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Relationship between color and composition of Cu-Mn-Zn alloys①

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[Abstract] The color of Cu-Mn-Zn alloys is quantitatively researched using the CIE $L^* a^* b^*$ color system. The color parameters such as L^*, a^* and b^* are employed to describe the color and are measured by a spectrophotometer. Based on the color data of 46 experimental alloys, a series of formulae are established to correlate color parameters changed with the alloy composition. Therefore, the color of the ternary Cu-Mn-Zn alloys can be calculated and forecast easily. The results show that Mn plays a more important role in the color of Cu-Mn-Zn alloys than Zn does. In particular, the chroma values of ternary Cu-Mn-Zn alloys mainly depend on the Mn content.

[Key words] Cu-Mn-Zn; chromaticity; color; regression

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1 INTRODUCTION

It is found that Ni can migrate from an alloy into the human skin because of its reaction with the sweat and can give rise to sensitization with the development of allergies[1~3]. Therefore, stricter standards and regulations are made to limit or prohibit the use of products with nickel[4, 5]. German silvers, which are Cu-Ni-Zn alloys and commonly used for the manufacture of clothing zippers, spectacles and costume jewellery, are facing great challenge at present. In order to develop a nickel-free white-color alloy to substitute for German silver, an emphasis is put upon the Cu-Mn-Zn alloy system[6, 7]. As a result, color should be one design criterion of such alloys.

Usually, color is evaluated by human eyes. Due to difference of individual sensation and method of expression, the color assessment became considerably ambiguous. Fig. 1 shows the color constitutional diagram of the ternary Cu-Mn-Zn alloy from the textbook[8]. It can be seen that there are three kinds of hue area, i. e. red, yellow and white in the Cu-Mn-Zn diagram. However, one's interpretation of "yellow", "red" and "white" may be considerably different from another's. Furthermore, it is unknown how much the color parameters of each alloy are and how the alloy colors change with the composition. It is necessary to study the surface color of alloys quantitatively and find out the relationship between the composition of the alloys and their color parameters.

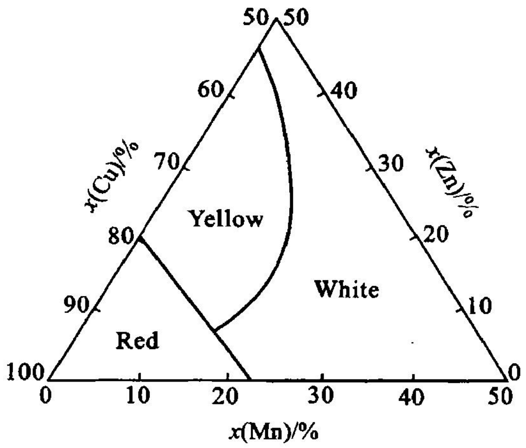

Fig. 1 Color constitutional diagram of Cu-Mn-Zn alloys

2 CIE 1976 UNIFORM COLOR SPACE

Up to now, the most important quantitative color order system is the CIE (Commission Internationale de l'Eclairage) system that is based on additive color mixing. It allows colorists worldwide to communicate colors in a common language. For this study, the CIE 1976 $L^* a^* b^*$ uniform color space[9, 10] is used. This is a three-dimensional color space containing lightness axis (L^*), red—green axis (a^*) and yellow—blue axis (b^*). Fig. 2 shows a schematic diagram of the CIE $L^* a^* b^*$ uniform color space. The L^* values can range from 0 at the bottom to 100 at the top. $L^* = 0$ represents black color and $L^* = 100$ means white color. The more the reflectance of the colored object, the larger the

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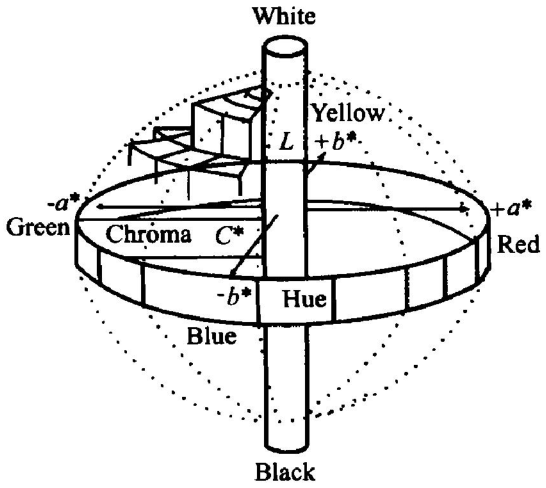

Fig. 2 CIE $L^* a^* b^*$ uniform color space

lightness value is. If the reflectance of one object is between 80% and 90%, it means that the object is white. If the reflectance is lower than 4%, it presents black. 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. According to the colorimetric formula concerned, chroma C^* is calculated as:

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

It represents the horizontal radial distance from axis L^* to a point in color space. The larger the C^* values, the larger the color saturation is.

3 EXPERIMENTAL

Experimental alloys were prepared to provide color data showing compositional effects on alloy color. This study included pure element Cu, binary Cu-Zn and Cu-Mn alloys and ternary Cu-Mn-Zn alloys with the Cu content more than 49% (mass fraction). The compositions of the samples were all confirmed by chemical analysis.

46 experimental alloys were melted at high temperature electric furnace and cast into moulds. The as-cast samples with size of d 24 mm × 15 mm were ground with wet abrasive papers (down to P 600) to a surface finish of 25.8 μm, then rinsed in alcohol and dried in desiccator. Color measurement was made within 24 h after the samples were finally ground and rinsed.

Color was measured on ELREPHO 2000 spectrophotometer. The D65 standard illuminant, CIE10° standard observer and 0/ d illuminating as well as viewing condition were adopted. Because the unpolished samples were used, the specular reflection data were excluded in the color measurements. The automated spectrophotometer provided a mean to objectively determine the spectral reflectance distribution from the sample and thereby compute its color parameters.

4 RESULTS AND DISCUSSION

The composition and color parameters of samples measured are listed in Table 1.

Based on the data in Table 1, Fig. 3 are obtained to describe the relationship between color parameters (L^*, a^*, b^* and c^*) and the alloy composition. Experimental results indicate that color parameters of one alloy are not the same as those of another. Each alloy possesses its own unique surface color. It is certain that colors of different alloys in the same hue area in Fig. 1 are not just the same. It is also shown that any small difference in any composition may cause the continuous variation of color parameters, that is, the alloy color changes with composition gradually but not suddenly. Especially speaking, when the Mn content is less than 10%, color parameters are changed rapidly with a little variation of Mn content. Therefore, Mn content (less than 10%) plays a more important role in color of Cu-Mn-Zn ternary alloys.

Fig. 3(a) shows the change of a^* with composition. The result exhibits that both Mn and Zn make a notable impact on a^*. When the Zn content is between 0 and 22% and more than 34%, a^* values of Cu-Mn-Zn alloys present positive; when the Zn content is 23% ~ 33%, they are negative. It can be clearly seen that with the increase of Mn, positive a^* values are decreased and negative a^* values are increased towards zero. It shows that the more the Mn content is, the less the red content or the green content of the surface color is in Cu-Mn-Zn ternary.

As shown in Fig. 3(b), when the Mn content is more than 10%, b^* values of ternary Cu-Mn-Zn alloys mainly depend on the Mn content and are decreased with the increase of Mn content; otherwise, b^* values are influenced by both Mn and Zn contents.

Mn influences C^* values in the similar way to b^*. However, the effect of Zn on C^* values is much less than that on b^*. Fig. 3(c) indicates that C^* values of ternary Cu-Mn-Zn alloys are only determined by the Mn element and have little to do with Zn element. The chroma tends to get progressively lower with the decrease of the Mn content. From the viewpoint of chromatics, Mn determines the color saturation of Cu-Mn-Zn alloys and turns the alloy from chromatic color to achromatic color.

Because the lightness varies with the experimental methods, color measuring condition, and samples preparation to a great extent[11], the L^* values obtained in our test present more scattered

Table 1 Composition and chromaticity parameters of experimental alloys (D65/10°, 0/d condition, ground surface)

Alloy No.		Composition (mass fraction) / %			Color parameter			
		Mn	Zn	Cu	L^*	a^*	b^*	C^*
1	600	0	0	Bal.	66.95	12.7	14.0	18.9
2	504	0	8.94	Bal.	65.48	4.7	8.1	9.4
3	515	0	19.83	Bal.	60.97	2.0	3.8	4.3
4	405	0	32.34	Bal.	58.42	1.3	2.8	3.1
5	516	0	39.00	Bal.	62.17	0.7	1.6	1.7
6	612	4.83	14.08	Bal.	65.51	1.9	7.6	7.3
7	613	5.11	17.78	Bal.	67.08	1.3	5.8	5.9
8	201	6.97	13.87	Bal.	67.32	1.5	6.8	7.0
9	306	7.13	14.51	Bal.	67.72	1.9	6.7	7.0
10	305	8.2	11.74	Bal.	71.52	2.1	8.2	9.4
11	517	8.97	0	Bal.	69.92	6.4	16.6	17.8
12	611	9.15	13.56	Bal.	67.35	1.2	7.0	7.1
13	406	9.51	10.19	Bal.	67.96	1.9	8.2	8.4
14	617	9.68	30.75	Bal.	62.41	0.4	3.0	3.0
15	510	9.74	12.85	Bal.	69.48	1.4	7.3	7.4
16	801	10.00	17.00	Bal.	66.94	0.7	6.8	6.8
17	614	10.53	17.43	Bal.	66.12	0.8	6.2	6.3
18	513	11.07	26.83	Bal.	64.51	0.9	3.4	3.5
19	618	11.37	39.05	Bal.	62.08	0.6	2.3	2.4
20	202	14.06	16.16	Bal.	68.56	0.5	6.4	6.4
21	610	14.17	14.02	Bal.	65.67	0.5	7.6	7.6
22	615	14.81	17.89	Bal.	66.64	0.4	4.6	4.6
23	203	18.17	12.37	Bal.	65.55	0.3	7.3	7.3
24	609	19.31	14.59	Bal.	67.46	0.3	7.8	7.8
25	402	19.36	0	Bal.	73.93	1.0	19.1	19.1
26	511	19.55	18.24	Bal.	64.40	0.2	5.2	5.2
27	507	19.96	9.47	Bal.	66.72	0.3	9.0	9.0
28	514	21.79	28.96	Bal.	61.70	0.2	3.2	3.2
29	608	24.45	14.62	Bal.	72.82	−0.1	6.6	6.6
30	607	25.03	9.31	Bal.	69.70	−0.1	9.6	9.6
31	508	26.81	7.61	Bal.	71.14	−0.4	10.8	10.8
32	512	27.89	16.39	Bal.	64.87	0	6.2	6.2
33	603″	28.72	4.53	Bal.	73.53	−0.6	14.0	14.0
34	403	29.33	0	Bal.	73.36	−1.7	20.3	20.4
35	616	29.49	18.72	Bal.	65.96	0	7.6	7.6
36	606	29.66	9.25	Bal.	71.47	−0.3	9.0	9.0
37	604	29.94	15.40	Bal.	69.73	−0.1	7.1	7.1
38	509	31.02	8.49	Bal.	68.40	−0.3	11.4	11.4
39	605	34.60	9.35	Bal.	72.90	0	9.1	9.1
40	603	34.73	4.86	Bal.	68.60	0.7	13.3	13.3
41	619	35.00	0	Bal.	71.88	0.2	19.0	19.0
42	518	37.90	0	Bal.	72.63	2.2	18.1	18.2
43	604′	38.22	9.64	Bal.	70.59	0.2	8.8	8.8
44	602	45.62	0	Bal.	74.03	1.6	17.9	18.0
45	601	48.92	0	Bal.	72.68	5.3	19.2	19.9
46	601′	50.62	0	Bal.	72.58	4.0	15.9	16.4

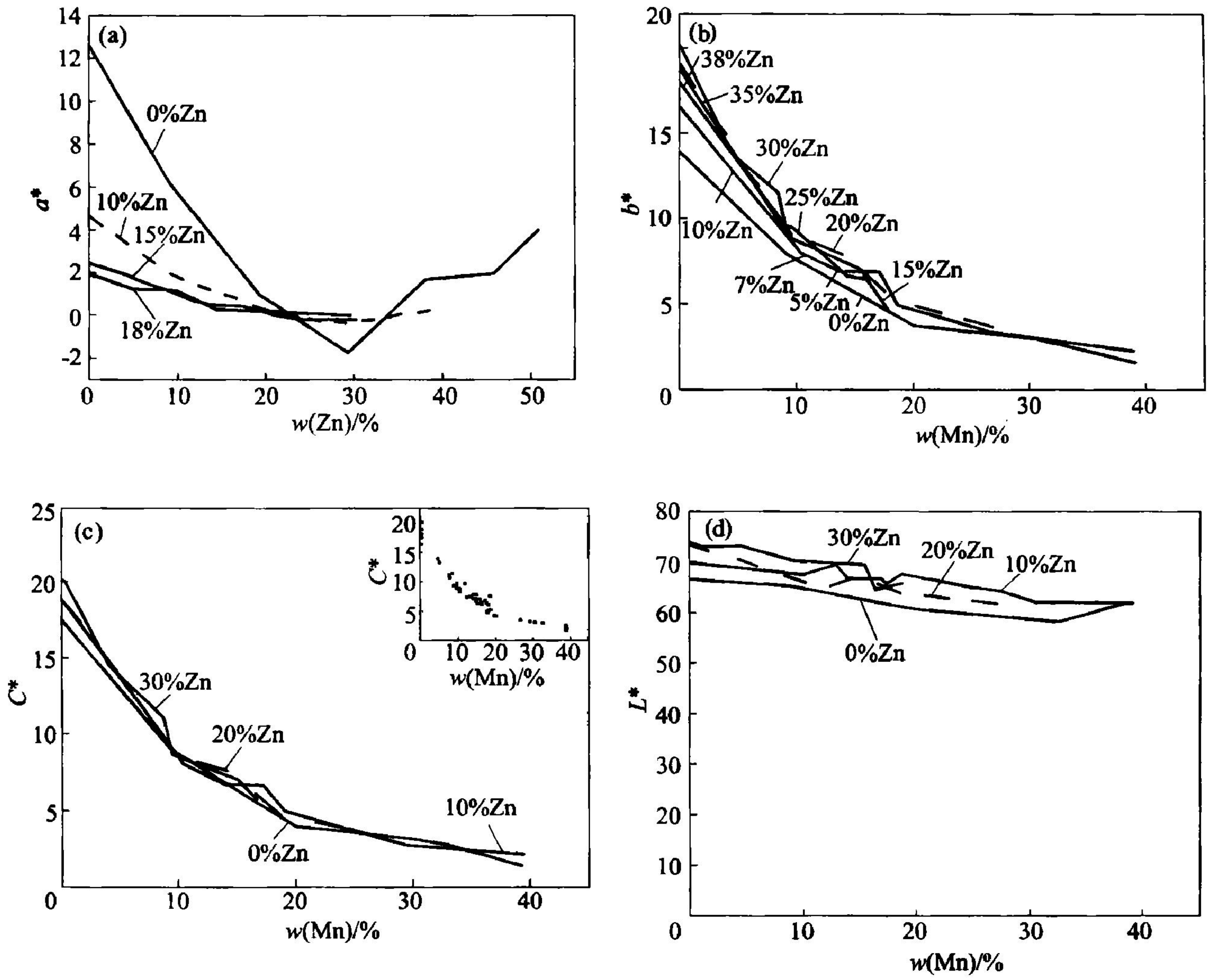

Fig. 3 Relationship between color parameters and composition of Cu-Mn-Zn alloys
(a) —a^* —w(Zn); (b) —b^* —w(Mn); (c) —C^* —w(Mn); (d) —L^* —w(Mn)

than other color parameters. Therefore, the CODs of fit curves for L^* values by the following regression analysis are less than those for a^*, b^* and C^*. However, it can be clearly seen from Fig. 3(d) that L^* values of alloys are decreased with the increase of Mn content. L^* values measured for these samples range from 61 to 74.

In order to quantitatively describe the relationship between color parameters(L^*, a^*, b^* and C^*) and Mn content, experimental alloys are classified into Cu-Mn, Cu-5%Zn-Mn, Cu-10%Zn-Mn, Cu-20%Zn-Mn, Cu-30%Zn-Mn, Cu-35%Zn-Mn, and Cu-38%Zn-Mn alloys by the Zn content. Regression analysis is made to establish some expression for the colors and the composition. It is found that polynomial fit can match the experimental results well. The equations of the corresponding fit curves are gained as follows.

For Cu-10%Zn-Mn alloys:

$$L^* = 69.857\,09 - 0.079\,24\,w(\mathrm{Mn}) - 0.009\,91\,[w(\mathrm{Mn})]^2 + 1.729\,29\times 10^{-4}\times [w(\mathrm{Mn})]^3 \quad (1)$$

R-square= 0.978 56

$$a^* = 6.409\,65 - 0.722\,85\,w(\mathrm{Mn}) + 0.033\,25[w(\mathrm{Mn})]^2 - 6.673\,19\times 10^{-4}\times [w(\mathrm{Mn})]^3 + 4.914\,26\times 10^{-6}[w(\mathrm{Mn})]^4 \quad (2)$$

R-square= 0.993 98

$$b^* = 16.449\,92 - 0.991\,95\,w(\mathrm{Mn}) + 0.026\,48[w(\mathrm{Mn})]^2 - 2.674\,72\times 10^{-4}\times [w(\mathrm{Mn})]^3 \quad (3)$$

R-square= 0.989 08

$$C^* = 17.634\,29 - 1.134\,74\,w(\mathrm{Mn}) + 0.032\,09[w(\mathrm{Mn})]^2 - 3.361\,23\times 10^{-4}\times [w(\mathrm{Mn})]^3 \quad (4)$$

R-square= 0.990 35

For Cu-20%Zn-Mn alloys:

$$L^* = 73.554\,11 - 0.692\,21\,w(\mathrm{Mn}) + 0.010\,03[w(\mathrm{Mn})]^2 \quad (5)$$

R-square= 0.928 38

$$a^* = 0.995\,89 - 0.115\,22\,w(\mathrm{Mn}) + 0.005\,78[w(\mathrm{Mn})]^2 - 9.507\,54\times 10^{-5}\times [w(\mathrm{Mn})]^3 \quad (6)$$

R-square= 0.985 97

$$b^* = 19.065\,08 - 1.532\,58\,w(\mathrm{Mn}) + 0.060\,83[w(\mathrm{Mn})]^2 - 9.276\,55\times 10^{-4}\times [w(\mathrm{Mn})]^3 \quad (7)$$

R-square= 0.990 19

$$C^* = 19.094\,79 - 1.534\,36\,w(\mathrm{Mn}) + 0.060\,81[w(\mathrm{Mn})]^2 - 9.257\,46\times10^{-4}\times[w(\mathrm{Mn})]^3 \quad (8)$$

R-square= 0.990 15

$b^* \approx C^*$

For Cu-30%Zn-Mn alloys:

$$L^* = 73.541\,9 - 0.389\,44\,w(\mathrm{Mn}) + 0.072\,27[w(\mathrm{Mn})]^2 - 0.004\,61[w(\mathrm{Mn})]^3 \quad (9)$$

R-square= 0.860 52

$$a^* = -1.699\,93 + 0.375\,25\,w(\mathrm{Mn}) - 0.034\,1[w(\mathrm{Mn})]^2 + 0.001\,07[w(\mathrm{Mn})]^3 \quad (10)$$

R-square= 1

$$b^* = 20.345\,62 - 1.672\,57\,w(\mathrm{Mn}) + 0.051\,76[w(\mathrm{Mn})]^2 - 6.472\,25\times10^{-5}\times[w(\mathrm{Mn})]^3 \quad (11)$$

R-square= 0.996 77

$$C^* = 20.415\,21 - 1.694\,74\,w(\mathrm{Mn}) + 0.054\,2[w(\mathrm{Mn})]^2 - 1.475\,86\times10^{-4}\times[w(\mathrm{Mn})]^3 \quad (12)$$

R-square= 0.996 86

$b^* \approx C^*$

As mentioned above, C^* values of Cu-Mn-Zn alloys are only determined by Mn content. Therefore, it can be estimated by one of Eqns. (4), (8) and (12) above. It can also be calculated by the Eqn. (13), which is based on all of C^* data in Fig. 3(c). The expression is as follows:

$$C^* = 18.830\,96 - 1.304\,04\,w(\mathrm{Mn}) + 0.039\,99[w(\mathrm{Mn})]^2 - 4.533\,53\times10^{-4}\times[w(\mathrm{Mn})]^3 \quad (13)$$

R-square= 0.979 93

It is found that the error between measured values and calculated values for C^* is about ±0.4, much less than the measured error (±0.85) by the spectrophotometer used in this study. Thus, such equations can be used to calculate the saturation of Cu-Mn-Zn alloys.

According to these equation, when the composition of the Cu-Mn-Zn ternary alloy is determined, the color parameters L^*, a^*, b^* and C^*, i. e., the color of the alloys will be obtained. On the contrary, if certain surface color is to be matched or if a color or a set of color parameters L^*, a^*, b^* is specified, one can also estimate the possible alloy composition for this ternary system. The present indication of affairs points to the possibility of controlling the color of Cu-Mn-Zn alloys quantitatively by the mathematical equations.

5 CONCLUSIONS

1) When the Zn content is less than 20% (mass fraction), color parameters such as L^*, a^*, b^* and C^* of Cu-Mn-Zn ternary alloys are reduced with the increase of Mn content. Less than 10% Mn (mass fraction) puts a greater influence on the alloy color.

2) C^* values of ternary Cu-Mn-Zn alloys mainly depend on the Mn content. Mn turns the color of Cu-Mn-Zn alloys from chromatic color to achromatic one.

3) The color of Cu-Mn-Zn alloy system changes continuously with Mn content. The relationship between color parameters of Cu-Mn-Zn alloys and their composition can be calculated by mathematical equations, Therefore, the color of ternary Cu-Mn-Zn alloys can be calculated and estimated quantitatively.

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