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Fabrication and properties of magnesium based alloys Mg-Ca

R. Nowosielski, A. Gawlas-Mucha*, A. Borowski, A. Guwer
Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
* Corresponding e-mail address: agnieszka.gawlas-mucha@polsl.pl

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ABSTRACT

Purpose: The paper describes the preparation, structure and mechanical properties of magnesium based alloys with chemical composition of Mg-1 (wt%) Ca prepared in the form of ingot.
Design/methodology/approach: The studied samples were prepared by the tubular resistance furnace melting in silicon crucible. The structure of the alloy was examined by X-ray diffractometry (phase analysis) and scanning electron microscope (chemical analysis of the micro-regions). Microhardness was measured using Vickers hardness testing machine with automatic track measurement. Microstructure was examined by optical light microscopy.
Findings: The X-ray diffraction investigations have revealed that the studied cast ingot the two-phase alloy structure. Chemical analysis confirmed the expected chemical composition. Values of the microhardness tests of materials were compared before and after remelting.
Practical implications: Magnesium alloys are new class of biodegradable materials other bioresorbable biomaterials for orthopedic applications. The potential benefits of ownership of Mg alloys are the closer modulus of elasticity to the bone than stainless steel or titanium, biocompatibility and bone- active properties and the elimination of necessity of a second operation to remove the implant body. Two- component Mg-Ca alloy is characterized in that a solid solution limit, and creates a stable intermetallic phase Mg_2Ca.
Originality/value: Fabrication and properties of magnesium based alloys to thermomechanical processing.
Keywords: Magnesium based alloys; Biomaterials; Magnesium; Calcium; Tubular resistance furnace melting

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1. Introduction

The increase in the production of magnesium alloys in the world is due to the industry's demand for lightweight structural components, that are used in automotive, aerospace, transportation and industrial automation. In the automotive industry magnesium alloys are used for engine blocks, fuel tank cover, seat frames and roof windows, steering columns, steering wheels, body parts, parts of the front and rear housing of the motor shaft, instruments, pedals brackets, grille, interior frame doors, gearbox, cylinder head covers [1-3]. Low weight (low specific gravity) of magnesium alloys is one of the main reasons for increasing their use of the computer cover, cover mobile phones, video cameras, and consumer electronics, home appliances, etc. [2,4,5]. Besides these applications the magnesium alloys has recently found using in medicine as biodegradable materials, with the possibility of resorption in the body. The accelerated pace of life, the extension of working age and lack of time as a result of physical activity in this population is increasingly exposed to various types of injuries. Injuries of the locomotor system is not rare to be subjected to intervention

surgeon and lead to different types of bone disease. So important is the development of materials to support the regeneration of bones [6-8].

Metallic materials play an important role as biomaterials designed to aid in the repair or replacement of bone tissue that is destroyed as a result of disease or mechanical damage. Metallic materials are more suitable for load-bearing applications in comparison with the ceramic materials or polymeric materials due to their combination of high mechanical strength and resistance to breakage. It is now widely used biomaterials metal which could include austenitic stainless steels, cobalt based alloys, titanium based alloys, alloys with shape memory. The currently used in medicine metalic materials are associated to the release of toxic ions and/or metal particles, which lead to disease states (inflammatory tissue) of the organism. It reduces are the undesirable effect of biocompatibility. In addition, mechanical properties such as modulus of elasticity, are not adequately matched to properties possessed by the natural bone tissue (Table 1) [35]. Increased mechanical properties of the material can lead to the implant causing a reduction in flexural modulus effect of bone tissue as a result of a mismatch between the elastic properties of the implant and the living tissue which can simulate the effect of reducing the growth of new tissue and bone remodeling, which reduces the stability of the implant. Current metallic biomaterials are essentially neutral in an in-vivo. These materials are used for implants, such as plates, screws, pins used to protect the fracture, must be removed during a second surgical procedure, at the appropriate time sufficient tissue healing. Repeat the operation increases the cost of the health care system and can lead to further complications in the patient [15-24].

Table 1.
Properties of various implant materials applied as biomaterials in comparison to the natural bone [35]

Properties	Natural bone	Magnesium	Ti alloy	Co-Cr alloy	Austenitic stainless steels	Synthetic hydroxyapatite
Density (g/cm^3)	1.8-2.1	1.74-2.0	4.4-4.5	8.3-9.2	7.9-8.1	3.1
Elastic modulus E (Gpa)	3-20	41-45	110-117	230	189-205	73-117
Compressive yeld strength (Mpa)	130-180	65-100	758-1117	450-1000	170-310	600
Fracture toughness (MPa m1/2)	3-6	15-40	55-115	N/A	50-200	0.7

Magnesium alloys are promising as new class of degradable structural biomaterials which provide beneficial properties such as high strength in relation to the weight of the alloy which, the elastic modulus (Young's modulus (Table 1)) proximal to the bone in comparison to titanium implants, biocompatibility, osseointegration (clinical stabilization of the implant anchored in the bone), improving the growth of apatite in the living system , increased osteoconduction (property file available biomaterial in contact with the playing bones which consists of supporting this process) and osteogenesis (and the elements contained in the alloy are also found in the body) and biodegradability. The advantage of the degradable materials is a necessity the only one operation, thus the time and expense of a second surgery and/or the cost of a new implant are eliminated. Additionally, implantation into the period is the period of exposure in a living organism or to the factors such as the tensile stress and inflammation of tissues. Magnesium metabolism and renal excretion process is a natural physiological process. Magnesium corrosion products are hydrogen bubbles that accumulate in a living system adjacent to the implant. This growth in the form of hydrogen gas and the formation of bubbles was a disincentive to further research. Controlled release of Mg in a living organism is a major challenge and should be resolved for the safe and efficient use of Mg alloys in orthopedics. Developing appropriate biodegradable implants is a multidisciplinary challenge. Currently, there is flexibility in the design of biomedical alloys, but we have to remember to keep certain restrictions related to the non-toxicity of the elements used as alloying elements. This excludes a large number of alloying elements such as rare earth elements, some heavy metals. A promising and biocompatible element is calcium [19,26,27].

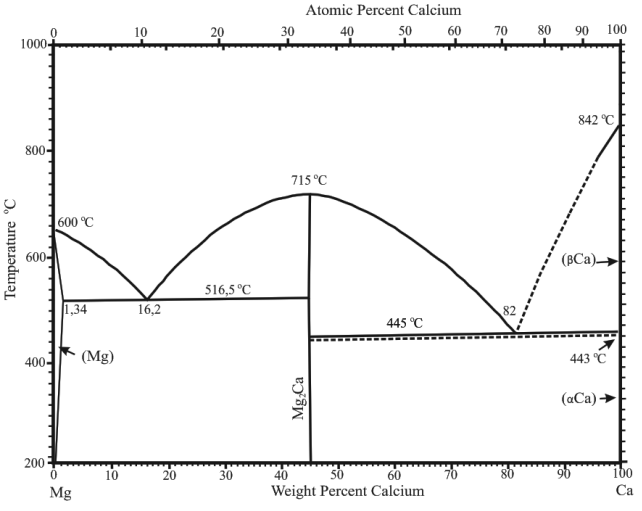

Fig. 1. Phase diagram of MgCa alloy [36,37,40]

Figure 1 shows the Mg-Ca phase system. Phase system of Mg-Ca alloy shows a two deep eutectic near low melting points and tends to form intermetalic phase Mg_2Ca Laves phase. The stable phases in Mg-Ca system are: the liquid, the Mg (hcp - hexagonal close packed while the packing of atoms in a value, the ABAB) solid solution, the Ca (bcc - body centered cubic), the Ca (fcc - the ABCABC arrangement is known as face

centered cubic), and the congruent intermetallic compound Mg_2Ca (A2B type Laves phase with C14). The alloy solidifies in eutectic composition when the calcium composition is on the level of 16.2 (wt)%. Electrochemically, Mg_2Ca phase is more active than α-Mg and assumes the role of anode contradicting other intermetallics which are cathode in relation to Mg. [10,11]. Additional alloying element which is the calcium is quite interesting in the context of biodegradable implants. Even a small addition of calcium increases the corrosion resistance and minimize grain growth and leads to a reduction grain size in casts [11,29-34,36-40].

Mechanical properties of magnesium alloys are of interest due to the fact that they are close to the mechanical properties of bone.

Figure 2 presents a comparison the mechanical properties of Mg-Ca alloys with other magnesium based alloys and cortical bone. Xuenan and coworkers published that the cortical bone has a Young's modulus of the order of 5-25 GPa, the compressive strenght in the range of 150-250 MPa [14]. Magnesium based alloys with calcium are characterized by a Young's modulus of 45-65 GPa level, and the compressive strength of in the range 300-200 MPa, these values are closer to the properties of the cortical bone compared to other currently used biomaterials. Presented in the Figure 2 group of materials base on metallic glasseshave closer Young's modulus to cortical bone but the compressive strength is bigger twice than compressive strength of cortical bone [11,14].

Li and coworkers repotred that the ultimate tensile strength (UTS) is at the level of 71.38 ± 3.01 MPa and elongation is about 1.87 ± 0.14% of as-cast Mg-1wt% Ca alloy [13]. Li and coworkers reported also that Vickers hardness of Mg-1% (wt) Ca was on the level 50 HV [25].

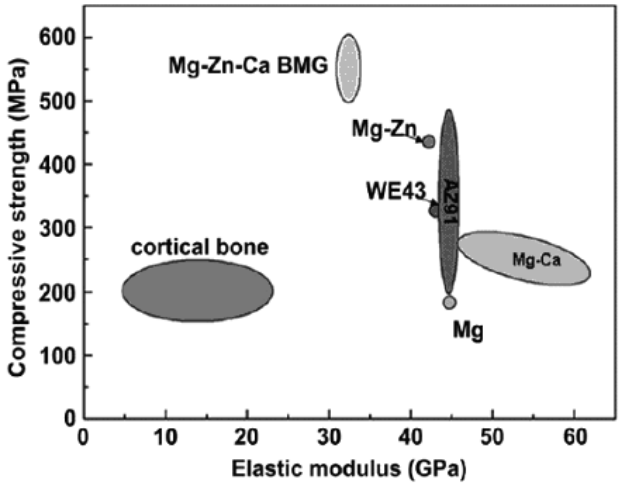

Fig. 2. The relation between Young modulus and compressive strength selected alloys and coprtical bone [14]

Figure 3 schows the Mg-Ca alloys witch different calcium concentraction in the range of 0-4.5 wt % with the increase in calcium concentration tensile strength increases. At a concentration of calcium equal to 0 wt % a tensile strength reached a value of 200 MPa. At a concentration of calcium is equal to 4.0 wt % can be observed an increase endurance by 40 MPa. Along with an increase of calcium concentration, the 0.2% elastic limit also increases. When the concentration of calcium equal is 1 wt% tensile strength is located at approximately is 180 MPa, and 0,2% elastic limit is located at approximately 145 MPa. With the increase of calcium concentration to 1 wt% also increases elongation at rupture, and elongation at the tensile strength. Then the value of property decreases with increasing concentrations of calcium [10,11].

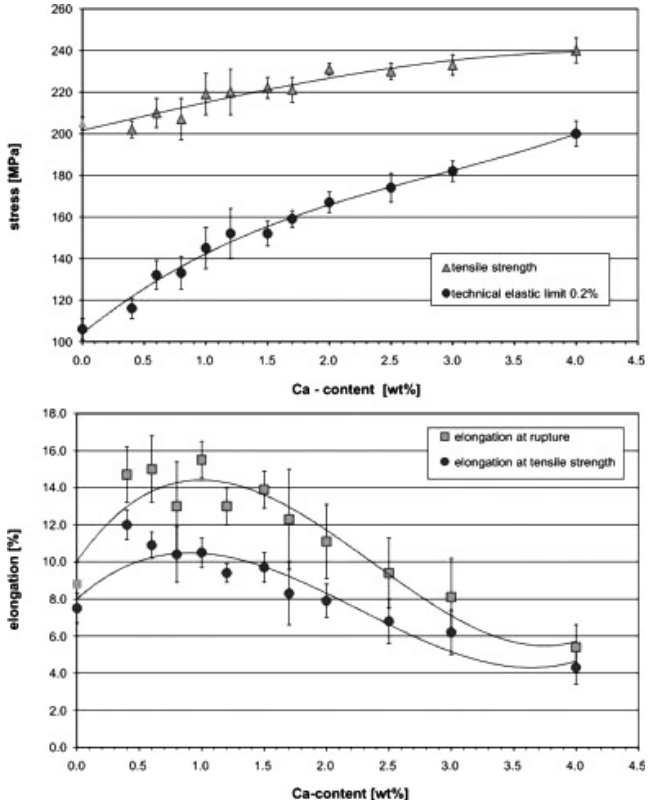

Fig. 3. The relation between Young modulus and compressive strength selected alloys and coprtical bone [10,11]

2. Experimental procedure

2.1. Materials

One sample with composition Mg-1% (wt) Ca was prepared using elemental lumps of magnesium (99.91% purity) and calcium (99.5% purity, 10 mm). Ingot was prepared with 20 grams properly weighed lumps. Weight mass of magnesium and calcium is presented in Table 2.

Table 2.
Characteristics of used elements

Element	Wt. [%]	mass per 20 [g]	T_m [°C]
Magnesium	99	19.8000	650
Calcium	1	0.1999	842

2.2. Research methodology

Melting and casting of magnesium alloys is a rather complicated process. The temperature of the casting is much higher than the point of ignition. The resulting of oxide layer on the surface does not form a molten tight barrier against further oxidation. This phenomenon makes it necessary to the use of melting of the protective layer [4].

Magnesium casting makes necessary to the use of a protective atmosphere, due to the strong oxidation of the magnesium during melting. The protective layer is obtained by various methods. Can be distinguish among others the use of protective gases or special protective fluxes. The main task of the protective atmosphere is to secure of molten metal prior to the formation of undesirable compounds [5].

Figure 4 shows a schematic of tubular resistance furnace using for melting alloys.

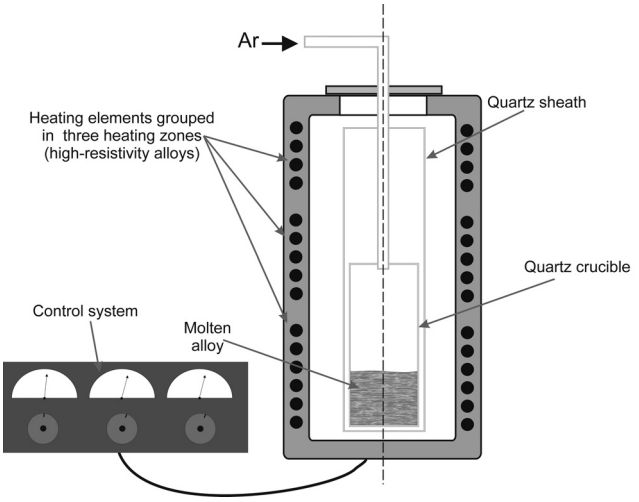

Fig. 4. Diagram of tubular resistance furnace used for melting of Mg1Ca alloy

Tubular resistance furnace has three heating zones: bottom, middle and upper. In each of them the heating temperature can be adjusted by using a control panel. The heating element is a resistance wire. In the middle of the heating chamber the material for melting and quartz crucible are placed. Around the crucible is quartz sheath, which protects the material from the atmospheric factors. Directly into the quartz crucible with the material the gas (argon) is supplied to protect the material from oxidation.

In the purpose of obtaining a sample for testing, the resistance melting in the tunnel furnace was used. Magnesium and calcium provided in the quartz crucible and then was inserted into furnace. Elements (Mg, Ca) blend were weighed on analytical high precision balance AS/X (four digits).

Resistance melting takes one hour. Melting temperature was 700 Celsius degrees. In each heating zone temperature was the same. After melting slow cooling with the furnace was used. Protective atmosphere was provided by the whole duration both of the melting process as well as cooling.

Figure 5 shows a ingot in as-prepared state Mg-1% (wt) Ca obtained by resistance melting.

The prepared sample was subjected to the following tests. X-ray diffractometer X'Pert Pro Panalytical with Cu Kα radiation (λ = 0.15418 nm) was used to study structure of fabricated ingot. The data of diffraction lines were recorded by "step-scanning" method in 2θ range from 20 to 80 and 0.05 step.

Chemical characterization of sample was analyzed by means of analytical technique - Energy Dispersive X-ray spectroscopy (EDS). EDS analyzer is part of the SEM. Values of the characteristic radiation energy permit to qualitative analysis in the test sample, and the intensity (peaks height) allows for quantitative analysis.

Microhardness of sample was measured by using Vickers hardness testing machine with automatic track measurement using image analysis FUTURE-TECH FM-ARS 9000. Microhardness measurements were made under load 0.97 N. The sample was tested seven times.

Observation of the structure of the prepared sample was carried out by using microscope metallographic inverted light ZEISS Axio Vert. A1 (this microscope has a magnification in the range from 25 to 2000) and the scanning electron microscopy (SEM) SUPRA 35 ZEISS.

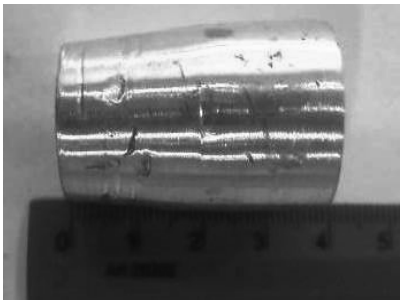

Fig. 5. Outer morphology of resistance melted Mg1Ca alloy as a roller with diameter of 20 and 30 mm and length 40 mm

3. Results and discussion

3.1. Microhardness

Microhardness measurements results of received ingot are presented in Table 4. The fabricated ingot was seven times examined. The largest value of microhardness which occurred was 51 HV, whereas the lowest value was 39 HV. The average value of microhardness was 43 HV. These results indicate a slight heterogeneity of different areas of the ingot.

Table 3.
Average microhardness values of pure element Mg and Ca in the form of slug in delivery status

Material	Average microhardness [HV]
Mg	57
Ca	81

However, in Table 3 compared the average microhardness of fabricated Mg1Ca alloy with microhardness of pure Mg and Ca in delivery status. Alloy Mg-1% (wt) Ca showed significantly lower microhardness (HV 43) than its individual components Mg (57 HV) and Ca (81 HV).

Table 4.
Results of measured microhardness Mg-1 (wt)%Ca sample after resistance melting

Number of measurement	Microhardness [HV]	Average microhardness [HV]
1	42	43
2	41	
3	46	
4	40	
5	43	
6	51	
7	39	

3.2. XRD analysis

Figure 6 demonstrates the XRD patterns of the Mg-1% (wt) Ca ingot after resistance melting. The XRD pattern of the prepared alloy can be attributed to the Mg and Mg_2Ca phases. According to the Mg -Ca phase scheme, the alloy should consist of the Mg and Mg_2Ca phases. Program PCPDFWIN v. 2.1 was used in order to identify phases formed of tested sample during resistence melting.

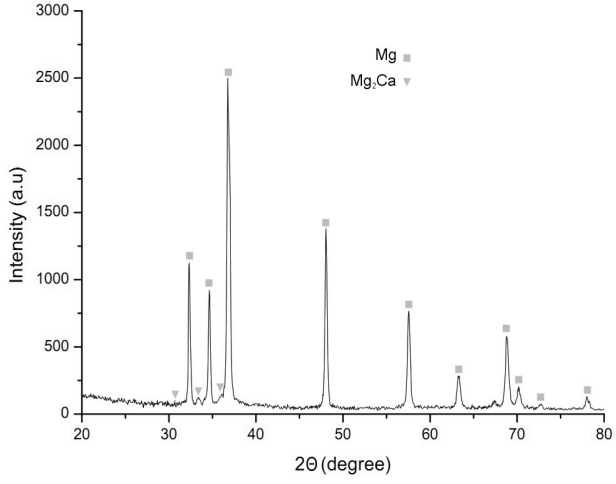

Fig. 6. X-ray diffraction pattern of Mg-1% (wt) Ca ingot in as-prepared state

3.3. Microscopic observation

Figure 7 (a-c) illustrates the microstructures of magnesium - calcium alloy at a concentration of 1% (wt) calcium obtained by light microscopy. Figure 7 (d-f) shows microstructures of the same alloy conducted by canning electron microscopy.

3.4. Microstructure

Figure 8 shows microanalysis of Mg1Ca ingot with marked area from the surface of the selected point in the fabricated samples. Energy dispersive X-ray analysis EDS shows existence of calcium and magnesium elements in studied sample. The chemical composition analysis was only a qualitative test and confirmed existing of main elements in alloy.

Table 5 presented detailed results of the chemical analysis for Mg1Ca ingot. In this sample was only basic components (Mg and Ca). The initial weight percentages of Mg equals 99% and Ca 1%. The investigation result have shown that the obtained ingot after induction melting have very similar weight composition to starting. The chemical composition of induction melted ingot confirms the possibility of exist the phases which were identified by the XRD analysis.

Table 5.
Results of chemical analysis from the surface of ingot

Sample	Element	At. [%]	Wt. [%]
Mg1Ca	Mg	99.17	98.63
	Ca	00.83	01.37

4. Conclusions

The results obtained of fabrication and testing Mg-1% (wt) Ca ingot allowed to state the following conclusions:

- it is possible to fabricated Mg1Ca alloy of a weight 20 grams by resistance melting in tubular furnace with argon atmosphere,
- the X-ray diffraction results confirmed the presence of two phases: Mg and Mg_2Ca,
- energy dispersive X-ray analysis EDS demonstrated occurrence only magnesium and calcium elements in studied alloys. Moreover the concentration of alloying elements is almost the same as the starting composition alloy,
- studies mapping the distribution of elements showed a uniform distribution of alloying elements. Map of the distribution of magnesium is more densely filled than maps of the distribution of calcium,
- Mg-1% (wt) Ca alloy has the average value of microhardness 43 HV. The difference between the measurements of the microhardness was 12 VH. The study of hardness is only a preliminary study. It is necessary to conduct further testing of mechanical properties,
- confirmation of literature reports on the potential use of these materials requires further study, among others, corrosive and tribological.

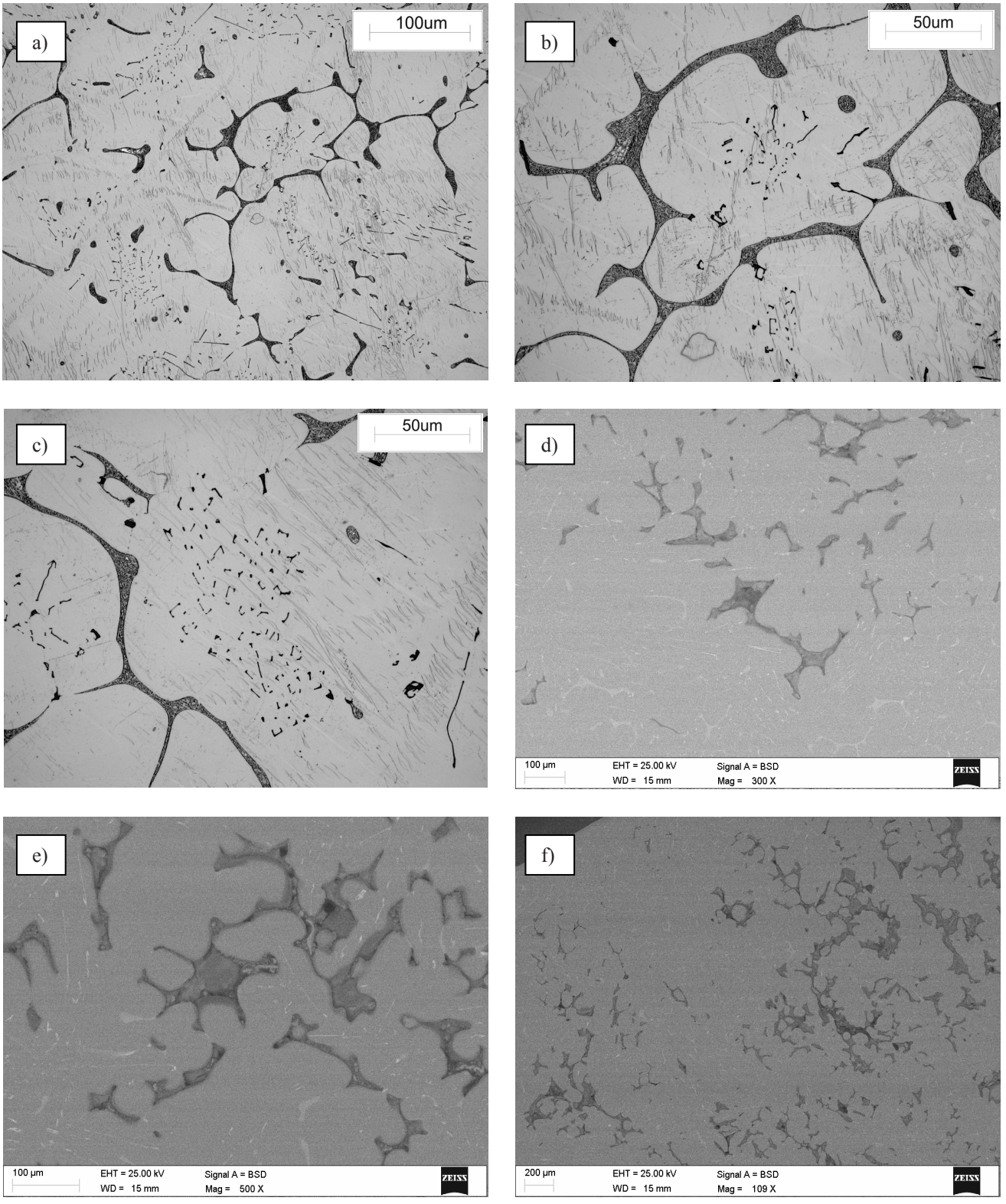

Fig. 7. Images of the Mg1Ca ingot structure conducted by a microscope metallographic inverted light (a-c) and scanning electron microscopy (d-f)

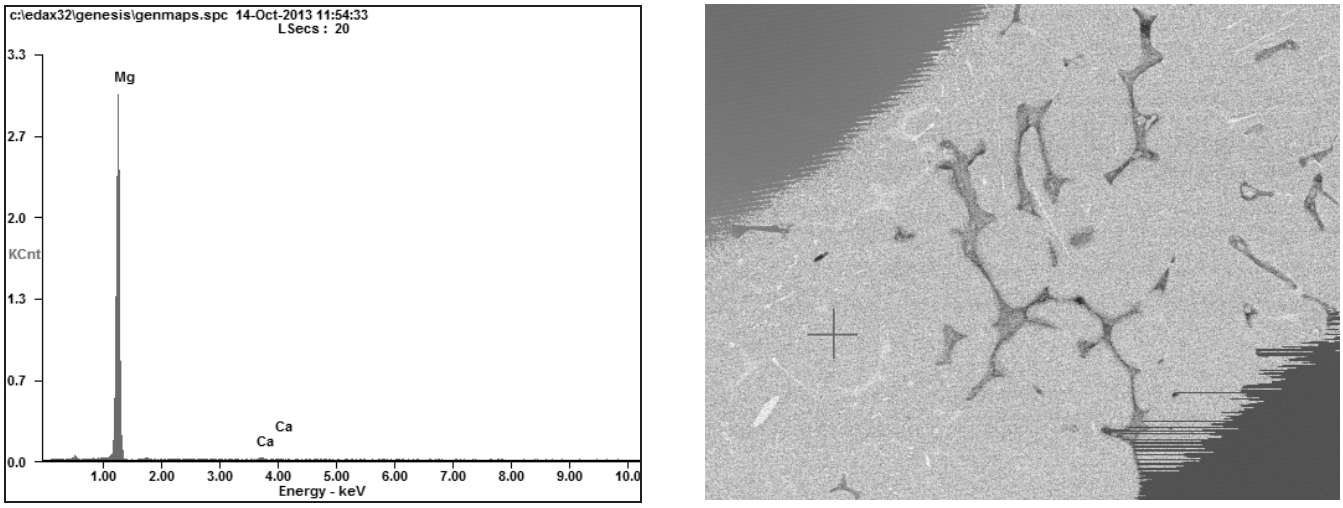

Fig. 8. SEM micrographs of Mg1Ca ingot after 1 h of resistance melting and next 1 h slowly cooling the with the furnace with marked area for which energy dispersive X-ray analysis (EDS) was performed from ingot of surface

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