

Corrosion Behavior of Copper-Steel Particulate Composite

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Abstract

This work was conducted to study the corrosion behavior of the steel particle reinforced copper matrix composites, under different conditions; namely heat treatment, concentration of corrosion media, and different weight percent of steel particles.

The density, corrosion rate, micro-structure, and Vickers micro-hardness, were investigated. The results showed that composites with limited steel particle contents can be used. The microstructure of the composites showed severe corrosion of the steel particles especially in the low steel particle content ones, which gave an effect more or less similar to the pitting corrosion. The Vickers micro-hardness showed a development in the hardness of the different zones of the composite due to the effect of the cold working and subsequent annealing, but yet with the same marked increment in micro-hardness at the particle-matrix interface. The later gave a strong indication that diffusion was taken place. Corrosion rate increased with increasing steel particle contents, because of severity corrosion in steel particles.

Keywords: Metal matrix composite, Heat treatment, Corrosion, Potentiostat polarization

1. Introduction

Metal matrix composites are materials with metals as a base and distinct, typically ceramic phases added to improve the properties. Although it is desired that these phases remain distinct and separate, reactions do occur between them. If this is the case, it affects the processing and final properties of the composites, regardless of which type of reinforcement is used (ASM Handbook. 2001). Reinforcement types include laminations, continuous fibers, discontinuous fibers, whiskers and particles of different morphologies are used. Each of these reinforcements affects the base metal in different subtle ways, but composites generally show improvement over the monolithic metal in, at least, one of the following properties: yield strength, hardness, tensile strength, wear resistance, coefficient of thermal expansion etc. Properties that depend on the system include thermal and electrical conductivities (William D. Callister, Jr. 2007). While metal matrix composites show great potential in these areas, they have only found limited use in actual industrial applications. Continuous fiber composites have been especially restrained, finding use only in high value parts in the aerospace field. This is due to the difficulty in processing of the materials, forcing manufacturers to offer them at high cost (Hatta, H., Aoi, T., Kawahara, I. and Kogo, Y. 2004). Discontinuous metal matrix composites, isotropic in nature, have more options and ease of preparation than continuously reinforced types, so that cost is lowered and acceptance is wider. However, even these materials are limited to a few industrial applications. For particle reinforced copper matrix composites, the main current commercial processing is done using the powder metallurgy technique i.e. mixing, compacting and

sintering. While this method has the advantage of controlling the volume fraction of the constituents it also has many drawbacks. These include tendency to segregate due to the difference in the atomic weight, particles desire to clump with each other, shrinkage and increased void formation. These all lead to higher cost (Pranav K. Deshpande, 2006).

Cu–Fe alloys are materials that are more and more extensively applied in industry. Firstly, they are utilized as master alloys to produce new copper alloys for very special purposes. They are used as materials for electrical device components, for example, semiconductor lead frames, electrical connectors, and electrical fuses. The phase diagram of the Cu–Fe system shows that copper solubility in iron is practically high at high temperatures. However, in the range of low temperatures, the copper solubility significantly drops to 1.88 at.% at the eutectoid temperature of 850 oC. A new melting process has been used to prepare Cu–Fe alloys with 10, 20, and 30 wt% Fe, but these alloys show a tendency to segregate. On determining and applying the proper parameters of the melting process, it is possible to produce Cu–Fe alloys with such high iron content (Z. J. Zhou, Y. S. Kwon, 2005).

Studies of the corrosion behavior of Cu–Fe alloys in aqueous media seem to be rare. It has been reported that iron-alloying addition to copper alloys may be used to improve their corrosion resistance. The mechanisms of the dissolution and passivation of bulk polycrystalline icosahedra Al₆₃Cu₂₅Fe₁₂ specimens during electrolytic corrosion in sodium hydroxide and sulfuric acid solutions were studied by El-Egamy (S.S. El-Egamy, 2008). He found that selective dissolution of Al and Fe from the alloy surface occurred at the open-circuit potential, which leads to precipitation of porous layer of re-crystallized copper. After anodic polarization, the dissolution of the alloy is followed by re-deposition of Cu and formation of Cu₂O (S.S. El-Egamy, 2008).

2. Experimental

The experimental procedures include heat treatment, corrosion test, scanning electron microscopy and finally hardness test. The composites consist of pure copper containing 99.99% Cu as a matrix and steel particles with chemical composition shown in Table (1) as a reinforcements phase. The steel particle reinforced copper matrix composite was prepared by stir casting processing method (Feras M.A. Kafiah, 2007). These composites contained different weight percent of steel particles, namely 10%wt, 20%wt, 30%wt, 40%wt and 50%wt (table 2).

In this project the specimens were cold worked using a cold-rolling process. It is noticed that the percentage amount of deformation decreases with increasing the wt% of steel particles as shown in Fig. (1).

Six cold rolled strips were produced; the maximum amount of cold working was different for each composite depending upon the appearing of the cracks on the surface. Six semi rectangular samples were taken from each strip, and so the overall number of samples used in this procedure was 36 samples. These 36 samples were divided into two categories (Annealed & Cold Worked Samples) 18 samples for each category. One temperature (750°C) was suggested to work for heat treatment for 1 hour; time was counted after 15 min to allow homogenizing the furnace atmosphere.

Carbolite furnace, model EML was used to anneal the samples. 9 samples were annealed for each run, for an hour; the same procedure was repeated for the other 9 samples & so on. The 36 sample demonstrated formerly (18 Annealed & 18 Cold worked) were prepared by grinding and polishing. All samples were cleaned by diluted hydrochloric acid, followed by acetone and Methanol to remove any impurities or scales that formed on the surface of the samples. The sample should be immersed in each solution for about 2 min and drying by air blower after each step.

A flat corrosion cell consist Reference electrode of Ag–AgCl saturate was used to determine the corrosion rate. The exposed surface area of specimens was 0.78 cm² in a medium of NaCl solution with different concentrations, namely, 1, 2 & 3.5% were used in this test. The potentiostat scan was operated using the same parameters for all samples and those were feed to the operating computer through the Princeton Applied research potentiostat wizard. The test was done at scan EI & EV of 0.1 (v) vs. open circuit potential, IT, 1.0 (mA), and scan rate of 1.0 mA/s. In the rescan definition steps an equilibration for 30 sec was adopted. And finally the IR compensation facility was enabled.

All samples were examined using scanning electron microscope. Electron micrographs were taken at different magnifications namely 12X, 100X and 600X before and after corrosion at different percentages of steel particles content. Vickers microhardness technique was used to measure the microhardness from matrix (Cu) along through the reinforcing phase (Steel particle) under a predetermined load of 25 gf. The separation between each reading of microhardness & the other was 0.03µm.

3. Results & Discussion

3.1 Corrosion Rate of Composites:

From Fig. (2) and Fig.(3) the increment in the solution concentration increases the corrosion rate; hence the conductivity of the solution is increased which provides more severity of chemical attack. The variation in corrosion rate in different concentrations is increased by increasing steel content; due to the availability of more active phase (steel) beside the increment in solution concentration both of which serves in favor of the increasing in corrosion rate.

Fig.(4), Fig.(5) & Fig.(6) show that annealing decreases the corrosion rate especially when steel content is higher than 20 wt% of steel particles, which gives an indication for stress corrosion phenomenon in cold worked samples, since cold working produces high dislocation density this increases the stored energy of the metal which in its turn increases the corrosion rate as a consequence. Since annealing eliminates dislocations by annihilation, the annealed samples gave lower corrosion rate values. But what should be mentioned is that the variation of corrosion rate (the slope of each line) at the same heat treatment condition which is greater for the cold worked samples than the annealed ones. That is attributed to the fact that copper content becomes lower with the increment in steel volume fraction this leads to high dislocation density as a result (S.S. El-Egamy, 2008). That makes the difference in corrosion rate between 40wt% sample and 30wt% sample, in case of cold worked one, greater than in case of annealed.

The higher corrosion rate after 20 wt% for both deformed and annealed samples could be due to the fact that the density of Fe (7.86 g/ Cm^3) is smaller than that for Cu (8.96 g/ Cm^3) i.e. the volume fraction of steel particles (anode) becomes higher (and then the area) than the corresponding volume fraction of Cu (cathode). This appears to be more clear with the volume fraction of 30 wt% and above. On the top of that the related total diffusion zone around the steel particles becomes larger; this effect leads to higher corrosion rate as well.

3.2 Microstructure Examination of the Composites:

From Fig. (7) the corrosion in copper-steel composite can be described as a selective corrosion behavior; since Cu is more noble than steel as a result the steel particles were corroded to a higher extent than copper matrix. This localized corrosion which is similar to pitting can be explained by the variation in the electro chemical potential of iron (the main component of steel) and copper, which means steel is more active than copper matrix, thus the steel particles are corroded selectively rather than the copper matrix. The difference in the density between steel and copper also affects the corrosion rate to be higher in the steel particles hence steel is of lower density than that of copper, so for a constant time of exposure to the corroding environment the steel particles will corrode faster than the copper matrix creating the localized pits (Feras M.A. Kafiah, 2007). And finally it should be mentioned that with increasing volume fraction of steel particles the severity of corrosion decreases in each particle and this can be seen in Fig.(8). That is due to the fixed number of ions in 3.5% NaCl, which means that the internal corrosion current is constant as well. And so the corrosion current intensity for steel particles will be higher with small number of particles per unit area & vice versa.

3.3 Micro-hardness measurements.

Fig. (9) Shows a scope of micro-hardness starting from the copper matrix through the diffusion area and finally to the core of the steel particle. From the figure the effect of heat treatment (annealing) was clear as expected i.e. hardness was lower by a certain margin indicating the decrement in dislocation density. This leads the corrosion rate to be lower than as cold worked ones. Another observation can be noticed from figure (9), namely, the variation in hardness values during moving from copper matrix to the steel particle (line slope between $0.12 - 0.18\mu\text{m}$) is greater in cold worked sample than annealed one, which indicate that annealing enhances the diffusion process on one hand and limits the effect of stress corrosion on the formation of copper steel composite pits on the other hand (ASM Handbook. 2001)(P. Deshpande, J. H. Li, R. Y .Lin, 2005).

4. Conclusions

- 1) Corrosion rate of copper-steel composite increases with the increasing in steel particle content;
- 2) For corrosive environment applications the highest suitable steel particle content is 20wt% for its low corrosion rate compared with the higher steel particle content.
- 3) Stress corrosion occurred in the composite when it was cold worked. Cold working affects the corrosion rate differently depending upon the volume fraction of steel particles.
- 4) Under uniform corrosive condition the corrosion reaction attacks the steel particle selectively rather than the copper matrix.

5) The corrosion severity in steel particle decreases with the increasing steel particle content.

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Table 1. Chemical composition of steel particles reinforcements

Fe wt%	C wt%	Mn wt%	Al wt%	Si wt%	P wt%	S wt%	Cr wt%
98.95	0.45	0.2	0.1	0.1	0.05	0.05	0.1

Table 2. Casts weight Details

Cast No.	Overall weight (g)	Reinforcement wt%	Reinforcement weight (g)	Copper weight (g)
1	1000	0%	0	1000
2	1000	10%	100	900
3	1000	20%	200	800
4	1000	30%	300	700
5	1000	40%	400	600
6	1000	50%	500	500

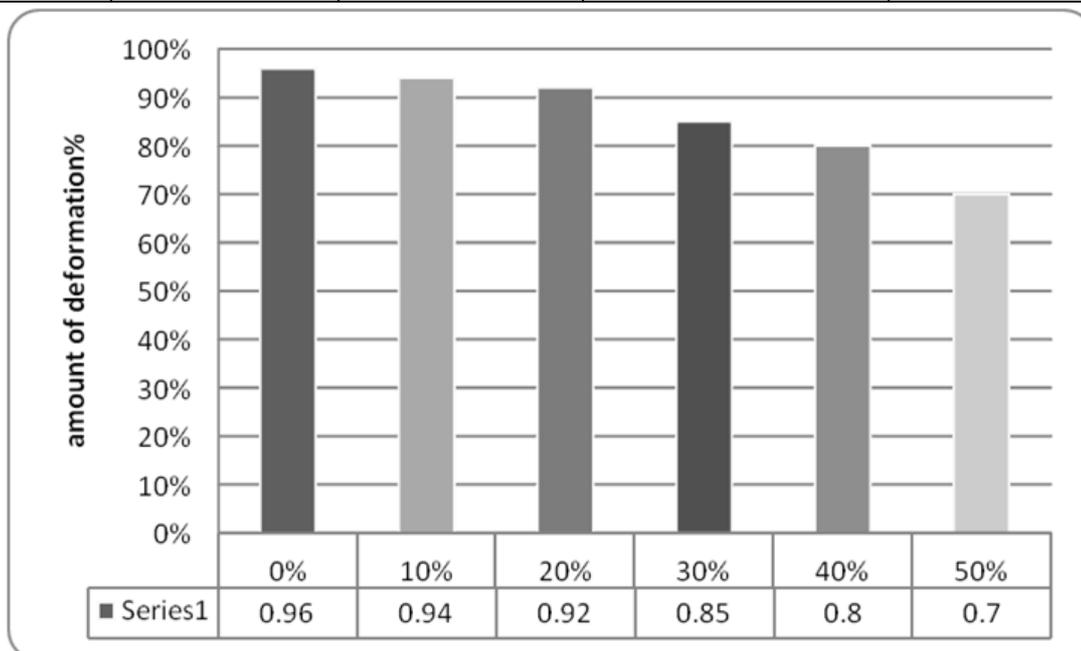


Figure 1. Deformability versus wt% of steel particles

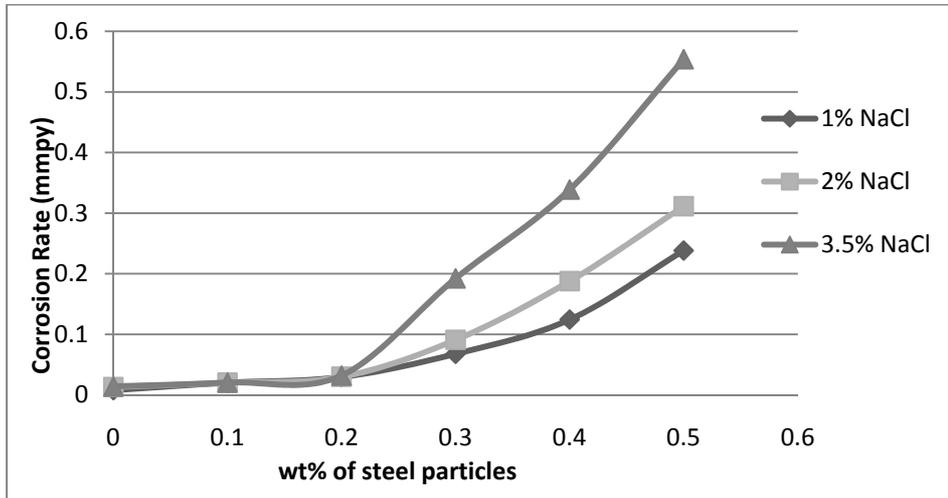


Figure 2. Corrosion rate at different concentration of NaCl for cold worked samples

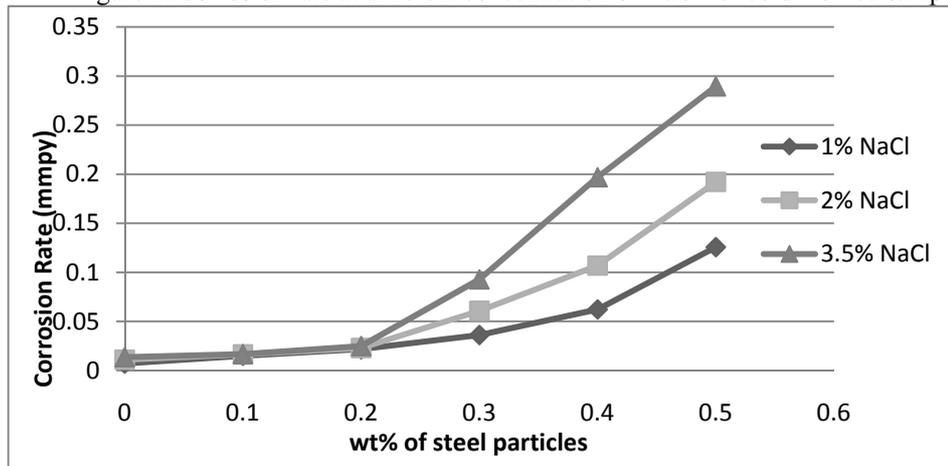


Figure 3. Corrosion rate at different concentration of NaCl for annealed samples

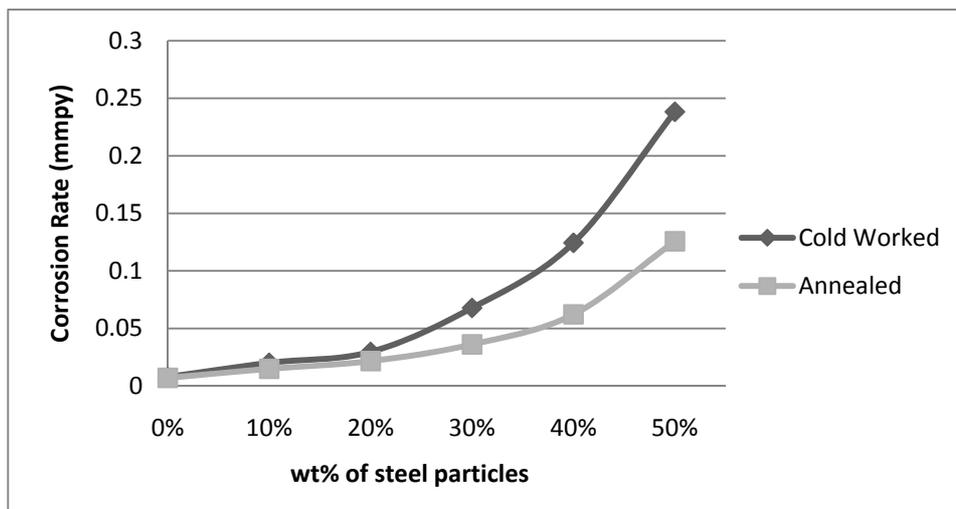


Figure 4. Cold Worked & Annealed Samples at 1%NaCl

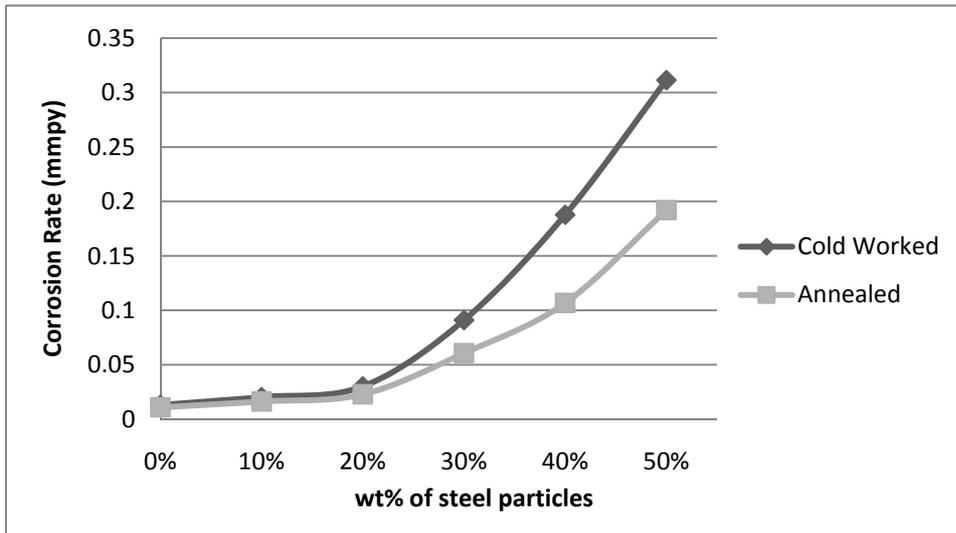


Figure 5. Cold Worked & Annealed Samples at 2% NaCl

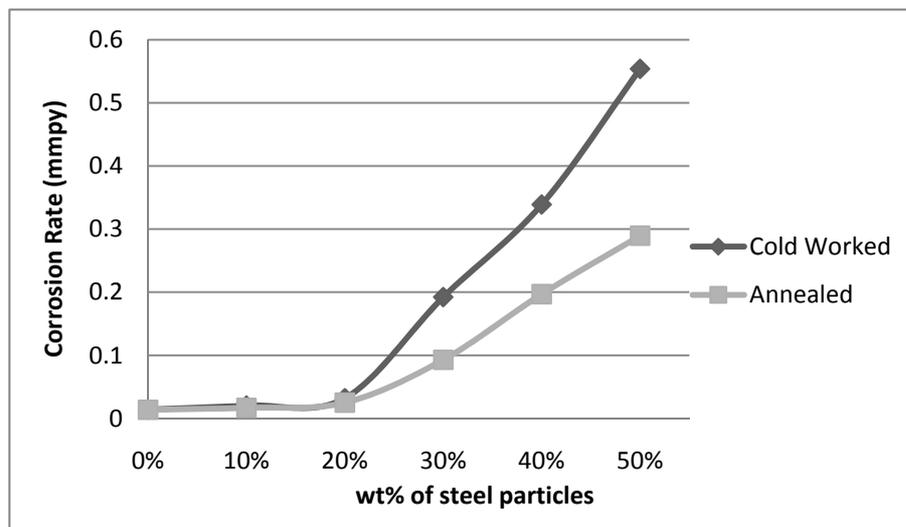
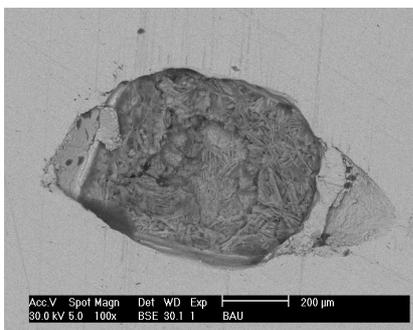
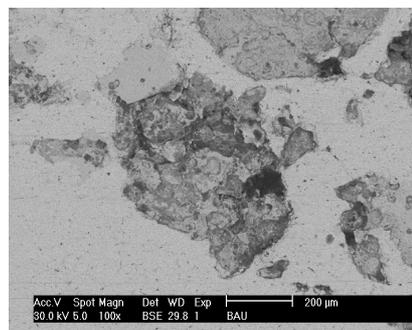


Figure 6. Cold Worked & Annealed Samples at 3.5%NaCl



(a)



(b)

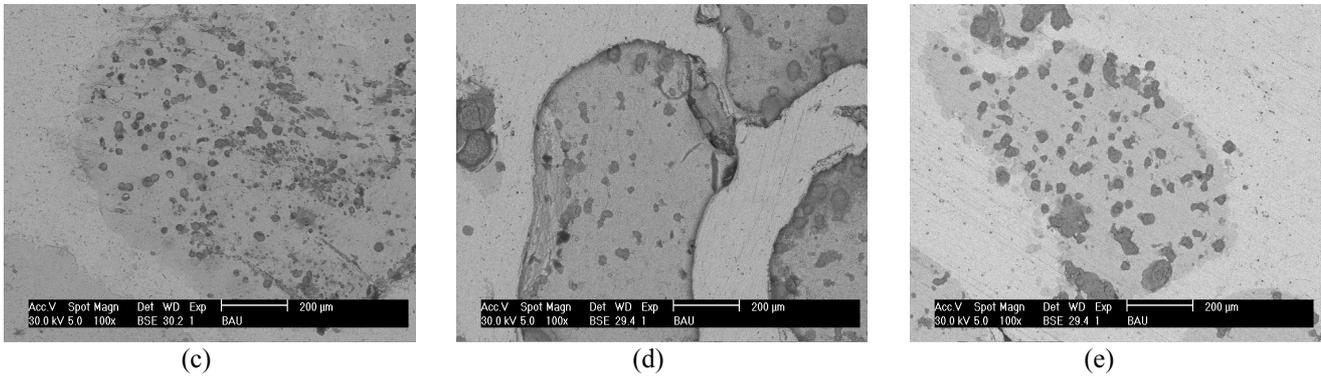


Figure 7. Scanning electron microscopy images show steel particles after corrosion in 3.5% NaCl solution at different weight percent of steel particles in Cu-matrix, (a) 10wt%, (b) 20wt%, (c) 30wt%, (d) 40wt% and (e) 50wt%

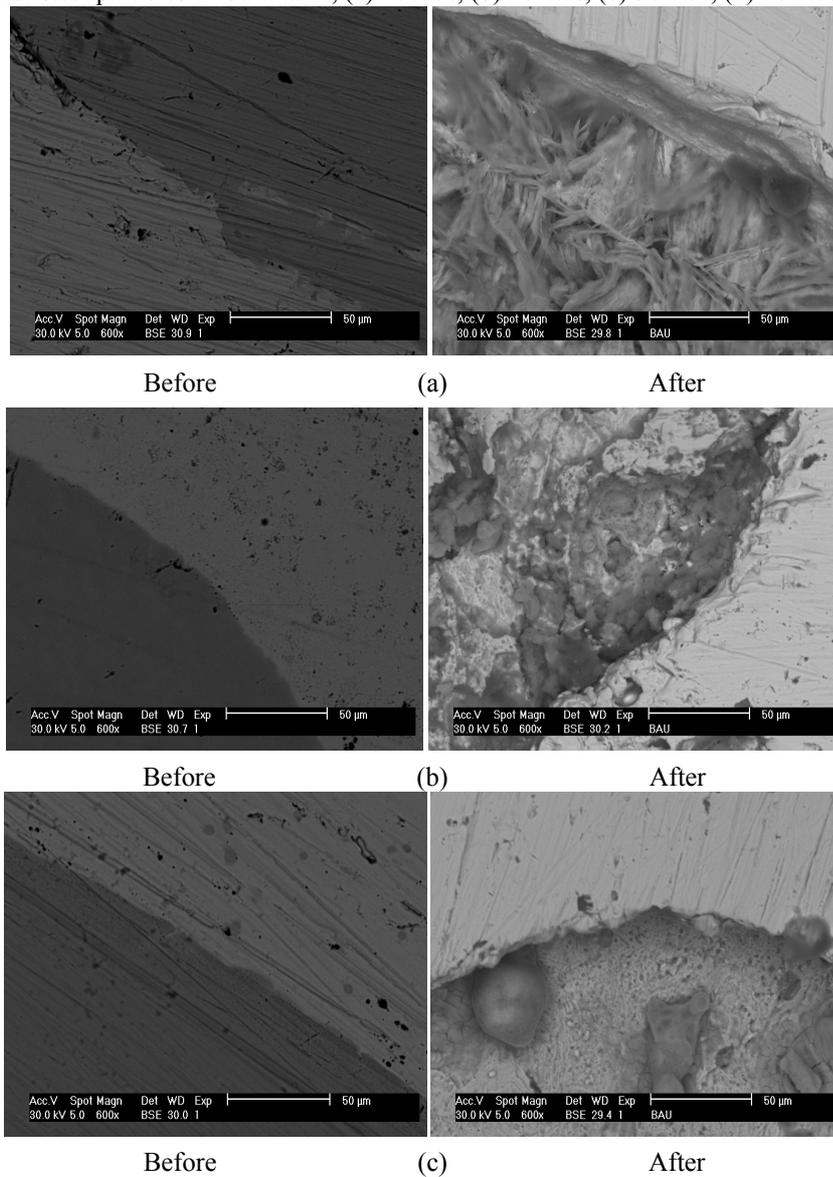


Figure 8. Scanning electron microscope images show steel particles before and after corrosion in 3.5% NaCl solution at different weight percent of steel particles in Cu-matrix, (a) 10wt%, (b) 20wt%, and (c) 30wt%

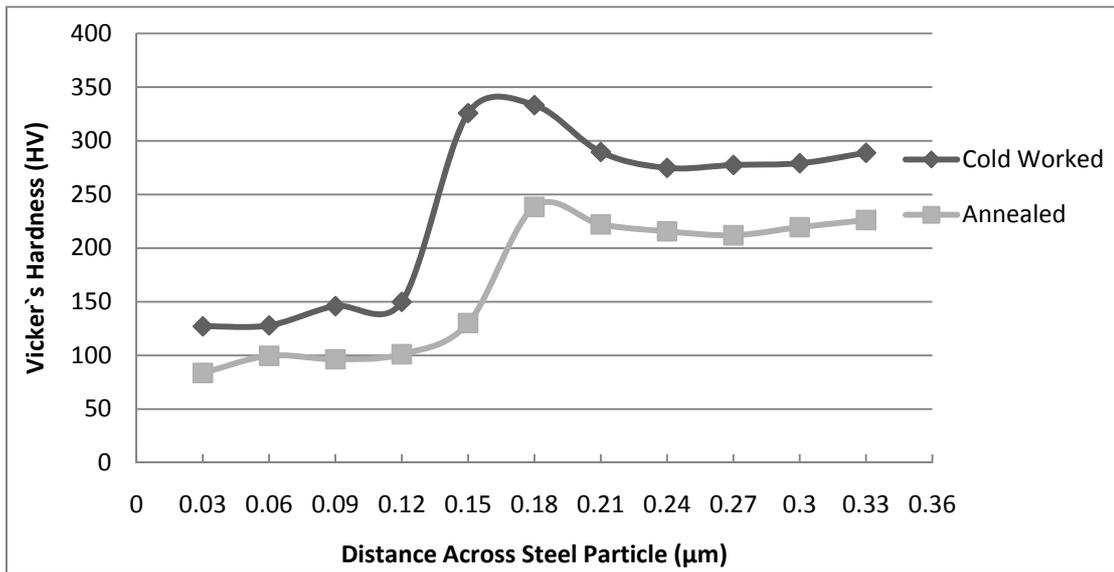


Figure 9. Vickers micro-hardness (HV) across the steel particle and the copper matrix