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Microstructural and mechanical properties of Cr-C reinforced Cu matrix composites produced through powder metallurgy method

Özgür Özgün*[1], Ali Erçetin[1]

Abstract

In this study, Cu matrix composite materials were produced by powder metallurgy technique (PM) by adding Cr and C at different ratios to pure Cu powder. Powder mixtures obtained by adding Cr and C at various ratios into the Cu powder were shaped by applying a pressure of 300 MPa. The specimens were sintered at different temperatures in order to determine the optimum sintering temperature. The success of the sintering process was evaluated by density measurements. The microstructure and mechanical properties of the produced composite specimens are characterized. Microstructural characterization was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) analyses. The effects of Cr and C addition on mechanical properties at different ratios were evaluated by hardness measurements and tensile tests. Density measurements have shown that the relative density values that can be achieved with increased Cr and C ratios are increased. XRD analysis showed that Cr formed carbide and nitride compounds in the microstructure during sintering. The hardness values obtained with these Cr and C ratios increased with the increase of these compounds.

Keywords: Cu, Cr-C, composite, microstructure, hardness, tensile strength

Toz metalurjisi metoduyla üretilen Cr-C takviyeli Cu matrisli kompozitlerin mikroyapı ve mekanik özellikleri

Özet

Bu çalışmada saf Cu tozu içerisine farklı oranlarda Cr ve C ilavesi yapılarak toz metalurjisi tekniği (T/M) ile Cu matrisli kompozit malzemeler üretilmiştir. Cu tozu içerisine farklı oranlarda Cr ve C ilave edilerek elde edilen toz karışımları 300 MPa basınç uygulanarak şekillendirilmiştir. Optimum sinterleme sıcaklığının tespit edilmesi amacıyla şekillendirilen numuneler farklı sıcaklıklarda sinterlenmiştir. Sinterleme işlemlerinin başarısı yoğunluk ölçümleri ile değerlendirilmiştir. Üretilen kompozit numunelerin mikroyapı ve mekanik özellikleri karakterize edilmiştir. Mikroyapısal karakterizasyon X-ışınları analizi (XRD), taramalı elektron mikroskobu (SEM) ve enerji dağılım spektrometresi (EDS) incelemeleri ile gerçekleştirilmiştir. Farklı oranlarda Cr ve C ilavesinin mekanik özelliklere etkisi sertlik ölçümleri ve çekme testleri ile değerlendirilmiştir. Yoğunluk ölçümleri artan Cr ve C oranıyla birlikte ulaşılabilen bağıl yoğunluk değerlerinin arttığını göstermiştir. XRD analizi, Cr'un sinterleme işlemi esnasında mikroyapıda karbür ve nitrür bileşikleri oluşturduğunu göstermiştir. Oluşan bu bileşiklere bağlı olarak artan Cr ve C oranıyla birlikte elde edilen sertlik değerleri de artmıştır.

Anahtar Kelimeler: Cu, Cr-C, kompozit, mikroyapı, sertlik, çekme dayanımı

1. Introduction

Due to excellent thermal and electrical conductivity [1], copper is one of the most common used metallic materials in the industrial applications [2]. Good corrosion resistance and oxidation resistance [3] with good ductility and toughness [4] are other outstanding features that copper has. Despite these superior properties, the most important deficiency limiting the usage of copper and its alloys is the low strength and inadequate wear resistance [5]. Copper is most preferred for applications requiring high thermal and electrical conductivity [6]. However, some applications require adequate hardness and wear resistance as well as good thermal and electrical conductivity [2]. Therefore, intensive researches have been done to improve the mechanical properties of copper. Alloying is one of the main ways to improve the mechanical properties of copper [7]. Another way to follow is to produce copper matrix composites with reinforcing elements such as oxides, borides, carbides and nitrides [8-10]. Through the use of reinforcing elements, mechanical properties such as hardness, strength, wear resistance and creep resistance can be improved considerably [11].

PM is a method of producing metallic parts in a homogeneous and fine-grained microstructure [12]. PM is the most cost-effective of all other production techniques possible in the production of any part [13]. Due to the use of

[1] Bingol University, Faculty of Engineering and Architecture, Department of Mechanical Engineering, 12000 Bingol, Turkey

*Corresponding author E-mail: oozgun@bingol.edu.tr

strategic elements [12,14], one of the most important advantages of PM is to increase the flexibility of the alloy system [14,15]. This makes it possible to produce parts from alloy systems with chemical compositions that cannot be combined with other production methods [16,17].

In this study, Cu matrix composites were produced by PM method by adding Cr and C into Cu powder at different ratios. The prepared powder mixtures were shaped under 300 MPa pressure and sintered at different temperatures. The sintered parts are characterized by density measurements, microstructure research and mechanical tests. Microstructural characterization is based on XRD, SEM and SEM/EDS. The change in mechanical properties was determined by hardness measurements.

2. Material and Method

In the studies, 99% pure Cu powder produced by Sigma-Aldrich was used. SEM image of the Cu powder with a particle size in the range of 14-25 μm and close to the particle-shaped spherical is given in Figure 1a. Cr powder added for composite production was obtained from Atlantic Equipment Engineers. This powder given in the SEM image is 99.8% pure and the particle size is 1-5 μm. The particle size of the graphite powder used is below 20 μm.

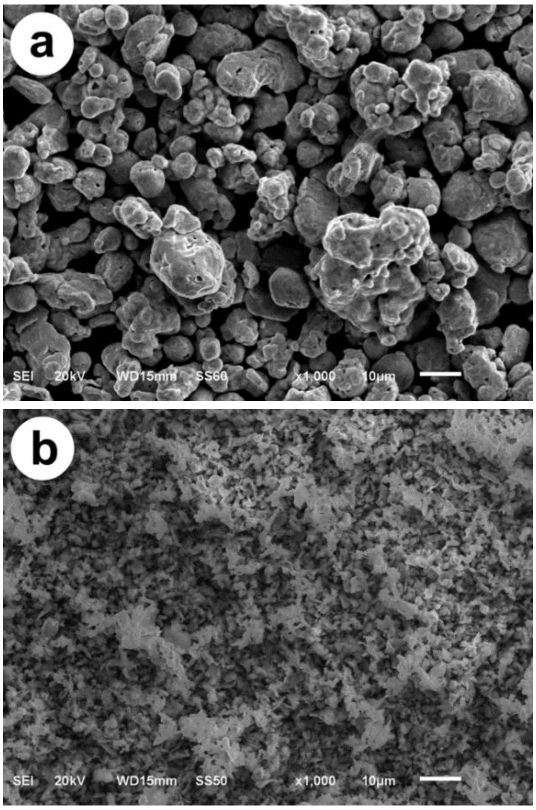

Figure 1. SEM images of **a)** Cu powder, **b)** Cr powder used in study

Table 1 presents chemical compositions of powder mixtures prepared for composite production. The powders were physically mixed after being weighed on a 0.0001 precision scale to provide the ratios indicated in Table 1. Cylindrical samples with a diameter of 13 mm were pressed by applying pressure of 300 MPa from the obtained mixtures. The pressed samples were sintered in high-purity nitrogen atmosphere at different temperatures between range of 1060-1100 °C (with 10 °C difference). Heating and cooling rate of 10 ^{o}C/min were used for sintering and samples were kept at sintering temperature for 150 min.

Table 1. Chemical composition of the prepared powder mixtures

	wt%		
Sample Name	**Cu**	**Cr**	**C**
CuCr10C1	89	10	1
CuCr20C2	78	20	2
CuCr30C3	67	30	3
CuCr40C4	56	40	4

The densities of the produced samples were determined according to the Archimedes principle. XRD analyses were performed at a scan rate of 0.002/0.4 degrees/sec using a Cu X-ray tube (λ=1.5405) on a Rigaku Ultima IV X-ray diffractometer. For microstructure studies, the samples were passed through the metallographic preparation stages and then were etched in 50% pure water + 50% HNO_3 solution. SEM and SEM/EDS studies were performed with JEOL JSM 6510 scanning electron microscope and IXRF 550 brand EDS system connected to this device. Hardness measurements were made with Vickers method and 25 g load on Wilson Hardness brand hardness meter. The samples to be used in the tensile tests are shaped with the mold prepared according to the ASTM E8 standard. Tensile tests were carried out using a Shimadzu AG-IC 50 kN model device at a constant speed of 0.5 mm/min using 3 samples per composition.

3. Results and Discussion

Figure 2.a shows the variation of the relative density of the composite materials produced due to the sintering temperature. When Cu-Cr phase diagram [18] is examined, it appears that there is an eutectic reaction at 1070 °C. Accordingly, it can be seen that the sintering process performed at 1070 ^{o}C provides the highest concentration of sintering performed at different temperatures for all compositions. In Figure 2.b, the relative density values of composites sintered at 1070 °C are given. It is seen from Fig. 2 that obtained relative density value is also increased with the increase in the amount of Cr amount. The highest relative density value was reached with a composition containing 40% Cr by weight, which was 95.51% on average.

Figure 3 shows XRD diffraction patterns of composites sintered at 1070 °C. When the figure is examined, the intensity of the peaks of Cu decreases with increasing Cr ratio. It is seen that the diffraction patterns of all the samples contain peaks belonging to the compounds formed by Cr. One of these compounds is the carbide compound of type $M_{23}C_6$, which is the result of coupling of Cr with added carbon during sintering. In this study, it was aimed to increase the hardness and hence the strength by forming carbide compounds in microstructure by adding C together with Cr into Cu and it has done. In addition to the carbide phase from XRD patterns, Cr appears to form nitride compounds by reaction with the selected nitrogen as sintering atmosphere during sintering. It has been reported that Cr produces oxide compounds in the sintering process using high purity inert gases in the production of different material groups containing Cr by PM techniques [19-21]. In accordance with this literature knowledge, in the present study, Cr oxide compounds were formed during sintering in a high purity nitrogen atmosphere. Along with the increase in the Cr ratio in the diffraction patterns, the intensity of the peaks of the compounds formed by Cr also increases.

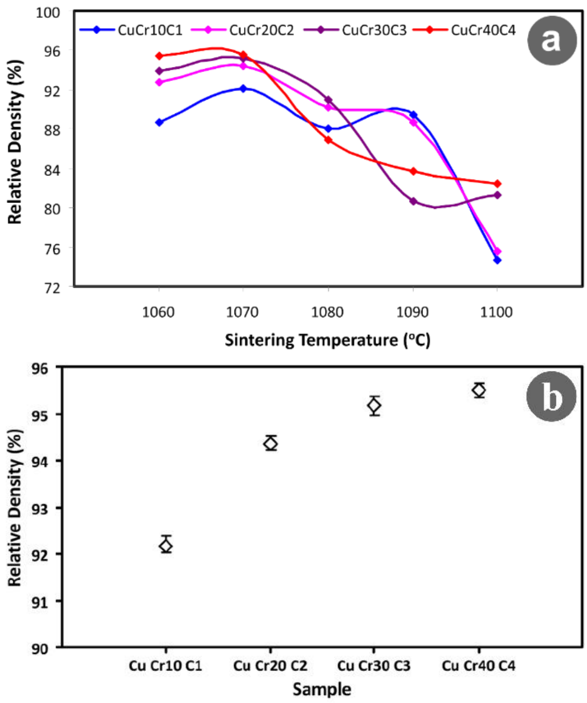

Figure 2.a) Change of relative density with sintering temperature in the produced composites, **b)** Obtained relative density values by sintering at 1070 °C

SEM images taken from the produced composites are given in Figure 4. SEM images were taken from the sintered samples at 1070 °C where the highest relative density was obtained. When images are viewed, it is seen that the porosity is lower in the samples with higher Cr content, consistent with the results obtained from the density measurements. According to the phase diagram [18], Cr does not dissolve in Cu at room temperature. Therefore, all of Cr added is found in grain boundaries and turns into a continuous film with increasing Cr ratio. It is seen that grain size in matrix is changed in the range of 20-30 μm. In the study, Cu powder having an initial particle size of 14-25 μm was used and there was no significant decrease in grain size, although the sintering was carried out for a long period of time like 150 min at 1070 °C. However, it is noteworthy that the matrix of the high-content Cr-containing composites is finer grained. It has been reported in the literature that hard phases in grain boundaries play a role in inhibiting grain blooming [22-24]. In the present study, the lower grain size in samples with higher Cr ratios suggests that the phases formed by Cr deposited at grain boundaries in the above information light in the literature prevent grain growth.

It has been reported that in most metal matrix composite systems produced by PM techniques, inadequate bonding at the matrix-reinforcement interface affects the properties of the produced composites negatively [25-27]. Inadequate soaking at the matrix-reinforcement interface results in both manufacturing difficulties and also in the service conditions causing the composite to be damaged from these interfaces [28]. In order to overcome this problem, it is necessary to take precautions to improve interface bonding in most composite systems [29-30]. When the SEM images are examined, it is seen that in the present study, a good bond is formed between the Cu matrix and the phases formed by Cr without applying any special measures. This is important in terms of mechanical properties.

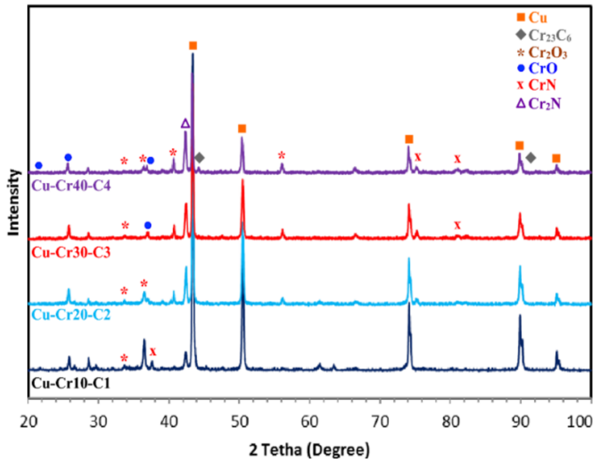

Figure 3. XRD diffraction patterns of the produced composites

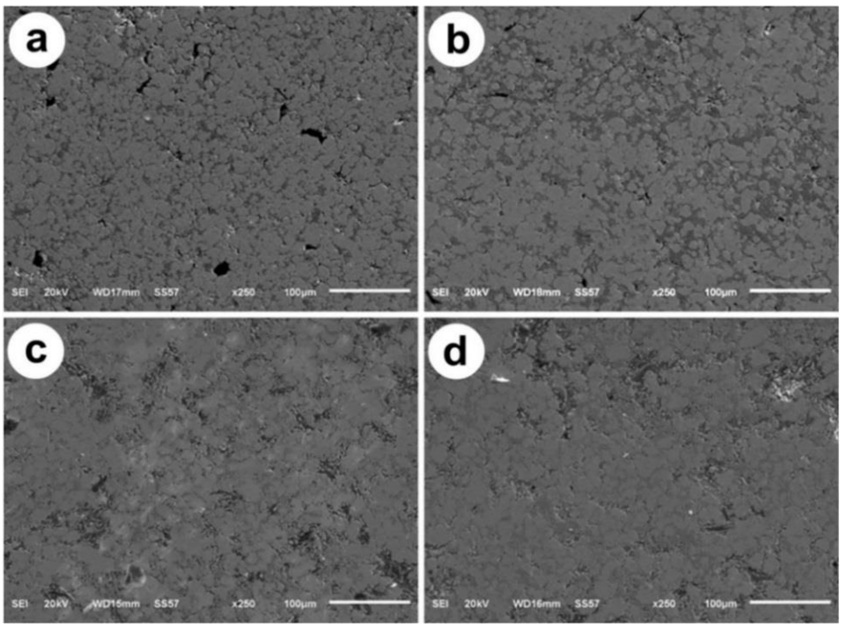

Figure 4. SEM images of the samples; **a)** CuCr10C1, **b)** CuCr20C2, **c)** CuCr30C3, **d)** CuCr40C4

Figure 5 shows images of SEM/EDS analysis taken from CuCr40C4 sample. In region 1, which is found in the Cu matrix, 97.2% by weight of Cu and 2.78% by weight of Cr are present. Considering that Cr is never soluble in Cu, there is no mention of the presence of a solid solution in this region. The low amount of Cr in this region is thought to be in the form of small-sized particles trapped in the matrix. According to the EDS analysis taken from area 2 at the border of the grain, there are 77.7 %wt Cr, 12 %wt Cu and a small amount of C and O elements in this region. This suggests that carbides and oxide compounds are formed by Cr in this region.

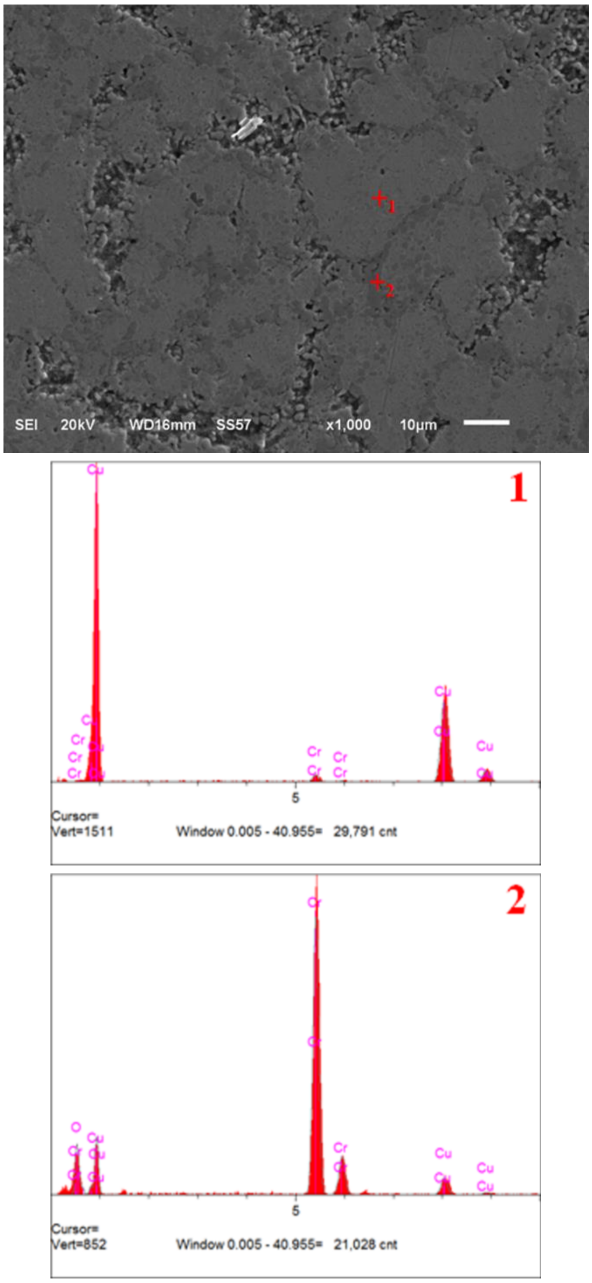

Figure 5. Images of the SEM/EDS analysis taken from the CuCr40C4 sample

Figure 6 shows the hardness values measured from the produced composites. Higher hardness values were achieved with increased Cr ratio. This is due to the increase in the presence and amount of hard phases detected by XRD and SEM/EDS analyses generated by Cr in the microstructure. The highest hardness value was obtained on the CuCr40C4 specimen, with an average of 273.13 $HV_{(0.025)}$.

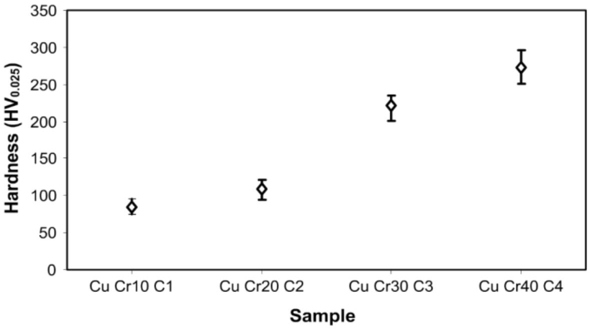

Figure 6. Hardness values of the produced composite samples

The average stress-strain curves obtained from tensile tests applied to the samples are given in Figure 7. With increasing Cr and C addition ratio, the ductility values of composite materials showed a remarkable decrease. This is due to the increase in the ratio of determined hard phases in microstructure by XRD, SEM and EDS analyses. Cr and C addition ratios increased to 30% Cr and 3% C addition ratios so yield and tensile strengths were also increased. The highest tensile strength is achieved with 30%wt Cr and 3%wt C added composites. The average tensile strain reached in these samples was 186.7 MPa. However, as the Cr content increased to 40% and the C content increased to 4%, the tensile strength decreased considerably. It is because of that addition at these ratios causes brittleness in samples which have these ratios.

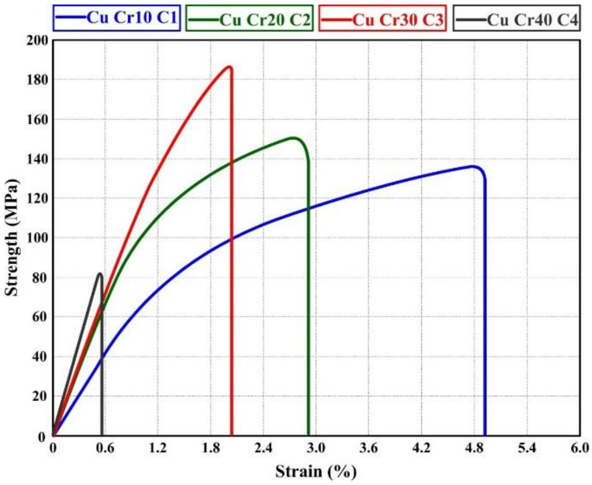

Figure 7. Average tensile strength and strain values of produced composite specimens

SEM images taken from the fracture surfaces after the tensile test are given in Figure 8. All samples have hard phases embedded in the matrix at the fracture surfaces. All the specimens except CuCr40C4 have dimple formations that indicate ductile fracture at fracture surfaces. The dimple formations are particularly noticeable at the fracture surfaces of specimens with low added Cr and C. It has been mentioned above that the addition of Cr and C increases the amount of hard phases formed in the microstructure. During fracture, these phases constitute the starting points in the formation of cracks. The increase in the amount of hard phases affects the fracture behaviour as much as the size is important. In the SEM image descriptions, the increased Cr and C addition ratio was reported to increase the size as well as increase the amount of hard phases. It is thought that large sized hard phases accelerate the formation of cracks because the hard phases in fracture lead to crack formation.

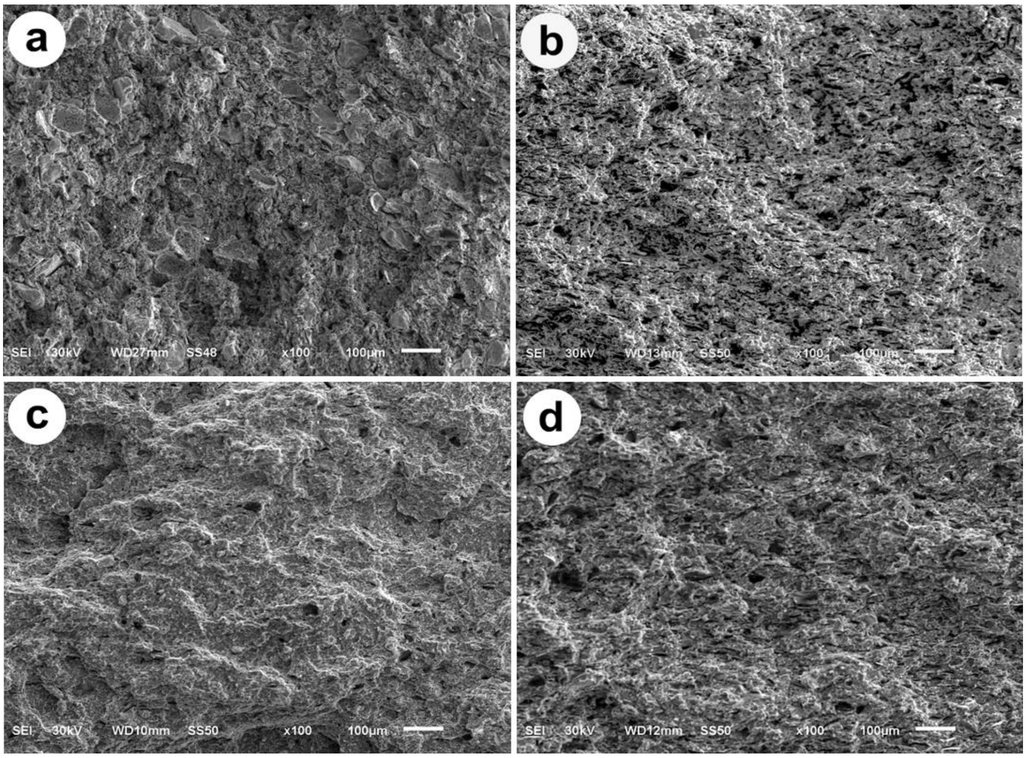

Figure 8. SEM images of fracture surfaces of samples

4. Conclusions

In this study, Cu matrix composite material with 4 different contents was produced by using PM method. The following results were obtained from the characterization processes applied to the produced composite materials.

1) The highest concentration of sintering performed at different temperatures was sintering at 1070 ^{o}C, the eutectic reaction temperature for Cu-Cr. The relative density values obtained with the increase in the amount of Cr added are also increased.

2) XRD analysis showed that Cr formed different compounds during sintering. One of these compounds is the carbide compound which is formed by the addition of graphite and Cr. Furthermore, the sintering process in the nitrogen atmosphere caused Cr to form different nitride compounds.

3) The phases formed by Cu matrix and Cr can be distinguished in composites produced in SEM examinations. The phases formed by Cr are usually located in grain boundaries and become a continuous film with increasing Cr ratio. It was observed that the grain size of the Cu matrix changed between 20-30 μm and these grains were surrounded by phases formed by Cr. In particular, in the sample containing 40% Cr, the phase formed by Cr turned out to be a continuous network surrounding Cu grains.

4) In the produced composites, higher hardness values were obtained due to the increase of the Cr and C ratio and the increase in the amount of hard phases in the microstructure.

5) In the produced composites, the strength values increased with the increase of Cr and C ratio (except CuCr40C4) and the elongation values decreased.

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