A Study on the Origin of Surface Reddening of 65/35 Brass during the Strip Production Process

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The surfaces of 65/35 brasses with normal and reddish color have been studied by XPS, EPMA and X-ray diffraction. Both brasses are covered by very thin surface films (2–3 nm thick) and reveal normal zinc contents at a depth of more than 10 μm . However, the surface region of less than 1 μm is fairly dezincified. The dezincification is most serious in the surface within a depth of 10 nm under the surface film, particularly in the reddened sample. The skin depth of light with a wavelength of 1 μm is about 4 nm for pure metallic copper and the thickness of the surface film is too small to cause the coloration. It was concluded, therefore, that the cause of the reddening is due to the enrichment of copper at the underlying alloy surface by the dezincification.

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I. Introduction

A brass with 35% Zn is known to have good rolling and drawing properties and is suitable for deep drawing such as radiator tube, fin, electric wiring and so on. A common name, yellow brass, of the 65/35 brass comes from its yellow color. However, this brass sometimes becomes reddish after the strip production process. The production process involves several cycles of rolling, annealing, and acid pickling. The surface is apt to be reddish when (1) a continuous annealing rather than an annealing in coil is adopted for the intermediate annealing process, (2) the reduction at the final rolling is less than *ca.* 50%, and (3) the grain size at the final annealing is less than 15 μm . Surface reddening is almost invariably observed when all of the above conditions are fulfilled. Some reasons can be assumed for the reddening phenomenon. One of the most probable reasons is the formation of a red-colored surface film, for example, Cu_2O . The other is the enrichment of copper by dezincification at the top of the alloy surface under the oxide film.

The purpose of this paper is to clarify the origin of the reddening by use of various techniques for surface analysis.

II. Experimental

Two kinds of samples were cut out from the final strip products, which were 0.25 mm thick. The chemical composition of both samples was nominally Cu–35 wt% Zn–0.03 wt% Pb–0.05 wt% Fe. One of the samples was apparently yellow and the other was reddish. The latter sample, (B), was produced through a continuous annealing process of unfastened strip in an electric furnace at 1020 K for *ca.* 60 s as the intermediate annealing, while the former sample, (A), was intermediately annealed in coil at *ca.* 850 K for *ca.* 29 ks. Both processes were followed by the same finishing, that is, acid pickling, finishing rolling (45% reduction), continuous annealing in unfastened strip at 1020 K for 20–30 s and again acid pickling. The acid pickling was made in 10% H_2SO_4 for 4–7 s at 313–333 K. Tolyltriasol was used as an inhibitor. The specimens were finally degreased in trichloroethylene.

Both samples were examined by means of X-ray photoelectron spectroscopy (XPS) with Mg $K\alpha$ radiation, electron probe micro-analysis (EPMA or XMA) with an electron accelerating voltage of 25 kV, and X-ray diffraction (XD). XPS measurement was carried out with an AEI-KEC-ES 200 electron spectrometer in a vacuum of *ca.* 4×10^{-7} Pa. The quantitative determination of the compositions of the surface film and the underlying alloy surface

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and the thickness of the surface film was performed with a similar method to that reported elsewhere⁽¹⁾, though the spectra of Cu and Zn used for this purpose were not the photoelectron spectra but the X-ray induced Auger electron spectra. For the quantitative analysis, the peak height intensities of the Cu $L_3M_{4,5}M_{4,5}$ and the Zn $L_3M_{4,5}M_{4,5}$ Auger lines were used. The sensitivity factors of the Auger electrons against the O 1s photoelectrons, corresponding to the photo-ionization cross-section ratio, for the Cu and Zn $L_3M_{4,5}M_{4,5}$ lines were determined from the data on Cu₂O and ZnO after Castle and Epler⁽²⁾ considering the spectrometer factor. Because of the difference in the spectral width of Auger lines between the oxidized and metallic states, the sensitivity factors of the metallic state were taken to be 1.2 times as large as those corresponding to the oxidized state. The spectra of Cu₂O by Larson⁽³⁾, ZnO by Schön⁽⁴⁾ and metallic Zn by Castle and Epler⁽²⁾ were used

for the standard $L_3M_{4,5}M_{4,5}$ Auger spectral shape which was necessary for the separation of the observed spectra into the oxidic and metallic components. The metallic spectrum of Cu was obtained by heating an emery polished copper sheet to 650 K in a high vacuum of the spectrometer. The calibration of electron energy detected was made against the Au $4f_{7/2}$ and $4f_{5/2}$, the Cu $2p_{3/2}$ and Cu $L_3M_{4,5}M_{4,5}$ peaks from pure gold and copper⁽⁵⁾⁽⁶⁾. EPMA was done with a JEOL U-3 type analyser with a take-off angle of $\pi/6$ rad. The $K\alpha$ lines of Cu and Zn were detected by a LiF crystal at an acceleration voltage of 25 kV. The absorption current was fixed to 2×10^{-8} A. During the EPMA measurement, the samples were mechanically scanned with $20 \mu\text{m}/60 \text{ s}$ in order to suppress the contamination with carbon deposits as low as possible. The diffractometer was used for the X-ray diffraction measurement with Cu $K\alpha_{1,2}$ radiation. For comparison, measurements with XPS and EPMA were also made on pure Cu, pure Zn and 65/35 brass polished in cyclohexane with SiC abrasive paper.

III. Results

1. XPS measurement

The photoelectron spectra from samples (A) and (B) showed the existence of S, Cl and C in addition to Cu, Zn and O. No detectable enrichment of Pb and Fe was observed.

As shown in Fig. 1, the Cu $2p_{3/2}$ electron spectrum gives a single peak. The Zn $2p_{3/2}$, Cu $3d$ and Zn $3d$ electron spectra were also measured and revealed single peaks. This fact results from very small chemical shifts between spectra of Zn⁰ in metallic zinc and Zn²⁺ in zinc oxide⁽⁴⁾ and between spectra of Cu⁰ and Cu²⁺, though the Cu $2p$ electron spectrum of Cu²⁺ in cupric oxide show a well-defined shift and characteristic large satellites⁽²⁾.

In contrast to the direct photoelectron spectra, the photo-excited Auger spectra corresponding to the $L_3M_{4,5}M_{4,5}$ transition exhibits distinguishable peaks as shown in Figs. 2 and 3; ones from the surface oxide and the other from the underlying metallic sub-

Fig. 1 The Cu $2p_{3/2}$ photoelectron spectra. (A); normal 65/35 brass, (B); reddish 65/35 brass, (E); 65/35 brass immediately after being scraped away about $20 \mu\text{m}$ of its surface with SiC abrasive paper in cyclohexane, and Cu; pure copper heated to 660 K in a vacuum of the spectrometer.

Fig. 2 The $\text{Cu } L_3M_{4.5}M_{4.5}$ Auger electron spectra. Curves (A), (B), (E) and Cu correspond to those in Fig. 1, respectively.

strate. The $\text{Zn } L_3M_{4.5}M_{4.5}$ Auger spectrum in the oxidized state seems to have two different states. The peak position of ZnO after Schön⁽⁴⁾ is indicated by an arrow in the Figure. The lower kinetic energy peak coincides with the ZnO peak. The other would arise from Zn(OH)_2 or some other oxide. The O 1s spectra of samples consisted of two peaks; one appeared at *ca.* 530 eV and the other, at *ca.* 532 eV. The former is inferred to the oxygen in metal-O-metal bond and the latter, in metal-OH and metal-OH₂ bonds by analogy with the iron-chromium-oxygen system⁽¹⁾⁽⁶⁾.

The S 2p photoelectron spectra were also composed of two peaks with binding energies of 168.4 and 162.7 eV. Bird and Galvin⁽⁷⁾ reported the binding energies of the S 2p electrons in pure sulfur, iron sulfide and iron (II) sulfate to be 164.3, 162.8 and 168.9 eV, respectively, where the binding energy of the C 1s electrons from contaminant hydrocarbon,

Fig. 3 The $\text{Zn } L_3M_{4.5}M_{4.5}$ Auger electron spectra. Curves (A), (B), and (E) correspond to those in Fig. 1, respectively.

285.0 eV, was taken as the energy standard. Larson⁽³⁾, though the energy calibration method was not described, gave the binding energy of the S 2p electrons in Cu_2S as 161.7 eV. The present authors have observed the S 2p spectra on a series of Fe-Cr alloys treated in sulfuric acid and on NiS having peaks at 169.3 and 162.6 eV, respectively⁽⁸⁾. The relationship between the apparent valency of S and the corresponding binding energy of electrons is given in Fig. 4. It can be said that the peak at 162.7 eV falls exactly on S^{2-} state; the other peak at 168.4 eV corresponds to the intermediate state between SO_4^{2-} and SO_3^{2-} . The spectral intensity ratio of the latter peak to the total S 2p intensity were 0.7 and 0.6 for samples (A) and (B), respectively.

The Cl 2p spectrum peak appeared at 198.8 eV which coincided with that from potassium chloride, at 198.6 eV⁽⁹⁾, and hence it was assigned to Cl^- . The C 1s spectrum at *ca.* 285.0 eV was all ascribed to the contaminant

Fig. 4 The relationship between apparent valency of S and binding energy of the S 2p electrons. *obs.*—in the figure indicates the observed peak positions on the S 2p spectra of brass samples.

hydrocarbon from diffusion pump oil.

The quantitative determination of the film thickness and composition of the surface oxide film and the composition of the underlying alloy were carried out assuming that Cu, Zn, O, S, H and Cl were homogeneously distributed through the oxide film which had a uniform thickness and was covered with a uniform contaminant layer. The homogeneous distribution was also assumed for Cu and Zn in the underlying alloy within the analysing depth.

The results of XPS are summarized in Table 1. The Zn content of both samples, (A) and (B), is significantly lowered in the surface film and the underlying alloy compared with their nominal composition. The dezincification is more remarkable in sample (B). One of the

most interesting characteristics is the fact that the weight ratio of Zn to the sum of Zn and Cu in surface film is 1.7 times as high as that in the underlying alloy for both samples. It is noticeable that the surface film on emery-polished brass consists mainly of Zn^{2+} as cationic species but the dezincification in the underlying alloy is not remarkable in comparison with samples (A) and (B).

2. Results of X-ray diffraction and EPMA

The lattice spacings obtained from the diffraction angles of (111), (200), (220), (311), (222), (400), (331) and (420) reflections were plotted against $(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$. The most probable values of the lattice spacing were determined by the least-squares method and were 0.36926 nm for sample (A) and 0.36919 nm for sample (B). The zinc contents for samples (A) and (B) were estimated from the lattice spacing measured, using the relationship between the composition and lattice constant which has been reported by Beck and Smith⁽¹⁰⁾. Compositions of samples (A) and (B) were determined to be 34.7 wt% and 34.4 wt% Zn, respectively. No oxide was detected on the diffraction charts.

Corrections for the EPMA measurements were performed with respect to the dead time of the proportional counter, efficiency of backscattering electrons, mass number effect, absorption and fluorescence. The zinc content of samples (A) and (B) were 30.5 and 28.9 wt%, respectively. A sample, with the top layer mechanically polished away by *ca.* 20 μm , was 34.64 wt% Zn. This Zn content probably corresponds to the bulk alloy composition.

Table 1 The results of quantitative XPS analyses of 65/35 brass. Colors of (A) and (B) are normal and reddish, respectively. Sample (E) is scraped away about 20 μm of its surface by abrasive SiC paper in cyclohexane immediately before the XPS measurement.

Sample	Film thickness (nm)	Composition							
		Surface film						Alloy	
		Cu	Zn	O (wt. %)	H	S	Cl	$\frac{[\text{Zn}] \times 100}{[\text{Zn} + \text{Cu}]}$	$\frac{[\text{Zn}]}{(\text{wt. \%})}$
(A)	2.7	55.4	17.4	21.2	0.8	2.7	2.6	23.9	14.1
(B)	2.0	66.0	9.6	17.9	0.6	1.3	4.6	12.8	7.4
(E)	0.7	6.7	61.8	30.5	1.0	—	—	90.3	24.7

IV. Discussion

The XPS results show that copper is contained as cuprous ion in the surface film on both samples (A) and (B). Chlorine and sulfur are contaminant elements. The former is possibly attached through degreasing by trichloroethylene. The latter may arise from sulfuric acid for acid pickling and the contaminated atmosphere containing SO_2 around the factory.

According to XPS analysis, for both the reddish and normal-colored samples, the weight ratio of Zn to the total cation, $(\text{Zn} + \text{Cu})$, in the surface film is *ca.* 1.7 times the weight fraction of Zn in the underlying alloy regardless of the degree of dezincification. This fact suggests that the cationic fraction of surface film is mainly determined by the surface composition of the underlying alloy prepared by acid pickling. On the other hand, the surface oxide is 3 nm thick at most as shown in Table 1. It is, therefore, natural that the XD method could not detect the existence of the surface oxide even if it is crystalline. Usually, this kind of thin surface film formed on brass is protective to further atmospheric corrosion and prevents film thickening, due mainly to its electrically insulating property⁽¹¹⁾. Such a thin insulator should be transparent to the most of electromagnetic waves including the visible light. Accordingly, the surface film which exists on both samples cannot be a cause of the difference in apparent color.

The dezincification was clearly observed in XPS results. It is, however, not significant in EPMA results and even not detected by XD. In XPS, the escape depth of photoelectrons is about a few nm when photoelectrons are excited by the Al or Mg $K\alpha$ radiation. Therefore, the analysing depth of the XPS is not more than a few tens of nm. On the other hand, the linear absorption coefficient of the Cu $K\alpha$ radiation in brass is about 45 mm^{-1} . In EPMA, the analysing depth is usually considered to be of the order of $1 \mu\text{m}$. The difference in composition among different analysing method with different analysing depth tells the existence of a large composition gradient in the

alloy surface of the brass product.

The analysing depth, L , is defined as follows: when the fraction G_L of the total signal intensity is detectable from the thickness range L of a homogenous substance of semi-infinite thickness, the thickness L is the analysing depth. In this report, G_L is taken as 0.78 for convenience, that is,

$$G_L = \int_0^L dI / \int_0^\infty dI = 0.78, \quad (1)$$

where I is the signal intensity. For XPS, the analysing depth is

$$L(\text{XPS}) = -\lambda \sin \theta \cdot \ln(1 - G_L), \quad (2)$$

where λ is the mean value of escape depth of the Cu and Zn $L_{3M_{4,5}}M_{4,5}$ Auger electrons, and θ is the take-off angle of photoelectrons. In the case of the diffractometer, $L(\text{XD})$ is expressed as follows using μ (the linear absorption coefficient of diffracting X-ray in brass), λ_x (the wavelength of the X-ray) and d_{hkl} [the lattice spacing with $(h k l)$]:

$$L(\text{XD}) = -(\lambda_x / 4d_{hkl}\mu) \cdot \ln(1 - G_L). \quad (3)$$

The analysing depth for EPMA cannot be expressed in a simple formula since it contains the ionization distribution function. Accordingly, $L(\text{EPMA})$ was obtained graphically under the condition of eq. (4):

$$\int_0^{\rho L(\text{EPMA})} \phi(\rho l) e^{-\chi \rho l} d(\rho l) / \int_0^\infty \phi(\rho l) e^{-\chi \rho l} d(\rho l) = 0.78, \quad (4)$$

where ϕ is the ionization distribution function, ρ is the density of the sample, l is the distance measured from the top of the sample surface, $\chi = (\mu/\rho)/\sin \theta_x$, μ is the linear absorption coefficient of the analysing X-rays, and θ_x is the take-off angle of X-ray. The analysing depths thus estimated are $1.6 \times 10^{-3} \mu\text{m}$ for XPS, $15 \mu\text{m}$ for XD and $0.57 \mu\text{m}$ for EPMA in this report.

The composition is plotted versus the analysing depth in Fig. 5. Figure 5, corresponding to an in-depth profile, shows explicitly the distribution of the dezincified region.

Metals and alloys are non-transparent to electromagnetic waves because of the existence

of high density of conduction electrons. It can, therefore, be said that the composition of the top-most thin layer about several nm thick controls the color of the metallic substance. For example, let's estimate an attenuation depth of light with wave length of $1\text{ }\mu\text{m}$, which belongs rather to infrared ray, in pure copper at 300 K. An amplitude E , at depth z in metal, of the electromagnetic wave incident to metal is expressed as follows⁽¹²⁾:

$$E \propto \exp(-z/\delta_0) \cdot \exp(iz/\delta_0), \quad (5)$$

where $\delta_0 = c/\sqrt{2\pi\sigma\omega}$, c : the light velocity, σ : the electrical conductivity, and ω : the angular frequency of incident wave. Taking $\sigma = 5 \times 10^{17}\text{ s}^{-1}$ (the d.c. conductivity of copper at 300 K), $\delta_0 = 4\text{ nm}$ for a light with a wavelength of $1\text{ }\mu\text{m}$. This means, from eq. (5), that the amplitude of the incident wave attenuates to e^{-1} at depth δ_0 compared with that out of metal. When the anomalous skin effect is taken into account, the attenuation depth corresponding to δ_0 is *ca.* 8 nm. δ_0 for visible light should be smaller because it is inversely proportional to $\sqrt{\omega}$. This fact suggests that brass may change its color even the dezincification is not serious except within the depth less than only 10 nm. The results shown in Fig. 5 actually shows that the dezincification of sample (B) is severer than that of sample (A) and the zinc content in (B) is nearly half of that in (A) in the surface region less deeper than δ_0 . It is conceivable that, when the surface of reddish brass

similar to (B) is scraped away *ca.* $1\text{ }\mu\text{m}$, it turns to normal yellow brass. The conditions which leads brass to be reddish can also be explained by the observed fact: the continuous annealing process in open atmosphere for relatively short time would give less chance, compared with the annealing process in coil for a long time, for zinc to diffuse from bulk alloy to the surface compensating the dezincified region; the rolling process would reduce the thickness of the dezincified region and particularly the softened dezincified region would preferably reduced. The lower the reduction by rolling, the more remarkable becomes the tendency to reddening; and the small grain size would facilitate the diffusion of zinc to the surface through the grain boundaries.

V. Conclusion

The 65/35 brass strips produced by a combination of rolling, annealing and acid pickling with inhibitor are covered with *ca.* 2–3 nm thick surface film, which contains Cu^+ and Zn^{2+} as cations. The ratio of $[\text{Cu}^+]/[\text{Zn}^{2+}]$ in the surface film is dependent on the composition of the alloy surface just beneath the surface film since it is formed by air-exposure of the bare alloy surface prepared by acid pickling.

The thickness of the surface film is so small that the existence of the surface film itself cannot be the origin of the reddening of brass.

The dezincification is observed on both normal and reddened brasses in surface region less than $1\text{ }\mu\text{m}$ deep, irrespective of their color. The zinc content in reddish brass is less than 10 wt% and is about a half of that in normal brass in the depth range of less than $10^{-2}\text{ }\mu\text{m}$, which is the same order of magnitude as the maximum depth for the attenuation of visible light. Thus, the severe dezincification, to less than 10 wt% Zn, of the surface region of less than $1\text{ }\mu\text{m}$ deep, is the main cause of brass reddening during the strip production process.

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Fig. 5 The relationship between zinc content and analysing depth. (A); normally yellow sample, and (B); reddened sample.

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