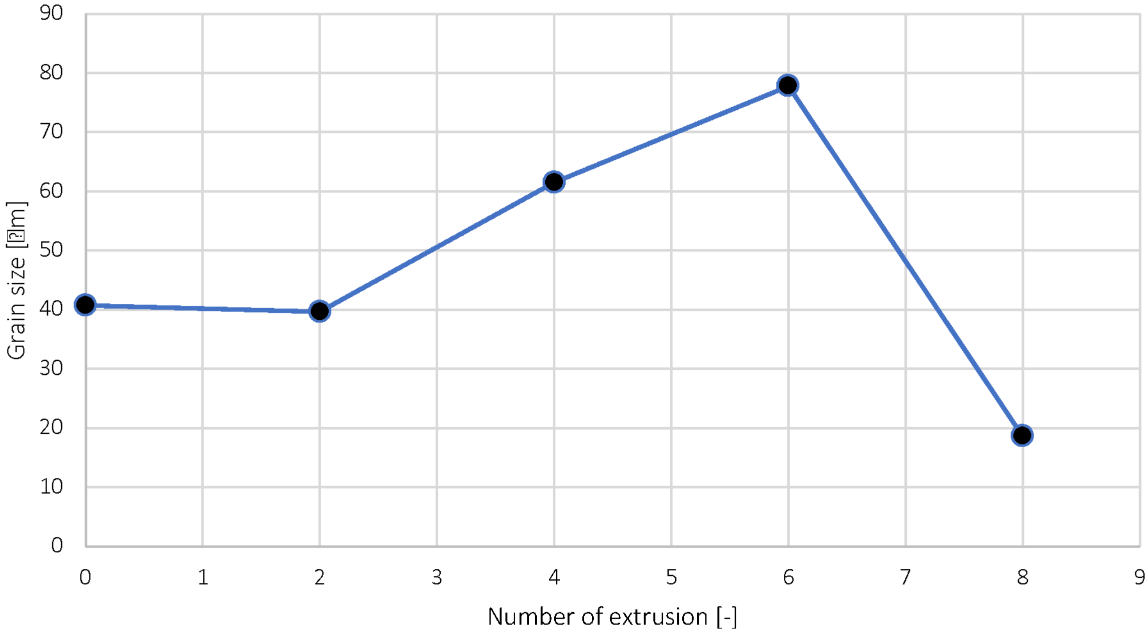

Fig. 4.3. Grain size of extruded Mg-3Zn-2Ca in the direction of extrusion, values from Table 4.2.

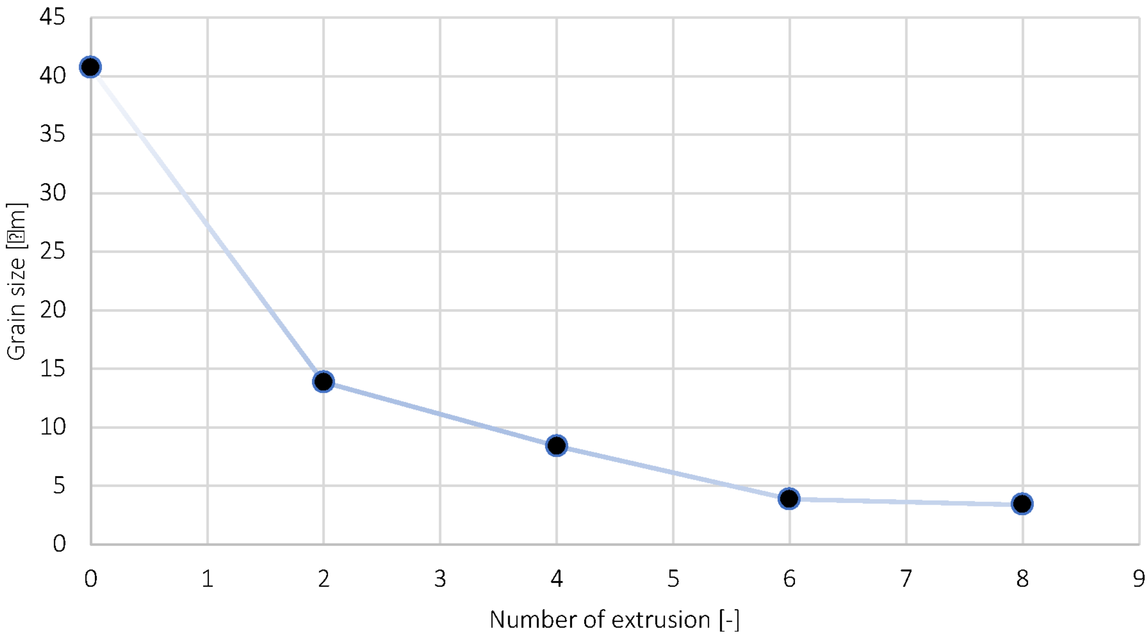

Fig. 4.4. Grain size of extruded Mg-3Zn-2Ca in the transverse direction to the extrusion values from Table 4.2.

From annex is obvious the tendencies of material after several number of equal channel angular pressing. Grain size in the direction of extrusion grows. However after 8th extrusion by rout Bc the extension is so big that the size of the gran boundary is no more energy advantageous (Annex 2). Deformation energy which is given in shear line to material is so big that it is enough for disruption of boundary and begins nucleation of new grain from the previous long one.

In transverse to direction is obvious that each pass through die is refinement of the previous refined grain. There is no change as in longitudinal direction. More refined grains means more mechanical barriers in distribution of dislocation. Dislocation concentrated in around grain boundary causes hardening of Mg-3Zn-2Ca. Homogenization of material raises as can be observed in annex 2.

4.5.2. Mechanical properties

True stress-strain curves recorded at room temperatures in tension are shown in Fig. 4.5. Characteristic values of yield stress, the ultimate tensile strength, strain to fracture are placed in Table 4.3. All Tensile test characteristics were estimated with the deviation of ± 5 %.

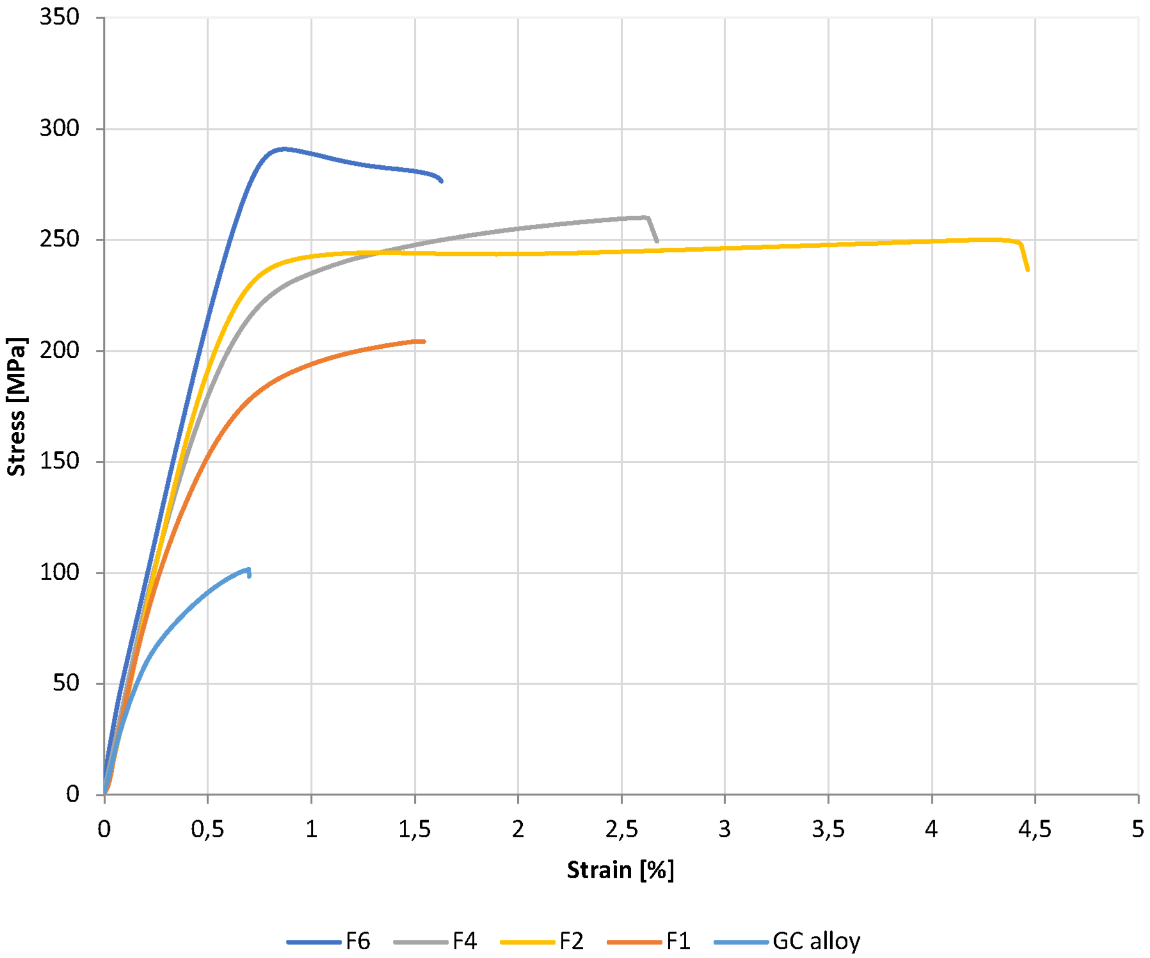

Fig. 4.5. True stress-strain curves obtained for ECAPed alloy and GC alloy.

The stress-strain curves of ECAPed alloy are introduced in Fig. 4.5. Significant differences was found between the yield stress of each specimen. Whole curves in diagram behaves more like fragile material that tough material with good plasticity. GC alloy reaches only 101 MPa of proof strength. The number of equal channel angular pressing makes great difference. F2 sample was extruded two times by path Bc. Sample was taken from the lower part of the specimen. For samples taken from upper part of material wasn't possible to measure tensile characteristics for a lot of defects. From the Table 4.3. and Fig. 4.5. is obvious that with the number of passes grows up ultimate strength, yield stress. Sample F2 reports great ductility and in the 240 MPa shows great stability till the fracture with forming small neck. In compare with the tensile curve with GC alloy it is obvious that toughness was enhanced. For sample F8 wasn't possible to perform mechanical test because of huge concentration of defect mostly occurred laps.

Table 4.3. Mechanical characteristics of the Mg-3Zn-2Ca alloy, E, proof strength, $R_{p0.2}$, ultimate tensile strength, R_m, elongation, A, contraction, Z:

Specimen ID	E	$R_{p0.2}$	R_m	A	Z
	[GPa]	[MPa]	[MPa]	[%]	[%]
GC alloy [7][8][18]	36,5	86	101	0,4	0,3
F1	40	162	204	1,1	2,8
F2	43	233	249	3,9	6,2
F4	40,1	218	260	2,1	4,8
F6	39,9	289	289	1	3,4
F8	-	-	-	-	-

Toughness was reduced by the number of passes after two passes. The biggest value of toughness reach sample F2. The smallest one value has GC alloy, which behave like fragile material. Elongation and contraction is Because of the intermetallic network of secondary phase. With small creation of neck after reaching ultimate tensile strength. Material Mg-Zn-Ca after ECAP behave like fragile material with small area of toughness but rising number of contraction after two passes through ECAP die. In reason that ultimate tensile strength isn't so obvious for each tensile curve in Fig. 4.5. I would rather chose for compering each passing proof strength as a defining characteristic of samples.

Highest value reached F6 with the value of 289 MPa. This amount of stress is four times more than proof strength of gravity cast alloy. Toughness of F4 has gone through a reduction in compare with F2.

If Table 4.2. and Table 4.3. is put together, it is obvious why there are such changes in mechanical behavior. Firstly, great grain change happened after equal channel angular pressing. Size of grains differs in direction to extrusion. In the direction to extrusion the grains are longer but in perpendicular direction to extrusion are smaller and their shape is round. So if the material is under great stress in the same direction as extrusion was done. Grains exposed great stress don't have chance to slip by the grain boundaries and also dislocation already concentrated in the grain itself won't let another taper of grain. The slip of grains is exhausted.

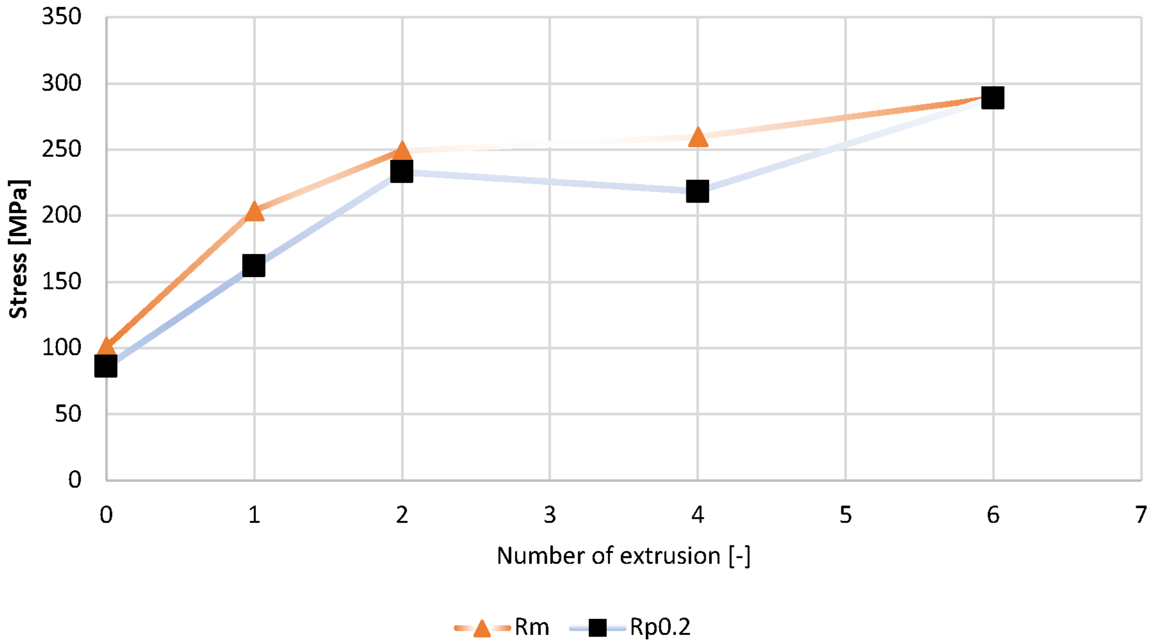

Fig. 4.6. Stress characteristics of Mg-3Zn-2Ca processed by ECAP.

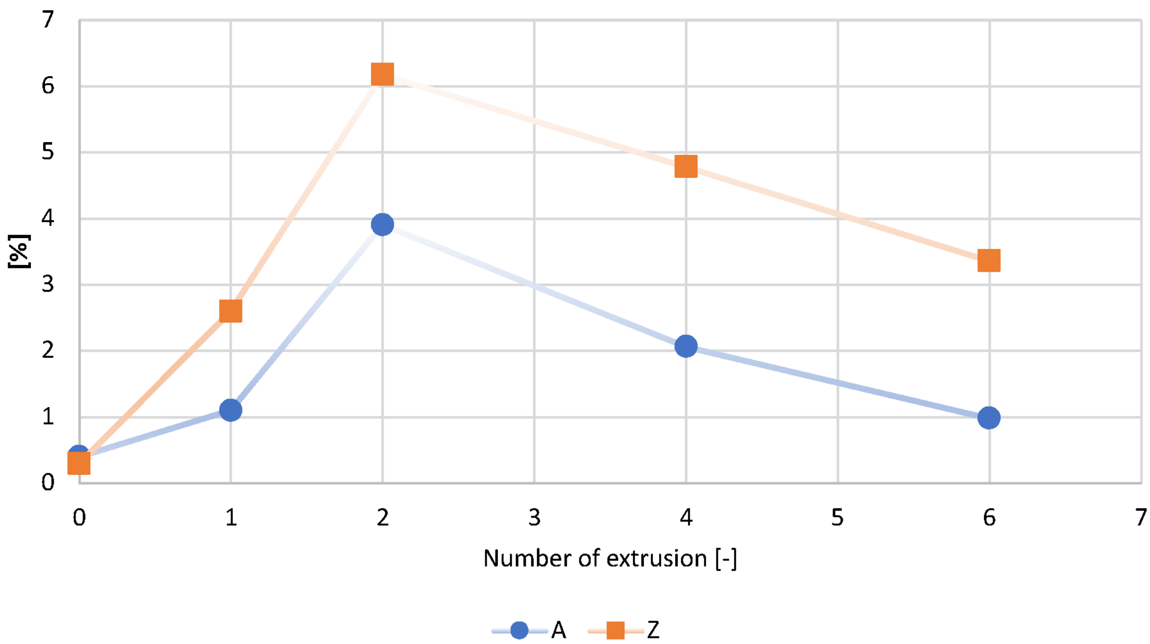

Fig. 4.7. Deformation characteristics of Mg-3Zn-2Ca processed by ECAP.

Deformation characteristics basically after first pass two enhance themselves this tendention continues to second passing. During fourth pass material shows decrease of deformation characteristics. That is basically caused by huge cumulation of dislocation implied to material during passing through equal channel angular pressing.

5. Discussion

Plastic deformation of HCP lattice is rapidly influenced by temperature. High temperatures gives enough energy to activate more slip planes and so the tensile strength reach smaller values. However the ductility raises with the temperature. Temperatures below room temperature causes low ductility and material starts to behave like fragile alloy. This behavior is unacceptable and so this alloy in this chemical composition is great for applying in areas where it is disposed to room temperatures or a bit higher, like human body.

The microstructure of Mg-3Zn-2Ca consist of alfa phase and secondary intermetallic phase particles Mg_2Ca and $Ca_2Mg_6Zn_3$ concentrated on grain boundaries. Grains are bounded by second phase with size of 40 μm. After extrusion by ECAP method was dissolved network of this phase and grains were elongated in direction of processing. Size in perpendicular direction to extrusion were decreasing by the number of passing. However size of grain in parallel direction to extrusion was raising till the number of eight passes, when the elongated grains reached the critical length and spheroidized. This led to extreme decrease of the size: see Table 4.2. and Annex 2 (with 8 passes). This issue occurs when the material is exposed to great plastic deformation during the process which gives enough energy to grain. The grain tries to have the smallest surface as possible.

Tensile test wasn't as successful as expected. 89% of samples have to be excluded in reason to defects. Main defect which occurred was lap. This caused several problems in experiments. From samples which survived till fraction was found that, number of passes fundamentally affects tensile curve. Mechanical properties raise with the number of passes (not elongation and contraction). After two passes the grain size is so refined that stress characteristics are doubled to GC alloy. Forth pass shows a small decrease to 218 MPa from 233 MPa. This could be caused by canceling deformation done by first extrusion. It happens every third extrusion and this means that than it's characteristic could much with the sample F2. 6^{th} pass by route Bc caused more deformation and enhanced UTS and proof stress to 289 MPa. Sample F8 have not pass thorough the quality control. After catting the specimen great laps in all specimen occurred. Ductility decrease with the growing number of passes. This means that from material which behaves in the room temperature toughly becomes fragile material: see Fig 4.6., Fig 4.8., Fig 4.7. The drop shown in Fig 4.8. is caused by premature fracture. Tensile specimen was defect. The lap defect was the reason for premature fracture. It wasn't discovered by quality control.

This rapid increase of tensile strength is caused by great grain refinement. Also with refinement of grains is connected increase of elongation. However main cause and source of premature time fracture was network of secondary phase. Dissolving this phase rapidly enhance every mechanical properties and also spreading homogenized sizes of this phases in material. With the raising number of passes the connectivity of second phase network was smaller and smaller and spheroidization resting secondary phase. When this phase is spread and homogenously distributed through the specimen, great enhancement on mechanical structure could be expected. Also main character in the material processed by ECAP is that the deformation rapidly changes with the distance from the upper and from bottom part of specimen. The deformation is better in upper part of specimen. That could be the reason concentrating of laps.

Defects in material which occurs in gravity cast state are after ECAP dissolved or reduced. It's sharp edges are spheroidized. Which means that this defects aren't such concentrators of stress as it used to be. Homogenization is also applied on this level. Microshrinkage or babbles are distributed along whole specimen in hand to hand with secondary phase.

Further investigation have to be done. Mostly because the laps which occurred during the process are source of a head of time fracture and also source of lubricant which is toxic to our body. And it would be applied to human body it have to be deprived of toxins. Also main problem which occurs during the experiment was that deformation would be expected in shear line and so it is, but depends of deformation differs with the distance to inner angle and outer angle. It is obvious, in spite the fact that in experiment haven't pass enough samples to reach verifying results, but the lower part is exposed lower deformation and also there is a problem of dead zone. Reaches better results in tensile strength than the upper part. This could be cause by higher number and bigger occurrence of defects in reason to exposing material higher deformation. So one question creates itself, that if we apply with smaller deformation but raise the number of passes could we reach higher mechanical properties without the risk of insertion of laps or other problems connected to ECAP.

6. Conclusion

The aim of this bachelor thesis was to specify changes in microstructure and mechanical properties of biodegradable alloy Mg-3Zn-2Ca processed by ECAP (Equal channel angular pressing. With raising number of passing through ECAP, raise disintegration of intermetallic network, amount of spheroidized intermetallic phase, extension of grains in extrusion direction, refinement in transverse direction to extrusion, spheronization of defects and also their refinement. Material became more and more homogeneous. Deformation characteristics are affected. Good ductile material became more fragile. In reason of exhaustion of plastic deformation and great concentration of dislocation mostly twins in matrix. Ductility is decreasing.

- The gravity cast alloy microstructure was dendritic with great intermetallic structure of Mg_2Ca and $Ca_2Mg_6Zn_3$. Concentrated on the grain boundaries. It caused non-use potentials of the alloy. For reduction of this characteristic, ECAP method was designed.
- After application of ECAP secondary intermetallic phase dissolve in α(Mg) matrix and concentrates in islands. Microstructure after two passes extruded by rout Bc reports preservation of the grain size in one direction (longitudinal) but in the transverse direction is the size downsize to 13,9 μm. Continuity of intermetallic phase network is disturbed by not dissolved. Elongation is observed in the direction of extrusion.
- Stress characteristic raise but after two processing ductility decrease till that time deformation characteristics grows.
- Sample after four passes shows bigger elongation in the direction of extrusion and decrease of grain size in transverse direction. Network of intermetallic phase is more disturbed but not homogeneously distributed in specimen.
- Stress and deformation characteristics a bit decrease. UTS in compare to sample after two passes is lower than for sample after four passes. That is caused by the canceling of the deformation every third passing. Material returns back to state after first pass.
- Six passes through die of ECAP refine material to such extend that it is still possible to observe texture caused by ECAP method. Size of grains grows in the extrusion direction but in transverse direction, Mg-alloy starts to spheroidized.
- Mechanical properties such as UTS, proof stress grow to 289 MPa. Ductility decrease. This great mechanical changes are caused by hardening texture and substantial grain size reduction.
- Microstructure of sample after 8^{th} ECAP shows huge homogenization of structure, spheronization of secondary phase. Elongated grains dissolves to smaller size grains in reason of instability of boundary.

- Deformation characteristics are affected. Good ductile material became fragile. In reason to exhaustion of plastic deformation and great concentration of dislocation mostly twins. Ductility grows and reaches maximum in second pass through ECAP than start to decrease and remain in this tendention
- Because of the huge concentration of laps haven’t passed through quality control 89 % of specimen.

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8. Glossary of all used terms and acronyms

Acronyms	Meaning
A	ductility [%]
Z	contraction [%]
E	elastic module [GPa]
ECAP	equal channel angular pressing
R_m	yield strength [MPa]
$R_{p0,2}$	proof strength [MPa]
SEM	scanning electron microscopy
SM	optical microscopy
XRD	X-Ray diffraction
GC	gravity cast

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Annex 1

Metallographic evaluation of gravity cast alloy Mg3Zn-2Ca

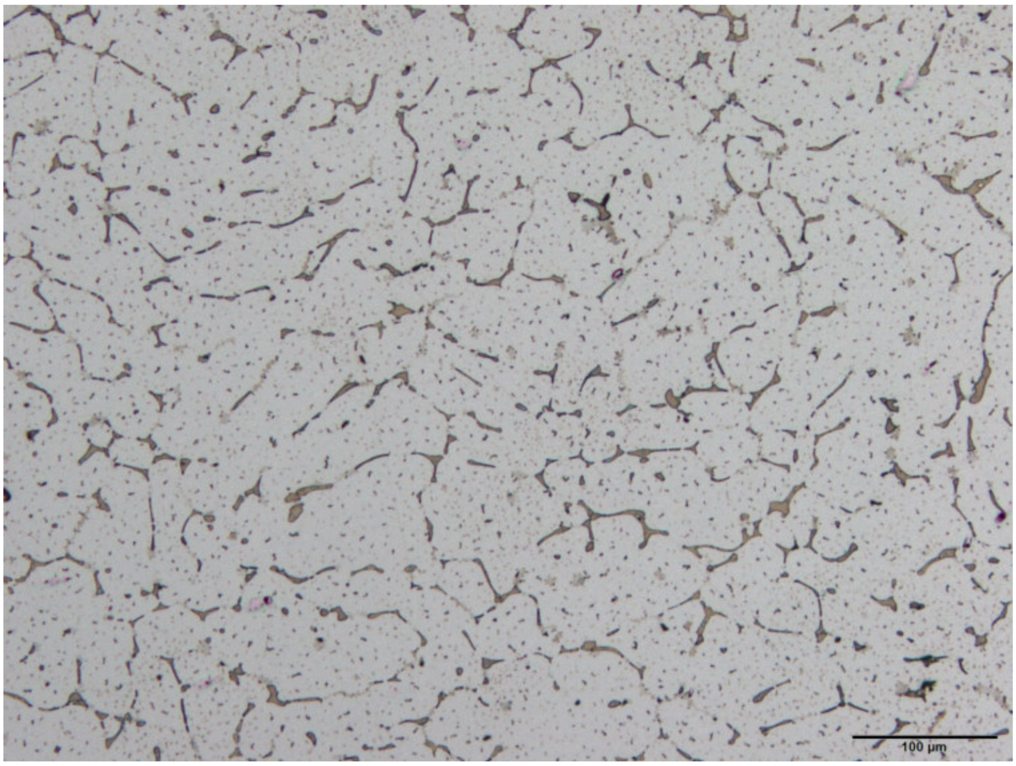


Fig. A1.1a.

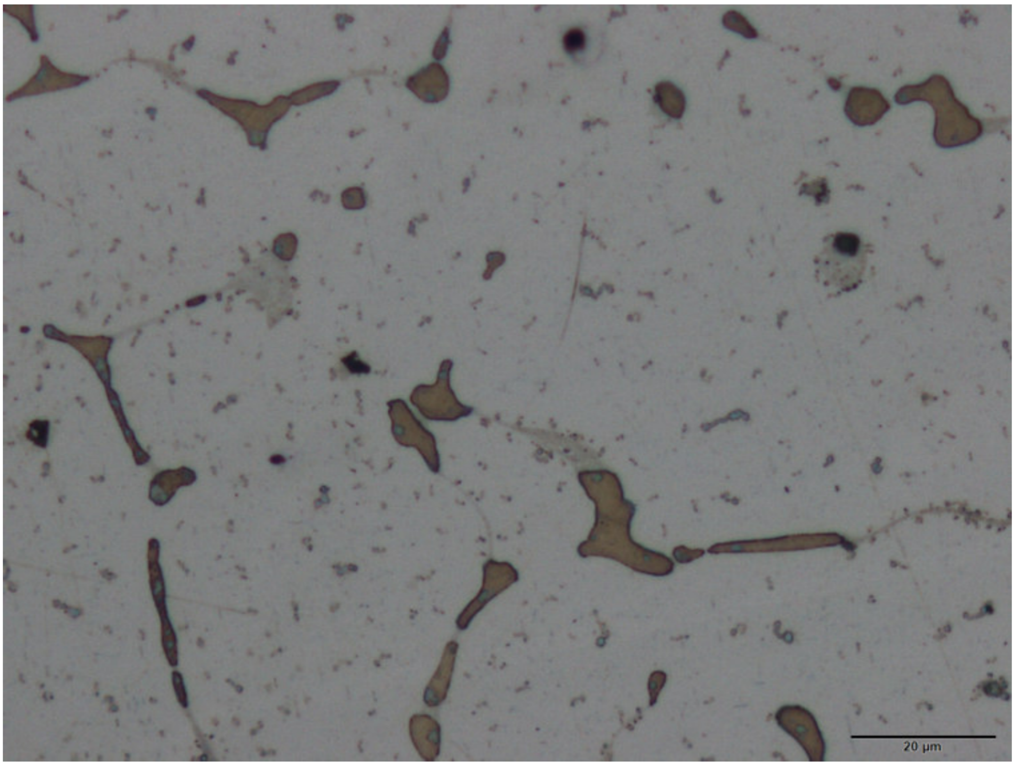


Fig. A1.1b.

Fig. A1.1 Microstructure of gravity cast alloy Mg-3Zn-2Ca

Annex 2

Metallographic evaluation of processed Mg3Zn-2Ca by ECAP

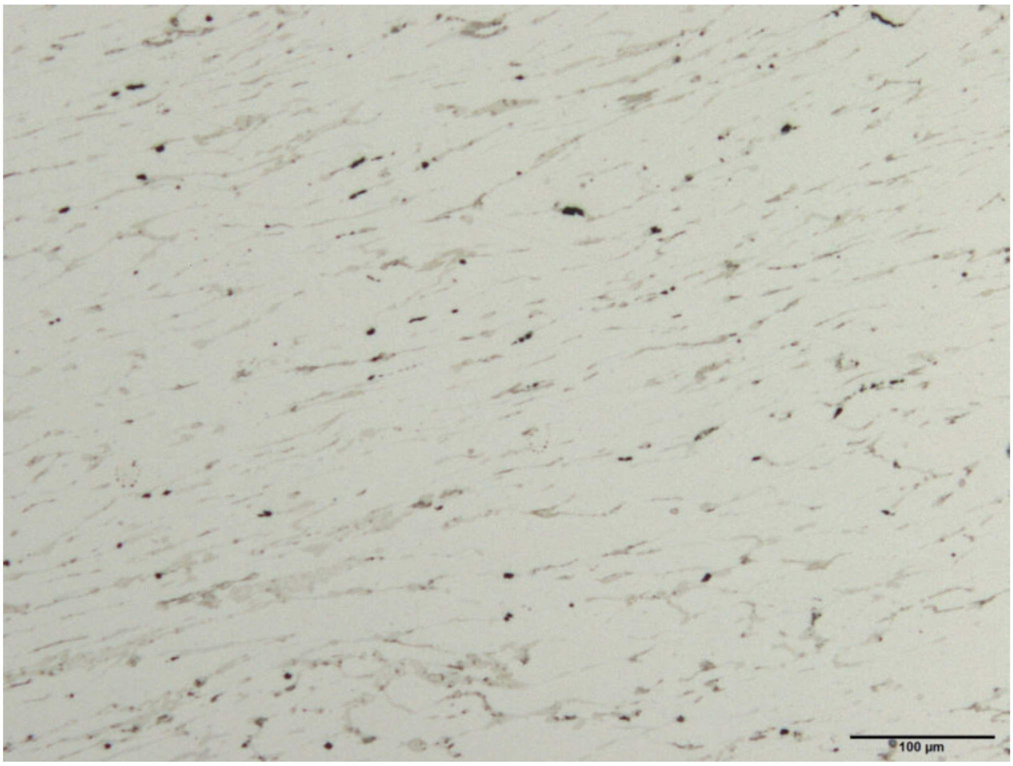


Fig. A2.1a.

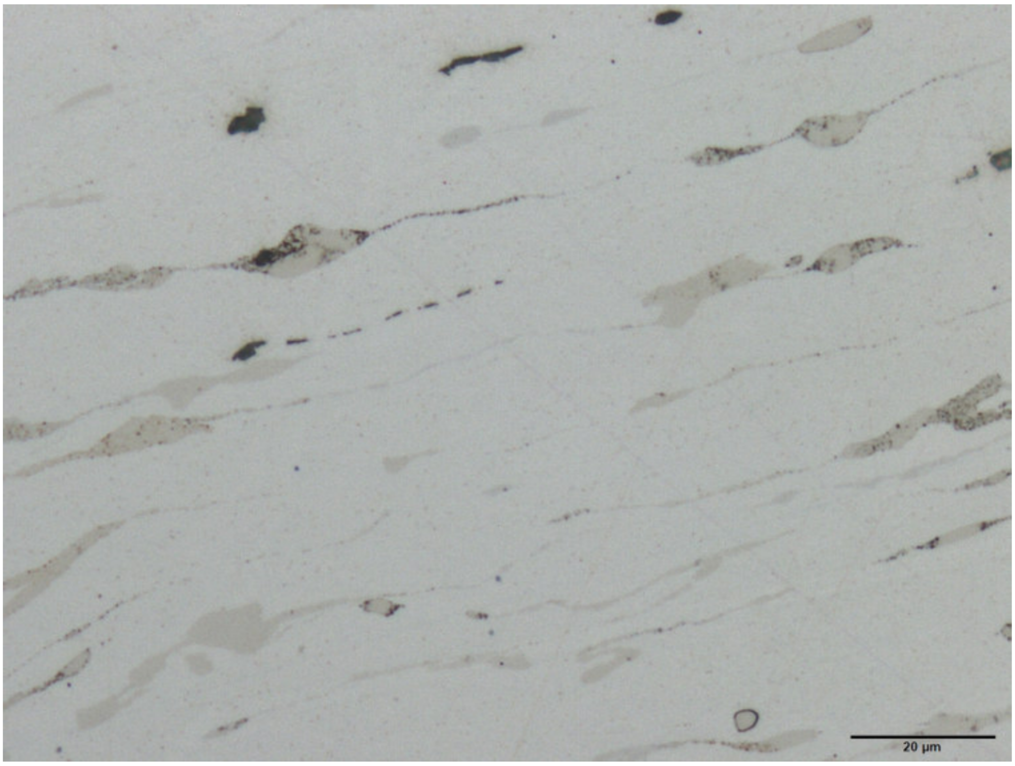


Fig. A2.1b.

Fig. A2.1 Microstructure of sample F2 Mg-3Zn-2Ca in Longitudinal direction to extrusion.

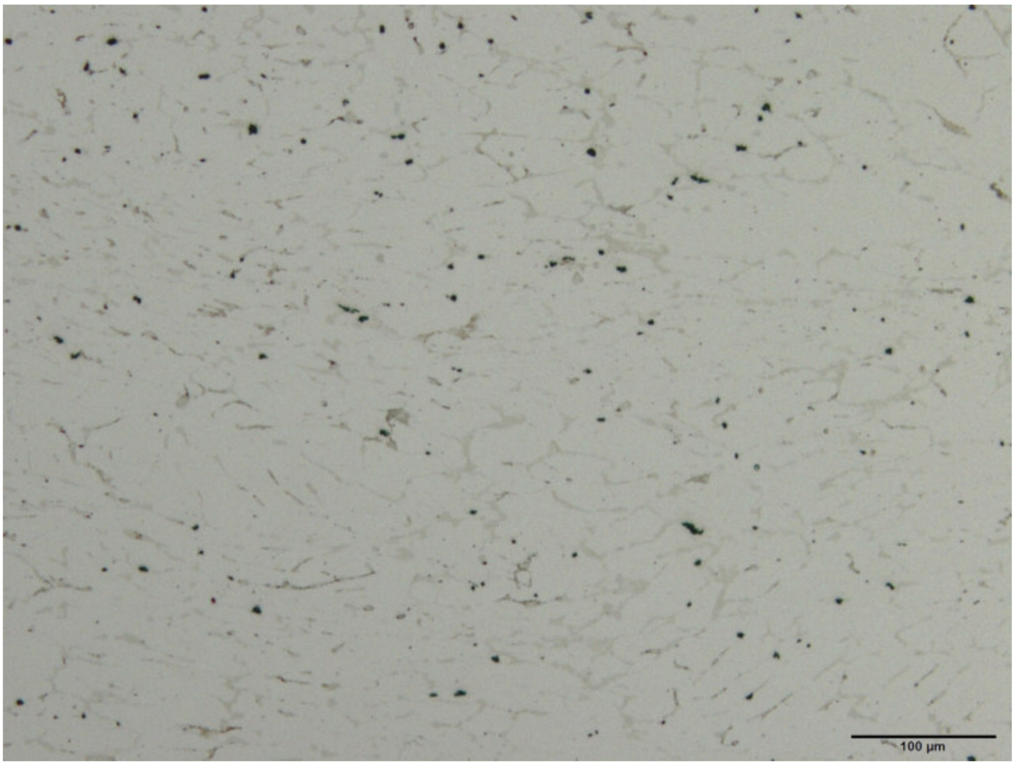


Fig. A2.2a.

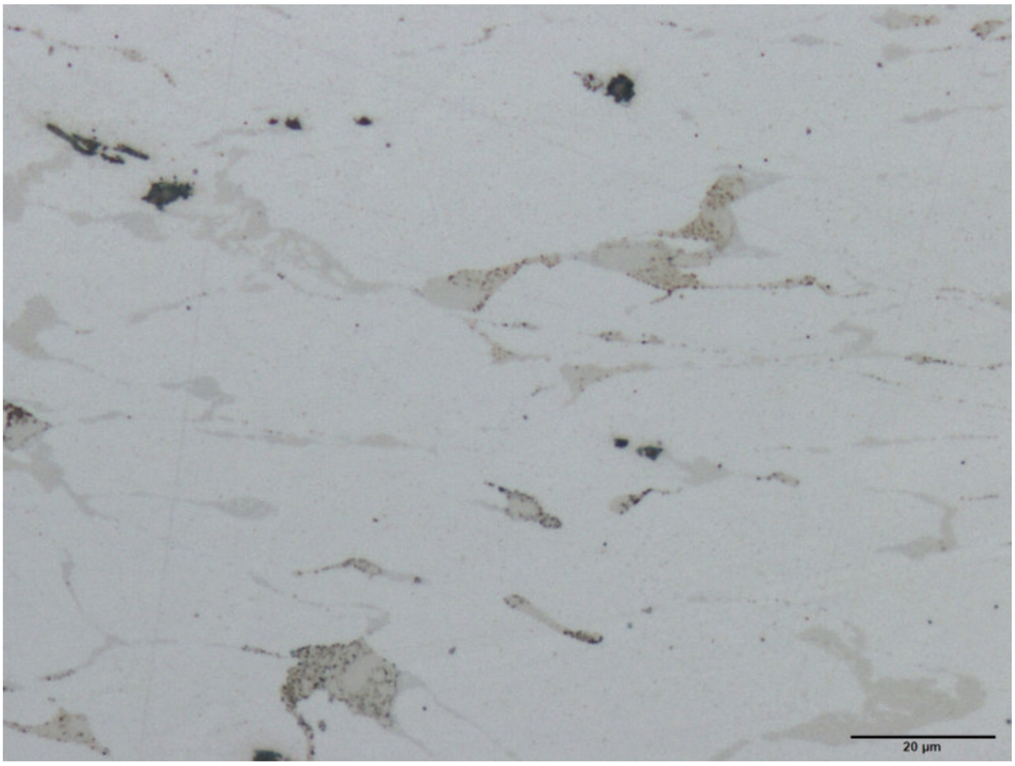


Fig. A2.2b.

Fig. A2.2 Microstructure of sample F1 Mg-3Zn-2Ca in transverse direction to extrusion.

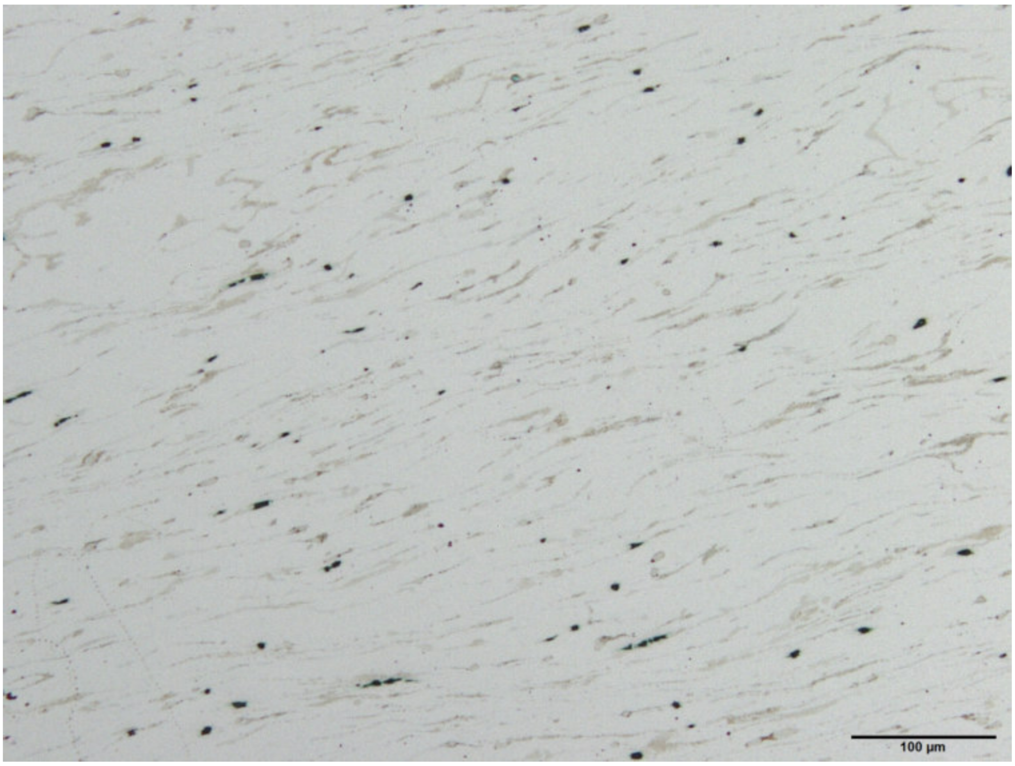


Fig. A2.3a.

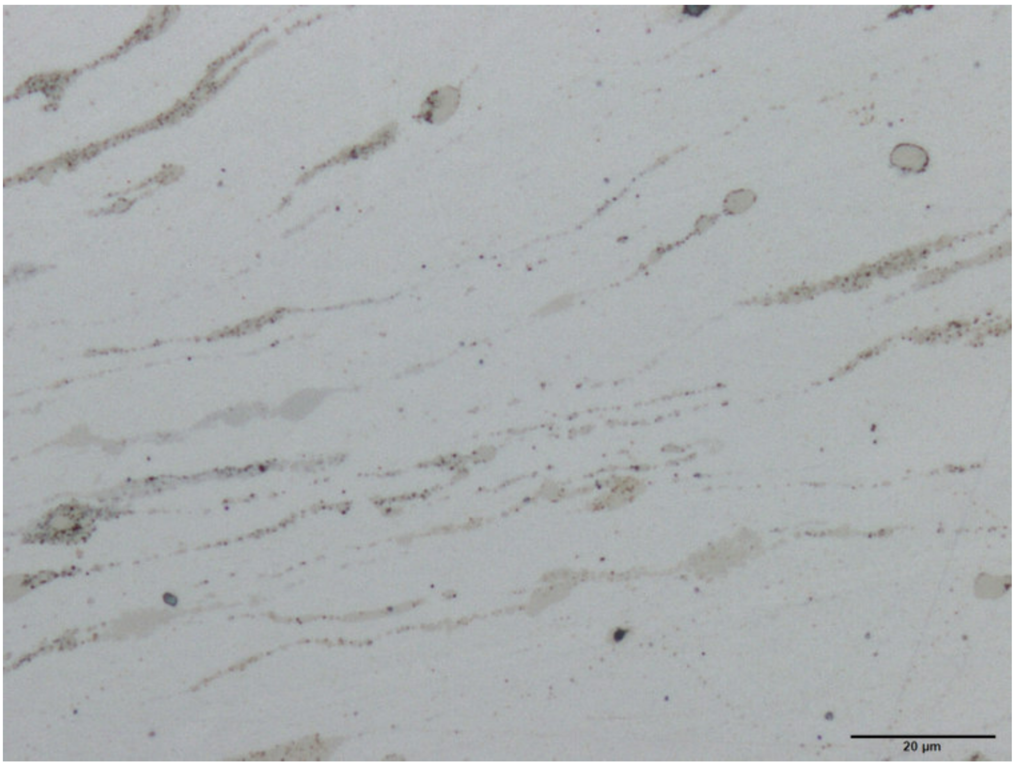


Fig. A2.3b.

Fig. A2.3 Microstructure of sample F4 Mg-3Zn-2Ca in Longitudinal direction to extrusion.

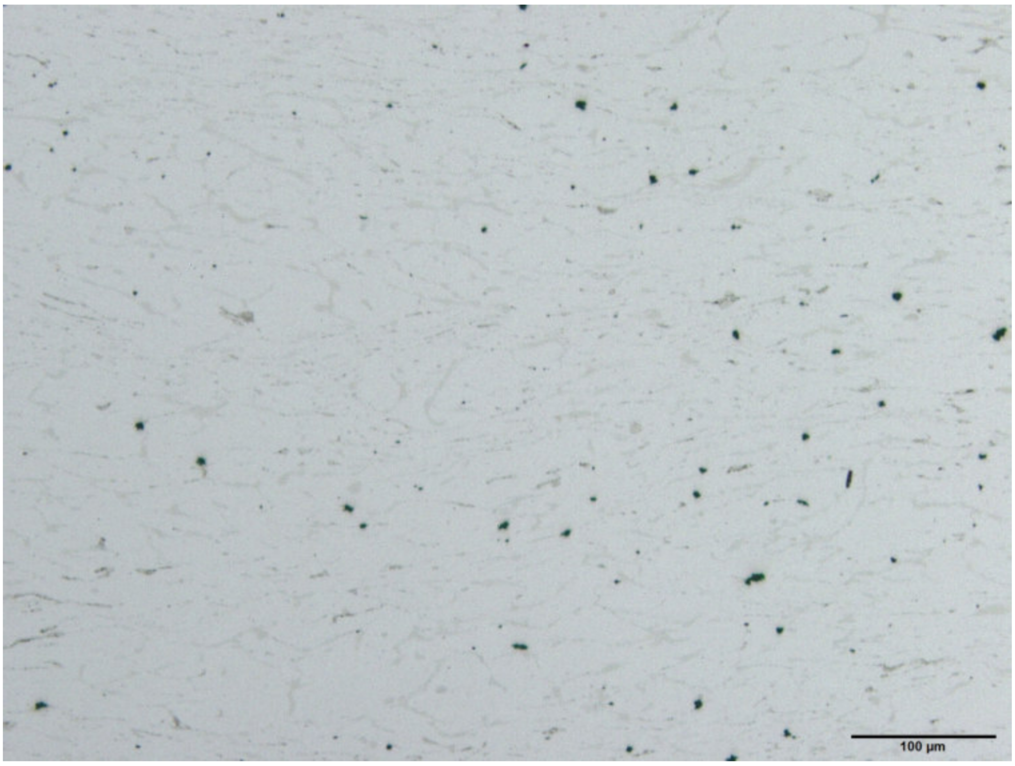


Fig. A2.4a.

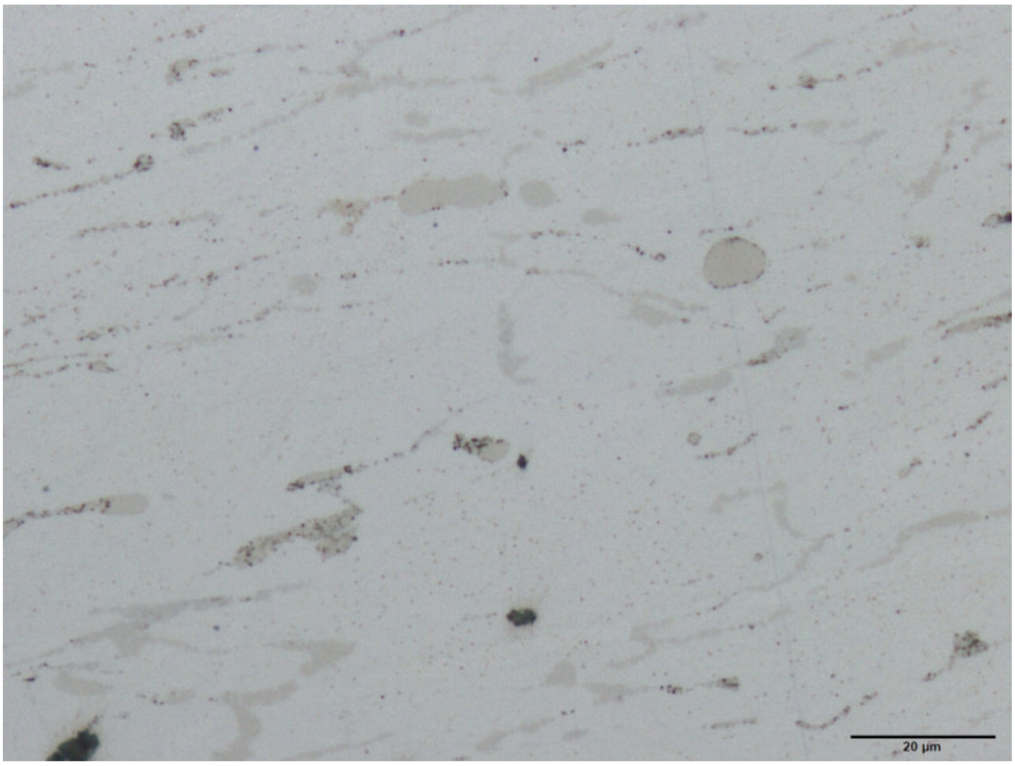
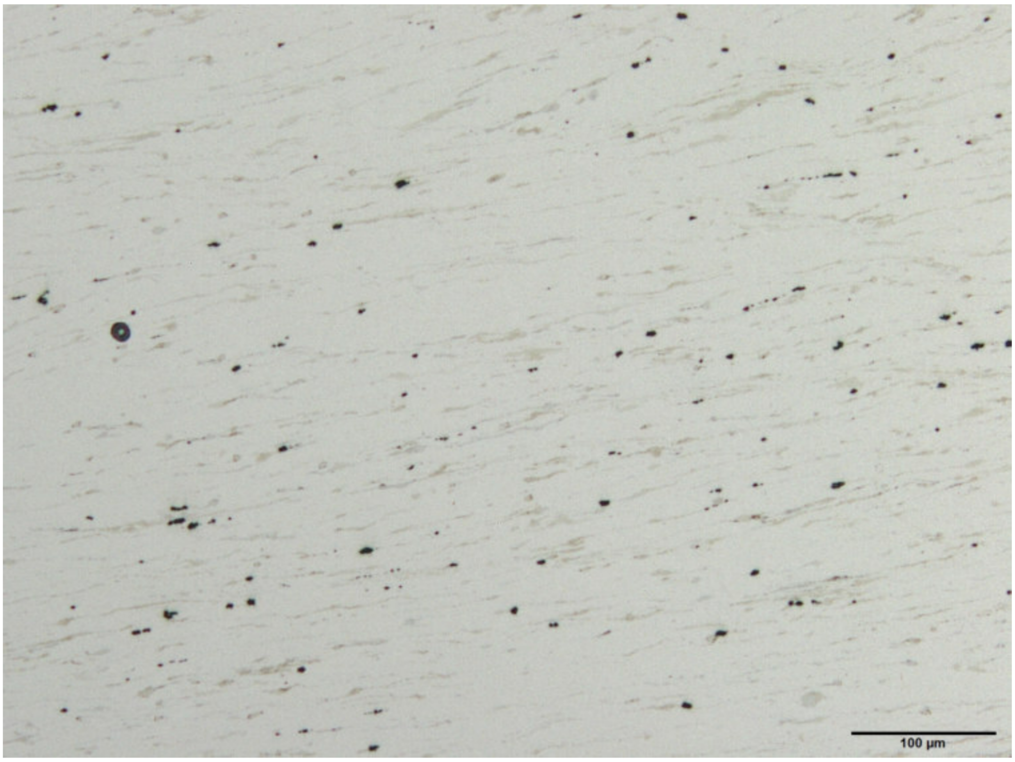


Fig. A2.4b.

Fig. A2.4 Microstructure of sample F4 Mg-3Zn-2Ca in transverse direction to extrusion.



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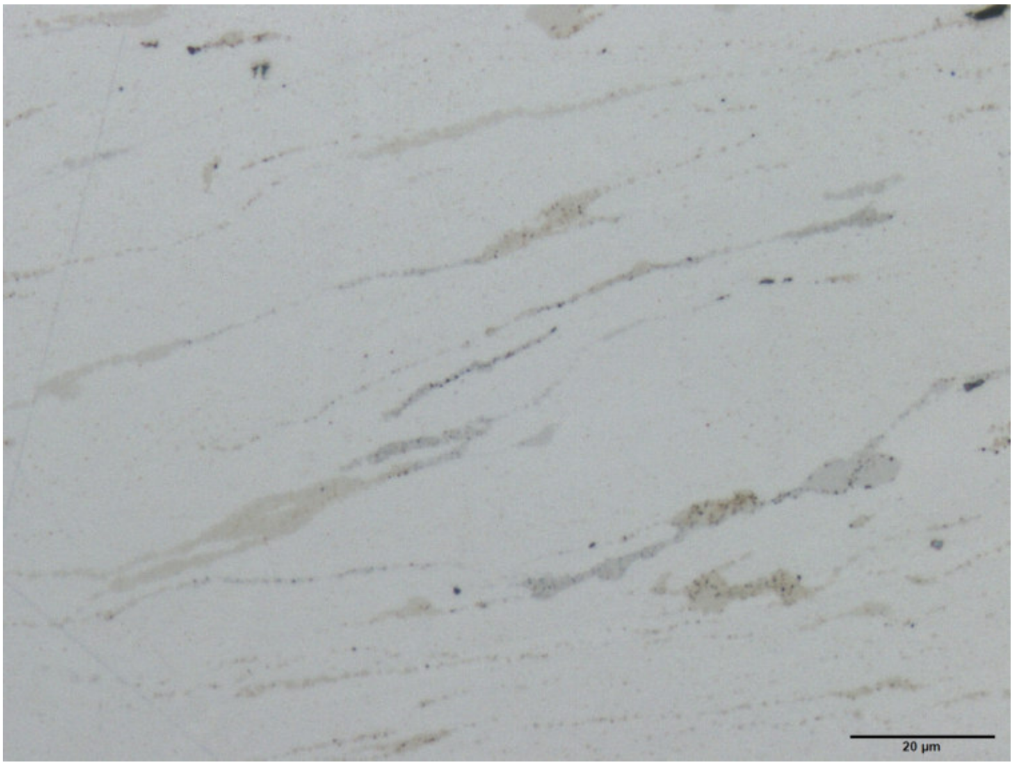

Fig. A2.5b.

Fig. A2.5 Microstructure of sample F6 Mg-3Zn-2Ca in Longitudinal direction to extrusion.

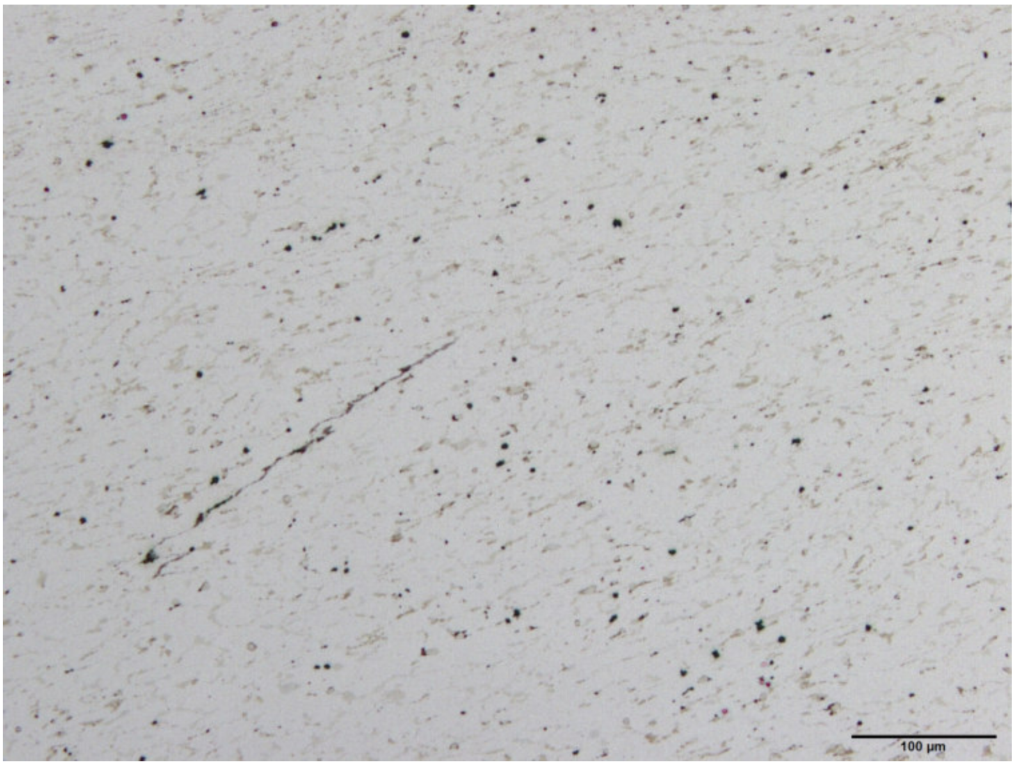

Fig. A2.6a.

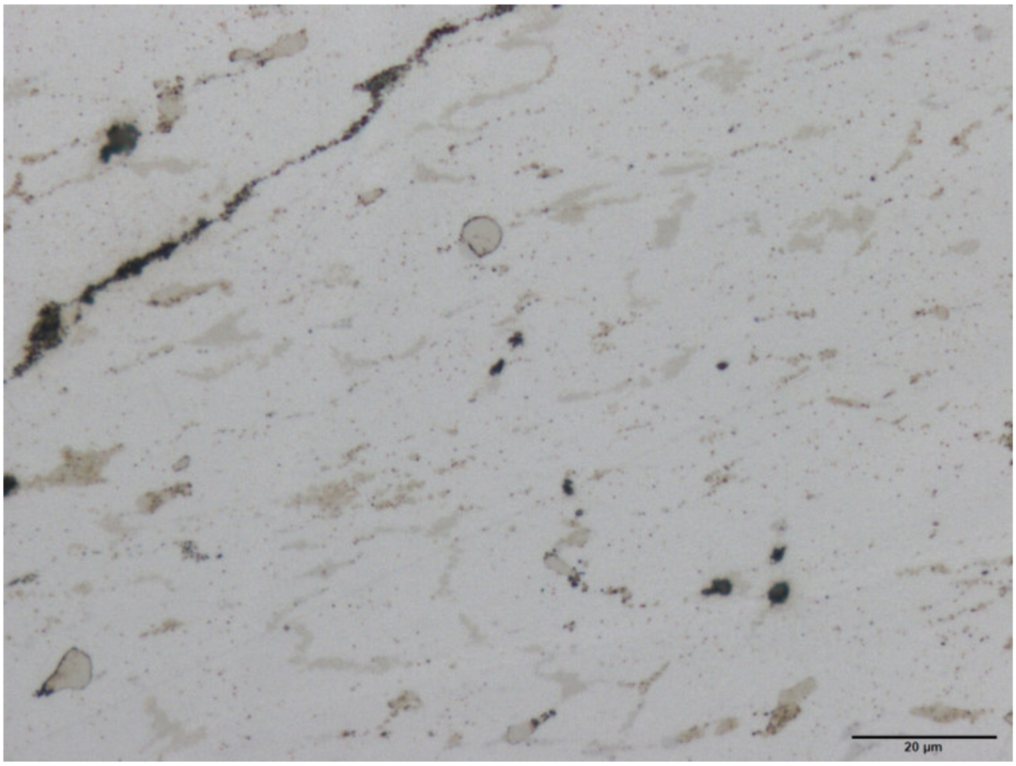

Fig. A2.6b.

Fig. A2.6 Microstructure of sample F6 Mg-3Zn-2Ca in transverse direction to extrusion.

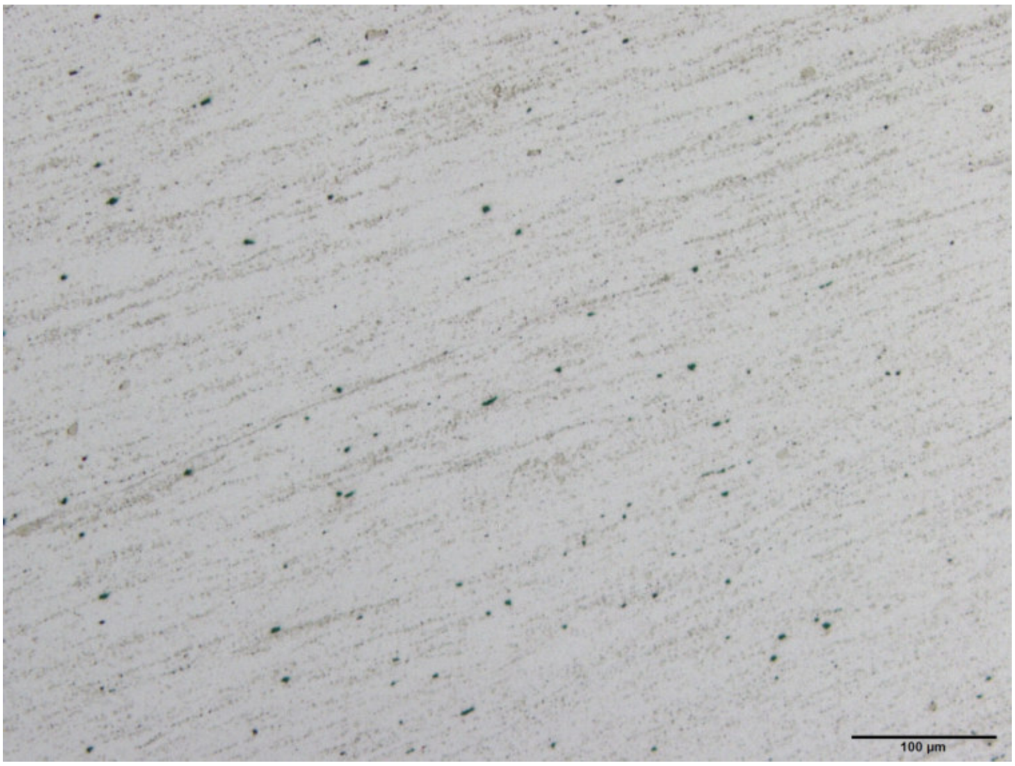

Fig. A2.7a.

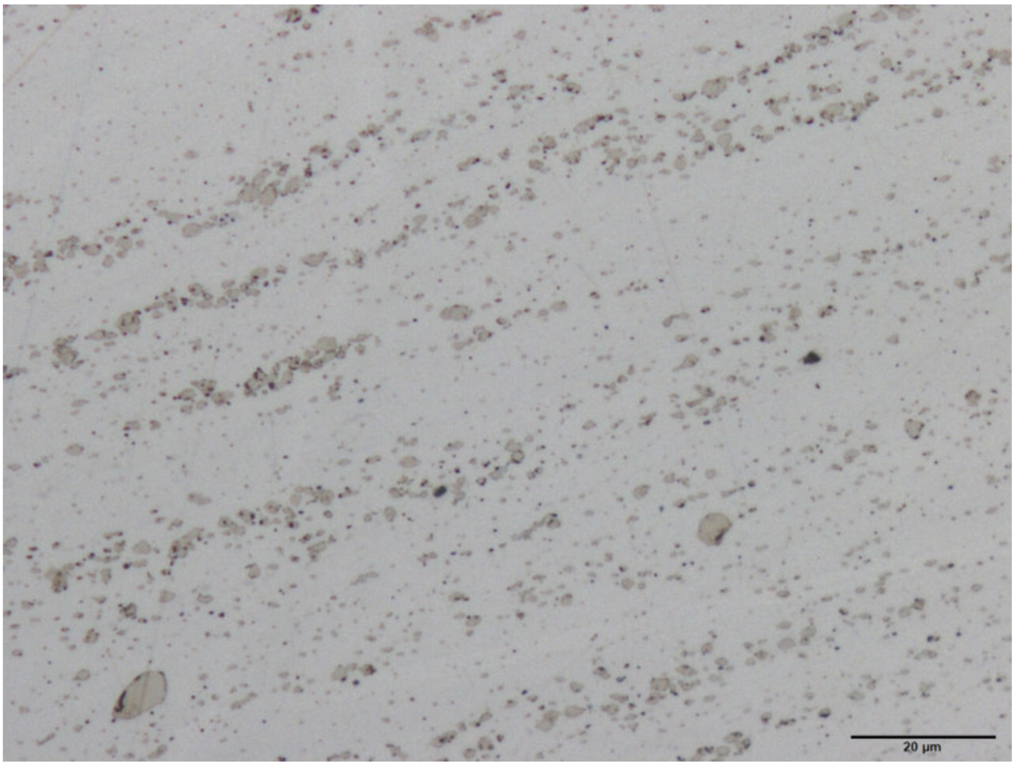

Fig. A2.7b.

Fig. A2.7 Microstructure of sample F8 Mg-3Zn-2Ca in longitudinal direction to extrusion.

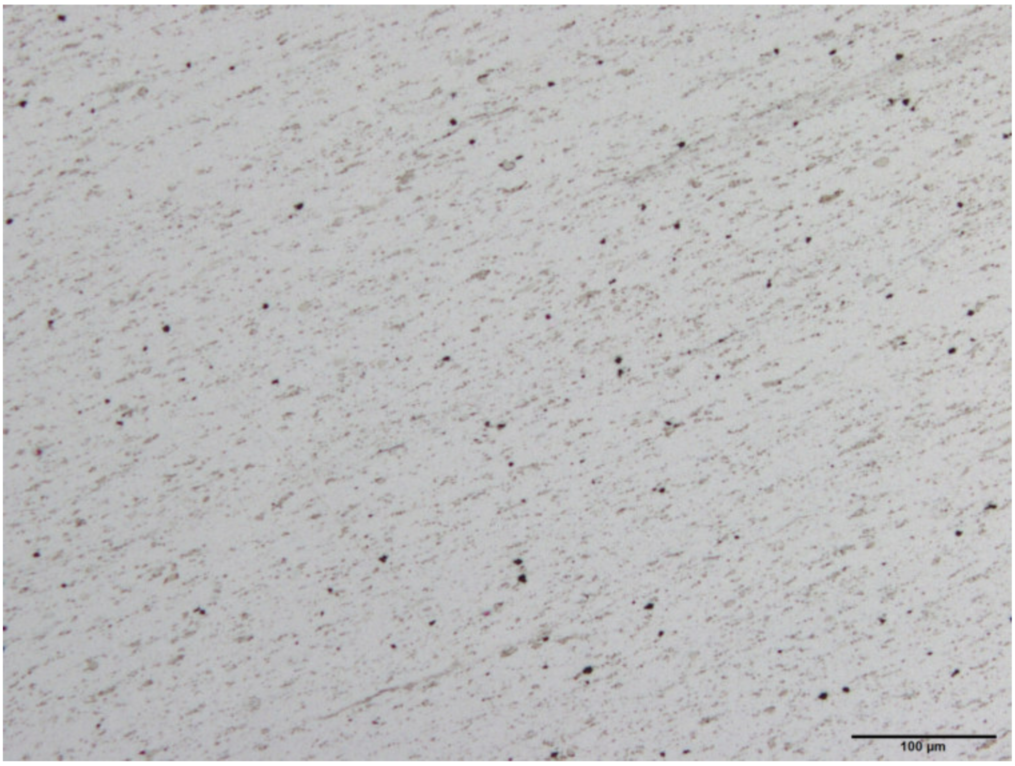

Fig. A2.8a.

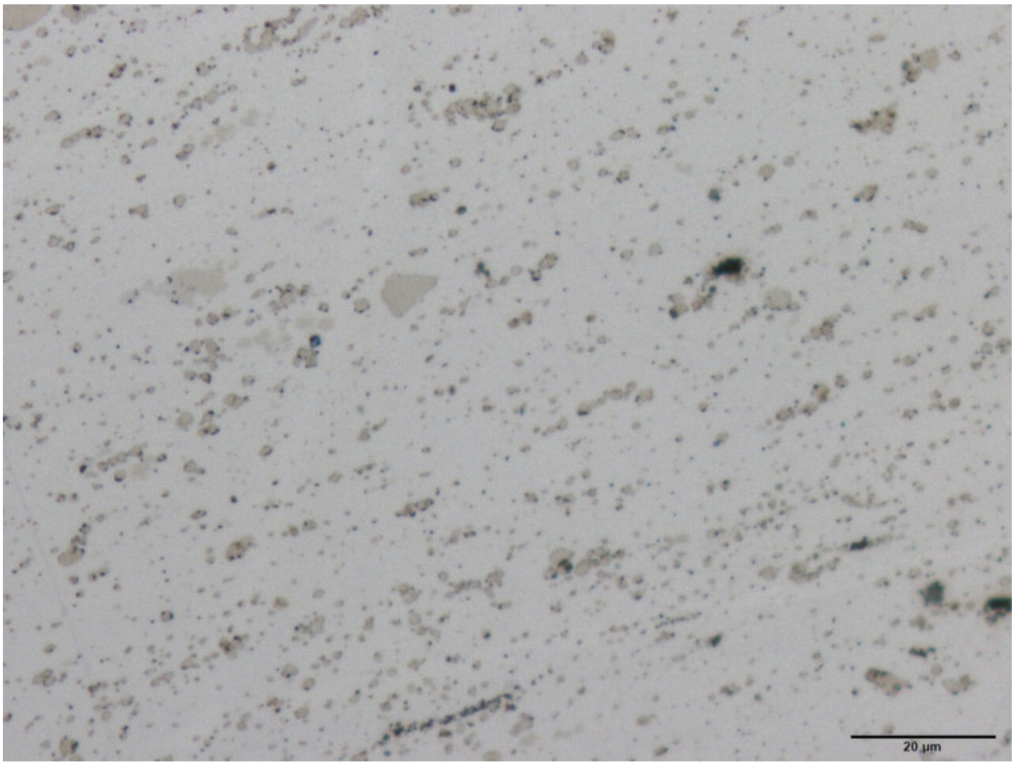

Fig. A2.8b.

Fig. A2.8 Microstructure of sample F8 Mg-3Zn-2Ca in transverse direction to extrusion.