Quantitative Research on Color of Cu-Mn-Zn Alloys

Yu-Ping Zhang^{1,2}, Jin-Xu Zhang¹ and Jian-Sheng Wu¹

 ¹Key Laboratory of the Ministry of Education for High Temperature Materials and Testing, Shanghai Jiaotong University, Shanghai 200030, P.R. China
²Department of Materials Science and Technology, Taiyuan Heavy Machinery Institute, Taiyuan 030024, P.R. China

In this paper, the color characteristics of ternary Cu–Mn–Zn alloys are investigated quantitatively and systematically. Using CIE LAB color system, the color parameters such as L^* , a^* and b^* , which were measured by a spectrophotometer, are used to describe the surface color of the forty-six experimental alloys. By the computer technique of data processing and graph editing, a set of the colorful color-composition diagrams of Cu–Mn–Zn alloys are established. The relationship between the chromaticity parameters and the composition is illustrated clearly. A series of equations are derived to correlate color parameters with the alloy compositions. As a result, the color of ternary Cu–Mn–Zn alloys can be calculated and estimated quantitatively.

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1. Introduction

It is well known that German silver is the Cu–Ni–Zn alloy, which is widely used in the field to make zipper, watches and spectacles. Because Nickel may cause skin allergy if people constantly contact with alloys containing Ni,^{1,2)} stricter and stricter standards and regulations have been made to limit or prohibit the use of products with nickel.^{3,4)} In order to develop a nickel-free white-colored alloy to substitute for German silver, an emphasis has been putting on the Cu–Mn–Zn alloy system.^{5,6)} Being different from normal engineering alloys, these Cu–Mn–Zn alloys must meet the need of white color besides good hardness, elongation and ductility. Therefore, during the composition design of nickel-free white copper alloys, color should be quantitatively described and investigated.

Quite often, color is appraised by human eyes. To express the color of alloys, words such as red and green are used. Let's take the color of ternary Cu-Mn-Zn alloys for example, as shown in Fig. 1, there are three kinds of hue areas, i.e. red, yellow and white.⁷⁾ However, as one person's response varies from another's, each observer interprets the color based on personal references and may describe the object's color differently. The interpretation of "yellow", "red" and "white" in Fig. 1 may be considerably different. Furthermore, Fig. 1 does not make known whether the colors of different alloys in the same color area are just the same or not and it seems quite difficult to fix the boundary between hue areas. It can be seen that Fig. 1 is merely a qualitative and ambiguous expression. From the viewpoint of Chromatics, color can be described by color parameters quantitatively and thus be communicated precisely. Therefore, it is necessary to make a quantitative investigation on the surface color of alloys.

So far, only primary research has been made on the surface color of the Au–Ag–Cu and Cu–Zn–Al ternary.^{8,9)} In this paper, the color characteristics of Cu–Mn–Zn alloys were measured and studied systematically. The accurate and basic data are provided for the decorative copper alloy and industry copper alloys.



Fig. 1 Color of Cu-Mn-Zn ternary alloys.

2. CIE 1976 Uniform Color Space¹⁰⁾

The perception of a color by the human eye is a psychological quantity. Therefore, for the indication of color as a physical quantity, some correlation would be necessary between the psychological and the physical quantity. At present, the most important quantitative color order system is the CIE system that is based on additive color mixing. It allows colorists worldwide to communicate colors in a common language. For this study, the CIE LAB uniform color space is used. This is a three-dimensional color space containing lightness axis (L^*) , red-green axis (a^*) and yellow-blue axis (b^*) . The L^* values can range from 0 to 100. $L^* = 0$ represents black color and $L^* = 100$ means white color. Positive a^* values correspond to red and negative a^* values mean green. In the same way, positive b^* values correspond to yellow and negative b^* values mean blue. Based on the colorimetric formula concerned, chroma C^* is calculated as:

$$C^* = (a^{*2} + b^{*2})^{1/2}$$

The larger the C^* values are, the larger the color saturation is.



Fig. 2 Composition of 46 experimental alloys in the Cu-Mn-Zn system.

3. Experimental Procedure

Figure 2 covered the 46 experimental alloys whose Cu content range from 50 mass% to 100 mass% including the pure Cu, binary Cu–Zn, binary Cu–Mn and ternary Cu–Mn–Zn alloys. The composition of the samples was all confirmed by chemical analysis.

The experimental alloys were melted at a high temperature electric furnace and cast into moulds. The as-cast samples of $\Phi 24 \text{ mm}^*15 \text{ mm}$ were ground with wet abrasive papers (down to 600 grit), then rinsed in alcohol and dried in a desiccator. Color measurement was made within 24 hours after the samples were finally ground and rinsed.

Color was measured on ELREPHO2000 spectrophotometer. The D65 standard illuminant, CIE 10° standard observer and 0/d illuminating-viewing conditions were adopted. Because the unpolished samples were selected, the specular reflection data were excluded in the color measurements.

4. Experimental Results and Discussion

4.1 The color-composition diagrams

Based on the color parameters measured,¹¹⁾ a set of colorful color-composition diagrams are established by the computer technique of data processing and graph editing (see Fig. 3 to Fig. 7). As shown in Fig. 3, with the increase of Mn, a^* values of alloys are changed towards zero; with the increase of Zn, a^* values decrease at first and then increase. For example, a^* values of the Cu–Zn binary decrease from positive 12.7 for pure copper to minus 1.7 for Cu-30%Zn alloy, and then increase to positive 5.3 for Cu-49%Zn. For most Cu-Mn-Zn alloys, there is a positive a^* , indicating red. However, for Cu-Mn-Zn alloys containing less than 5%Mn and about 30%Zn, there is a negative a^* , indicating green. Especially in the copper-rich (Cu%>80) part of the ternary diagram, a^* values diminish greatly as Mn or Zn is increased. Figure 3 also shows that a^* contours go in the similar direction to the demarcation line between the yellow and red area in Fig. 1.

Since b^* values measured are much larger than a^* values, the color of Cu–Mn–Zn alloys is dominated by positive b^* values or yellow hue. Figure 4 clearly indicates that Zn has a strong yellow effect. It can also be drawn that C^* values



Fig. 3 a^* projection on the Cu–Mn–Zn ternary diagram.



Fig. 4 b^* projection on the Cu–Mn–Zn ternary diagram.



Fig. 5 C^* projection on the Cu–Mn–Zn ternary diagram.



Fig. 6 L* projection on the Cu-Mn-Zn ternary diagram.



Fig. 7 Color-composition diagram of the Cu-Mn-Zn ternary alloy.

 $[C^* = (a^{*2} + b^{*2})^{1/2}]$ are slightly larger than or nearly equal to b^* values, that is why Fig. 4 is looked like Fig. 5. From these two figures, it can be seen that the effect of Mn on b^* and C^* values is much larger than that of Zn. With the increase of Mn content, b^* and C^* values of alloys decrease. Especially speaking, when the Mn content is less than 10%, the contour lines in Fig. 4 and Fig. 5 appear more densely, which means that b^* and C^* values will decrease greatly with a little addition of Mn. In other words, Mn less than 10% has a greater influence on b^* and C^* . From the viewpoint of chromatics, Mn decreases the yellow content and the saturation of the surface color, and turns Cu-Mn-Zn alloys from chromatic color to achromatic color. The relationship between L^* values and compositions is more complex (see Fig. 6). Both Mn and Zn affect the lightness of copper alloys. Figure 6 clearly demonstrates that L^* values of alloys reduce when adding Mn or reducing Zn content. Therefore, copper alloys containing less Mn and more Zn show high luminance and appear lighter.

So far, no reference has been found to express the color of the ternary alloy system quantitatively and qualitatively in one graph. In our study, the computer technique of graph editing and synthesizing is used to establish the colorful colorcomposition diagram of the Cu–Mn–Zn alloy (Fig. 7). Com-



Fig. 8 3D graphs of Color parameters of Cu-Mn-Zn alloys.

paring with Fig. 1, not only does Fig. 7 illustrate the alloy color qualitatively, but also it reveals the color parameters of each alloy quantitatively. It also details that each alloy owns its unique surface color and color parameters in Cu–Mn–Zn diagram vary gradually with compositions. It is obvious that the color of ternary Cu–Mn–Zn alloys could be classified into three kinds of hues: bronze, brass and silver-white, which are similar to red, yellow and white hue shown in Fig. 1. How-ever, there is no sudden color change in Fig. 7. Therefore, it could be concluded that the demarcation line in Fig. 1 is the artificial one according to some judgment.

4.2 Regression

Figure 8 demonstrates the 3D graph of color parameters of the Cu–Mn–Zn ternary. In order to describe the relationship between the color and the compositions, the multivariate regression is applied. The corresponding equations are as following:

$$L^{*} = 67.295 + 0.410^{*}(Zn\%) - 0.181^{*}(Mn\%)$$

- 6.140^{*}10^{-3*}(Zn%)² - 7.800^{*}10^{-3*}(Zn%)^{*}(Mn%)
(1)
R Sqaure = 0.881
$$a^{*} = 11.059 - 0.686^{*}(Zn\%) - 0.560^{*}(Mn\%)$$

+ 7.577^{*}10^{-3*}(Mn%)² + 1.100^{*}10^{-2*}(Zn%)²
+ 1.465^{*}10^{-2*}(Zn%)^{*}(Mn%) (2)
R Square = 0.892

$$b^{*} = 14.624 - 0.829^{*}(Mn\%) + 0.246^{*}(Zn\%)$$

- 3.850^{*}10^{-3*}(Zn\%)^{2} + 1.352^{*}10^{-2*}(Mn\%)^{2}
- 5.650^{*}10^{-3*}(Zn\%)^{*}(Mn\%) (3)

R Square
$$= 0.976$$

$$C^* = 18.035 - 1.022^*(\text{Mn\%}) + 1.605^*10^{-2*}(\text{Mn\%})^2 \quad (4)$$

R Square = 0.977

These formulae correlate color parameters (L^*, a^*, b^*) and C^*) with the alloy composition (Mn and Zn content). In this case, the compositions are on a mass percentage basis and R Square is the multiple determination coefficient between 0 to 1. The latter shows how the dependent variable correlates with the independent variables. The larger the R Square is, the better the regression equation fits the experimental data. Therefore, eqs. (3) and (4) can forecast b^* and C^* of Cu-Mn-Zn alloys more exactly. They indicate that L^* , a^* and b^* are the function of Mn% and Zn% but C^* is only determined by Mn%. It can also be seen that Mn plays a much more important role in b^* values than Zn. Based on these expressions, the color of Cu-Mn-Zn alloys can be calculated and estimated quantitatively.

According to the equations and the color-composition diagrams above, one can obtain the color parameters $(L^*, a^*, b^*$ and C^*) and the corresponding color if the composition of an alloy is given. On the contrary, if certain surface color is to be matched, one can choose the most suitable composition in this alloy system. These results will be important in developing the new type of the nickel-free white copper alloys.

In the same way, the color-composition diagrams and color-composition equations of other ternary alloys can be established. It will be helpful to the field associated with color as a design criterion.

5. Conclusions

(1) A series of color-filled 2D and 3D color-composition diagrams of the Cu–Mn–Zn ternary are established. They illustrate the color parameters and the color appearance quantitatively and qualitatively. The hue of the Cu–Mn–Zn ternary could be divided into three kinds: bronze, brass and silver-

white.

(2) The mathematical expressions are derived by the multivariate fitting analysis. The relationship between color parameters of Cu–Mn–Zn alloys and their compositions can be calculated. As a result, the color of ternary Cu–Mn–Zn alloys can be forecast quantitatively.

(3) L^* and a^* of Cu–Mn–Zn alloys are the function of Mn and Zn content. b^* values mainly depend on Mn content but C^* is only determined by Mn content. For most Cu–Mn–Zn alloys, there are a positive a^* and b^* , indicating red and yellow. Their colors are dominated by yellow hue.

(4) Cu has a strong red effect while Zn has yellow and light effects. Mn has a strong gray effect and turns the color of Cu–Mn–Zn alloys from chromatic color to achromatic color.

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