



SAKARYA ÜNİVERSİTESİ

FEN BİLİMLERİ ENSTİTÜSÜ DERGİSİ

Sakarya University Journal of Science
SAUJS

ISSN 1301-4048 e-ISSN 2147-835X Period Bimonthly Founded 1997 Publisher Sakarya University
<http://www.saujs.sakarya.edu.tr/>

Title: Effect of Heat Treatment on Microstructure of Zinc Aluminum Hybrid Composite Cast Alloys

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Received: 2021-08-14 00:00:00

Accepted: 2021-09-27 00:00:00

Article Type: Research Article

Volume: 25

Issue: 5

Month: October

Year: 2021

Pages: 1218-1234

How to cite

Serdar ASLAN; (2021), Effect of Heat Treatment on Microstructure of Zinc Aluminum Hybrid Composite Cast Alloys. Sakarya University Journal of Science, 25(5), 1218-1234, DOI: 10.16984/saufenbilder.982948

Access link

<http://www.saujs.sakarya.edu.tr/en/pub/issue/65589/982948>

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Effect of Heat Treatment on Microstructure of Zinc-Aluminum Hybrid Composite Cast Alloys

Serdar ASLAN*¹

Abstract

The matrix material ZA-27 alloy was used in the production of metal matrix composite material. SiC and graphite were used as reinforcement materials in the study. ZA27 alloy with 10% SiC, 2.5% , 5% , 7.5% and 10% graphite and 10% SiC + 2.5% , 5%, 7.5%, 10% graphite reinforcement by weight hybrid composite material was produced. The microstructures were examined by SEM and EDS and the results were discussed. In the investigations, SiC and graphites had a heterogeneous nucleating effect during the solidification of the alloy. In addition, thin dendrites showed a tendency to become spherical by heat treatment.

Keywords: ZA alloy casting, Heat Treatment, Composite, Hybrid Casting

1. INTRODUCTION

In 1979, a unique family of alloys, hypereutectic zinc-aluminum alloys with high aluminum and copper contents, were developed from Zamak alloys that widely used. ZA-27 is the recently developed Zn-Al based alloy [1].

Zinc aluminum (ZA) alloys are the alloys containing zinc as the base metal with higher aluminum concentrations compared to conventional zinc alloys (ZAMAK). Other metals found in these alloys are magnesium and copper.

Zinc aluminum alloys are high performance metallic composites thanks to their good strength, good hardness, high corrosion resistance under atmospheric conditions, excellent casting properties, easy processing and good tribological properties. Some of the zinc aluminum alloys are

ZA8, ZA12 and ZA27, the numbers in these expressions indicate the aluminum concentration.

ZA27 alloy is a lightweight alloy suitable for applications requiring optimum strength. It exhibits good strength, stiffness, maximum friction and creep resistances [2-3].

Zinc-aluminum based alloys have many advantages over some ferrous and non-ferrous alloys [1]. Among these advantages are ideal casting properties, requiring little additional processing after casting, high specific strength (strength/density ratio), wear resistance and corrosion resistance. The composite's alloying elements are cheap and easy to obtain which shows they are financially affordable and environment friendly. ZA alloys were developed as replacements for bronze during periods when the copper content was insufficient [4]. The addition of copper, aluminum and silicon enabled zinc-based alloys to exhibit low coefficient of

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friction and high wear resistance properties in lubricated medium. Although copper showed a better effect than silicon in case of increased strength, it did not show the same effect in terms of increased wear resistance. Because zinc aluminum alloys contain copper and silicon, their use as bearing materials has gained commercial importance. Bearings made of these alloys are widely used in plain bearings with low speed and high load [5]. However, the limited operating temperature of 100 °C and the low impact resistance are among the factors limiting the use of this alloy. These considerations have led to studies to determine the appropriate composition, heat treatment and the addition of second particles [5].

In general, zinc aluminum alloys are used in many engineering fields such as construction machines, lathes, hydraulic lift cylinders, water pumps, automobile and textile industry [6]. Zamak alloys, which have a very high usage area in the construction and automotive industry electronic devices; household goods, ready-to-wear; toys, sports, office machinery; hardware, tools used in agriculture and mining which are frequently preferred as raw materials. Especially thanks to the high strength Zamak2 [7] exhibits, it can be used in shaft bearings as well as metal plates, where the wear effect is high. Zamak2, which is used in plastic injection equipment, metal forming molds, is the best example of this [8]. Finally, Zamak5 alloy, which is preferred in the areas of usage where tensile performance is important, is also used in areas where slightly higher performance is expected compared to Zamak3 [8].

2. EXPERIMENTAL STUDIES

2.1. Matrix and Reinforcement Materials

The matrix material used in the production of the metal matrix composite in this present work was

ZA-27 alloy. In the production of ZA-27 matrix alloy, 99.99% pure Zn, Cu, and Mg and 99.95% pure Al were used and the prepared matrix alloy composition was poured into a permanent mold. The melting process was carried out under argon gas in a graphite crucible in an electric resistance furnace. The chemical analysis of the produced alloy in the absorption device is as follow; 26.7% Al, 2.1% Cu, 0.03% Mg, 0.035% Fe, 71.135% Zn by weight (w/w). SiC and graphite were used as reinforcement materials into the previously prepared matrix alloy during the experimental work. Together with ZA-27 alloy, hybrid composite materials (HCM) consisting of 10% SiC+2.5%, 5%, 7.5% and 10% graphite reinforcements by weight were produced. The diameter of SiC particles used in the production of composites and hybrid composites is 62.5 µm, and the diameter of graphite particles is about 40-90 µm. Despite a tough addition of graphite particles into the matrix is well-known in the literature due to the high surface tension between ZA 27 alloy and graphite, copper metal coating on graphite particles was performed to control surface tension of graphite particles to make them suitable for hybrid composite production. In order to reduce a surface tension, the graphite particles were coated with copper metal.

The purpose of the coating is the metal/reinforcement phase interface structure; converting from graphite/metal to metal/metal. Surfaces of graphite particles were activated by addition of 0.2 M CuSO₄.5H₂O solution in a 380 °C furnace and a thin copper layer was formed on the particle surface based on the cementation of copper [9]. The surface and cross-sectional images of the coated graphite particles are given in Figure 1.

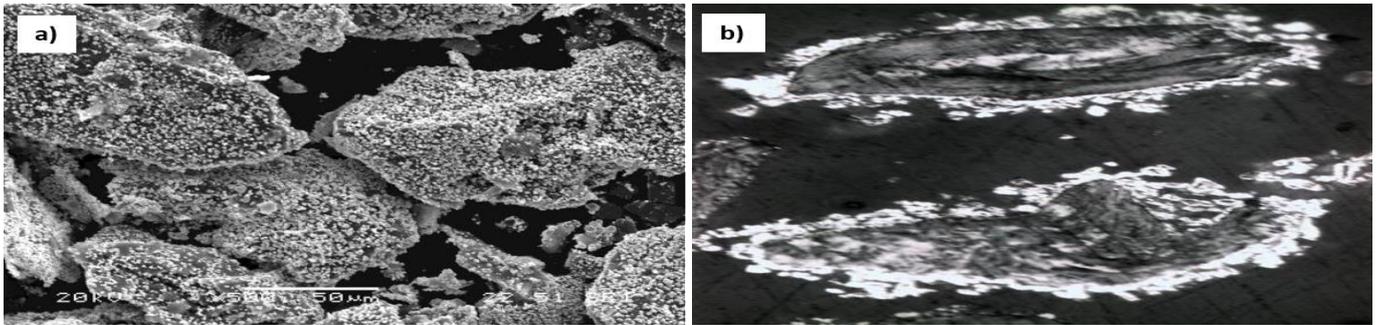


Figure 1 SEM micrograph of the graphite particles coated with Cu: a) surface image of starting graphites, b) cross sectional image of the graphite with Cu coating layer.

2.2. Heat Treatment of the Composite Materials Produced

The samples prepared for heat treatment were placed in an oven and subsequently the temperature inside was set at 330 °C and kept constant for 5 hours, and then the specimens were cooled in water.

2.3. Metallographic Studies

The samples to be used for metallographic investigation after casting and heat treatment were first prepared by cutting with a diamond disc with the help of a cutting device.

Unlike ZA 27, while composite materials consist of two components, hybrid composite materials consist of three main components: matrix, graphite particles and hard ceramic SiC particles. The metallographic preparation of these materials is a difficult process, since each of these components has their own unique hardness. Sanding and polishing processes must be done very sensitively so that the soft graphite particles and the hard and brittle ceramic reinforcement phases are not removed from the matrix by the abrasive. Specimens used for this examination were sanded in accordance with standard sample preparation methods. The specimens, which were cleaned from abrasives that may come from the sanding step by washing thoroughly, were polished with 1µm alumina.

The dried samples were etched in Keller's solution (1cm³ hydrofluoric acid; 1.5 cm³ chloric acid; 2.5 nitric acid; 95 cm³ water) for optical and SEM examination with EDS analysis. After etching, the

specimens were washed and dried again, and SEM examinations were made.

3. CONCLUSIONS AND DISCUSSIONS

3.1. Microstructure of the ZA-27 Alloy, Reinforcement Materials and the Hybrid Composites Produced

SEM image of the microstructure of the ZA-27 alloy after casting is given in Figure 2a. In Figure 2b, the microstructure image of the ZA alloy after heat treatment is given. The particle visible in Figure 2b is the η phase, which is rich in net region consisting of black thin lines, and the very thin ϵ s in this phase are in the ground.

In ZA 27 alloy, unlike other alloys, peritectic and eutectic and eutectoid reactions are seen together. During the solidification process, aluminum-rich α phase occurs in the liquid first. At 443 °C, α dendrites form a peritectic reaction with the liquid. During the formation of α dendrites containing 60% aluminum in the structure, the liquid phase becomes enriched with zinc. As a result of peritectic reaction of α dendrites with the liquid at 443 °C, zinc-rich β phases form around the dendrites. The α and β phases are in FCC structure and differ in terms of composition and lattice parameter [5]. Solidification is completed by the eutectic transformation of the remaining zinc-rich liquid. As a result of the eutectic reaction at 377 °C; aluminum-rich α phase, zinc-rich η phase and intermetallic (CuZn₄) ϵ phases are formed. This ϵ (CuZn₄) phase in the ZA 27 alloy is in a metastable state intermetallic. This phase, which is present in η as precipitate particles, contributes to the mechanical properties

positively. At 268 °C, the triple stable phase of Al_4Cu_3Zn (T') occurs as $\epsilon + \alpha \rightarrow \eta + T'$ [5,18]. $Al_4Cu_3Zn(T')$ phase contains 12.7% Zn, 31.6% Al and 55.7% Cu in content and has a rhombohedral structure. The aluminum-rich β phase, which is unstable under 275 °C, forms the α and η stable phases as a result of the eutectoid reaction. Figure 2a and 2b show the microstructures of the ZA 27 alloy after casting and heat treatment, respectively. When the cast structure is investigated, it is seen that the β phase formed as a result of the peritectic reaction

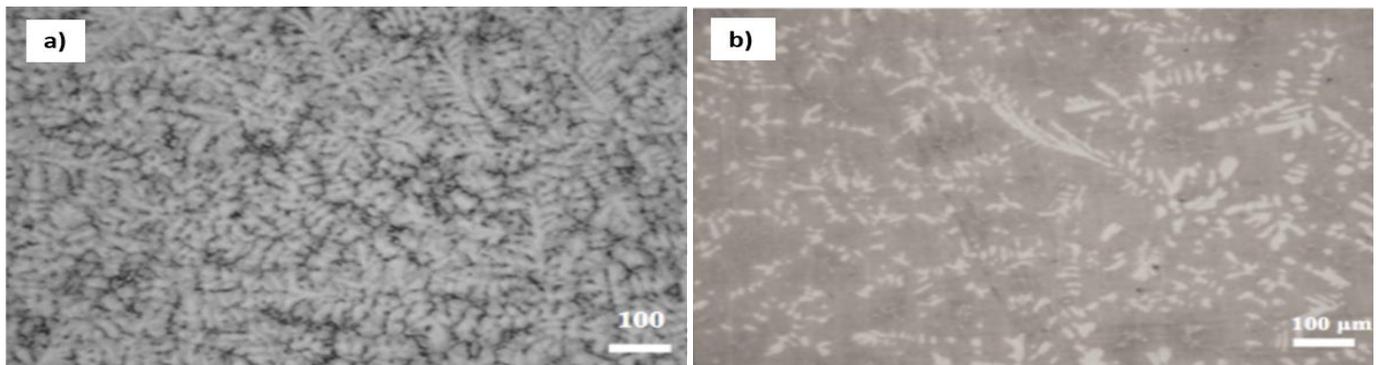


Figure 2 a) ZA 27 alloy casting state, b) thermal post heat treatment microstructure micrographs

In Figure 3, the microstructures of SiC reinforced composite materials (SRC) after casting and heat treatment are given. The matrix in the SRC casting structure is similar to the microstructure of the alloy given in Figure 2. SiC particles are homogeneously dispersed in the structure.

It is seen that the matrix microstructure of the heat-treated SRC material in Figure 2b degenerates compared to the cast structure in Figure 2a, and the dendrites are thinner.

Figure 4–7 shows the microstructures of graphite reinforced composite (GRC) materials containing 2.5-5-7.5-10% graphite by weight, after casting and post heat treatment, respectively. Due to the increase in graphite percent, segregation did not occur in 5, 7.5 and 10% graphite by weight reinforced composites. The difference in crystallization system, density difference and high surface tension between graphite and metal prevents the metal from wetting the graphite and thus forming a good bond [9]. Thanks to the copper coating, the metal and graphite bond is very well. Since the bond structure of graphite in

surrounds the first formed α dendrites. It is known that the dark colored part in the microstructures contains the α , η and ϵ phases formed as a result of the eutectic reaction of the final liquid [15]

When the heat treated microstructures in Figure 2b are investigated, It is seen that the alloy structure becomes homogeneous and the α dendrites become spherical and coarse. A similar situation has been observed in the heat treatment of Altupak's short fiber reinforced Al alloy and composites [16].

the c direction has Van der Waals bond structure, weak bonds in this direction were broken as a result of squeeze casting and liquid metal was filled in this region. In Figure 4a-5a, this structure is seen on graphite. Figure 6a-6b show the microstructures of casting and post-heat treatment of graphite reinforced composite (GRC) materials containing 2.5, 5, 7.5 and 10 % graphite by weight, respectively. Due to the increase in graphite percent, segregation did not occur in 5, 7.5 and 10% by weight reinforced composites. The difference in crystallization system, density difference and high surface tension between graphite and metal prevents the metal from wetting the graphite and thus forming a good bond [9].

Thanks to the copper coating, the metal and graphite bond very well. Since the bond structure of graphite in the c direction has Van der Waals bond structure, weak bonds in this direction were broken as a result of squeeze casting and liquid metal was filled in this region. Figure 4a-5a shows this structure on graphite.

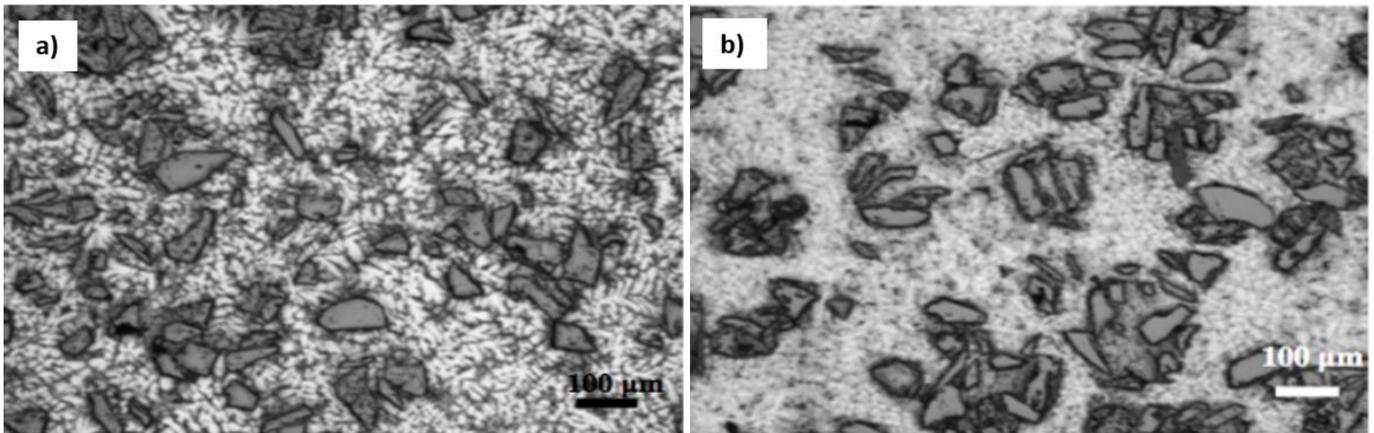


Figure 3 Microstructure photographs of a) casting state of 10% SiC reinforced composite, b) post heat treated graphite reinforced composite

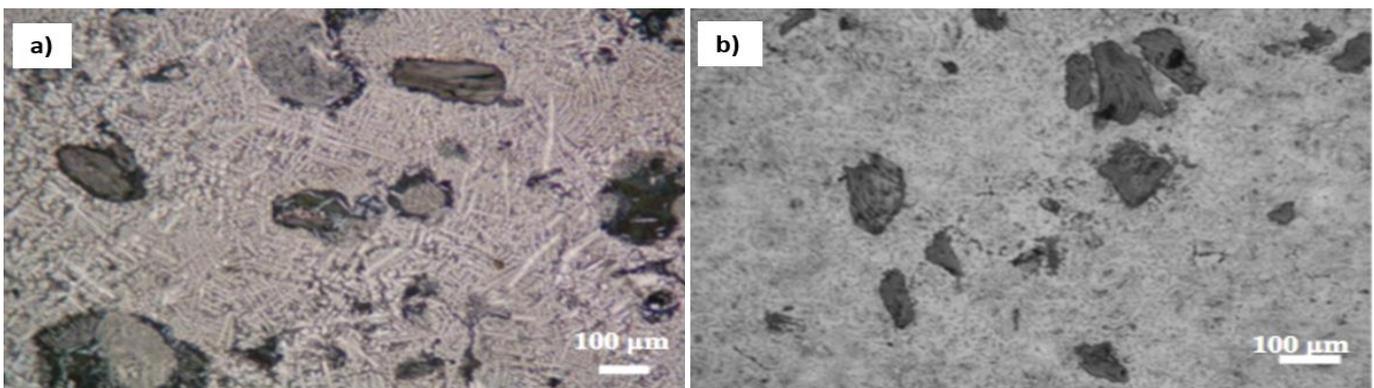


Figure 4 Microstructure pictures of a) casting of 2.5% graphite reinforced composite b) post heat treated graphite reinforced composite

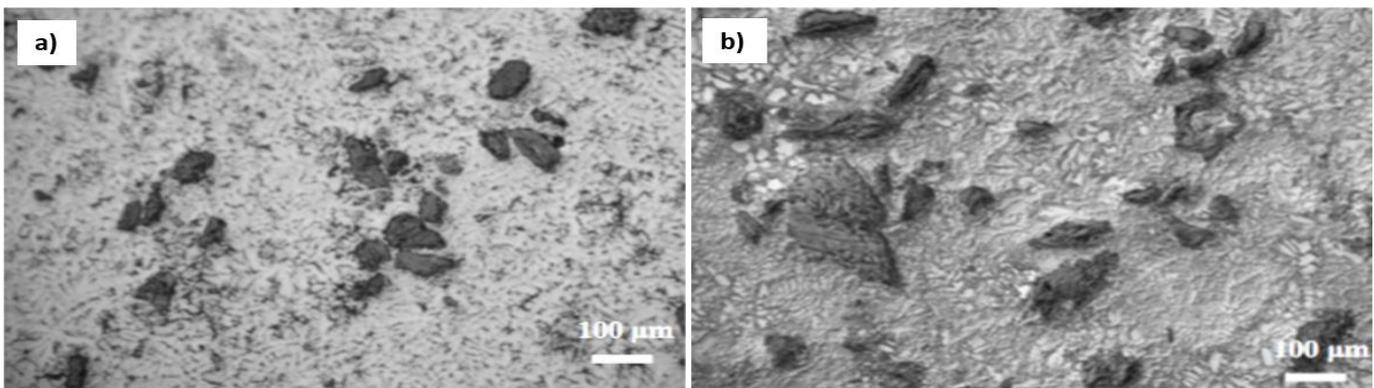


Figure 5 Microstructure photographs of a) casting state of 5% graphite reinforced composite, b) post heat treated graphite reinforced composite

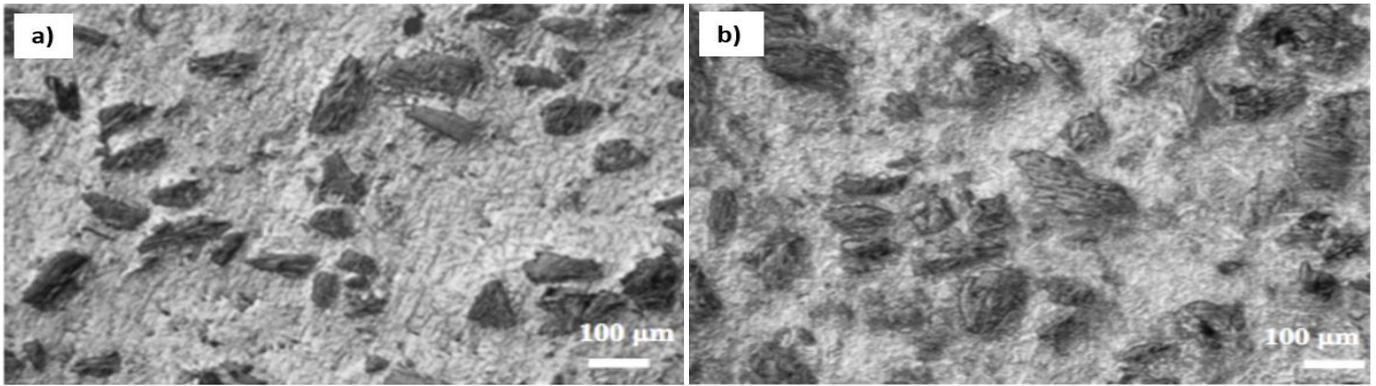


Figure 6 Microstructure photographs of a) casting state of 7.5% graphite reinforced composite, b) post heat treated graphite reinforced composite heat

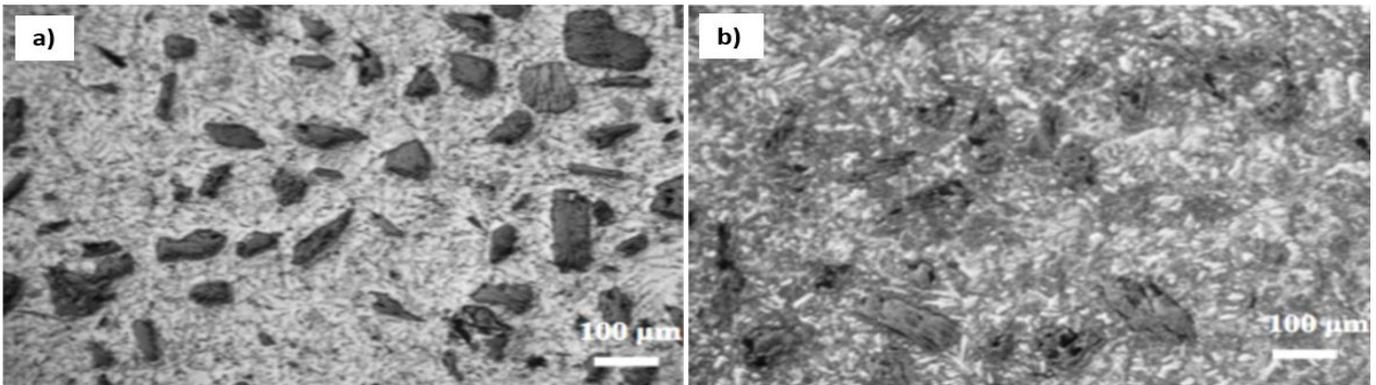


Figure 7 microstructure pictures of a) 10% graphite reinforced composite casting state, b) post heat treated graphite reinforced composite

In Figure 8-11, casting and heat treated microstructures of hybrid composite (HCM) materials containing 10% SiC and 2.5-5-7.5-10% graphite by weight respectively, are given. In addition, in Figure 9a and 10a, finer dendritic structure is seen around graphite with much higher heat conductivity, while coarser dendrites grow around SiC. Figure 8b-10b clearly shows the microstructure formed post heat treatment. The resulting white areas are primary α and around

them $\alpha+\eta$ structure is seen. After heat treatment, primary α phases in the form of dendrites become spherical. In the HCMs in Figure 8-11, this spheroidization size is at a lower order compared to the heat-treated microstructure of the alloy in Figure 2b. The same behavior was detected in 10% SiC reinforced and graphite reinforced materials. Increasing reinforcement ratio prevents coarsening of primary α dendrites.

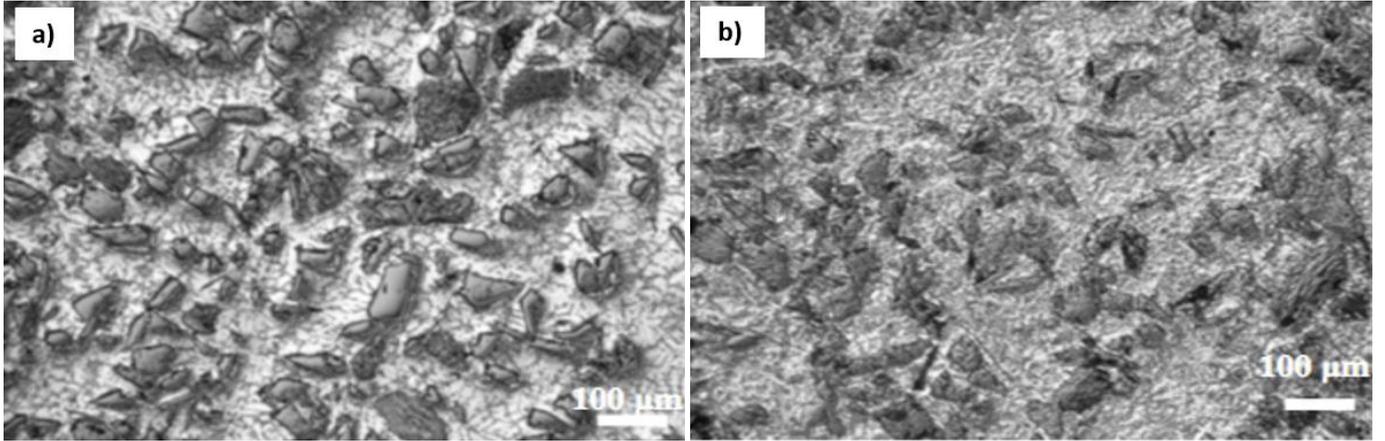


Figure 8 Microstructure photographs of a) casting state of 10% SiC + 2.5% graphite by weight reinforced hybrid composite b) heat treated state

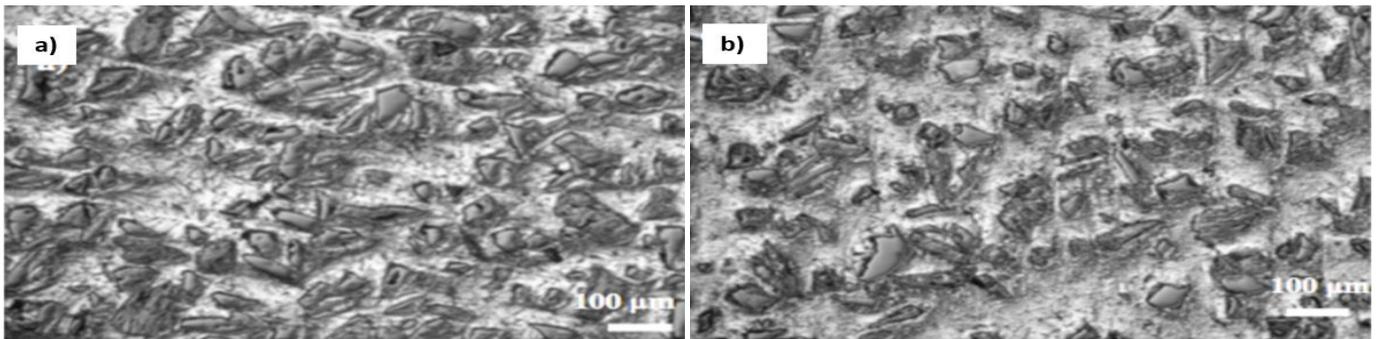


Figure 9 Microstructure photographs of a) 10% SiC + 5% by weight graphite reinforced hybrid composite as casting, b) heat treated state

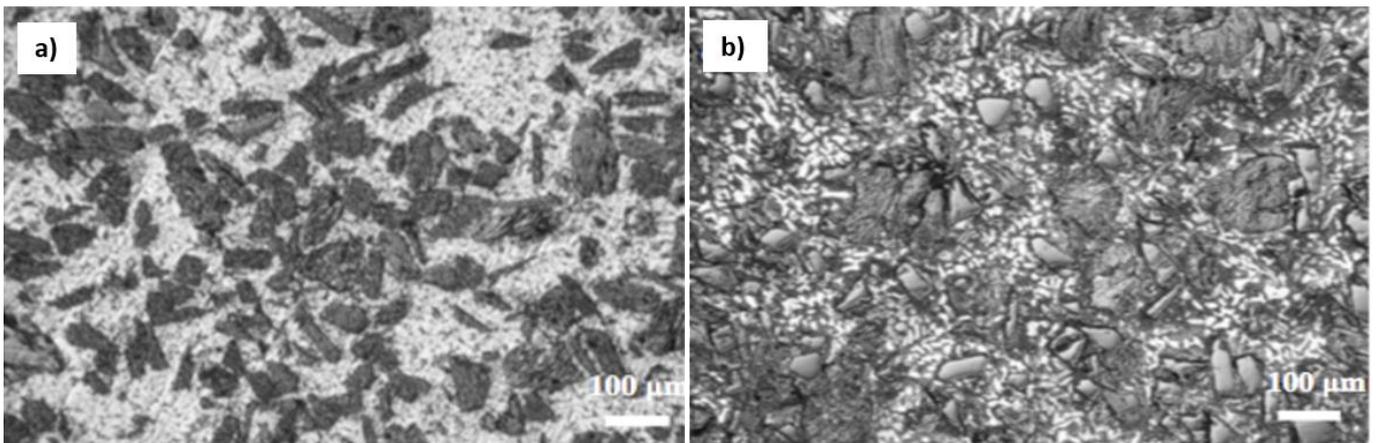


Figure 10 Microstructure photographs of a) 10% SiC + 7.5% by weight graphite reinforced hybrid composite casting state, b) heat treated state

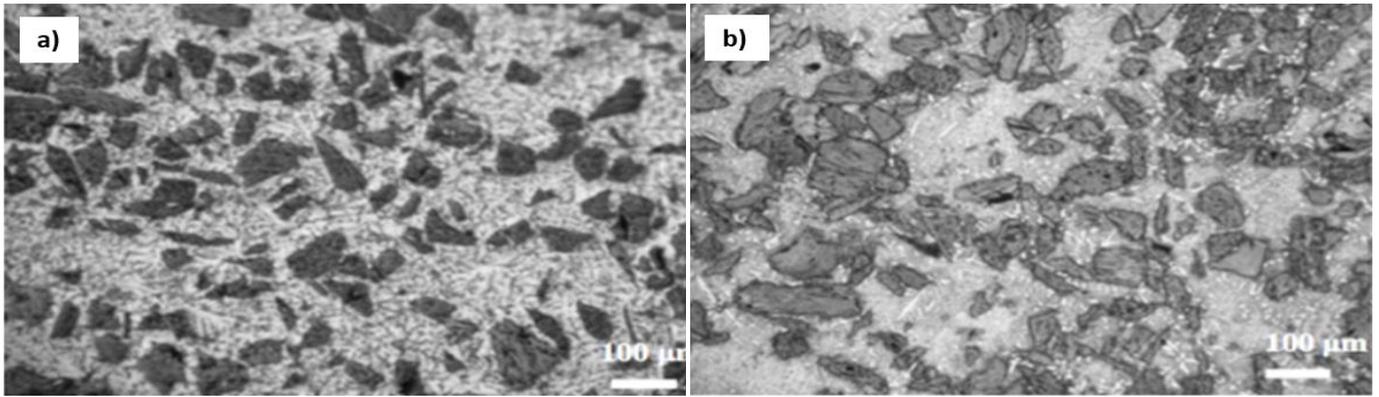


Figure 11 Microstructure photographs of a) 10% SiC + 10% by weight graphite reinforced hybrid composite casting state, b) heat treated state

Electron microscope images of ZA 27 alloy, SRC, GRC and HCM and EDS analysis of these images are given in Figure 12-24. In electron microscope (SEM) images, Zn-rich phases were detected in light tones, while Al-rich phases were detected in dark tones. Durman and Murphy [17] showed that the ϵ phase contains 84% Zn and 14.8% Cu by weight. In our study, EDS analyzes taken from the ϵ phase in electron microscope images give 82-85% Zn and 14-15% Cu content by weight, in accordance with the literature. Durman and Murphy, in their studies, showed that Cu in the alloy in the metastable ϵ phase, Zn rich eutectic η and high temperature phase β precipitated as very small particles in the η matrix formed as a result

of the eutectoid transformation and preserved its metastable existence for a very long time, for more than five years. It has been proven in the examinations made on samples aged at room temperature. The ϵ phase is not stable at temperatures below 268 °C and must be transformed into the T' phase. The T' phase consists of 58% Cu, 30% Al and 12% Zn, and accordingly, the transformation of the ϵ phase to the stable T' phase requires diffusion of aluminum into the ϵ phase. However, due to the very low aluminum solubility in the η matrix and the similar crystal structures of the η and ϵ phases, it can maintain its metastable existence in the ϵ phase and η matrix for long periods of time

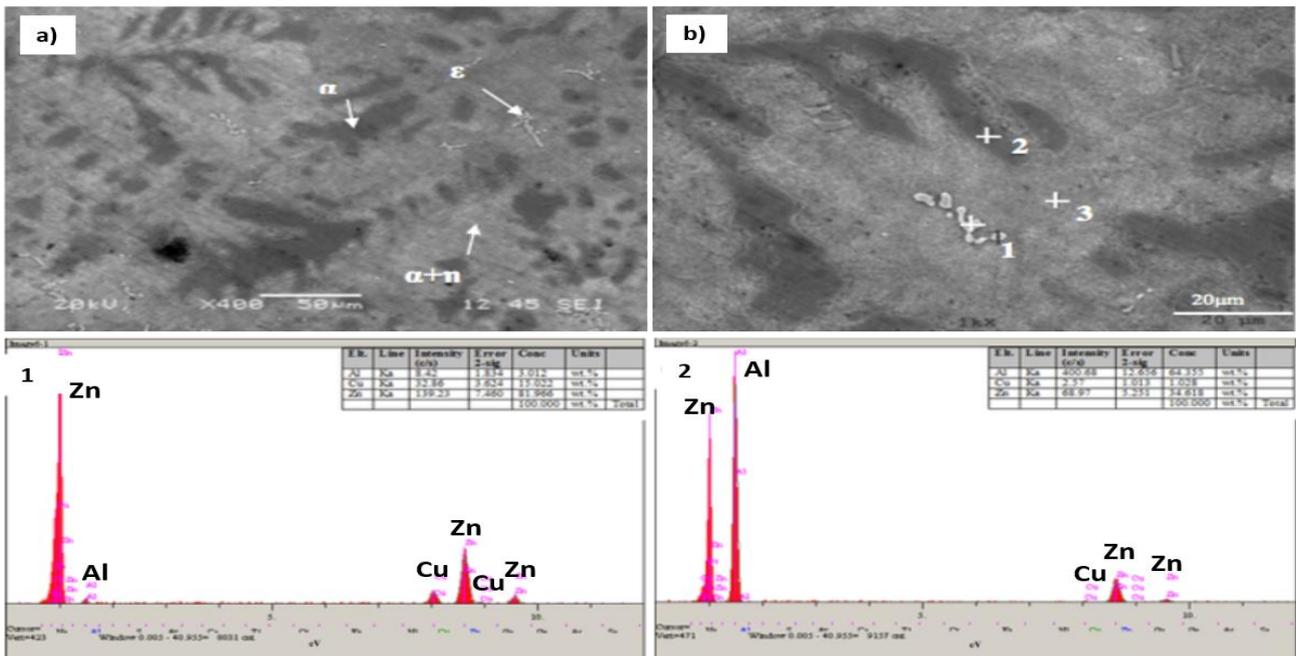
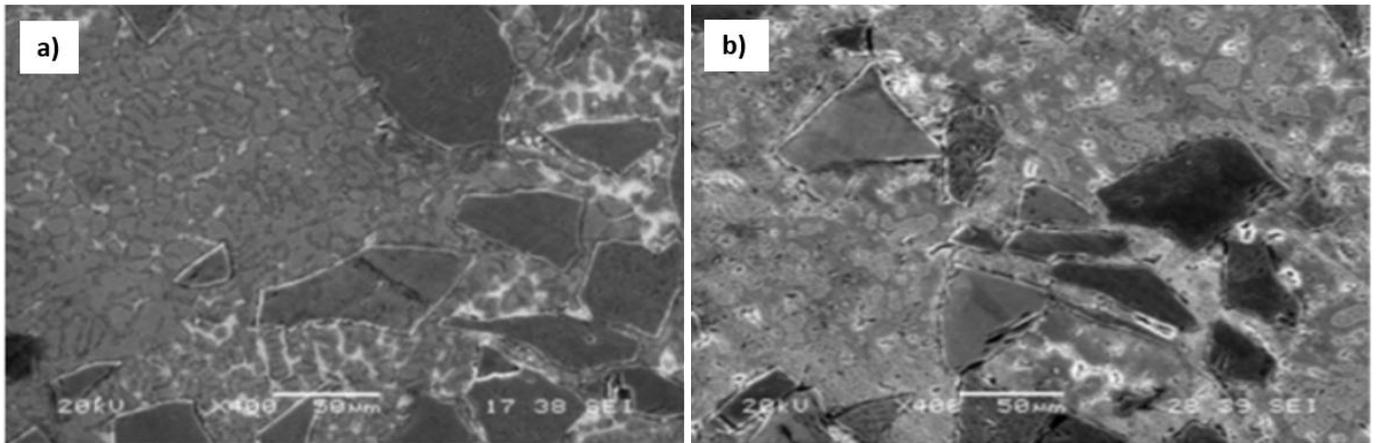
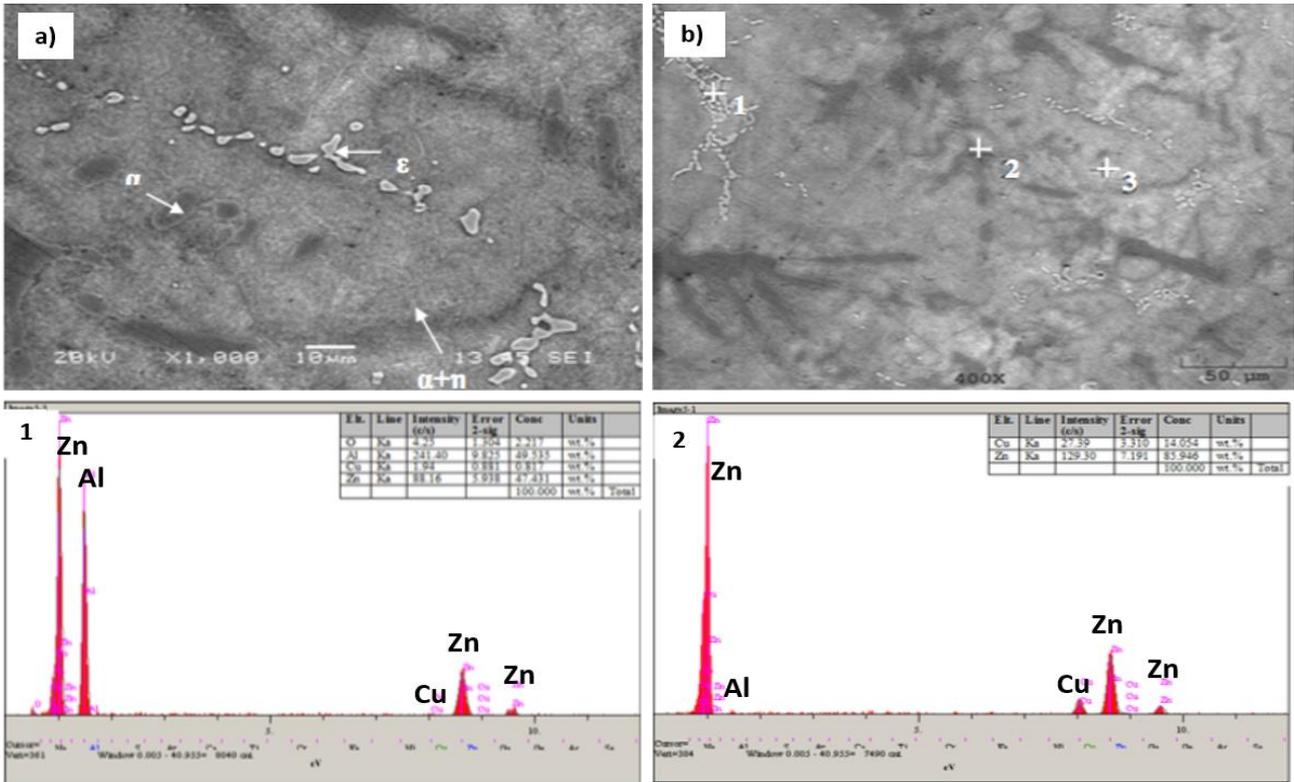


Figure 12 a-b) SEM structure of cast ZA 27 alloy, 1-2) EDS analysis of cast ZA 27 alloy



In Figure 15–19, it is seen in SEM images that it consists of islet-shaped primary α phases and surrounding $\alpha+\eta$ phase structure as in standard

ZA 27 alloys. After the heat treatment in the structure, the ϵ phases remain intact.

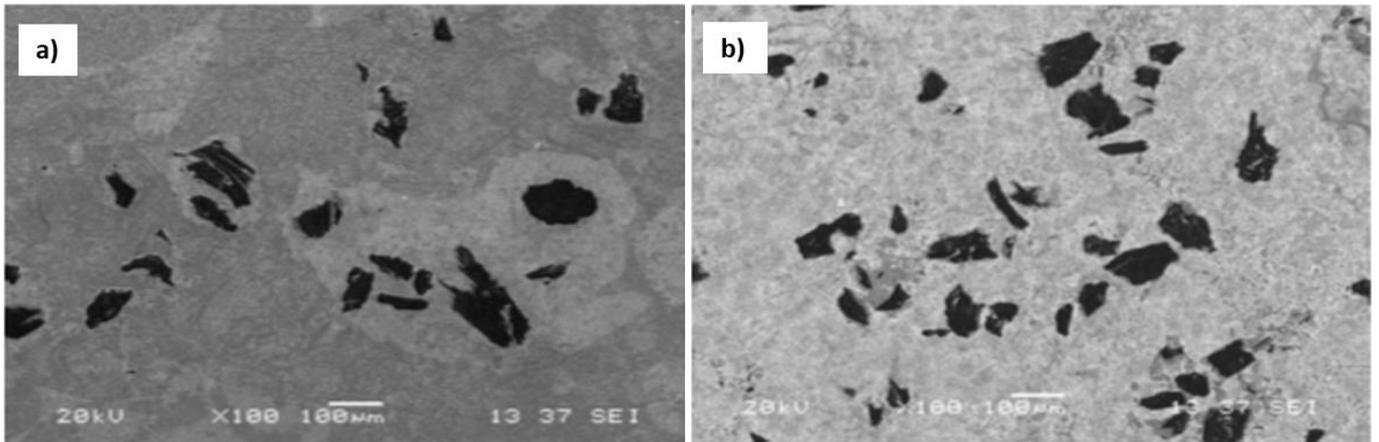


Figure 15 SEM structure of 2.5% by weight graphite reinforced composite material (GRC) a) casting state b) heat treated state

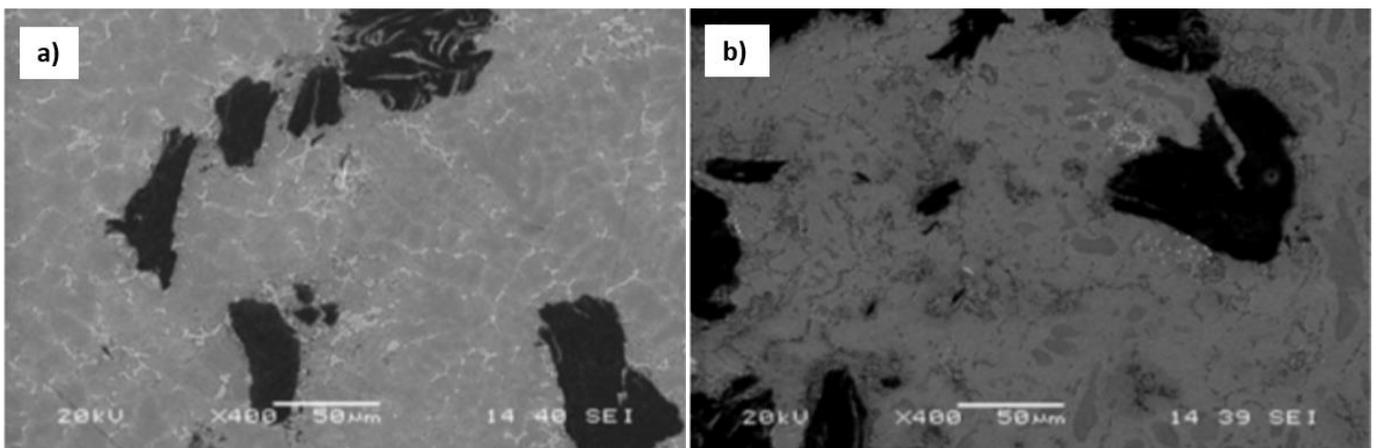


Figure 16 SEM structure of 5% graphite by weight reinforced composite material (GRC): a) Casting state, b) Heat treated state

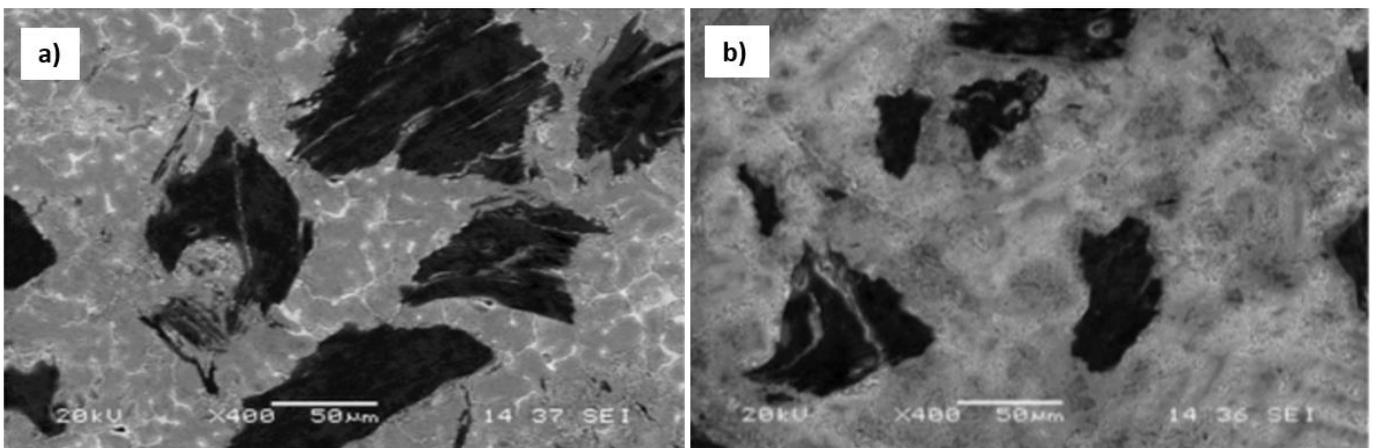


Figure 17 SEM structure of 7.5% Graphite by weight reinforced composite material (GRC): a) casting state b) heat treatment state

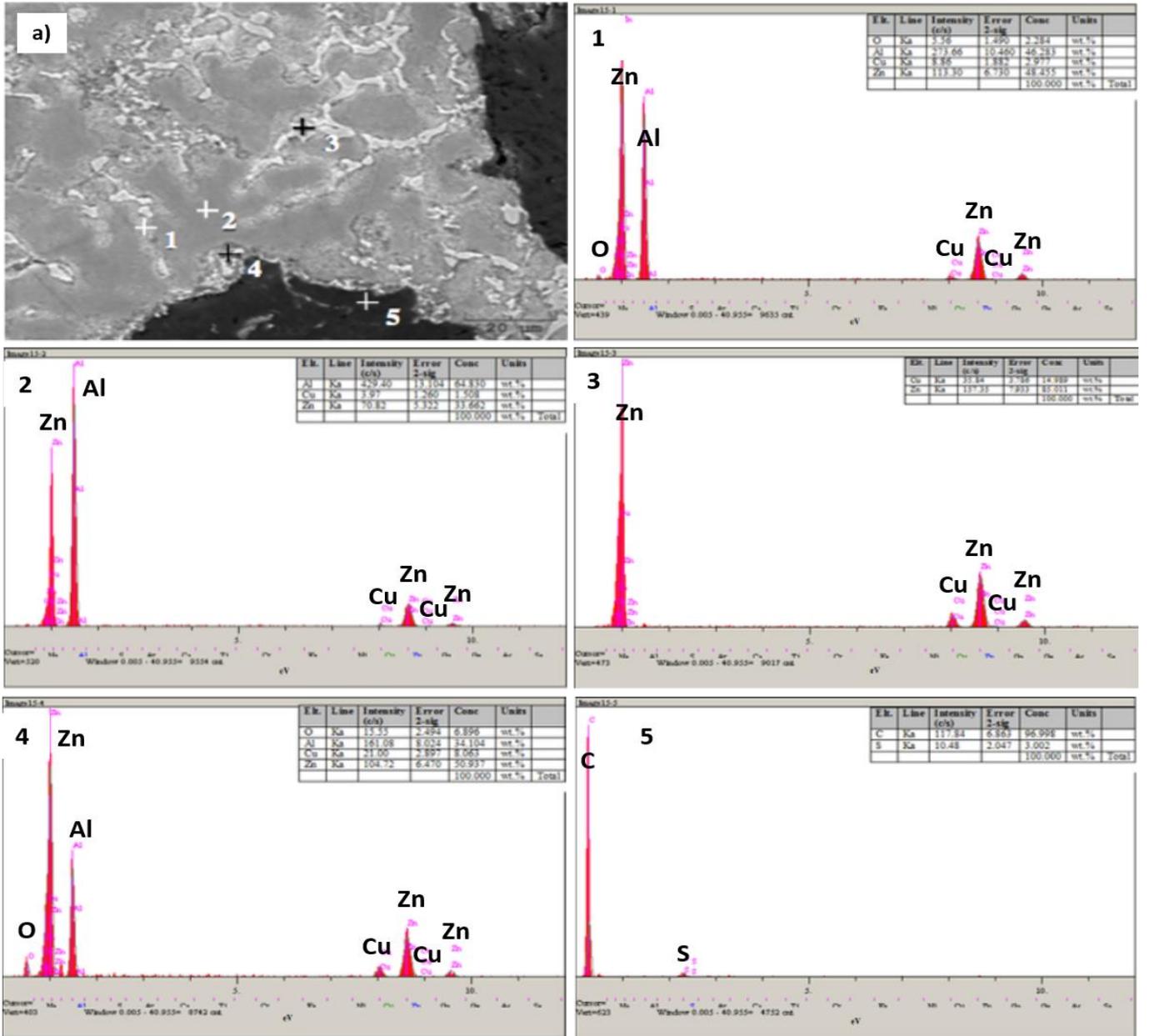


Figure 18 SEM structure of 10% graphite by weight reinforced composite material (GRC) a-b) cast state, 4-5) EDS analysis

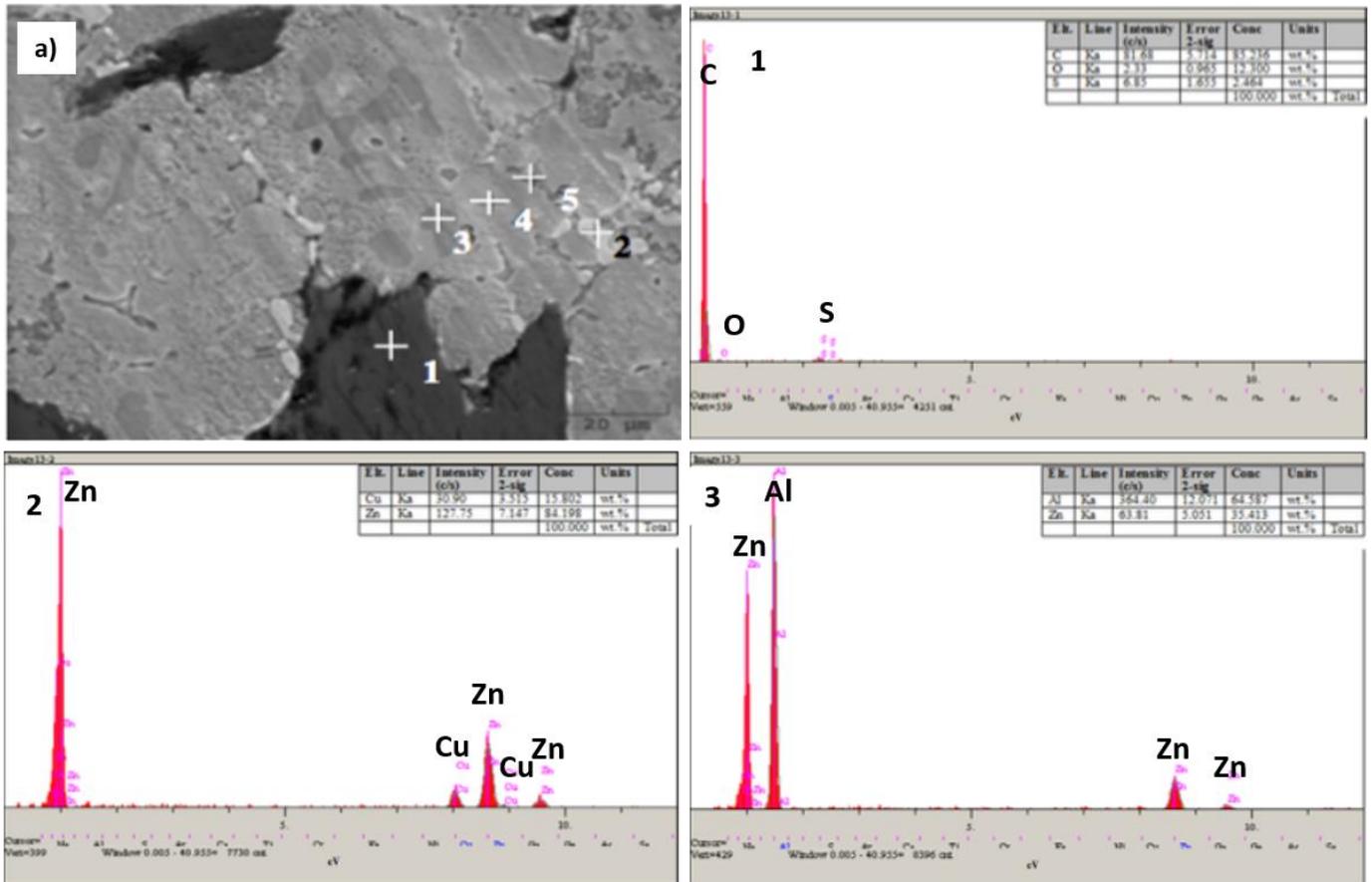


Figure 19 SEM structure of 10% graphite by weight reinforced material (GRC) b) heat treated state 1-3) EDS analysis

Electron microscope images and EDS analyzes of hybrid composite materials (HCM) containing 10% SiC and 2.5-5-7.5-10% graphite, respectively, are given in Figure 20-24. The matrix shows the same properties as in the ZA 27 alloy, SRC and GRC. When the HCM structures are examined, it is seen that the graphite and SiC particles are homogeneously dispersed in the matrix and the matrix and particle interface is very good. Hibrit kompozit malzemelere ilave edilen grafitler aynen As with GRC composites, it is very well wetted by the matrix. The images that prove this are the matrix phase infiltrating the

graphite in Figure 21 and 22. The high strength bearing feature of the SiC reinforcement phase in the hybrid composites has preserved its physical stability during the vortex method and compression casting production. When both SRC and HCM are examined, it is seen that most of the SiC particles remain in the matrix without deformation. However, it was determined that very little SiC and graphite were fragmented during the production of the composite by vortex and during the production by high pressure compression casting method.

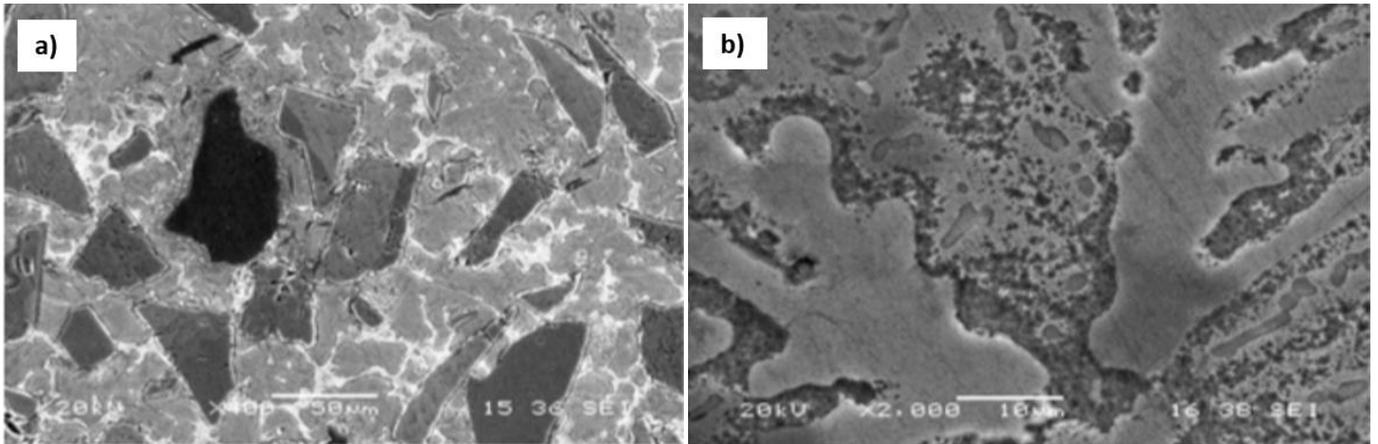


Figure 20 SEM structure of 10% SiC and 2.5% graphite by weight reinforced hybrid composite material (HCM) a) casting state b) heat treated state

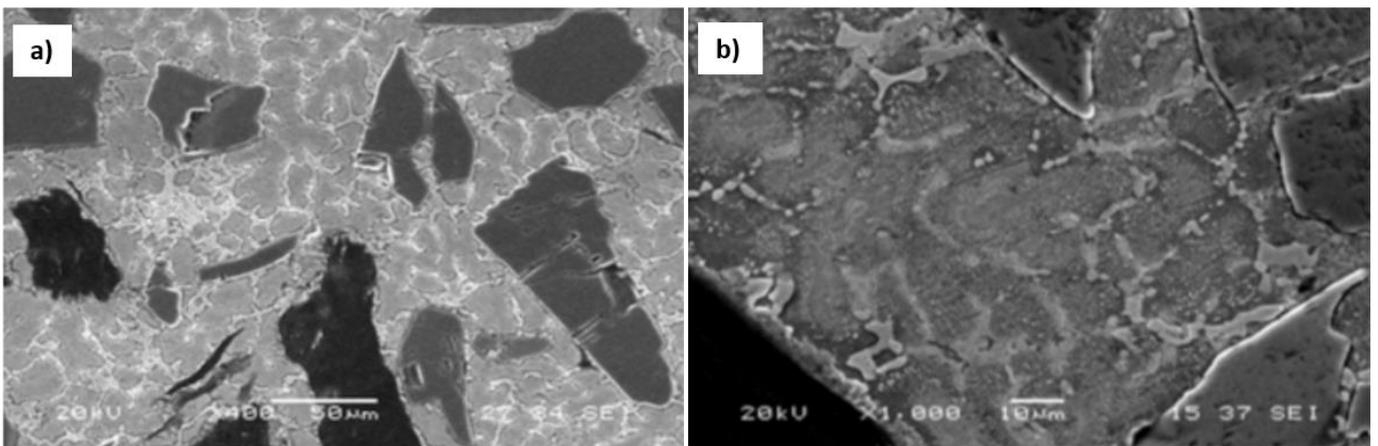


Figure 21 SEM microstructure of 10%SiC and 5% graphite by weight reinforced hybrid composite material (HCM) a) casting state b) heat treated state

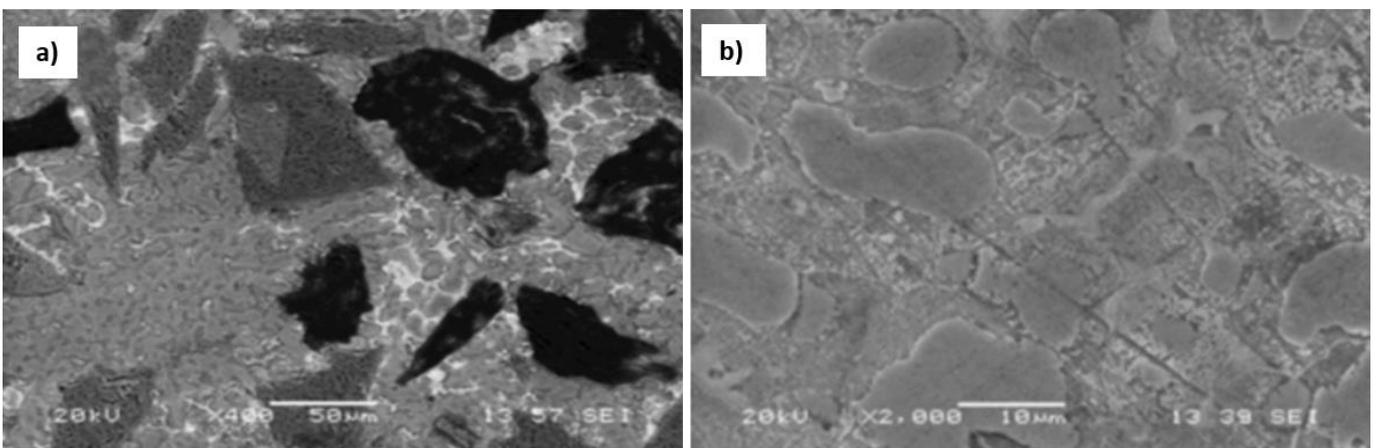


Figure 22 SEM structure of 10% SiC and 7.5 % graphite by weight reinforced hybrid composite material (HCM) a) casting b) heat treated state

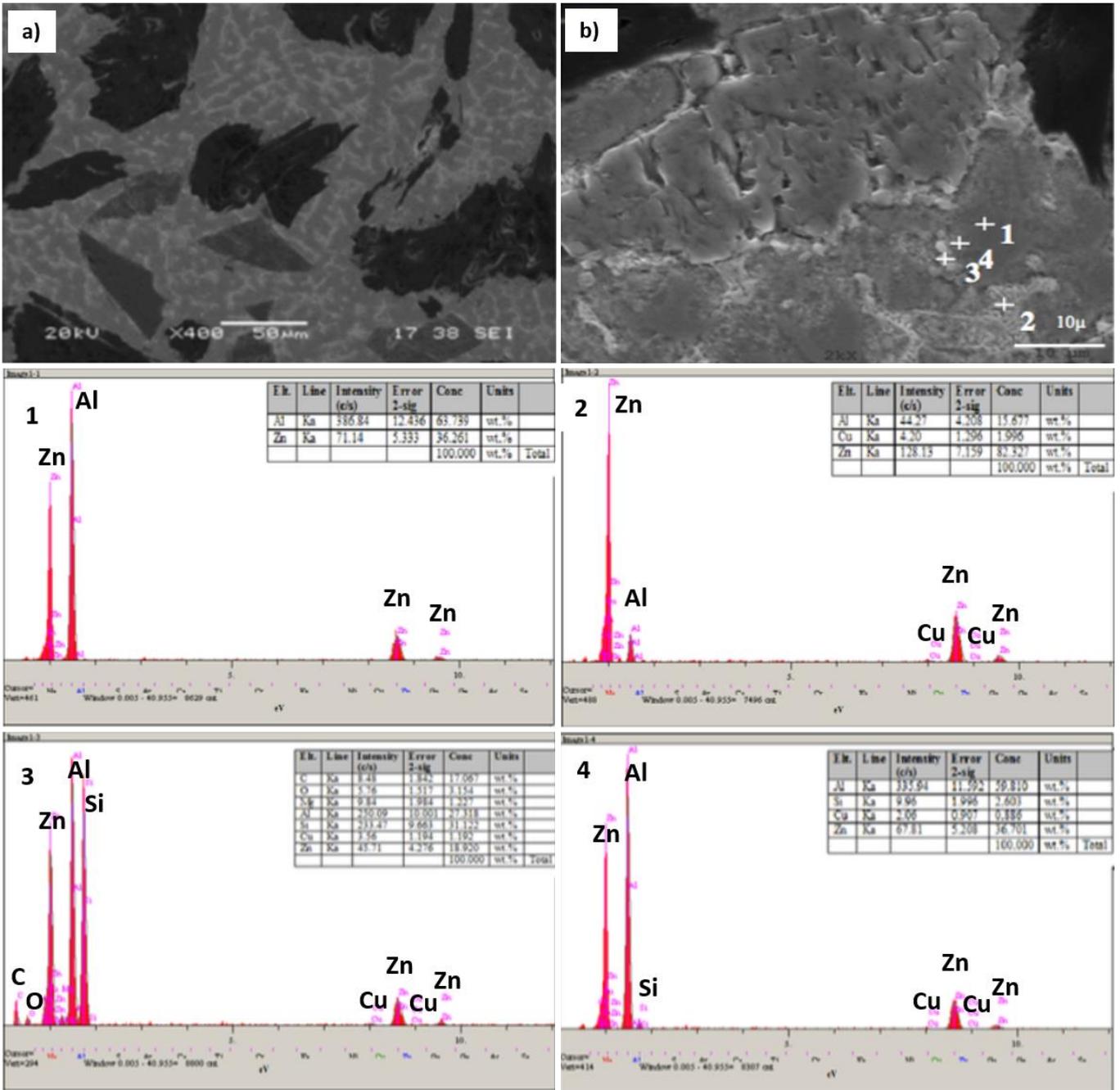


Figure 23 SEM microstructure of a-b) cast hybrid composite material containing 10%SiC and 10% graphite by weight 1-4) EDS analysis

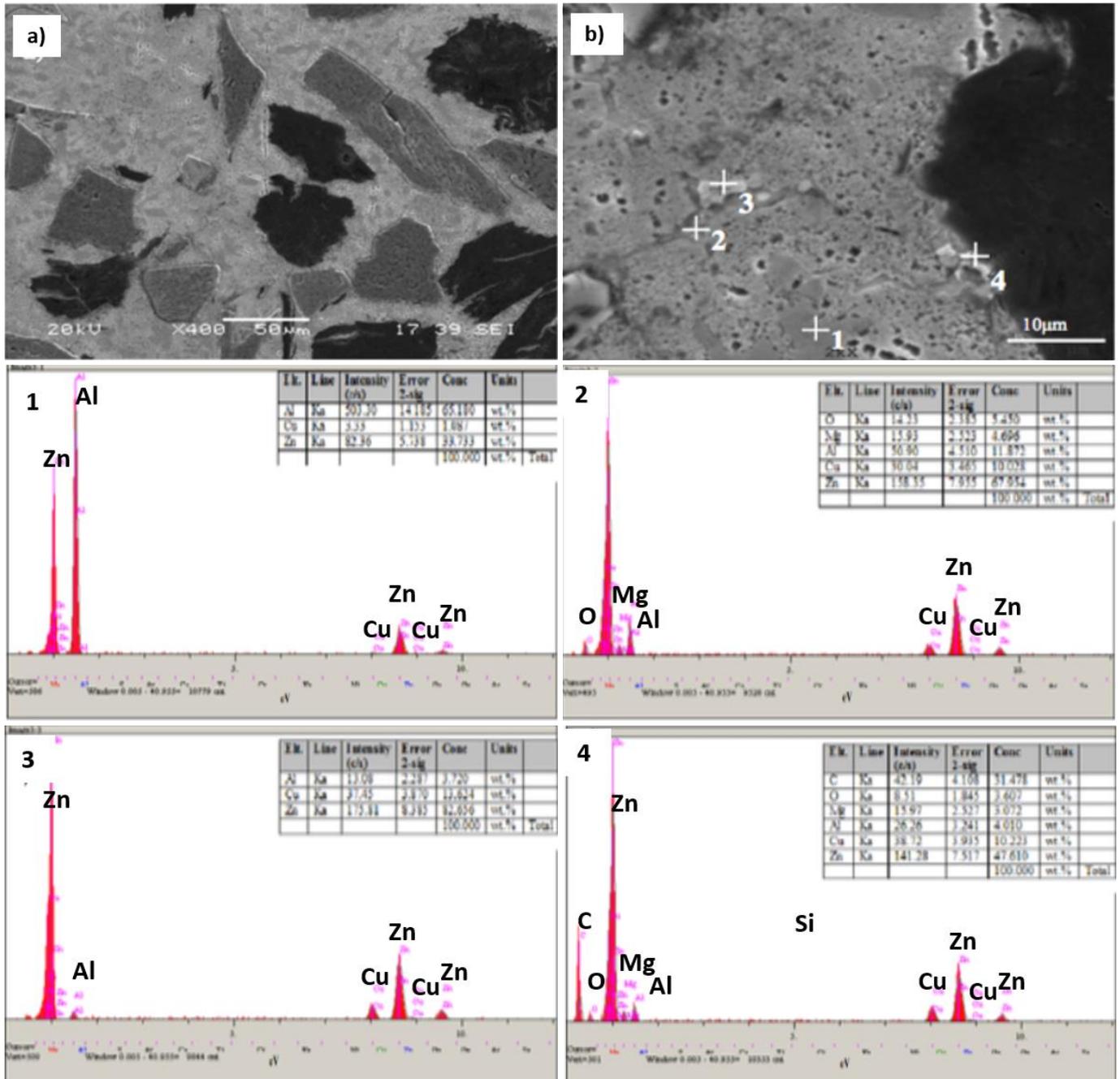


Figure 24 SEM microstructure of the hybrid composite material (HCM) a-b) heat treated state containing 10%SiC and 10% graphite by weight 1-4) EDS analyzes

4. CONCLUSION

1- The ZA-27 metal matrix alloy and hybrid composite materials with an addition of SiC and graphite particles produced by the vortex method and casted by the compression casting method which allows reinforcements generally homogeneously distributed in the matrix. In the optical investigation, it was determined that very little particle segregation occurred in 2.5%

graphite reinforced composite (GRC), and this segregation disappeared with an increase in graphite addition.

2- SiC and graphite particles added to the 2-ZA-27 alloy which had a heterogeneous nucleating effect during solidification.

3- Thin dendrites tend to become a spheroid shape after heat treatment.

3-Thin dendrites tend to spheroid after heat treatment.

Acknowledgments

We would like to thank Prof. Dr. Hatem Akbulut and Assoc. Prof. Dr.. Mehmet Uysal for providing laboratory facilities.

Funding

The author (s) has no received any financial support for the research, authorship or publication of this study.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

The first author contributed 80%, the second author 20%.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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