EFFECT OF WC REINFORCED ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CUALMN ALLOYS PRODUCED BY HOT PRESSING METHOD

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In this study, the effect of WC reinforcing particles on the microstructure and mechanical properties of CuAlMn and CuAlMn-WC alloy produced by powder metallurgy method was investigated by adding 5 %, 10 % and 15 % by volume WC to CuAlMn alloy. Cu, Al, Mn and WC powders of approximately 99.9 % purity with a grain size of 325 mesh were used in the production of the alloys. The samples were produced by hot pressing method at 900 °C temperatures under 35 MPa pressure for 6 minutes. Microstructure, phase formation, hardness and corrosion properties of the samples were investigated in detail. Scanning electron microscopy (SEM) was used for microstructure analysis and X-ray diffractogram (XRD) was used for phase formation detection. The hardness measurements of the samples were measured by microhardness measuring device. The corrosion tests were performed potentiodynamic polarization curves of the composite materials in 3.5% NaCl solution. As a result, it has been determined that the mechanical properties of WC reinforcing particles added to CuAlMn matrix increase with increasing volume ratio.

Key words: CuAlMn alloys, hot press, mechanical properties, microstructure properties, reinforced WC

1. Introduction

With the rapid development of technology, many new types of materials are being developed and used. These materials are more suitable for today’s conditions and their usage is becoming widespread. Metal matrix composite materials have also been studied in recent years and new types of materials are derived. Production method with PM is a method used to produce full or semi-finished products [1]. It has been stated that some composite materials, such as super alloys and hard metals, can only be produced by the PM method, because the melting temperatures of the metals are very high and it is very difficult to reach these temperatures under industrial conditions [2,3,4]. Many different Cu alloys are used in the chemical industry and electro technologies [5-7]. Cu alloys have high corrosion and oxidation resistance in addition to their good thermal resistance and electrical resistance. In addition, copper has a good ductility and toughness [8]. Composites with Cu matrix have high thermal conductivity and electrical conductivity. In addition, the mechanical properties and tribological properties of these composites are good [9-12].

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Metal matrix composites have many positive properties such as high elastic modulus, high strength and reproducibility [13]. In addition, these materials have very good abrasion resistance due to particle reinforcements [14,15]. There is also a lot of research on composites with copper matrix [16]. In a study, the abrasion resistance was improved by adding Ni₃Al particles to the copper matrix [9]. CuCr SiC composite material has been produced and it has been stated that the hardness increases in the examination [17]. In addition, FeMnp and FeCrp were added to the Cu matrix to investigate their microstructure and mechanical properties [18]. By adding different additions to the Cu matrix, its hardness, strength, abrasion resistance and conductivity can be improved [19]. In addition, tensile strength increased up to 4% within the varying Cu matrix ratios; It was observed that after 4% it decreased and the hardness increased with increasing Cu matrix ratio [20].

Although powder metallurgy (PM) is not a newly known process, it was only used as an industrial process in the early 20th century. PM method has been used extensively in different fields since the beginning. As an example to these; tool steels, stainless steels, superalloys, aluminum and titanium alloys, copper and copper alloys, nuclear materials and cerments can be given [1-5,21]. Parts produced by this method have a smoother surface than parts produced by other methods and often do not require secondary treatment. It was determined that approximately 97% of the first material used in mass production with PM was used. Accordingly, the production of the part is cheaper and in the desired composition, and some parts that are difficult to produce and process by other methods are easily produced. By making fluctuations on the value of the punch pressure, it is possible to produce products in various forms in a better quality and in a proper manner [4].

Demand increases for copper (Cu) based alloys, especially Cu-Al-Ni, CuZn-Al and Cu-Al-Mn alloys due to their cheap cost and good shape recall effects and superelasticity in engineering applications [22-24]. Cu-based shape recall alloys have been in great demand after the 1960s and have been used as alternatives to NiTi alloys, because they have good electrical and thermal conductivity [25,26]. Cu based shape remembering alloy systems are in great demand in the practical applications of shape remembering alloys. Because it can be produced both cheaply and easily. However, as the high Al additive to this alloy causes the grain boundaries to weaken, it creates a very fragile alloy. It is important to add new elements to strengthen the Cu-Al alloy with a good ductility [27,28]. The addition of new elements to Cu-Al alloys made this alloy group more useful and attractive. However, in addition to the elementary additive, CuAl based shape recall alloys can improve the performance of the applied heat treatment. Generally, high temperature shape recall alloys are important in the robotics, automotive and aircraft industries. The application temperatures of these alloys should be above 390 K [29,30]. In this study, the effect of heat treatment temperature and heat treatment time on the conversion temperature and crystal structure of CuAlMn alloy, which is a new high temperature shape remember alloy, will be examined. There are some studies in the literature about the production of Cu-Al-Mn alloys with the PM method and the relationship between the microstructure and mechanical properties [31,32]. For example, Yu-Yang Gao et al. [33,34] in their study, they made a characterization study by adding different ratios of SiC to Al-Cu-Mg-Si-Mn composites by using PM method. They determined that the particles were dispersed homogeneously and the tensile strength increased. This has been linked to the formation of precipitates of SiC particles during sintering and post-sintering cooling. Yan et al. In their study, they investigated the change of martensitic phase by adding Ni to Cu-Al-Mn shape memory alloy casting method. They found that when 2% Ni was added, the triple Cu-Al-Mn alloys increased the shape memory from 85% to 92%. Cu-Al-Mn alloys have a high tensile strength. It is used in the production of
machine parts, vehicles, lifting gear, railway wagons in constructions where high strength is required. Strength in Hardened State It has been determined that it reaches the strength of 52 steel [32].

2. Experimental Procedure

In the starting matrix powders, Cu, Al, Mn and WC an average particle size 44 μm were used. The matrix in produced segments that was sintered by hot pressing process. Powder mixtures were weighed by using precision scales and mixing process was applied for 30 minutes by using a turbula mixer (Celmark Group 7T, Turkey). PEG 400 (Polyethylene Glycol) at a rate of 1,5 wt% was added in the powder mixture in order to reduce friction forces during hot pressing and to provide a homogenized mixture. Previously, powders were weighed 20 grams, and then CuAlMn-WC were produced with a pressure of 300 MPa by using double-effect hydraulic press (Dim-Net WP-45SA, Korea). After that, CuAlMn-WC were placed within graphite dies and hot pressed under vacuum atmosphere by a PLC controlled direct hot pressing machine (Zhengzhou Golden Highway, SMVB 80, China) (Fig. 1).

Figure 1. PLC controlled direct hot pressing machine.

Following that production process was completed by applying a sintering to the samples in a furnace (Prothem, PLF 120/27, Turkey) under argon atmosphere at 900 °C and under pressure 35 MPa and for 4 minutes. Composite parameters of production were given in the Tab. 1.

Table 1. Hot pressing production parameters.

| Sample | Pressure (MPa) | Temperature (°C) | Time (min.) | Chemical Composition |
|--------|---------------|------------------|-------------|---------------------|
| 1      |               |                  |             | CuAlMn              |
| 2      | 35            | 900              | 4           | CuAlMn - 5 % WC     |
| 3      |               |                  |             | CuAlMn - 10 % WC    |
| 4      |               |                  |             | CuAlMn - 15 % WC    |

The produced composite samples were characterized for hardness, optical microscope. Surface of the samples were polished with 200, 400, 600, 800, 1000 and 1200 mesh wet sandpaper by using grinding device (Metkon Forcimat, Turkey). Microhardness of the samples were measured in Vickers
microhardness terms (HV$_{0,1}$) by using 16 second time and 0,1 kg of load. Surface of the samples were etched by a special etcher which consists of 50 gr. (FeCl$_3$ – 6H$_2$O) + 960 ml. methanol + 200 ml. HCl after polishing and then microstructure investigations were performed. The SEM images and EDS analyzes of the materials were obtained from the “FEI” brand “Quanta FEG 250” in model device at Kastamonu University Central Research Laboratories (Fig. 2a). The XRD analyzes of the samples were taken from “Bruker” brand “D8 Advance” model device at Kastamonu University Central Research Laboratories (Fig. 2b).

![Figure 2. (a) FEI QUANTA 250 FEG SEM analyzer, (b) Bruker D8 Advance XRD analyzer.](image)

The hardness measurements of the materials were done by using “SHIMADZU” brand “HMV-G21” model microhardness measurement device (Fig. 3a) under 16 min. waiting time and 100 g load. Corrosion tests of the produced materials were made by “Gamry” brand Potentiostat / Galvanostat device (Fig. 3b).

![Figure 3. (a) SHIMADZU HMV-G21 model microhardness measuring device, (b) Reference 3000 Potentiostat / Galvanostat / ZRA device.](image)

3. Results and Discussion

The SEM images of the CuAlMn-WC composites produced by the powder metallurgy method (Fig. 4) were taken and evaluations were made according to the obtained images.

When the SEM images are examined, it is seen that WC particles are distributed homogeneously in the interior of the sample containing CuAlMn. Samples produced are non-cracked and partially porous. As the addition of WC increases, the pore amount decreases and it is seen from SEM
photographs. The homogeneous dispersion may be sufficient due to the sintering temperature [35]. Represents the WC powders are uniformly separated on the CuAlMn in the Fig. 4 [36].

Figure 4. SEM images CuAlMn-WC composites produced: (a) CuAlMn, (b) CuAlMn - 5% WC, (c) CuAlMn – 10% WC and (d) CuAlMn - 15% WC.

Fig. 5 shows hardness as a function of the WC content in the composites.

Figure 5. Microhardness graph of samples.

Hardness values were determined by taking the average of six different measurements on each composite. Hardness of the composites increased with increasing WC content. This may be explained by rule of mixture, applied to composite materials [37]. The hardness measurement values were 206 HV$_{0.1}$ for CuAlMn, 248 HV$_{0.1}$ for CuAlMn – 5% WC, 322 HV$_{0.1}$ for CuAlMn – 10% WC and 490 HV$_{0.1}$
for CuAlMn – 15% WC. They are almost identical in the CuAlMn and CuAlMn – 5% WC hardness of composites by addition of WC. But CuAlMn – 15% WC composite is sharply increased in the hardness increased the amount of WC.

Fig. 6 shows SEM-EDS analysis taken from the samples.

![SEM-EDS analysis of the samples](image)

When the analysis results given in Fig. 6 were examined, it was figured out that the material was CuAlMn and WC. When the analysis results given in Fig. 6 were examined, the peaks of Cu, Al, Mn, W and C that were present also in the samples were clearly seen. The matrix phase acquires a brighter backscattered electrons contrast level in splats where WC dissolution was more pronounced. Fig. 7 shows XRD graphs of the CuAlMn-WC composites produced by hot pressing method.

When the XRD graphs given in Fig. 7 were examined, the peaks of Al<sub>77</sub>Mn<sub>23</sub>, Al<sub>5</sub>Cu<sub>2</sub>Mn<sub>3</sub>, AlCu<sub>4</sub>Mn, AlCu, Mn, Al<sub>3</sub>Mn<sub>3</sub>, Cu<sub>0.6</sub>W<sub>0.6</sub> and WC were determined. In this study, the phases formed are shown by XRD analysis; The formation of other phases has been revealed according to the results of EDS analysis. In their study on the effect of CuAlMn/ WC ratio on the plastic deformation in
strengthening mechanism, Ji et al., determined similar peaks [38]. The dominant phases were seen to be Al$_{77}$Mn$_{23}$, Al$_5$Cu$_2$Mn$_3$, AlCuMn and AlCu$_4$ in the graphs. When all peaks were examined, it was found that as WC amount increased in the samples.

![XRD graphs of the samples.](image)

Figure 7. XRD graphs of the samples.

The corrosion tests of the samples were carried out in the prepared 3.5% NaCl solution. Potentiodynamic polarization curves resulting from the experiments are given in Fig. 8.

![Tafel curves of samples.](image)

Figure 8. Tafel curves of samples.

The potential was applied to the open circuit potential after -0.5 mV to 0.5 mV. Immersion time of 30 minutes was applied. $E_{\text{corr}}$ (corrosion potential), $I_{\text{corr}}$ (corrosion current), $\beta_a$ (anodic tafel curve), $\beta_c$ (cathodic tafel curve) and corrosion rate were determined from tafel curves. $R_p$ (corrosion resistance) was calculated using Stern and Geary equation (equation 1) [39].

$$R_p = \frac{\beta_a \times \beta_c}{2.303 \times I_{\text{corr}} (\beta_a + \beta_c)}$$ (1)
The electrochemical results of the samples are given in Tab. 2.

| Materials | Ecorr (mV) | Icorr (µAcm\(^{-2}\)) | \(\beta_a\) (mV) | \(\beta_c\) (mV) | Corrosion rate (mpy) | \(R_p\) Corrosion resistance (kΩ.cm\(^2\)) |
|-----------|------------|------------------------|----------------|----------------|---------------------|----------------------------------|
| 1         | -302       | 16.72                  | 95             | 512            | 10.76               | 2.08                             |
| 2         | -354       | 21.8                   | 124            | 759,8          | 18.54               | 2.12                             |
| 3         | -367       | 10.5                   | 127            | 188            | 10.23               | 3.13                             |
| 4         | -391       | 14.2                   | 142.9          | 404.9          | 14.12               | 3.22                             |

As a result, there is a reaction between Cu, Al, Mn and WC. When the Tab. 2 is examined, the \(R_p\) (corrosion resistance) of the sample CuAlMn was 2.08 kΩ.cm\(^2\), while the value for the sample CuAlMn + 5% WC was calculated as 3.22 kΩ.cm\(^2\). It is clear from the data obtained that as the amount of WC in the reinforced increases, the corrosion resistance of the samples increases. Similar results have been found in the literature for composites of reinforced WC [28].

4. Conclusion

The effects of WC on the microstructure and mechanical properties of composites fabricated by hot pressing were investigated.

- Microstructure observation demonstrates a relative homogenous distribution in CuAlMn of WC particulates.
- The hardness measurement values were 206 HV\(_{0.1}\) for CuAlMn, 248 HV\(_{0.1}\) for CuAlMn – 5% WC, 322 HV\(_{0.1}\) for CuAlMn – 10% WC and 490 HV\(_{0.1}\) for CuAlMn – 15% WC.
- The analysis of EDS the peaks of Cu, Al, Mn, W and C that were present also in the samples were clearly seen.
- The dominant phases were seen to be Al\(_{77}\)Mn\(_{23}\), Al\(_5\)Cu\(_2\)Mn\(_3\), AlCu\(_2\)Mn and AlCu\(_4\) in the XRD graphs.
- It is clear from the data obtained that as the amount of WC in the reinforced increases, the corrosion resistance of the samples increases.

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