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Phase equilibria of the Co-Cu-Zn system at 600 °C and 450 °C

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ABSTRACT

The 600 °C and 450 °C isothermal sections of the Co-Cu-Zn ternary system have been investigated experimentally by means of scanning electron microscopy coupled with energy dispersive x-ray spectroscopy, and x-ray diffraction. Five three-phase regions were confirmed in the 600 °C isothermal section and six three-phase regions existed in the system at 450 °C. The γ-Co_5Zn_{21} and Γ-Cu_5Zn_8 phases formed a continuous solid solution, which is designated as the γ/Γ phase. No ternary compound was found in the present work. The solubility of Co in δ and β is up to 1.8 and 8.8 at% respectively, and the maximum solubility of Cu in γ_1 and β_1 is 14.7 and 7.9 at% respectively at 600 °C. The maximum solubility of Co in ε and β' is 8.5 and 6.7 at% respectively, and the solubility of Cu in γ_2, γ_1 and β_1 is up to 12.9, 14.4 and 11.2 at% respectively at 450 °C.

1. Introduction

Hot-dip galvanized products are widely used in the world because of their good corrosion resistance and appearance [1]. However, Si existing in steels leads to results in Sandelin effect [2], which is a worldwide problem in the hot-dip galvanized industry [3]. The common method to solve the problem is adding alloying elements into the zinc bath [3–8]. Li et al. [9] found that the addition of Co into the molten zinc bath could reduce the thickness of the ζ phase in coatings and improve the corrosion resistance. Katiforis et al. [10] discovered that the addition of Cu into the molten zinc bath could suppress Fe/Zn reaction and improve the atmospheric corrosion resistance of the clad layer. In order to investigate the controlling mechanism of Co or Cu alone in bath on the Fe/Zn interface reaction during hot-dip Si-containing steel, the phase equilibria of the relevant systems have been studied, such as Co-Si-Zn [11], Zn-Fe-Co-Si [12], and Zn-Fe-Cu [13]. In order to achieve a good understanding of the synergistic effect of Cu and Co on Fe/Zn interface reaction during hot-dip galvanizing, it is necessary to determine the phase relations of the Co-Cu-Zn ternary subsystem in the Zn-Fe-Cu-Co-Si system at the galvanizing temperature. The present work is intended to obtain experimentally the isothermal sections of the Co-Cu-Zn ternary system at 600 °C and 450 °C using scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD).

2. Literature data

There are three groups of binary subsystems in the Co-Cu-Zn ternary system, namely, Co-Zn, Cu-Zn and Co-Cu binary systems. Massalski et al. [14] indicated that three intermediate phases exist in the Co-Zn system at 600 °C, namely, β_1-CoZn, γ-Co_5Zn_{21} and γ_1-$CoZn_{7.5}$, and four intermediate compounds, β_1-CoZn, γ-Co_5Zn_{21}, γ_1-$CoZn_{7.5}$ and γ_2-$CoZn_{13}$ at 450 °C. Vassilev and Jiang [15] evaluated the Co-Zn binary system, the results indicated that the varieties of the intermediate phases existing in this binary system are consistent with that presented by Massalski [14]. However, the composition range of β_1 is controversial [14,15]. Recently, Zhao et al. [16] confirmed experimentally that the range of β_1 is 49.1–59.1 at%, which agrees well with the results of Vassilev and Jiang [15].

The Cu-Zn binary system has been collected in Massalski's Handbook of Binary Phase Diagram [14]. Three intermetallic compounds, namely, β-CuZn, δ-$CuZn_3$ and Γ-Cu_5Zn_8, existed at 600 °C. β'-CuZn, ε-$CuZn_4$ and Γ-Cu_5Zn_8 three binary phases were found in Cu-Zn binary system at 450 °C. The Cu-Zn binary system was evaluated repeatedly by researchers [17–19]. All of them suggested that the Cu-Zn binary system contains the compounds as mentioned above, and the temperatures of the β'- β order-disorder transformation range from 454 °C to 468 °C.

Compared with the Cu-Zn and Co-Zn binary subsystems, the Co-Cu binary system is quite simple. Massalski et al. [14] and Palumbo et al. [20] showed that no intermediate compound exists in the Co-Cu binary system.

The incomplete isothermal sections of the Co-Cu-Zn ternary system at 25 and 672 °C were collected by Villars et al. [21], as shown in Fig. 1. The crystallographic data of the binary compounds in the Co-Cu-Zn system are listed in Table 1 [22–30].

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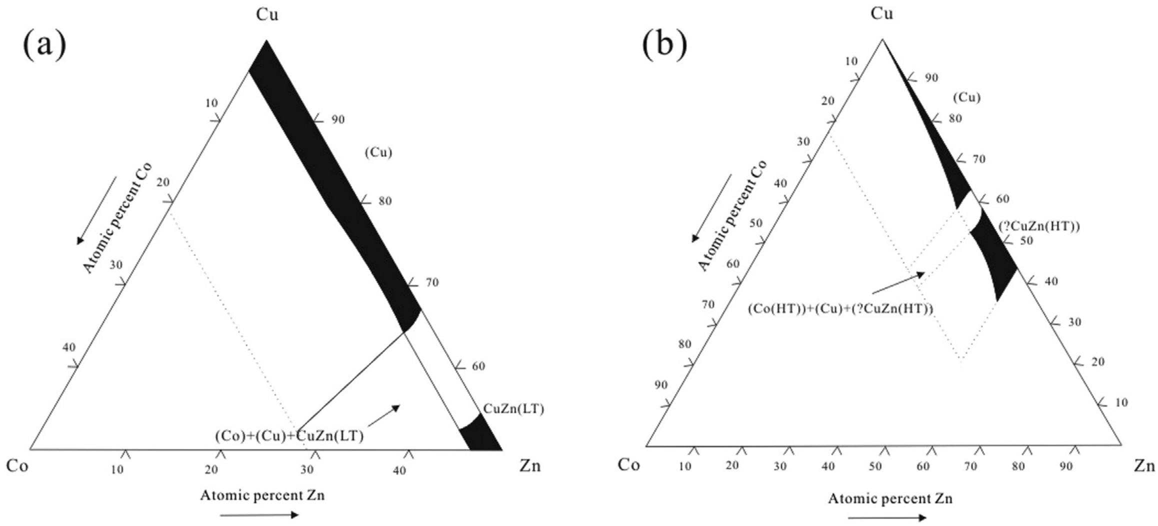

Fig. 1. Incomplete isothermal sections of the Co-Cu-Zn ternary system at 25 and 672 °C collected by Villars et al. [21].

Table 1
Crystallographic data of the binary compounds in the Co-Cu-Zn ternary system.

Compound	Crystal system	Space group	Cell parameters (pm)			Reference
			a	b	c	
Γ-Cu_5Zn_8	Cubic	$I\bar{4}3m(217)$	886.6			[22]
γ-Co_5Zn_{21}	Cubic	$I\bar{4}3m(217)$	895.25			[23]
γ-Co_5Zn_{21}	Cubic	$P\bar{4}3m(215)$	892.70			[24]
β_1-CoZn	Cubic	$P4_132(213)$	634.50			[24]
γ_1 -$CoZn_{7.5}$	Monoclinic	$F2/m(12)$	903.00	433.80, β = 89.90°	1251.10	[25]
γ_2-$CoZn_{13}$	Monoclinic	$C2/m(12)$	1330.60	753.50, β = 126.47°	499.20	[26]
β´-CuZn	Cubic	$Pm\bar{3}m(221)$	295.0			[27]
β-CuZn	Cubic	$Im\bar{3}m(229)$	294.5			[28]
δ-$CuZn_3$	Hexagonal	$P\bar{6}(174)$	427.5		259.0	[29]
ε-$CuZn_4$	Hexagonal	$P6_3mmc(194)$	276.7		428.9	[30]

3. Experimental methods

The phase relationships of the Co-Cu-Zn ternary system at 600 °C and 450 °C are deduced by studying the phase constitutions of the equilibrated alloys. The designed nominal compositions of the alloys are listed in Tables 2 and 3 (Column 2). Every sample was prepared using Zn block (1 × 1 × 2 mm), Co powder, and Cu particle, 4 g in total. The purity of all the starting materials is 99.99%. Each mass was weighed to an accuracy of 0.0001 g. The raw materials were mixed and sealed in an evacuated quartz tube. All alloys were heated to 1100 °C, and kept for 15 h in the high temperature melting furnace, followed by quenching in water using a bottom-quenching technique to reduce Zn loss and sample porosity [31]. Each quenched sample was resealed in evacuated quartz tube and then annealed at 600 °C for 25 days and 450 °C for 40 days. At the end of the treatment, all alloys were quenched rapidly into water to preserve the equilibrium state at the annealing temperatures.

The samples were polished with conventional metallographic techniques. Different corrosion agents were used to reveal the microstructures of the alloys. When Cu content in alloys was high, the etchant solution was composed of 0.625 g $FeCl_3$, 0.25 ml HCl, and 100 ml H_2O. However, a nital solution was adopted as the Cu content was low. A JSM-6360LV SEM equipped with an OXFORD INCA EDS was utilized to observe the microstructure and measure chemical compositions of various phases in the samples. The phase constitutions were further verified by means of the Rigaku Vltima IV X-ray diffraction at 40 kV and 40 mA with Cu K_α radiation.

4. Results and discussion

More than 40 alloys were prepared for studying the phase equilibria of the Co-Cu-Zn system at 600 °C and 450 °C. All phases existing in the alloys are summarized in Tables 2, 3 (column 3), respectively, together with their chemical compositions determined by SEM-EDS (column 4–6). The listed compositions are the average of five measurements. Zn-rich solid solution phase, marked as “L” in the paper, is in liquid state at 600 °C and 450 °C. Each phase in alloy can be differentiated by the relief, color and chemical compositions obtained by SEM-EDS. The relevant X-ray diffraction was used for the final identification of the phase.

4.1. The X-ray diffraction pattern analyses and cell refinement of the continuous solid solution (γ-Co_5Zn_{21}) / (Γ-Cu_5Zn_8) phase

A continuous solid solution γ/Γ phase was found in the isothermal sections at 600 and 450 °C, which was confirmed by SEM-EDS and XRD. To identify its structure, eight alloys with the single phase were prepared. The X-ray diffraction patterns obtained from alloys A1~A4 along