



Osama Kriewah

Kastamonu University, osamakrewa00@gmail.com, Kastamonu-Turkey

Serkan Islak

Kastamonu University, serkanislak@gmail.com, Kastamonu-Turkey

DOI	http://dx.doi.org/10.12739/NWSA.2022.17.2.2A0187	
ORCID ID	0000-0002-9991-3517	0000-0001-9140-6476
Corresponding Author	Serkan Islak	

CORROSION PROPERTIES OF Cu-Cr-B₄C-CNF HYBRID COMPOSITES PRODUCED BY PM

ABSTRACT

In this study, corrosion properties of Cu-Cr-B₄C-CNF hybrid composites produced by powder metallurgy method were investigated. After cold pressing, hybrid composites were sintered at 900°C in an argon atmosphere for two hours. SEM analysis was used to obtain information about the distribution of reinforcement elements in the Cu matrix. SEM photographs showed relatively homogeneous distribution of Cr, B₄C and CNF reinforcement elements in the Cu matrix. In addition, the formation of pores in the microstructure draws attention. The corrosion properties of the composites were determined using the potentiodynamic method. For potentiodynamics and corrosion rate, Cu-Cr-B₄C-CNF hybrid composites were immersed in a 3.5 wt% NaCl solution at pH 6-7. Corrosion current density, corrosion potential and corrosion rate of hybrid composites were calculated from the Tafel curves read directly from the corrosion device. Corrosion test results showed that Cu matrix had the best corrosion resistance. It was determined that when the reinforcement was added, the corrosion resistances decreased partially, but the Cu-8B₄C-6Cr hybrid composite had the best corrosion resistance among the composites.

Keywords: Hybrid Composite, Corrosion, Microstructure, Copper, Powder Metallurgy

1. INTRODUCTION

Copper, which has good electrical, thermal and corrosion properties, has limited mechanical properties. Therefore, it is difficult to use in applications where mechanical strength is desired. In order to overcome this disadvantage, it is generally tried to increase the strength by precipitation hardening mechanism by adding small amounts of alloying elements such as Cr, Zr, Ag or Fe [1]. However, these alloys lose their strength under operating conditions at 500°C due to the deterioration of the precipitates [2]. Therefore, metal matrix composites (MMC) are candidate materials to overcome these disadvantages. MMCs are produced by adding ceramic reinforcements such as oxides, carbide borides and carbon fiber to the copper matrix [3 and 4]. The inclusion of ceramic particle reinforcement can significantly improve the high temperature mechanical property and wear resistance of the matrix, without serious deterioration in the thermal and electrical conductivity of the matrix [5] Among various ceramic particles, Al₂O₃, SiC, B₄C and TiB₂ particles are widely used to support ductile metal matrix composites. is used.

Recently, great attention has been paid to the synergistic reinforcement of MMCs with hybrid reinforcement. Hybrid reinforcements consisting of two or more reinforcements have been shown to significantly

How to Cite:

Kriewah, O. and Islak, S., (2022). Corrosion Properties of Cu-Cr-B₄C-CNF Hybrid Composites Produced by PM. Technological Applied Sciences, 17(2):39-45.
DOI:10.12739/NWSA.2022.17.2.2A0187.



improve the mechanical properties of MMCs compared to those strengthened with a single reinforcement [6, 7 and 8]. Compared to unreinforced metal matrix, metal matrix composites offer a wide variety of applications with improved mechanical and tribological properties in the aerospace, automotive, marine and defense industries [9, 10, 11 and 12]. Composite products are highly accepted due to features such as high specific strength, Young's modulus, high strength, low coefficient of thermal expansion and wear resistance [13].

In this study, materials such as copper matrix, boron carbide, chromium and carbon nanofiber were chosen as reinforcements. The corrosion properties of the produced hybrid composite materials were experimentally investigated in detail.

2. RESEARCH SIGNIFICANCE

Pure copper is widely used in various electrical applications due to its high electrical conductivity and high thermal conductivity. In addition, copper has a number of properties such as high corrosion resistance, low cost and easy manufacturability. In copper matrix composites, on the other hand, electrical conductivity decreases and strength increases. However, studies on the determination of corrosion properties are very rare. Considering the working conditions of copper materials, the investigation of corrosion properties reveals the importance of the study.

Highlights:

- Cu-Cr-B₄C-CNF hybrid composites were successfully produced by PM.
- The reinforcements are relatively homogeneously dispersed in Cu.
- Cu-8B₄C-6Cr has the best corrosion resistance among composites.

3. EXPERIMENTAL METHOD

In this study, hybrid composites were produced by adding Cr, B₄C and CNF to Cu by powder metallurgy method. Cu as matrix material with -325 mesh grain size and 99.99% purity, as reinforcement B₄C with -325 mesh grain size and 99.99% purity, Cr with -325 mesh grain size and 99.99% purity and CNF with D×L 100 nm×20-200µm in size and 98% purity were used. The mixtures prepared in the ratios in Table 1 were mixed in the mechanical alloying device. It was then produced in a cold press with a diameter of 20mm and a height of 10mm. It was then sintered in an argon atmosphere tube furnace at 900°C for 2 hours. The mechanical alloying, pressing and sintering stages of the samples are shown in Figure 1. The microstructures of the samples were analyzed by SEM.

Table 1. Powder mixture ratios (% by vol.)

No	Cu	B ₄ C	Cr	CNF
1	100	0	0	0
2	92	8	0	0
3	90	8	2	0
4	88	8	4	0
5	86	8	6	0
6	85	8	6	1
7	84	8	6	2
8	83	8	6	3

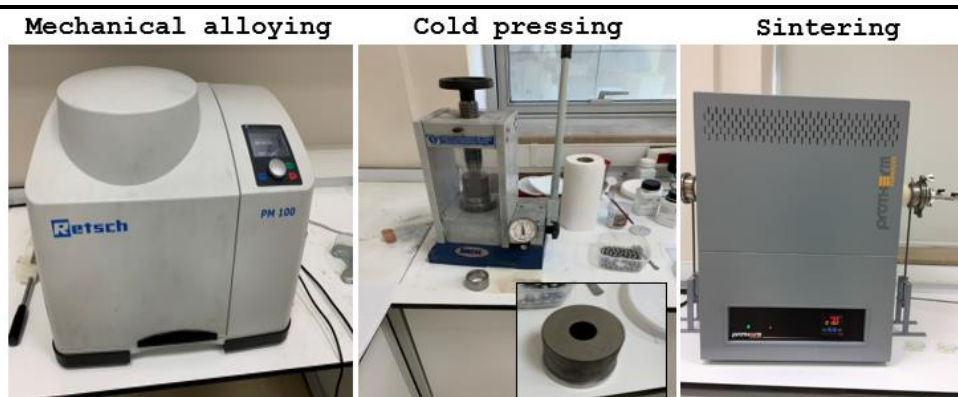


Figure 1. Mechanical alloying, pressing and sintering steps

Corrosion experiments were carried out under NaCl solution conditions. For the solution, 35g of NaCl was mixed with 1 liter of distilled water in a magnetic stirrer. The cleaned samples were kept in a 3.5 wt% NaCl solution for about 1 hour to stabilize. The electrochemical/corrosion cell consists of three electrodes applied in electrochemical experiments. Graphite was used as the counter electrode. The reference electrode consists of Ag/AgCl. The working electrode consists of hybrid composite samples. Corrosion Tests consisting of potentiodynamic polarization (PDP) were carried out in 3.5% NaCl solution at room temperature after 300 seconds until equilibrium was reached at the open circuit potential (OCP). Galvanostat (Partstat 4000) was used to perform the Tafel measurement. The corrosion test system used in the corrosion test is shown in Figure 2. The scanning range is +0.5 and -0.5V and the scanning rate is 1.5mV/s. Before each experiment, the working electrode surface was sanded with 400, 600, 800 and 1200 silicon carbide sandpaper, then; The surfaces of the samples were polished with the help of diamond spray and then carefully cleaned with pure water. The epoxy resin was then used to protect the sample, leaving an area of 0.12cm² that could be used for solution exposures. All current and potential measurements were normalized to the surface area of the electrode. After the corrosion tests, the sample surfaces were examined by SEM.

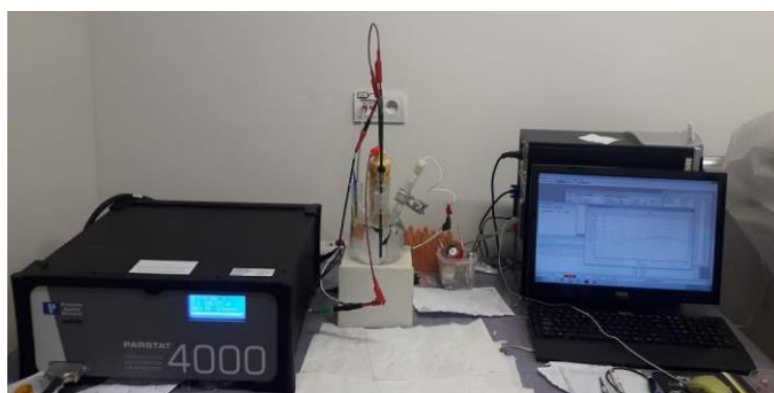


Figure 2. Corrosion test setup

4. FINDINGS AND DISCUSSIONS

SEM images of Cu-B₄C-Cr-CNF hybrid composites produced by powder metallurgy technique are given in Figure 3. SEM photographs showed relatively homogeneous distribution of Cr, B₄C and CNF reinforcement elements in the Cu matrix. B₄C has sharp corners and is well surrounded by the matrix. Since Cr is softer than B₄C, it was coated with Cu powders

during mechanical alloying and completely homogeneous mixing became difficult. Since CNF is a nano-sized reinforcing element, it is very difficult to see at small magnifications. The distribution of the reinforcements in the matrix affects the physical, chemical and mechanical properties of the composite. While in homogeneous dispersion, this has a positive effect, in homogeneous dispersion, the properties are negatively affected [14 and 15] In addition, the pores that are inevitable in the samples produced by the powder metallurgy method were also formed in the hybrid composite samples in our study.

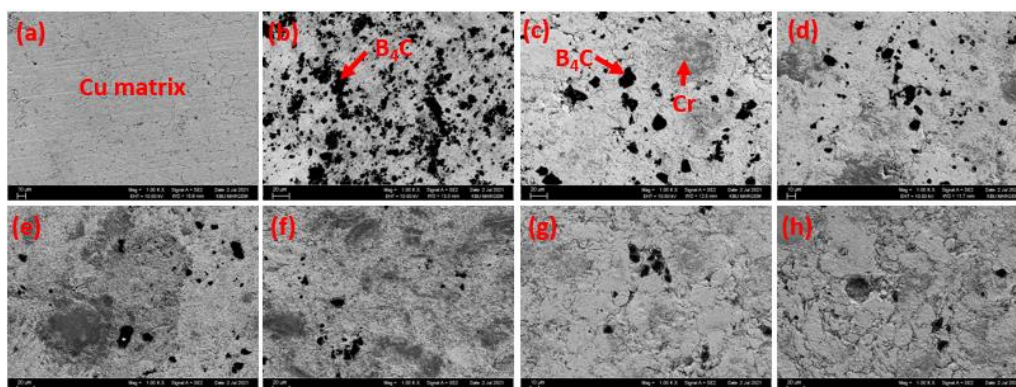


Figure 3. SEM images: (a) Cu, (b) Cu-8B₄C, (c) Cu-8B₄C-2Cr, (d) Cu-8B₄C-4Cr, (e) Cu-8B₄C-6Cr, (f) Cu-8B₄C-6Cr-1CNF, (g) Cu-8B₄C-6Cr-2CNF, and (h) Cu-8B₄C-6Cr-3CNF

The Tafel curve drawn between corrosion current and corrosion potential during corrosion tests of hybrid composites is given in Figure 4. The corrosion potential (E_{corr}), corrosion current density (I_{corr} density), corrosion current (I_{corr}), anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) in Table 2 were taken from the Tafel curve. The corrosion rate (CR) was calculated with the following formula (1) [16].

$$CR = \frac{I_{corr} \cdot K \cdot EW}{d \cdot A} \quad (1)$$

Here, I_{corr} is the corrosion current, K is the constant, EW is the equivalent weight, d is the density, and A is the contact area of the sample. Corrosion resistance (R_p) was calculated by Stern and Geary equation (2) [17].

$$i_{corr} = \frac{\beta_a \cdot \beta_c}{2.303 \cdot R_p (\beta_a + \beta_c)} \quad (2)$$

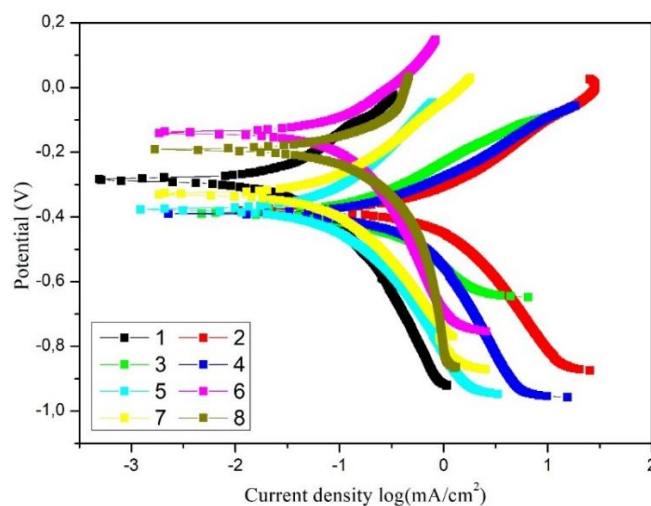
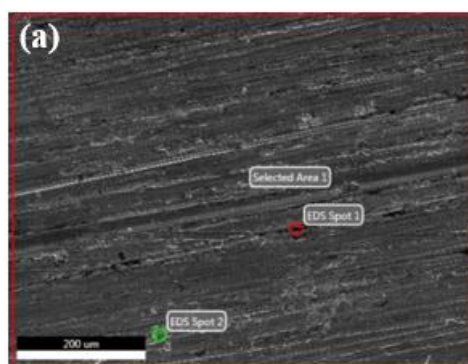


Figure 4. Tafel curve

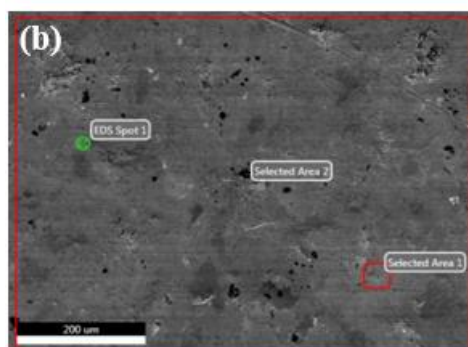
As seen in Table 2, the corrosion potential, corrosion current, corrosion rate and corrosion resistance of hybrid composites vary depending on the type and amount of reinforcing element. The sample with the lowest corrosion rate (most resistant to corrosion) was found to be pure copper. The important point here is the absence of foreign elements in the matrix. Because foreign element, impurities and pores show anodic effect. The sample with the lowest corrosion rate among the composites is the Cu-8B₄C-6Cr sample. Cr forms a very thin film on the surface of the material against corrosion attacks. This layer of film is the protective film called passive layer or passive film. Partial addition of CNF also increased the corrosion resistance, but the resistance decreased at the addition of 3%. The reason for this can be explained as the addition of large amounts of CNF will cause heterogeneous distribution and inhomogeneous corrosion may occur on the sample surfaces. The increase in corrosion resistance at the addition of up to 2% CNF can be partially explained as the pore-filling effect of CNF. When the post-corrosion SEM-EDS analyzes are examined in Figure 5, Na⁺, Cl⁻, O₂⁻ ions from the solution are seen in point and area EDS. Corrosion is more intense around particles, porosities and microcracks. Aggressive chlorine ions from the solution damaged the material.

Table 2. Electrochemical Measurements

Specimen	E _{corr} (V)	I _{corr} density (μA/cm ²)	I _{corr} (μA)	β _a (V/decade)	B _c (V/decade)	CR (mm/year)	R _p × 10 ⁻³
1	-0.29	65.83	7.90	0.217	0.285	0.76	6.77
2	-0.37	1294.5	155.34	0.751	0.972	15.01	1.18
3	-0.38	444.5	53.34	0.162	0.156	5.15	0.65
4	-0.39	612.75	73.53	0.17	0.477	7.105	0.74
5	-0.37	93.16	11.18	0.277	0.345	1.08	5.97
6	-0.14	137.33	16.48	0.231	0.493	1.59	4.14
7	-0.33	109.83	13.18	0.248	0.344	1.27	4.74
8	-0.19	229.83	27.58	0.284	0.518	2.66	2.89



Element	Spot 1 Weight %	Spot 2 Weight %	Area 1 Weight %
O K	6.26	-	-
NaK	23.93	-	2.41
ClK	7.85	-	0.33
CuK	61.97	100	97.27



Element	Area 1 Weight %	Spot 1 Weight %	Area 2 Weight %
B K	11.51	16.11	12.81
C K	9.06	7.17	8.60
NaK	1.68	1.38	1.54
CrK	4.03	7.57	12.75
CuK	73.72	67.77	64.30

Figure 5. SEM-EDS analysis of corroded sample surfaces: (a) Cu, and (b) Cu-8B₄C-6Cr-1CNF



5. CONCLUSION AND RECOMMENDATIONS

SEM photographs showed relatively homogeneous distribution of Cr, B₄C and CNF reinforcement elements in the Cu matrix. In addition, pores were also formed in the hybrid composite samples in our study. Corrosion tests of the samples showed that there was a change in corrosion resistance depending on the type and amount of reinforcing element, the most resistant material was pure copper, and the most resistant material among composites was Cu-8B₄C-6Cr. In addition, it has been observed that Na⁺, Cl⁻ and O₂⁻ ions attack and damage the material.

CONFLICT OF INTEREST

The authors declared no conflict of interest.

FINANCIAL DISCLOSURE

The authors declare that this study has received no financial support.

DECLARATION OF ETHICAL STANDARDS

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

REFERENCES

- [1] Correia, J.B., Davies, H.A., and Sellars, C.M., (1997). Strengthening in rapidly solidified age hardened Cu-Cr and Cu-Cr-Zr alloys. *Acta Materialia*, 45(1):177-190. [https://doi.org/10.1016/S1359-6454\(96\)00142-5](https://doi.org/10.1016/S1359-6454(96)00142-5).
- [2] Zhan, Y. and Zhang, G., (2003). The effect of interfacial modifying on the mechanical and wear properties of SiCp/Cu composites. *Materials Letters*, 57(29):4583-4591. [https://doi.org/10.1016/S0167-577X\(03\)00365-3](https://doi.org/10.1016/S0167-577X(03)00365-3).
- [3] Lu, J., Shu, S., Qiu, F., Wang, Y., and Jiang, Q., (2012). Compression properties and abrasive wear behavior of high volume fraction TiCx-TiB₂/Cu composites fabricated by combustion synthesis and hot press consolidation. *Materials & Design*, 40:157-162. <https://doi.org/10.1016/j.matdes.2012.03.050>.
- [4] Efe, G.C., İpek, M., Zeytin, S., and Bindal, C., (2012). An investigation of the effect of SiC particle size on Cu-SiC composites. *Composites Part B: Engineering*, 43(4):1813-1822. <https://doi.org/10.1016/j.compositesb.2012.01.006>.
- [5] Efe, G.C., Altinsoy, I., İpek, M., Zeytin, S., and Bindal, C., (2012). Effects of SiC Particle Size on Properties of Cu-SiC Metal Matrix Composites. *Acta Physica Polonica*, 121(1):251-253.
- [6] Mallikarjuna, H.M., Ramesh, C.S., Koppad, P. G., Keshavamurthy, R., and Sethuram, D., (2017). Nanoindentation and wear behaviour of copper based hybrid composites reinforced with SiC and MWCNTs synthesized by spark plasma sintering. *Vacuum*, 145:320-333. <https://doi.org/10.1016/j.vacuum.2017.09.016>.
- [7] Qu, J.P., Zhang, C.J., Han, J.C., Zhang, S.Z., Yang, F., and Chen, Y.Y., (2017). Microstructural evolution and mechanical properties of near α -Ti matrix composites reinforced by hybrid (TiB+ Y₂O₃) with bimodal size. *Vacuum*, 144:203-206. <https://doi.org/10.1016/j.vacuum.2017.08.001>.
- [8] Zeng, X., Yu, J., Fu, D., Zhang, H., and Teng, J., (2018). Wear characteristics of hybrid aluminum-matrix composites reinforced with well-dispersed reduced graphene oxide nanosheets and silicon carbide particulates. *Vacuum*, 155:364-375. <https://doi.org/10.1016/j.vacuum.2018.06.033>



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- [9] Somani, N., Tyagi, Y.K., Kumar, P., Srivastava, V., and Bhowmick, H., (2018). Enhanced tribological properties of SiC reinforced copper metal matrix composites. *Materials Research Express*, 6(1):016549. <https://doi.org/10.1088/2053-1591/aae6dc>.
- [10] Miracle, D.B., (2005). Metal matrix composites—from science to technological significance. *Composites science and technology*, 65(15-16):2526-2540. <https://doi.org/10.1016/j.compscitech.2005.05.027>.
- [11] Torralba, J.D., Da Costa, C.E., and Velasco, F., (2003). P/M aluminum matrix composites: an overview. *Journal of Materials Processing Technology*, 133(1-2):203-206. [https://doi.org/10.1016/S0924-0136\(02\)00234-0](https://doi.org/10.1016/S0924-0136(02)00234-0).
- [12] Moghadam, A.D., Schultz, B.F., Ferguson, J.B., Omrani, E., Rohatgi, P.K., and Gupta, N., (2014). Functional metal matrix composites: self-lubricating, self-healing, and nanocomposites—an outlook. *JOM*, 66(6):872-881. <https://doi.org/10.1007/s11837-014-0948-5>.
- [13] Rohatgi, P.K., Tabandeh-Khorshid, M., Omrani, E., Lovell, M.R., and Menezes, P.L., (2013). Tribology of metal matrix composites. In *Tribology for scientists and engineers*. Springer, New York. https://doi.org/10.1007/978-1-4614-1945-7_8.
- [14] Islak, S., Kir, D., and Buytoz, S., (2014). Effect of sintering temperature on electrical and microstructure properties of hot pressed Cu-TiC composites. *Science of Sintering*, 46(1):15-21. <https://doi.org/10.2298/SOS1401015I>.
- [15] Li, Q., Turhan, M.C., Rottmair, C.A., Singer, R.F., and Virtanen, S., (2012). Influence of MWCNT dispersion on corrosion behaviour of their Mg composites. *Materials and Corrosion*, 63(5):384-387. <https://doi.org/10.1002/maco.201006023>.
- [16] Yousif, H.A., Al-Hadeethi, F.F., Al-Nabilsy, B., and Abdelhadi, A.N., (2014). Corrosion of steel in high-strength self-compacting concrete exposed to saline environment. *International Journal of Corrosion*, 2014:1-11. <https://doi.org/10.1155/2014/564163>.
- [17] Stern, M. and Geary, A.L., (1957). Electrochemical polarization: I. A theoretical analysis of the shape of polarization curves. *Journal of the electrochemical society*, 104(1):56-63. <https://doi.org/10.1149/1.2428496>.