Wear-Resistant Coating of Copper for Energy Applications

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***Abstract* – Copper is a metal that is often used as a mold for the continuous casting where the application temperature is significantly high. Because it is hard to predict mechanical properties of Cooper at the elevated temperature, actual investigation on its properties should be entailed. High temperature mechanical performance and inter-diffusion effect of copper-based alloys that had Ni or Ni/Co as the coating were investigated to estimate changes of their structure at the elevated temperature, which is similar to the environment of their application. In-situ high temperature Vickers hardness testing was conducted at 100℃, 200℃, 460℃ and room temperature. For ABNC, a rapid drop of HV at 460℃ was observed (HV: 463, 430, 330, and 72 at room temperature, 100°C, 200°C, and 460°C, respectively). From the inter-diffusion measurement, for N+ it was observed that about 10 atomic % of Ni was diffused into the copper substrate near the interface, after 28 days of heat treatment at 400℃. However for NC and ABNC, Ni and Co were not diffused into the Cu substrate. For better understanding, Vickers hardness test and optical microscopy for inter-diffused specimens and wear/scratch test and TEM work for coatings will be conducted in the future.**

# INTRODUCTION

Copper and its alloys are used in numerous energy applications because of their high thermal and electrical conductivity.1

One of the applications of copper is as a mold for continuous casting. Continuous casting is one method of casting that has unique features. Unlike other casting processes where each step of casting is sequential (heating and melting metal, pouring the molten metal into casts, solidification and cast removal), in continuous casting all steps occur at the same time. Hence continuous casting saves a lot of processing time.2 Copper molds play an important role in the continuous casting process. When the molten metal is received by the copper mold, because of the high thermal conductivity of copper, heat is removed rapidly from the molten metal and this guarantees quick solidification.

However low wear resistance of copper sometimes induces constraint. There are several methods that can enhance wear resistance properties of copper. One important aspect is that in the continuous casting process the high thermal conductivity of copper should not be reduced. Introducing external wear resistant coating on the copper is one way to enhance the wear resistance without compromise of the thermal conductivity of the copper.

For more advanced investigation and to understand materials properties and behavior in the application environment, at high temperature environment, in-situ experiments can be conducted. This is the method of experiment where operations or procedures perform while testing.

At elevated temperature, between different metals, inter-diffusion at the interface can occur. At the diffusion interface, new alloy phases can be formed. Because the interfacial bonding at the interface changes, wear resistance of the alloy also changes.3

Diffusion Coefficient can indicate the diffusion rate of a material and it is a function of temperature and $D\_{0}$ which is a material constant.

|  |  |  |
| --- | --- | --- |
|  | $$D=D\_{0}exp⁡(-\frac{Q\_{d}}{RT})$$ | (1) |

Where D is the diffusion coefficient of material, $D\_{0}$ is a temperature-independent pre-exponential, $Q\_{d}$ is the activation energy for diffusion, R is the gas constant, and T is absolute temperature.

|  |  |  |
| --- | --- | --- |
|  | $$\sqrt{Dt }≈x $$ | (2) |

Where t is time and x is the diffusion distance in the equation 2.4

In this research project, three copper based alloys, N+, NC, and ABNC, were investigated. The coating layer was nickel, 0.8Ni0.2Co, and 0.6Ni0.4Co for N+, NC, and ABNC respectively.

# METHOD

Scanning Electron Microscope (SEM) is one of the electron microscopes that can provide high resolution images of sample’s surface. The surface of a specimen is scanned with an electron beam, and the reflected or back scattered beam of electrons is collected. Then the collected beam is displayed at the same scanning rate on a cathode ray tube. Different types of mode can be operated in SEM; Secondary electrons imaging (most common), Backscattered-electron imaging. The specimens that are observed in as SEM should be conductive and usually observed in high vacuum.5

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique that is used for the elemental analysis or chemical characterization of a sample. From the interaction from the sample and X-ray excitation, the result of the analysis can be derived. This is possible because each element has a unique atomic structure that allows a unique set of peaks on its electromagnetic emission spectrum. When a high-energy beam (electrons, protons, or X-rays) is focused into a sample, it stimulates the emission of characteristic X-rays from the specimen. At rest, an atom within the sample contains ground state electrons. When an energetic incident beam hits, it will excite an electron in an inner shell and an electron hole is made where the electron was. An electron from an outer, high energy shell then fills the hole. The energy difference between the higher-energy shell and the lower energy shell is released in the form of an X-ray (characteristic X-ray). The number and energy of the X-rays can be measured by an energy-dispersive spectroscope. Because the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured.6

Hardness of a specimen is a measure of the resistance to localized plastic deformation induced by mechanical indentation or abrasion. Vickers hardness test is one of the hardness test methods and is used for measuring micro-hardness; Vickers hardness (HV). Vickers hardness test can be conducted under various magnifications and it is well suited for measuring the hardness of small, selected specimen regions. A calibration block for Vickers test can be used for the calibration. The absolute Vickers hardness value of the calibration block is 700HV. By using the calibration data obtained, it is possible to measure a more precise HV.4, 7

Hot hardness testing is the measurement of material hardness while at elevated temperature. Hot hardness can be valuable for assessing and comparing materials, such as tool steels and wear resistant coatings, which are used in high temperature applications. Vickers hardness tester can be used for hot temperature hardness testing, usually combined with a vacuum chamber to prevent oxidation of the sample.8

Figure 1 shows the experiment setup for the Hot Hardness testing that was conducted using Vickers Hardness tester.

**A**

**B**

**E**

**C**

**D**


## Experimental setup for Hot Hardness testing (A: Stage Micrometer, B: Insulated Stage with Coolant Circulation C: Heating element, D: Tungsten Carbide Indenter, E: Water Injection as Coolant for Indenter)

# RESULTS & DISCUSSION

From the Hot hardness test result of N+, it was noticeable that the HV dropped fairly linearly as temperature dropped, as seen in table 1. It was also denoted that at 460℃, the HV result showed the least standard deviation.

## Hot Hardness test result of N+, value of HV, Average HV value, and Standard deviation

|  |
| --- |
| **Hot Hardness test, specimen - N+** |
| **Temperature**  | **HV 1** | **HV 2** | **HV 3** | **AVG** | **STD** |
| **RM Temp (20.4°C)** | 279 | 239 | 251 | 256.3 | 20.5 |
| **200°C** | 248 | 207 | 210 | 221.7 | 22.9 |
| **460°C** | 110 | 106 | 98.7 | 104.9 | 5.7 |

For NC, values of HV at elevated temperature (100℃ and 200℃) showed fairly high consistency; both showed small standard deviation (about 5 and 7 respectively). HV values of NC showed linear property with respect to temperature, denoted in table 2.

##  Hot Hardness test result of NC, value of HV, Average HV value, and Standard deviation

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| --- |
| **Hot Hardness test, specimen - NC** |
| **Temperature**  | **HV 1** | **HV 2** | **HV 3** | **AVG** | **STD** |
| **RM Temp (20.4°C)** | 433 | 402 | 424 | 419.7 | 15.9 |
| **100°C** | 369 | 370 | 361 | 366.7 | 4.9 |
| **200°C** | 279 | 280 | 291 | 283.3 | 6.7 |

The HV value of ABNC in table 3 was slightly decreased from the Room temperature to 200℃ then dropped rapidly at 460℃. The rate of change of HV was least for the Room temperature to 100℃ as 0.42[HV/C]. And for 100℃ to 200℃ and 200℃ to 460℃, it was slightly larger as 0.98[HV/C] and 1.00[HV/C] respectively.

## Hot Hardness test result of ABNC, value of HV, Average HV value, and Standard deviation

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| --- |
| **Hot Hardness test, specimen – ABNC** |
| **Temperature**  | **HV 1** | **HV 2** | **HV 3** | **AVG** | **STD** |
| **RM Temp (20.4°C)** | 467 | 477 | 444 | 462.7 | 16.9 |
| **100°C** | 449 | 430 | 409 | 429.3 | 20.0 |
| **200°C** | 328 | 324 | 343 | 331.7 | 10.0 |
| **460°C** | 72.2 | 70.2 | 74 | 72.1 | 1.9 |

Generally, the three specimens showed a common behavior where the value of HV dropped at elevated temperature. However the rate of change of HV of each specimen was different. The general slope of specimen of HV-Temp curve (figure 2) was achieved. It was denoted that N+ showed a slope meanwhile NC and ABNC showed steeper slope than N+; about twice of N+.

## General plot of average HV of N+, NC, and ABNC and standard error

For each specimen, N+, NC, and ABNC, the coating layer and the Cu substrate that were close to the interface region were investigated. It was observed that for NC, the overall composition of the coating observed was 0.8Ni0.2Co however the region of the coating close to the interface showed a greater Ni content. This is seen in table 4.

##  EDS data of specimens, before inter-diffusion

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| --- |
| **EDS data of specimens, before inter-diffusion** |
|   | **N+** | **NC** | **ABNC** |
| **Phase (at%)** | Cu | Ni | Cu | Ni | Co | Cu | Ni | Co |
| **Coating**  | . | 100 | . | 92.4 | 7.6 | . | 62.7 | 37.3 |
| **STD** | . | 0 | . | 1.1 | 1.1 | . | 1.2 | 1.2 |
| **Substrate (Cu)** | 100 | . | 100 | . | . | 100 | . | . |
| **STD** | 0 | . | 0 | . | . | 0 | . | . |

For N+, after 28 days of heat-treatment at 400℃, the composition of the Cu substrate showed an obvious change. About 10 atomic percent of nickel was observed at the Cu substrate. For every specimen, the coating layer generally had not been changed from the original composition, dictated in table 5.

## EDS data of specimens, after inter-diffusion at 400℃ for 28 days

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| --- |
| **EDS data of specimens, after inter-diffusion; 400℃ for 28 days** |
|   | **N+** | **NC** | **ABNC** |
| **Phase (at%)** | Cu | Ni | Cu | Ni | Co | Cu | Ni | Co |
| **Coating** | . | 100 | . | 93.3 | 6.7 | . | 56.1 | 43.9 |
| **STD** | . | 0 | . | 0.8 | 0.8 | . | 21.7 | 21.7 |
| **Substrate (Cu)** | 90.6 | 9.4 | 99.8 | 0.1 | 0.1 | 96.8 | 0.4 | 2.8 |
| **STD** | 10.2 | 10.2 | 0.4 | 0.4 | 0.4 | 5.7 | 8.8 | 10.8 |

From the figure 2, the comparison of HV value of each specimen at different temperatures, it was observed that every specimen showed linear function at low temperature; temperature below 200℃. However ABNC showed dramatic decreased of HV at the 460℃ and the slope of ABNC was also not linear.

Hardness is one measure of strength of material and testing at elevated temperatures provides materials strength and abrasion resistance at elevated temperature. It is also possible from the results of Hot Hardness test to identify critical temperature for properties degradation.9

ABNC showed severe drop of HV at 460℃ and it referred to that ABNC may not have appropriate wear resistant coating at the elevated temperature. Hence if the application environment can heat the coating layer above fairly high temperature (above 200℃), the coating layer of ABNC should be reconsidered whether it can be used or not.

For N+, after 28 days of heat-treatment, it was observed that about 10at% of Ni diffused into the Cu substrate. However Cu did not diffuse into the Ni coating. It can be explained using the diffusion coefficient of each element.

Diffusion coefficient of Ni and Cu at Cu-Ni system at elevated temperature, 1000℃ is known. The intrinsic diffusion coefficient of Ni and Cu at the 80 atomic percentage of Cu system is $7×10^{-15}[m^{2}s^{-1}]$ and $2×10^{-14}[m^{2}s^{-1}]$, respectively.10

The diffusion coefficient of Cu is approximately 3 times larger than that of Ni. And the diffusion coefficient is highly related with the diffusion rate as well as the temperature (equation 1). From the equation 2, it is denoted that the material with high diffusion coefficient has higher diffusion rate which means it takes shorter time to diffuse in.

It was expected that because Cu has higher diffusion coefficient than Ni, observation of small portion of Cu in the coating layer of N+. However the result, table 5, came out reversely; Ni diffused into the substrate. Considering the diffusion coefficient of materials and grain size of the coating and substrate, this unexpected result cannot be explained. Hence further research should be conducted; e.g. X-ray map of the elements.

It is known that activation energy for diffusion changes as the concentration of alloying changes. For FCC Ni-Co system, the activation energy increases with increasing Co content.11

Hence the Ni-Co system, NC and ABNC, showed more stability at the elevated temperature than pure Ni; N+ (table 5).

It was mentioned that inter-diffusion can affect the wear resistance of a material, and the wear resistance of a coating can be compared by comparing the Hardness. Thus, for N+ that was heat-treated, HV values are needed to be measured and compared with the original value.

# CONCLUSION

The coating of N+, NC, and ABNC showed the common behavior that their HV value decreased as the temperature increased. For ABNC, the HV value after 200℃ was significantly dropped and hence the further research and reconsideration of its stability as wear resistant coating should be conducted. For N+ and NC, for more accurate comparison and to understand their mechanical behaviors that are related to wear resistance, HV measurement at more various temperatures should be conducted. For N+, it was found that approximately 10 atomic percent of Ni was diffused into Cu substrate. However in NC and ABNC this diffusion trend was not observed. This is because the diffusion coefficient of Ni tends to be decreased as Co content increases. From this result, it was considered that NC and ABNC, Ni-Co alloy, are more stable at the elevated temperature in a long term, compare to N+; pure Ni. Inter-diffusion of alloy system can affect its wear resistance. Hence the measurement of HV that is highly related with its wear resistance or wear-scratch testing should be conducted on the inter-diffused specimens and needs to be compared with the original specimens. For NC, from the EDS data, the composition of coating layer was not uniform but it contained higher Co content at the top part and contained less Co near the interface. It was due to the processing method, electroplating, which affected its composition.

From this experiment, it was able to obtain the mechanical properties of the alloys at the elevated temperature and the effects of diffusion on the alloys. However as mentioned, it was not able to explain the diffusion of Ni into Cu after 28 days of heat treatment (table 4) and a few points were missing in the figure2. Furthermore, wear resistance of the alloys needs be more clarified by conducting scratch testing. Finally, the micro-structure of the Ni, Ni/Co coating layers were not able to be observed by SEM. The structure of the coating layers should be observed because it can explain the trend of hardness of the coatings at various temperatures. Thus, microscopic analysis using TEM needs to be conducted in the future.

# REFERENCES

1. *Sohan L. Chawla, R.K.Gupta. 1993. Materials Selection for Corrosion Control. ASM. pp 210*
2. *Basics of Continuous Casting of Steel -Steel Casting Process. https://www.calmet.com/basics-of-continuous-casting-of-steel/. Accessed 26 Oct. 2019.*
3. [*Li,*](https://www.researchgate.net/publication/337096502_Interfacial_Bonding_and_Abrasive_Wear_Behavior_of_Iron_Matrix_Composite_Reinforced_by_Ceramic_Particles) *Tang, et al. Nov 6, 2019. Interfacial Bonding and Abrasive Wear Behavior of Iron Matrix Composite Reinforced by Ceramic Particles. MDPI*
4. *William D. Callister, Jr., David G. Rethwisch. “Materials Science and Engineering an Introduction(8”). Wiley. 2009.*
5. *Scanning Electron Microscopy. (n.d). Nanoscience Instruments. Retrieved June 19, 2020, from https://www.nanoscience.com/techniques/scanning-electron-microscope/*
6. *Serap Yesilkir Baydar, Olga N. Oztel, et al,”Nanobiomaterials Science, Development and Evaluation”, Elsevier, pp 211 ~ 232, 2017.*
7. *Theory of hardness testing. (n.d.) Retrieved June 19, 2020, from https://www.emcotest.com/en/the-world-of-hardness-testing/hardness-know-how/theory-of-hardness-testing/*
8. *John Tartaglia. March 17, 2017. What is Hot Hardness Testing. Element*.
9. *SJ Shaffer. March 31, 2014. Hardness Testing at Elevated Temperatures. Bruker*
10. *Yoshiaki, Hirano, et al. “Determination of Intrinsic Diffusion Coefficients in a Wide Range of a Cu-Ni Couple by the Multiple Markers Method”: Japan Institute of Metals: Vol 23, No 1, Oct 8, 1981.*
11. *Hideki Hagi.. Diffusion Coefficient of Hydrogen in Ni-Cu and Ni-Co alloys. Japan Institute of Metals. Research Gate. Apr 1, 1984.*