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作品名稱 Dependence of Alloy Composition in Color Change of Brass Foil by Oxide Thin Layer Formation

得獎獎項 大會獎 三等獎

國　　家 Japan

就讀學校 Sendai Daisan High School, Miyagi Prefecture

指導教師 Yusuke Sugawara

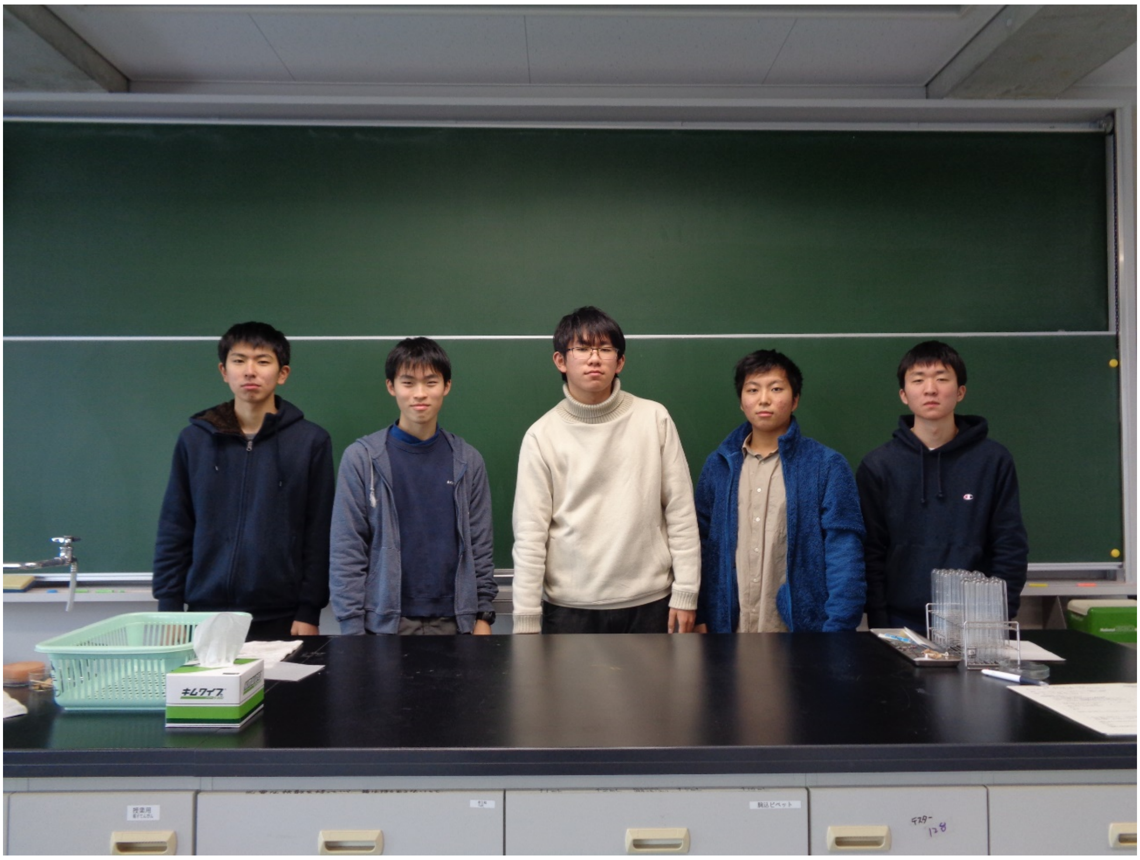
作者姓名 Yuki Kawakatsu

Masahiro Kimura

Tomoaki Nikaido

關鍵詞 diffusion length

作者照片



1. Abstract

It is known that copper foil undergoes a color change in heating by oxide thin layer formation. Therefore, we focused on the color change by the oxidation of brass foil. Brass foil (Akaguchi (Cu87%Zn13% alloy) and Aoguchi (Cu85%Zn15% alloy)) also undergoes color change by oxidation, and it shows heating time and temperature dependence. Brass foil need longer heating time to appear color change than copper foil, and we can visually confirm that the brass has corrosion resistant. In addition, color change of brass foil depends on the percentage of copper in the brass, and Aoguchi shows rapidly color change in same heating condition. We show that brass has different physical properties than copper, even with a high percentage of copper in brass, and this was verified through comparison using diffusion length and RGB data in Aoguchi and Akaguchi. We demonstrate these colored brass foils are used as art materials, and our results expanded material using possibility of brass foil.

2. Background and Purpose

From previous research[1), when copper foil is heated below 400°C, copper(I) oxide is formed, and a color change appears on the copper foil according to the thickness of the oxide film. The color change can be expressed by the diffusion length of oxygen atoms, which is calculated by heating temperature and heating time. Therefore, we expected oxidation also changes the color of copper alloys. To realize color change in brass foil, we heated the brass to see the relationship between time and temperature in the color change.

Akaguchi (Cu87% Zn13% brass foil) and Aoguchi (Cu85% Zn15% brass foil) are well-known as art materials in Japan, and wider variety of colors in these brass foil expands the material using possibilities. In this research, color change of Aoguchi and Akaguchi by heating was observed, and relationship between composition of brass foil and color change was discussed.

3. Color Change of Akaguchi and Aoguchi

3.1 Color Change of Akaguchi and Aoguchi by Heating

Experimental Conditions

Akaguchi (Composition: Cu87%Zn13%)

Aoguchi (Composition: Cu85% Zn15%)[2)]

Sample size: 20mm×20mm

Thickness: 0.4μm

Heater equipment: Muffle furnace (KENIS, FO100)

Applied temperature: 160°C to 400°C with 10°C intervals.

Applied heating time: 10, 20, or 30 minutes.

Experimental Method

I. Raise the temperature in the muffle furnace to the set temperature.
II. Quickly place the sample into the muffle furnace and heated it at low temperature.
III. After a set time, remove the sample from the furnace and cool to room temperature.
IV. Observe the discoloration on the surface of the brass foil.

3.2 Experimental Result

The results are shown in **Fig. 1** and **2**. Color change of copper foil by heating from the previous study [1)] are shown in **Fig. 3** for comparison.

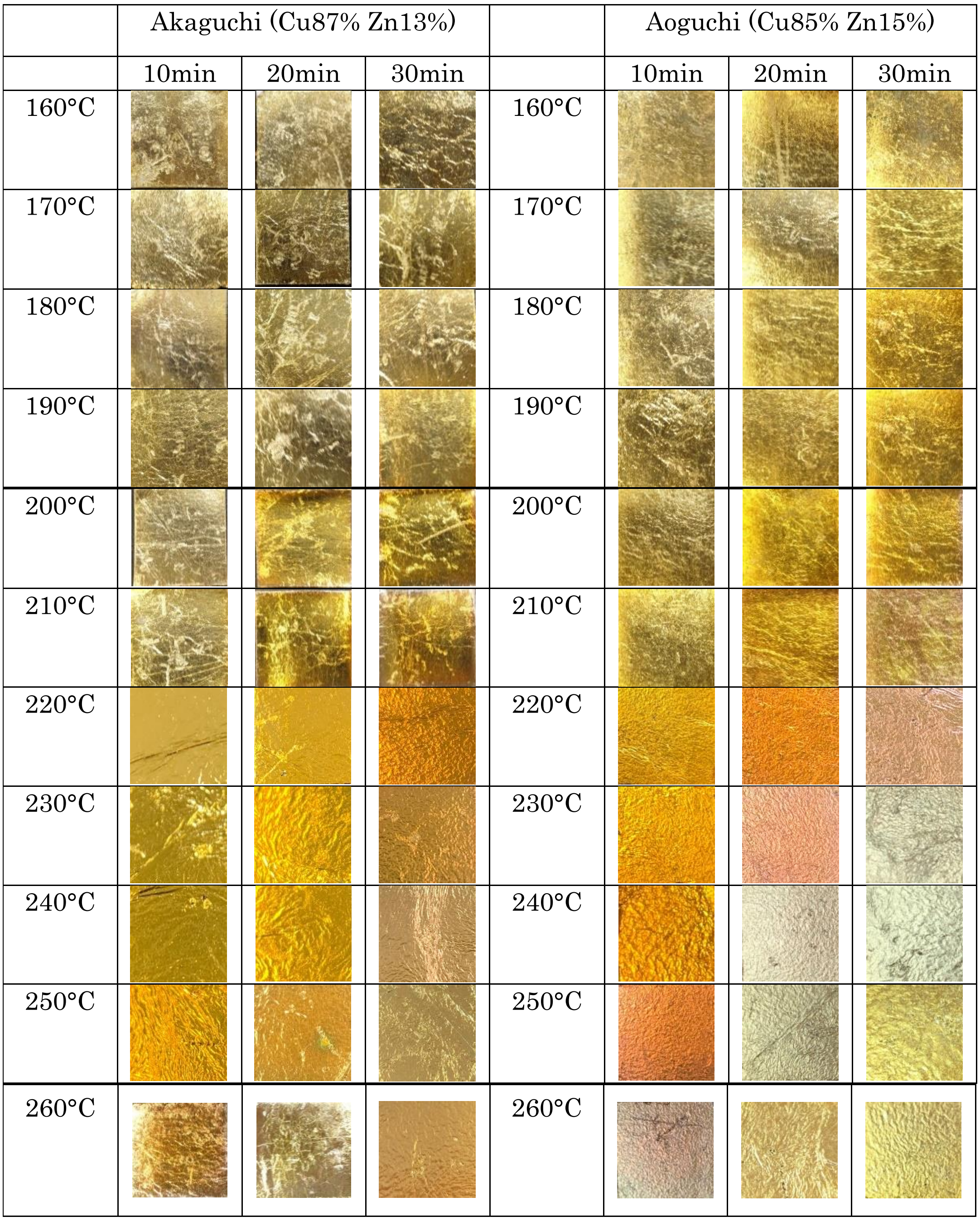


Fig. 1 Colors of heated Akaguchi and Aoguchi (160°C to 260°C)

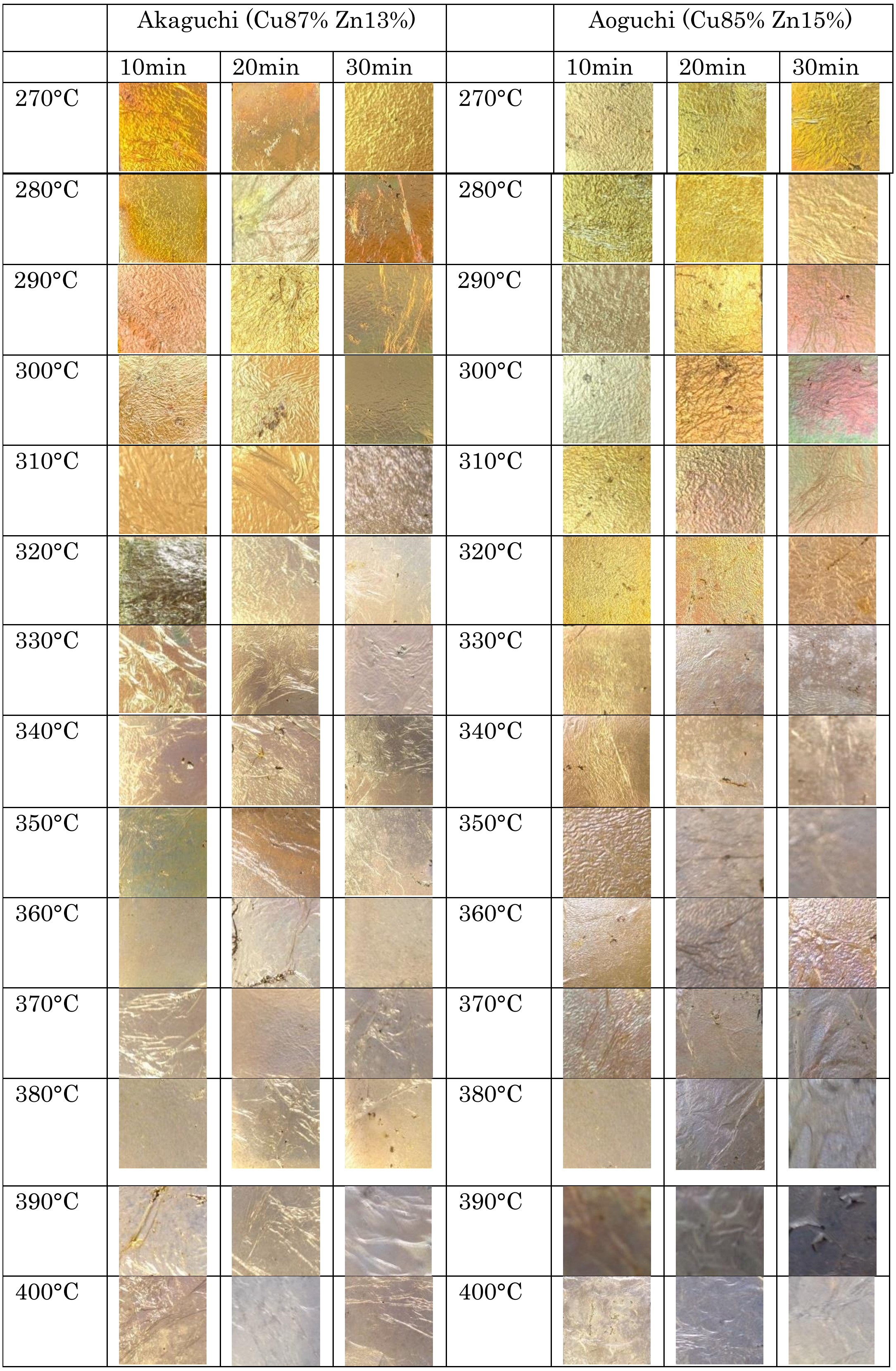


Fig. 2 Colors of heated Akaguchi and Aoguchi (270°C to 400°C)

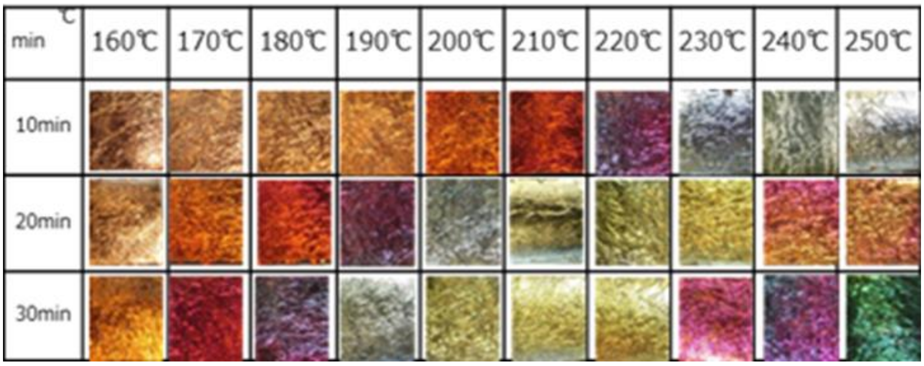


Fig. 3 Colors of heated copper foils[1]

The color of Akaguchi and Aoguchi changed in the following order: golden yellow, yellow, orange, peach, light yellow, silver, light peach, gray, and black. There was little color change in Akaguchi and Aoguchi at 160°C to 200°C. The brass required higher temperature and longer heating time than the copper foil for color change.

Compared to copper foil, brass showed light pastel colors and metallic colors. In addition, between Akaguchi and Aoguchi, Aoguchi (Cu85% Zn15%) is more similar to copper foil in color change.

3.3 Discussion

3.3.1 Brass foil requires higher temperature and longer time than copper foil for color change

In brass, there is a large difference in the ionization tendency between copper and zinc, hence zinc is oxidized faster. Therefore, higher temperature and longer heating time are required for color change than copper, and brass has higher corrosion resistance than copper. This experiment allows us to visually confirm the corrosion resistance of brass

3.3.2 Light pastel colors and metallic colors of Aoguchi and Akaguchi

The color change in the brass showed pale shades, shiny brown and gray. The reason for these colors is due to the presence of zinc oxide ZnO inside the brass. Zinc oxide is white, which-dull the reflection of light and make the color pale. In addition, the observed brown and gray brass foil are shiny and similar to the colors used in car paint. The luster of the colors used in car paint appears when aluminum pieces are sprinkled in the paint film[3]. Although this has not been found to be the same principle as the zinc oxide that is sparsely present inside the brass, we have certainly succeeded in producing the colors used in car paint by heating brass foil

3.3.3 Color change of Aoguchi has more similarity to copper foil

The color of copper foil changes with copper(I) oxide forming. Therefore, it was expected that the color change of Akaguchi, which contains more copper, would be similar to that of copper foil. However, the experimental results showed that the color change of Aoguchi was more similar to copper. Therefore, we focused on the composition dependence of the color change of brass foil.

4 Comparison of Color Change between Akaguchi and Aoguchi

From **Fig. 1**, we have achieved to understand the color change by making a table of the color change of brass foil with heating temperature and heating time. Furthermore, there is a difference in the susceptibility to oxidation between Akaguchi and Aoguchi because there is a difference in their color changes. However, we used a muffle furnace to heat them. That way we could not directly observe the process of color change during heating. Therefore, we could not determine the susceptibility to oxidation. Hence, we used a hot plate for heating. In this way, we can directly observe the process of color change. We heated copper foil in order to compare it with brass foil.

4.1Color Change of Brass Boil by Hot Plate.

Experimental Conditions

Akaguchi (Composition: Cu87%Zn13%)

Aoguchi (Composition: Cu85% Zn15%)[2)]

Copper foil

Sample size: 20mm×20mm

Thickness: 0.4μm

Heater equipment: Hot plate (Yamazen, IH-H1400 (B))

Applied temperature: 250 °C

Applied heating time: 20 minutes

Experimental Method

I. Set the temperature of the hot plate to 250°C and raised it.
II. When the temperature reached 250°C, place a piece of brass foil in the center of the plate.
III. Observe the color change for 20 minutes.

4.2 Experimental Result

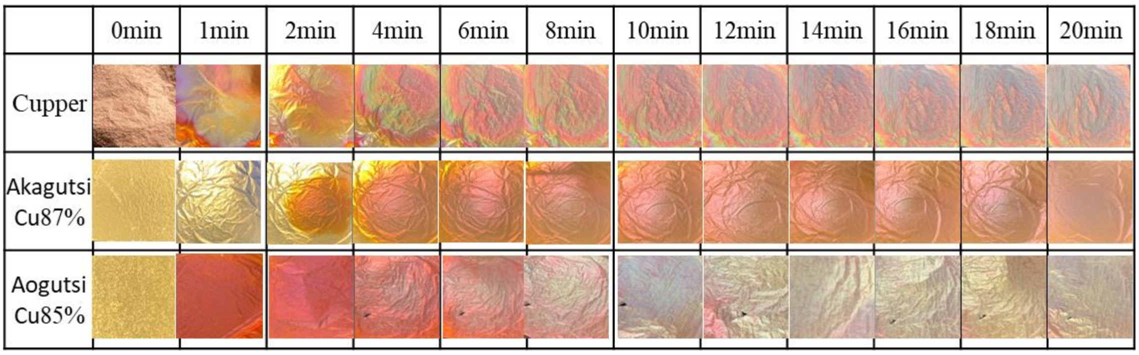


Fig. 4 Color change of brass foil and copper foil on the hot plate

The results are shown in **Fig. 4**. The copper foil color changed to red, purple, silver, and gold in one minute. The color of Aoguchi changed to red rapidly. On the other hand, Akaguchi color remained their original color. We can see that the order in which color changes are most likely to occur is copper, Aoguchi, and Akaguchi. This means that Aoguchi, with less copper, changes color more easily than Akaguchi.

4.3 Discussion

4.3.1 Color change progresses in the following order: Copper > Aoguchi > Akaguchi.

From a reference[4)], the magnitude of ductility of brass with 90% copper percentage is closer to that of copper than that of brass with 80% copper percentage. This does not mean that a higher copper percentage is closer to the properties of copper. We had assumed that higher copper content is closer to copper properties. However, the color change of brass is not proportional to the percentage of copper. We were led to believe that the alloys have a complex relationship. **Fig. 5**, shown below, was found in a reference[4)]. The meaning of the vertical axis is cross-sectional shrinkage. Cross-sectional shrinkage means ductility. “OFHC" means pure copper.

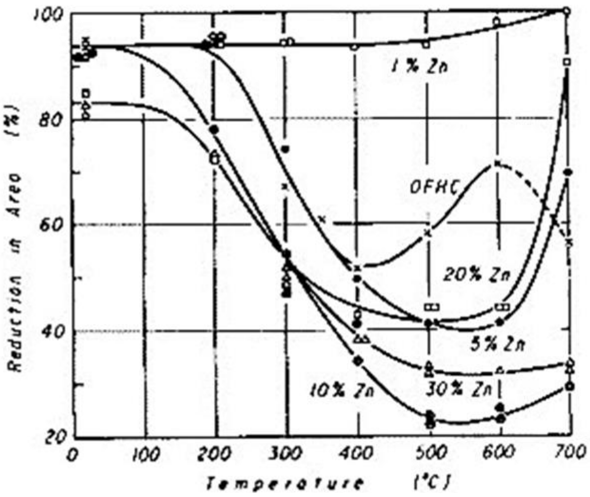


Fig. 5 Cross-sectional shrinkage vs. temperature curve of brass at low temperature test

5.On the Comparison of Aoguchi and Akaguchi Using the Diffusion Length of Oxygen Atoms

5.1 Relationship between Color Change and Diffusion Length in Brass

From this experiment, the order in which color changes are most likely to occur is copper, Aoguchi, and Akaguchi. Therefore, to compare the differences, we calculated the diffusion length of oxygen atoms used in previous study[1)]. The color change occurs when oxygen molecules reach the surface of the brass, enter from the surface, and diffuse into the brass, oxidizing it. The diffusion length indicates the distance that oxygen molecules can enter. By using the diffusion length, the degree of oxidation of brass can be quantitatively expressed.

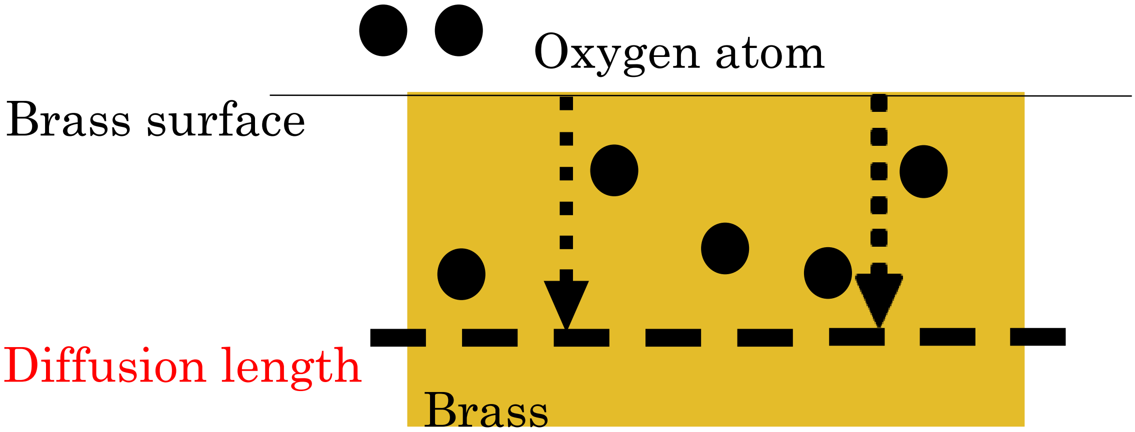


Fig. 6 Penetration and diffusion length of oxygen atoms on brass surface

$D = D_0 \exp\left(-\dfrac{E_a}{RT}\right)$	D:Diffusion coefficient D_0:Diffusion constant E_a:Activation energy R:Gas constant T:Temperature
$L(t) = 2\sqrt{Dt}$	$L(t)$:Diffusion length t:Time

Formula for diffusion length of oxygen atom

After much searching of the literature, we found that Aoguchi diffusion constant was 4.88×10^{-7} m^2/s (500K~1240K) and activation energy was 40.2 kJ/mol in NIMS[5)]. However, there were none data for the Akaguchi. The relationship among heating time, temperature, diffusion length, and color change for the Aoguchi is shown in **Fig. 7**.

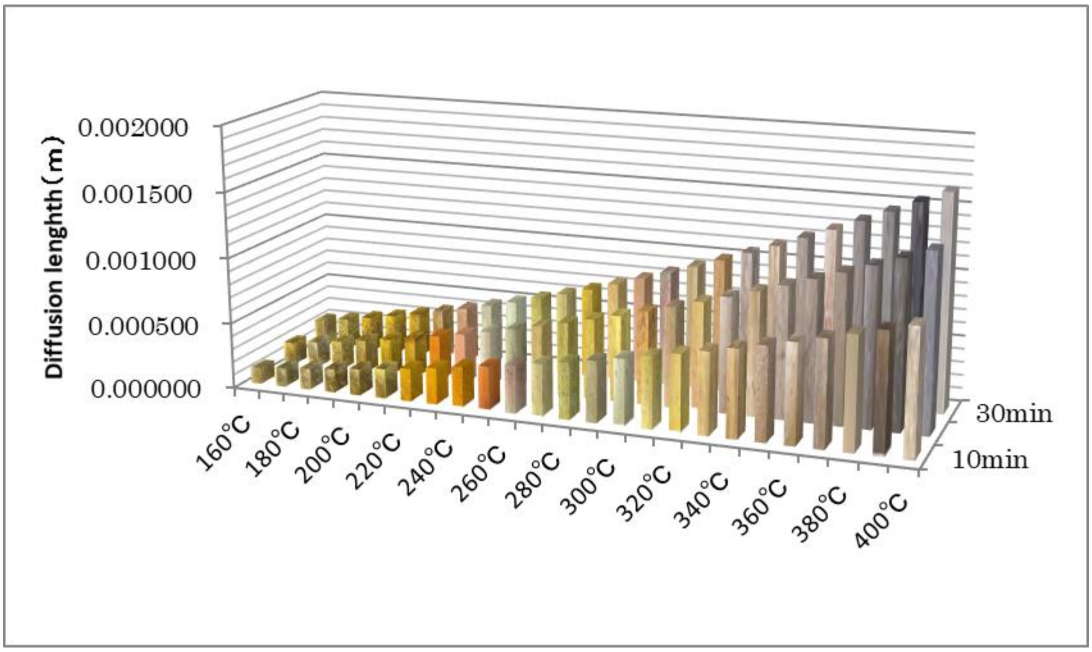


Fig. 7 Relationship among heating time, temperature, diffusion length of oxygen atoms, and color change in Aoguchi

Fig. 8 shows the data in **Fig. 7** classified by heating time.

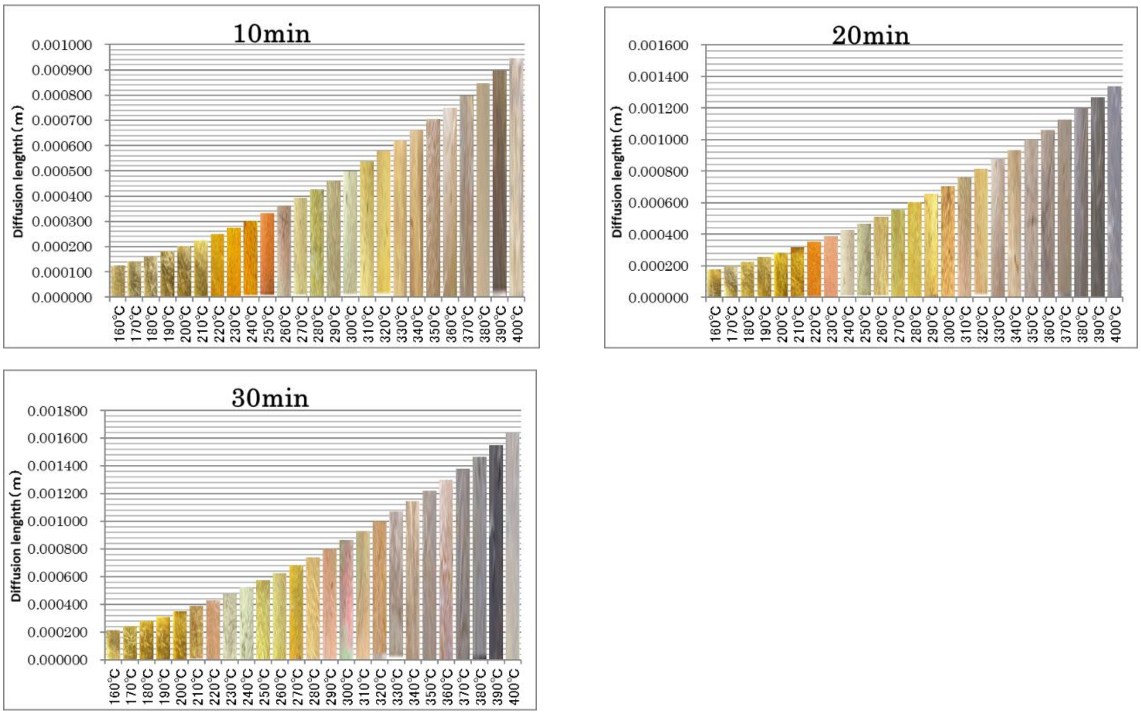


Fig. 8 The relationship between the temperature and diffusion length in Aoguchi

From previous study[1], we can see that there is a correlation between the color of copper foil and the diffusion length of oxygen atoms. If the diffusion lengths of oxygen atoms in similar colors are close in brass foil, there is a correlation between the color of brass foil and diffusion length of oxygen atoms. Therefore, we measured the RGB data and diffusion lengths of orange, which has similar Akaguchi and Aoguchi.

Table. 1 and **Fig. 9** below show the diffusion length of oxygen atoms around the orange color. The results of measuring the RGB data of the orange color, the photograph, and the value of diffusion length are shown in **Fig. 10** below. From the measurement results, the color change is similar when the diffusion length is close. Therefore, the diffusion length of oxygen atoms is related to the color change of the brass.

Table. 1 Diffusion length of oxygen atoms around the heating temperature and heating time when the orange color appears on Aoguchi. ($\times 10^{-4}$ m)

	10min	20min	30min
160°C	1.24	1.76	2.15
170°C	1.41	2.00	2.45
180°C	1.60	2.26	2.77
190°C	1.80	2.54	3.11
200°C	2.01	2.84	3.48
210°C	2.24	3.17	3.88
220°C	2.48	3.51	4.30
230°C	2.74	3.88	4.75
240°C	3.02	4.27	5.23
250°C	3.31	4.68	5.73

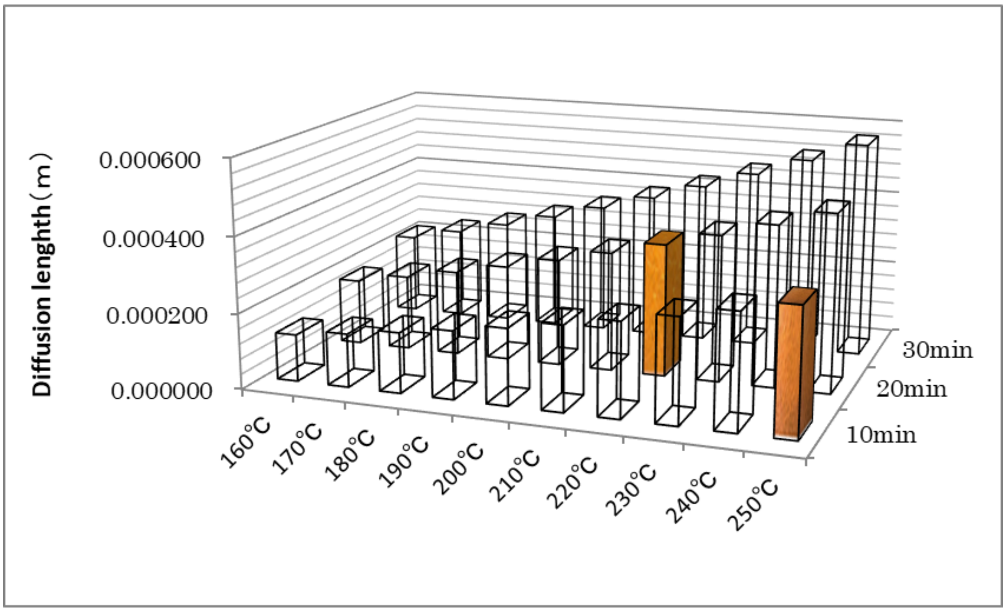


Fig. 9 Diffusion length of oxygen atoms around the heating temperature and heating time.

Condition	220°C　20min (Akaguchi)	250°C　10min (Aoguchi)
Photograph		
RGB data	R:207 G:118 B:14	R:211 G:120 B:50
Diffusion length	3.51×10^{-4} m	3.31×10^{-4} m

Fig. 10 RGB data of orange, diffusion length and its photograph

The activation energy and diffusion constant are different for Akaguchi and Aoguchi. However, we used the same values for our comparison. It is true that the values of the constants are different between Akaguchi and Aoguchi. Nevertheless, since we are comparing them relatively on the same basis, we can think of the difference as representing the difference between Akaguchi and Aoguchi. It is thought that they are oxidized to the same degree when the brasses are the same color. If the colors are similar at close values of the diffusion length, we can conclude that the 2% difference in copper content between Akaguchi and Aoguchi is not significant. On the contrary, if the colors become different at close values of the diffusion length, the difference can be judged to be the effect of the copper content of 2%. The relationship among heating time, temperature, diffusion length of oxygen atoms, and color change in Akaguchi is shown in **Fig. 11**.

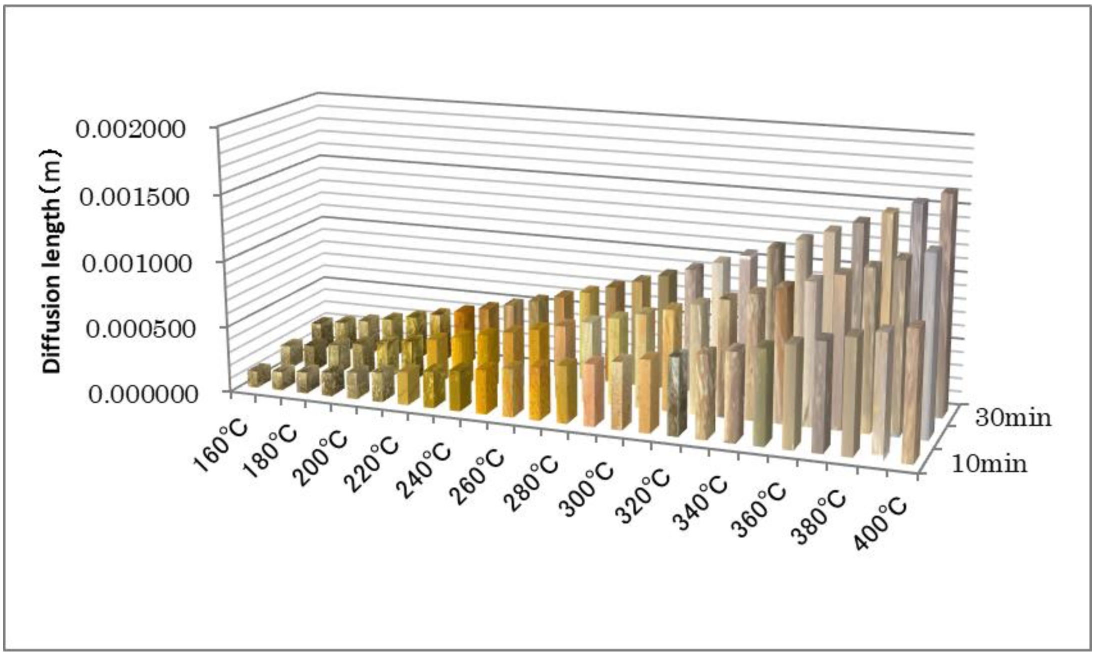


Fig. 11 Relationship among heating time, temperature, diffusion length of oxygen atoms, and color change in Akaguchi.

Fig. 12 shows the data in **Fig. 11** classified by heating time.

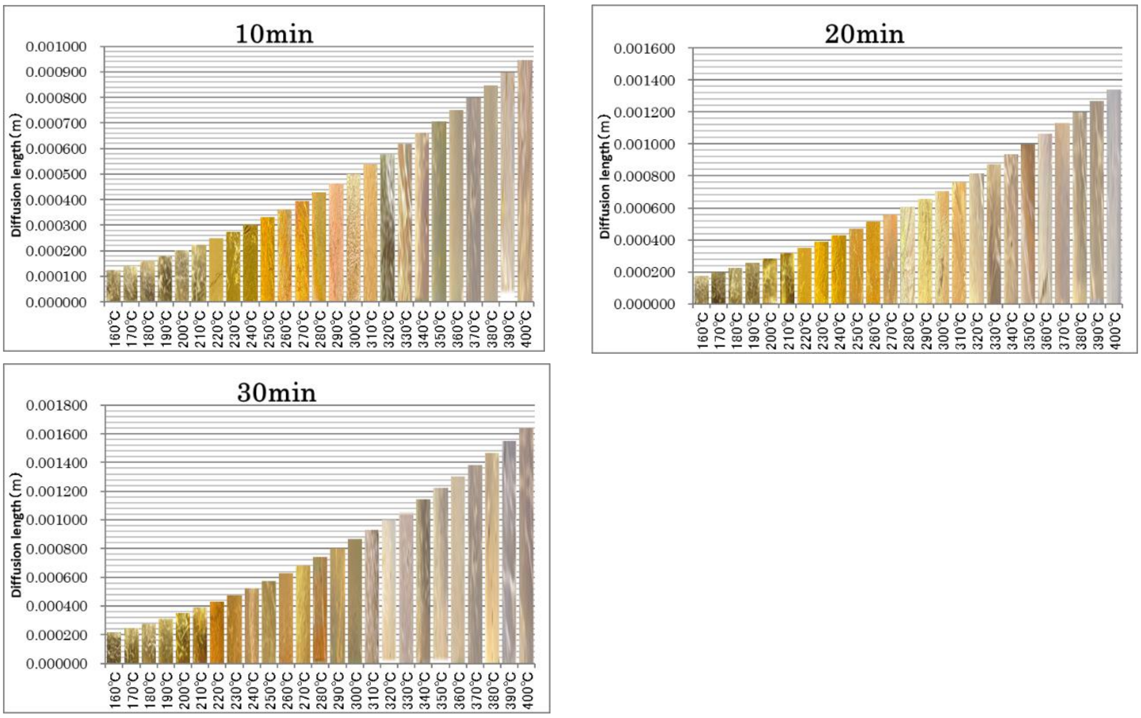


Fig. 12 Relationship between temperature and diffusion length in Akaguchi when time is kept constant

Fig .7 and **11** show that under the conditions of the first experiment, there were few similar colors in Akaguchi and Aoguchi. Among them, the orange color appeared as a similar color change in Akaguchi and Aoguchi. We decided to compare Akaguchi and Aoguchi using brass, which showed orange color.

5.2 Relationship between the Diffusion Length of Aoguchi and Akaguchi

From the RGB data, the color of Akaguchi heated at 220°C for 30 minutes and Aoguchi heated at 220°C for 20 minutes are similar. **Fig.13** below shows the data for Akaguchi and Aoguchi respectively, under those conditions. The diffusion lengths of Akaguchi and Aoguchi are 4.30×10^{-4} m and 3.51×10^{-4} m, respectively. The value of diffusion length of Akaguchi was 1.23 times larger than that of Aoguchi. For copper contained in brass to be oxidized and have the same thickness of copper(I) oxide, Akaguchi requires a longer diffusion length than Aoguchi. Therefore, although it is a simple comparison, Akaguchi is 1.2 times more resistant to oxidation than Aoguchi.

Condition	220°C 30min (Akaguchi)	220°C 20min (Aoguchi)
Photograph		
RGB data	R:198 G:111 B:11	R:207 G:118 B:14
Diffusion length	4.30×10^{-4} m	3.51×10^{-4} m

Fig. 13 Measurement results of RGB data of orange, diffusion length and its photograph

Now, to find out if other similar colors produce similar values, we examined the ratio of the diffusion length of oxygen for peach color at 290°C for 10 minutes for Akaguchi and 230°C for 20 minutes for Aoguchi. The measured peach color photographs, RGB data, and diffusion lengths are shown in **Fig. 14** below.

Condition	290°C 10min (Akaguchi)	230°C 20min (Aoguchi)
Photograph		
RGB data	R:254 G:204 B:153	R:230 G:179 B:137
Diffusion length	4.63×10^{-4} m	3.88×10^{-4} m

Fig. 14 Measurement results of RGB data of peach color, diffusion length and its photograph

It is obvious from the RGB data that colors of these two samples are similar. Moreover, the diffusion lengths for Akaguchi and Aoguchi are 4.63×10^{-4} m and 3.88×10^{-4} m, respectively. The value for Akaguchi is 1.19 times that for Aoguchi, suggesting that Akaguchi is 1.19 times resistant to oxidation than Aoguchi. This value is similar to that of the aforementioned value for orange, which means that is Akaguchi about 1.2 times more resistant to oxidation than Aoguchi. By using this value, we can predict the diffusion constant and activation energy of Akaguchi. Following this idea, we calculated the diffusion constant at Akaguchi to be 3.36×10^{-7} m^2/s at all temperatures. However, the value of the activation energy was different for each temperature and could not be determined. In this case, we used the activation energy of Aoguchi to find the diffusion constant of Akaguchi, and the diffusion constant of Aoguchi to find the activation energy. This was done to reduce the number of variables to one and simplify the calculation. From the above, we can assume that there is no significant difference in the activation energy, which changes with temperature, between Akaguchi and Aoguchi. Therefore, there is a large difference in the value of the diffusion constant between Akaguchi and Aoguchi. The value of the diffusion constant is considered to be about the same as the above value.

6. Application as Art Materials

In this study, various colors appeared on the brass foil that did not appear on copper foil in previous studies. Since colored brass foil by oxidation shows almost no discoloration over time, it is expected to be valuable for industrial use such as art materials. Therefore, we named it "Stained Brass," inspired by stained glass. **Fig. 15** shows the commercial sticker used as the source, and **Fig. 16** shows an example of using colored brass foil as a decorative material for the sticker.

Fig. 15 Before decorating[6)]

Fig. 16 After decorating (Stained Brass)

7. Conclusion

Various color changes appear by heating and oxidation of brass foil, and from the comparison of color changes between brass foil and copper foil, it is possible to visualize that brass is more resistant to oxidation than copper. Moreover, comparing Akaguchi and Aoguchi, Aoguchi with a smaller percentage of copper, are more easily oxidized than Akaguchi. Furthermore, the color change of brass foil is expressed by the diffusion length of oxygen atoms, as in the previous study using copper foil. In addition, we demonstrated the application of brass foil as art materials. We expect that this research will expand the application range of brass foil.

8. Future Work

In this study, we used the diffusion length to investigate the color change. However, it is a calculated value and not the actual film thickness. Therefore, we have to investigate the actual relationship between the color change and film thickness. We will measure the mass difference between the unheated and heated brass foil. In addition, we will calculate the film thickness from the surface area and density of the brass. Finally, we will investigate whether those values corresponded to the diffusion length and the color change.

9. Acknowledgement

We would like to express our sincere gratitude to our advisor, teachers, and senior students for their support in this research. We would like to take this opportunity to express our deepest gratitude.

10. References

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【評語】030028

In this work, the students tried to work on the oxidation of copper/zinc alloy with different ratios and monitor the color change. Although simple, the research is interesting and the students are motivated. They can know and explain the scientific principle more clearly. However, they created beautiful color patterns with the heating on different corners/parts of the alloy. This is really smart and appreciated.