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LETTER

Experimental Zn-rich corner of the Fe–Zn–Cu ternary phase diagram at 460 °C

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The presence of alloying elements in the galvanizing bath has been shown to affect the properties of the zinc coatings during the galvanizing process [1, 2]. However, only a few studies have examined the use of copper in the process of galvanizing [3].

Two patents reported on an adhesive coating comprising a ternary alloy (55–75 wt% Cu, 15–45 wt% Zn and 0.1–10 wt% Fe) that is useful for coating steel wire. The chemical nature of the alloys elaborated by sequential electroplating and heating of copper, iron and zinc layers avoids a separation between the coating and steel wires during wire drawing [4, 5].

In the present study, the emphasis is placed on the Zn-rich corner of Fe–Zn–Cu ternary system, which, up to date, remains unknown.

Before galvanizing, two low-carbon steel substrates were classically prepared [6]. The first substrate was rolled with copper wire. A copper piece was hammered in the middle of the second one to make a rivet (Fig. 1). As-prepared samples were then batch galvanized at 460 °C for one hour in a zinc bath saturated with iron and added with 2.9 at% Cu.

The two specimens were then either air cooled or water quenched.

The microstructure of the coatings was characterized by scanning electron microscopy (SEM) and analysed by energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) gave an insight on the nature of the different phases. All the chemical compositions were finally reported in the isothermal section at 460 °C of the Fe–Cu–Zn ternary phase diagram.

When a steel substrate is dipped in a pure zinc bath saturated with iron, the coating is constituted by three intermetallic phases Γ (Fe_3Zn_{10}), δ_1 ($FeZn_7$) and ζ ($FeZn_{13}$), and pure η-Zn phase [6, 7]. In presence of copper in zinc bath, some changes of microstructure were observed in the galvanized coatings.

Concerning the water-quenched rivet, a succession of phases in equilibrium were observed between copper, steel

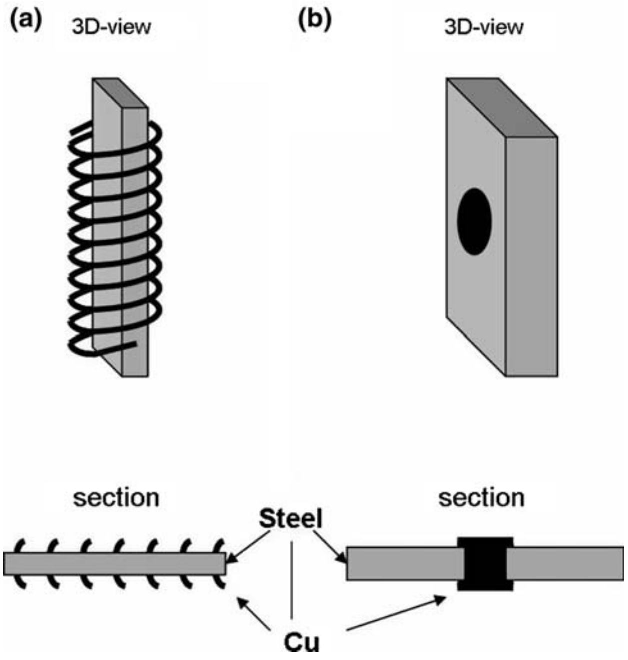

Fig. 1 (**a**) Steel rolled with copper wire, (**b**) rivet of steel with copper in its middle

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and the outer galvanized layer (Fig. 2). Between copper and the galvanized layer, β, γ, ε intermetallic compounds of the Cu-Zn system and solidified liquid (η-Zn) with about 3 at% Cu in equilibrium with dross were successively detected. Between copper and steel, β, γ and Γ compounds were successively observed. Finally, between steel and the outer layer, Γ, δ_1 enriched with Cu, dross and then solidified liquid (η-Zn) with about 3 at% Cu in equilibrium with dross were formed. All the compositions of the latter phases are supplied in Table 1.

In (η-Zn) with about 3 at% Cu, that is in the outer layer of the coating, drosses and dendrites with a flower morphology (Fig. 2) are also observed. Drosses are related to the δ_1 phase enriched with copper (Table 1). The nature of the latter crystals was confirmed by XRD after polishing the batch-galvanized sample (Fig. 3). Dendrites, whose composition is indicated in Table 1, originate from the peritectic transformation ε + liquid → η-Zn at 425 °C in the Zn–Cu binary diagram [8].

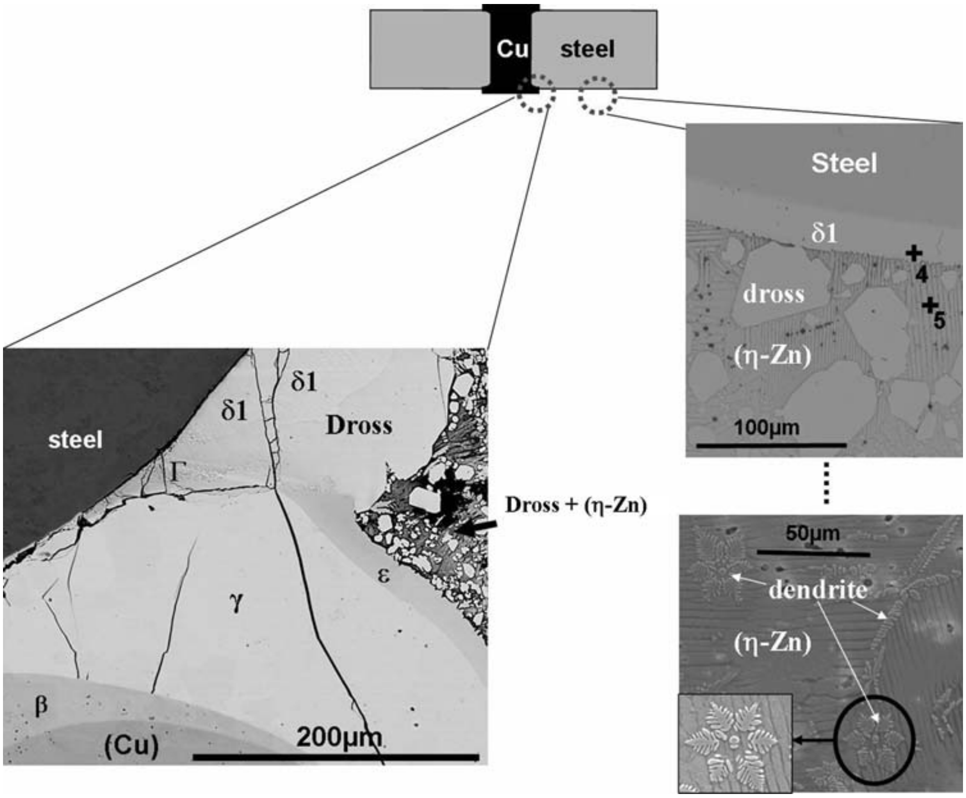
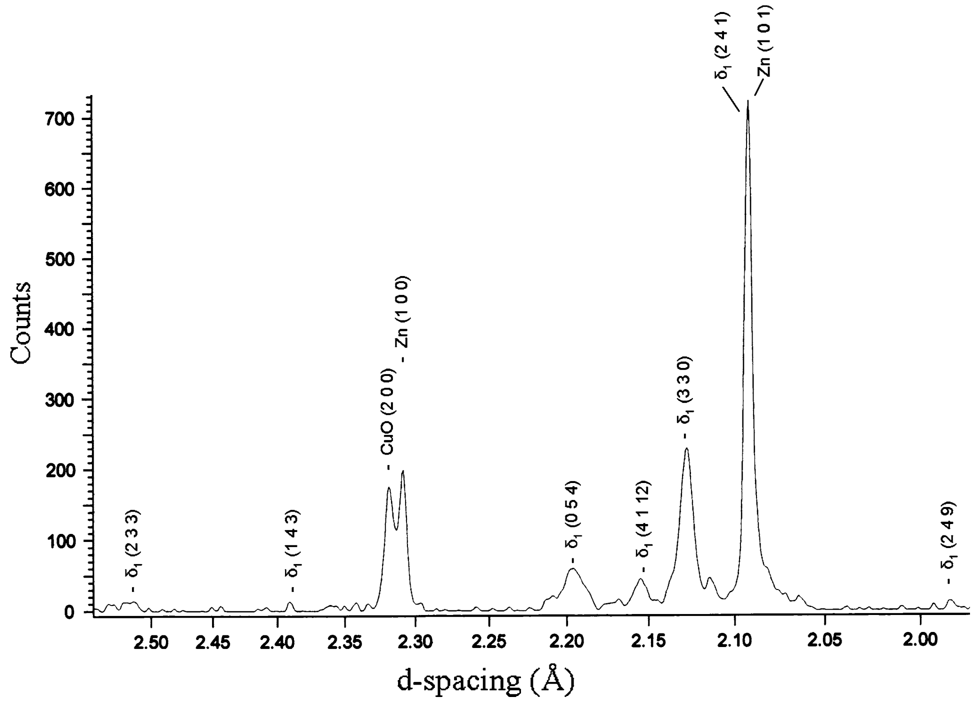


Fig. 2 Various phases obtained in a water-quenched rivet

Table 1 Chemical composition range of various phases

Sample	Phase	At% Fe	At% Zn	At% Cu
Water-quenched batch galvanized rivet	β	–	~46.1	~53.9
	γ	–	$64.3 < Zn < 67.7$	$32.3 < Cu < 35.7$
	ε	–	~81.6	~18.4
	$\Gamma = \Gamma_1 + \Gamma_2$	$5.5 < Fe < 14.2$	$79.7 < Zn < 84.0$	$0.5 < Cu < 14.8$
	δ_1 compact	$5.7 < Fe < 15$	$84.6 < Zn < 88.9$	$0.5 < Cu < 6.5$
	δ_1 dross	$4.7 < Fe < 8.4$	$88.6 < Zn < 90.0$	$5.1 < Cu < 6.5$
	Dendrites	–	$85.0 < Zn < 88.3$	$10.8 < Cu < 14.4$
Batch galvanized steel strip rolled with copper wire	γ	–	$66.1 < Zn < 66.3$	$33.7 < Cu < 33.9$
	ε	–	$81.2 < Zn < 83.2$	$16.8 < Cu < 18.8$
	δ_1 dross	$5.4 < Fe < 5.9$	$88.6 < Zn < 89.4$	$5.2 < Cu < 5.7$
	Dispersed δ_1	$4.9 < Fe < 5.0$	$91.5 < Zn < 91.6$	$2.5 < Cu < 3.5$
	δ_1 compact	~6	~92	~2

Fig. 3 XRD pattern of δ_1 dross and solidified liquid Zn enriched with Cu (batch-galvanized sample, slightly polished)



Moreover, Fig. 2 shows the existence of lines in the more external layer composed of (η-Zn) + dross + dendrites. They may result from stress concentration between larger dross, which are quite hard and brittle intermetallic compounds; they also may be twins induced by plastic deformation and which are often observed in closely packed hexagonal metals [9], among which zinc can be considered. They are very likely to present various orientations according to the crystal orientations of zinc grains in which they appear.

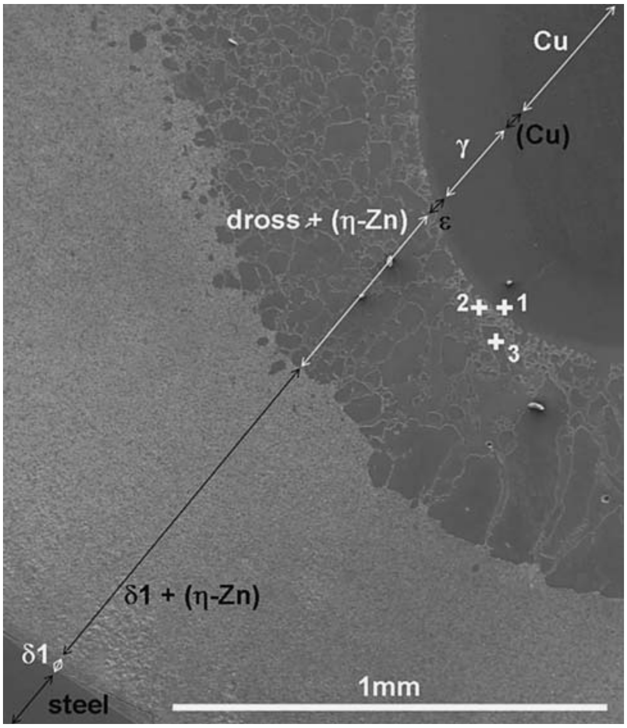


Fig. 4 Batch galvanization of a steel strip rolled with copper wire

In the case of batch-galvanized steel strip rolled with copper wire (Fig. 4), the interface between copper and steel substrate is composed of six layers, namely (Cu) with 1.5–1.7 at% Zn, γ, ε, (η-Zn) with 2.8–3.2 at% Cu and dross, an intimate mixture (η-Zn) + δ_1, and finally δ_1 compact.

Analyses of the different phases formed in galvanized samples at 460 °C pointed out a Zn-rich region of the diagram (Fig. 5). The chemical composition of key points is listed in Table 2. According to Fig. 2, three ternary phase equilibria were identified, namely (ε, liquid, dross that is δ_1 containing dissolved Cu), (δ_1, liquid, ζ) and (γ, Γ, δ_1). Γ represents a mixture of two phases Γ_1 and Γ_2 of similar crystal structures (Γ_2 is a superstructure of Γ_1) [6] and is scarcely seen in galvanized coatings.

The above experiments show that the coating solidification mechanism depends on the copper amount in the galvanizing bath.

In pure zinc bath saturated in iron and without added copper, the ζ phase appears first in the liquid phase. δ_1 and Γ layers then develop due to the diffusion of Fe and Zn from steel substrate and ζ phase, respectively [6].

In agreement with Katiforis et al. [3]'s observations, we did not detect any ζ phase in layers galvanized in Zn baths added with 1–3% Cu. Since the solubility of copper in the

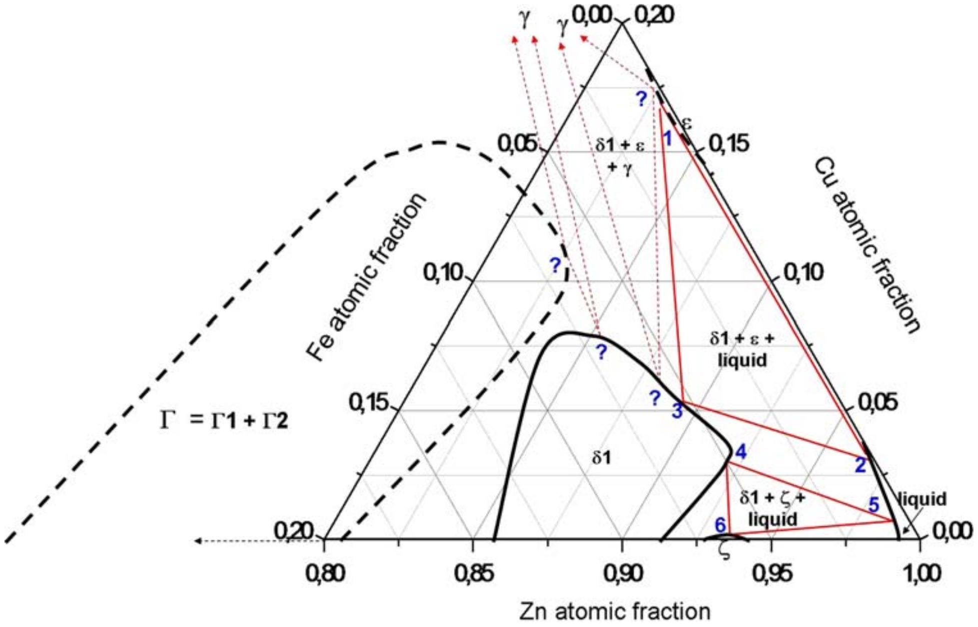


Fig. 5 Experimental Zn-rich corner of the Fe–Cu–Zn phase diagram at 460 °C

Table 2 Chemical compositions of some phases observed in the zinc-rich corner

Point	Phase	At% Fe	At% Zn	At% Cu
1	ε	–	$81.2 < Zn < 83.2$	$16.8 < Cu < 18.8$
2	Liquid	$0.0 < Fe < 0.2$	$96.0 < Zn < 96.4$	$3.2 < Cu < 3.9$
3	δ_1 dross	$5.4 < Fe < 5.9$	$88.6 < Zn < 89.5$	$5.2 < Cu < 5.7$
4	δ_1	$4.9 < Fe < 5.0$	$91.5 < Zn < 91.6$	$2.5 < Cu < 3.5$
5	Liquid	–	~98.7	~1.3
6	ζ (not detected)			<0.5

δ_1 phase is larger than that in the ζ phase (not detected), the content of Cu at the neighbouring surrounding steel substrate may be quite large. As a result, it inhibits the development of a ζ phase and the δ_1 phase is formed rather than Γ phases.

Contrary to another previous work where no copper was detected in Γ phase [3], we observe that the Γ layer, which occasionally may form between the substrate and δ_1, may dissolve up to 14.8 at% Cu.

In Fe–Zn system, the δ_1 phase is a non-stoichiometric compound (from ~85 to 92.5 at% Fe at 460 °C) which appears under two morphologies. The Fe-rich δ_1 has a so-called compact morphology, whereas the Zn-rich δ_1 is termed 'palisade'. In the ternary Fe–Zn–Cu system, the Zn-rich δ_1 which is dispersed in (η-Zn) had still a different morphology. The Cu solubility in the Zn-rich δ_1 (~5.3 at% Cu) is higher than its solubility in the compact form (~3 at% Cu) which is consistent with previous observations [3]. This behaviour appears clearly on the ternary phase diagram (Fig. 4).

Because of the quenching, Cu solubility in η-Zn phase corresponds to the solubility of Cu in liquid.

In conclusion, this study shows for the first time to our knowledge, the description of the zinc-rich corner of the Fe–Cu–Zn system at 460 °C.

The salient feature of this ternary system is the great solubility of Cu in intermetallic Γ and δ_1 phases, compared with its low solubility in the ζ phase. As a consequence, an equilibrium δ_1 liquid is easily reached, which hinders the precipitation of ζ. Moreover, various equilibria between different phases with specific compositions were found. When Cu is added to the zinc bath, the liquid phase enters in equilibrium successively with ζ, δ_1 and ε phases.

After having determined the phases and components present in the Fe–Cu–Zn system, future experiments will be planned to model the galvanizing process and to complete the exact description of the entire diagram, particularly the reaction between Γ(Fe, Zn) and γ(Cu, Zn) which have the same crystal structure, type Cu_5Zn_8.

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