Study of the Zinc-Rich Corner of the Zn-Fe-Cr System at Galvanizing Temperatures

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The Zn-rich corner of the Zn-Fe-Cr system was experimentally determined at temperatures relevant to galvanizing. The liquid phase was found to be in equilibrium with the ternary extensions of the ζ-FeZn$_{13}$ phase and the θ-CrZn$_{17}$ phase. The solid solubility limits of Cr in the ζ phase and of Fe in the θ phase are 3.1 and 4.2 at.%, respectively, at 450 °C. The invariant liquid composition of the liquid-ζ-θ three-phase equilibrium changes noticeably with temperature, shifting from 0.18%Cr and 0.019%Fe at 450 °C to 0.161%Cr and 0.011%Fe at 440 °C. The θ-CrZn$_{17}$ phase is the only intermetallic phase in the binary Zn-Cr system, and the Cr solubility in molten Zn was grossly overestimated by previous investigators. A schematic Cr-Zn phase diagram is proposed.

Introduction

In continuous galvanizing, 316L stainless steel is being used as guiding rolls submerged in molten Zn-Al alloys and as the cladding material for pots holding the molten metal. Although this steel possesses an excellent corrosion resistance in an oxidizing atmosphere at elevated temperatures, its suitability for applications as submerged rolls or pot-cladding materials in continuous galvanizing is being questioned. The rolls, if not coated with materials that are resistant to the corrosion of molten Zn-Al alloys, react readily with the bath metal. As a result, intermetallic compounds build up on the roll surface, and the coating quality is adversely affected. Rolls made of 316L stainless steel are frequently removed from the galvanizing pot for cleaning and refurbishing at a significant cost. The life span of galvanizing pots clad with 316L stainless steel could vary significantly with pot chemistry, suggesting that the corrosion resistance of 316L stainless steel is sensitive to the Al content of the coating alloy. The reaction of 300 series stainless steels with molten Zn-Al alloys has been the subject of many investigations (Ref 1-4). However, due to the lack of a fundamental understanding of the available equilibrium states in the Zn-Fe-Al-Cr system, the interpretations of the test results were frequently inadequate and confusing. Chromium is frequently added to high-strength steels for automotive applications. The interaction of Cr dissolved from the steel substrates with the molten Zn-Al alloy is a concern for galvanizers (Ref 2). The addition of Cr to molten Zn-Al alloys was found to facilitate the galvannealing process (Ref 5). Apparently, Cr is an element that is closely related to the galvanizing industry. To assist galvanizers in their endeavor to improve product quality and production profitability, Teck Cominco Metals Ltd. (Mississauga, ON, Canada) has launched a research program to study the fundamentals of phase equilibria in Zn-Fe-related systems (Ref 6-9). The current study constitutes the first step in the investigation of the Zn-rich corner of the Zn-Fe-Al-Cr quaternary system.

Experimental

Molten Zn-Fe-Cr alloys were prepared in a ceramic crucible that was placed in a resistance furnace. Special high-grade (SHG) Zn was used to prepare the alloy. Fe and Cr were added in the form of master alloys produced in-house using high-purity Fe and Cr metal shots and SHG Zn. The chemical compositions of the alloys were analyzed using atomic absorption spectrophotometry. Bath samples were taken using glass tubes from the middle section of the bath to avoid entrapping intermetallic particles. Samples also were taken from the bottom of the bath to analyze the intermetallic compounds coexisting with the liquid. Sections of the samples were prepared in the conventional way for metallurgical examination. A nital solution was used for revealing the microstructural details. Intermetallic compounds in the samples were analyzed using a scanning electron microscope (SEM) (model JSM-5800, SEM: JEOL, Tokyo, Japan) that was equipped with a Princeton Gamma Tech, NJ (PGT) IMIX x-ray energy-dispersive spectroscope (EDS). The SEM was operated at a voltage of 20 kV; the ZAF method was used for matrix correction, and pure Zn and Fe were used as the standards in the EDS analysis. The composition of the compounds reported here was the average of at least ten measurements. X-ray diffraction of the intermetallic compounds was carried out on a Philips (Amsterdam, the Netherlands) x-ray diffractometer using Cu-K$_\alpha$ radiation.

To maximize the efficiency of the experimental work, an alloy with a given composition was used for measuring Fe solubility at several temperatures ranging from 430 to 470 °C. Bath sampling always took place in the morning after the molten alloy had been held at the temperature overnight.

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After samples were taken for analyzing the liquid composition and the intermetallic compounds coexisting with the liquid, the temperature of the bath was increased to 520 °C and was held at this temperature for 5 to 6 h. During this period of time, the bath was regularly stirred to ensure the full dissolution of the intermetallic particles and to homogenize the bath composition. The bath temperature was then reset at the end of a working day and was maintained at the desired temperature overnight. The desired temperature was obtained through controlling the furnace temperature rather than that of the melt due to the limitation imposed by the available furnace-controlling system. The actual melt temperature was measured at the time when samples were taken, and the deviation of the actual temperature from the set temperature was always within ±2 °C. The variation of the bath temperature overnight and over long weekends was monitored using a computer system. It turned out that the bath temperature was quite stable, remaining within ±2 °C of the set temperature.

Results and Discussions

Chromium Solubility in Molten Zn

In preparing master alloys, the dissolution of Cr shots in molten Zn was found to be extremely sluggish, as reported by Heumann (Ref 10). The designed composition of the master alloy was 1%, which is lower than the reported Cr solubility of 1.2% (1.5 at.%) at 500 °C (Ref 11). After being held at 560 °C for over 1 week, the Cr metal shots in the master alloy were still not totally dissolved, although the alloy had been stirred at regular intervals. The chemical analysis of a bath sample taken from the middle of the bath indicated that the Cr content of the liquid phase was only 0.576%. A metallurgical examination of the bath sample revealed that it was free of intermetallic particles. On the other hand, samples taken from the bottom of the bath were found to contain numerous intermetallic particles and undissolved Cr shots. These observations indicated that the master alloy was oversaturated with Cr, and that the Cr solubility limit in molten Zn was only 0.576% at 560 °C. Consequently, Cr solubility in molten Zn seems to have been grossly overestimated by Heumann (Ref 10) and others (Ref 11). Those investigators prepared Zn-Cr alloys by reducing chromium chloride with molten Zn, and the alloys contained solid Cr particles. Knighton and Dorsey (Ref 12) also have studied Cr solubility in molten Zn, and they reported much lower Cr solubilities. However, their results are still higher than the values obtained in the present investigation. It is worthwhile to mention that in the early 1950s Harding and Raynor (Ref 13) successfully prepared Zn-Cr alloys without free Cr through reducing chromium chloride at temperatures ranging from 750 to 800 °C. The maximum Cr content of the alloys, however, was only 0.54% (0.68 at.%), which is very close to the result obtained in the current study.

Cr particles that survived in the master alloy were fragmentary and porous. The microstructure of one surviving Cr particle is shown in Fig. 1. SEM-EDS analyses indicated that Zn diffused into Cr particles, forming a solid solution
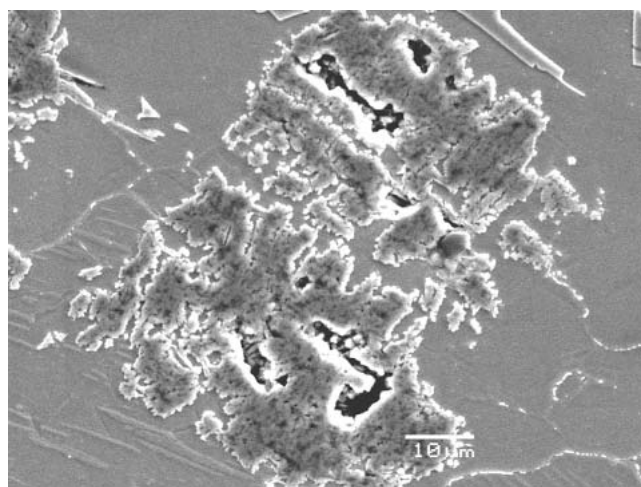

Fig. 1 A surviving Cr shot in the master alloy. SEM-EDS analyses indicated that the Zn solid solubility in Cr exceeded 65 at.% at 560 °C.

Table 1   Cr solubility at various temperatures

Solubility	Temperature °C							
	560	**535**	**510**	**492**	**470**	**464**	**450**	**420**
at.%	0.576	0.543	0.511	0.461	0.424	0.414	0.356	0.143
wt.%	0.723	0.682	0.642	0.579	0.533	0.520	0.447	0.180

phase with Zn content generally decreasing from as high as more than 65 at.% on the outskirt of the particle to about 1 at.% at their center. This finding suggests that the Zn solid solubility limit in Cr was more than 65 at.% at 560 °C. It is worthwhile mentioning that only one type of intermetallic compound, the θ-CrZn$_{17}$ phase, was found in the vicinity of the dissolving Cr particles.

By gradually reducing the temperature of the master alloy, Cr solubility in molten Zn as a function of temperature was determined. The data were recorded in Table 1.

The solubility data (in at.%), plotted in a natural logarithmic scale, can be separated into two groups. Both decrease approximately linearly with the reciprocal of temperature in Kelvin, as shown in Fig. 2. Linear regression analyses indicated that the two lines intersect at approximately 464 °C. The high-temperature part can be described by:

$$\ln[\text{Cr}] = 2.33 - 2.19 \times 10^3/T\,(\text{K}) \qquad R^2 = 0.9861$$

and the low-temperature part can be expressed as:

$$\ln[\text{Cr}] = 12.9 - 9.90 \times 10^3/T\,(\text{K}) \qquad R^2 = 0.9172$$

A similar trend was observed by Heumann (Ref 10) and Chiotti and Parry (Ref 11).

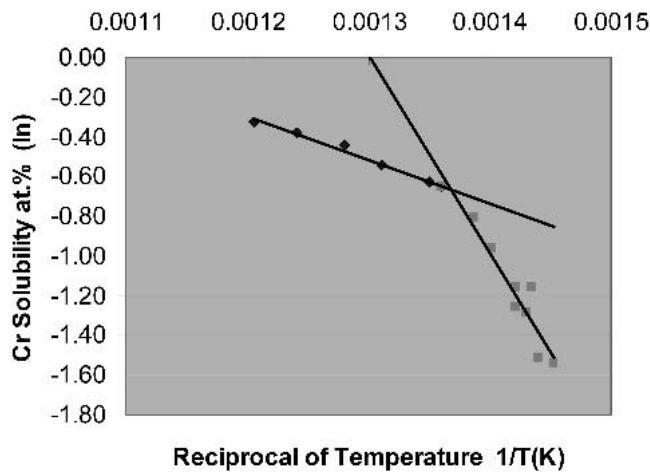Intermetallic particles formed in the master alloy mostly settled to the bottom of the bath. EDS analyses indicated

Fig. 2 Cr solubility in molten Zn can be divided into two groups. The turning point signals the dissolution of the $CrZn_{17}$ phase.

Fig. 3 The x-ray diffraction pattern of the hexagonal $CrZn_{17}$ phase

that the particles contained about 5 at.% Cr. An x-ray diffraction pattern obtained from a melt sample taken from the bottom of the bath is shown in Fig. 3. An analysis of the pattern confirms that the intermetallic compound is the $CrZn_{17}$ phase, which has a hexagonal unit cell with $a = 1.289$, $c = 3.056$ Å. SEM-EDS and x-ray diffraction studies indicated that $CrZn_{17}$ is the only intermetallic compound in the Zn-Cr system. As shown in Fig. 4, one $CrZn_{17}$ particle coexists with the Cr-rich solid solution phase that evolved from a Cr particle. No other intermetallic phase exists between the two phases. This observation substantiates the above conclusion that $CrZn_{17}$ is the only intermetallic phase in the Zn-Cr system. The turning point in Fig. 2 corresponds to the melting point of the $CrZn_{17}$ phase, as reported by Heumann (Ref 10) more than 5 decades ago.

To further confirm the above conclusion, two alloys, both containing 10 wt.% Cr, were prepared. These alloys were kept at 600 °C for over 1 week. Afterward, one sample was furnace-cooled to the ambient temperature, and the other was quenched in water. The microstructures of the alloys were examined, and x-ray diffraction studies were carried out on the samples. Again, only undissolved Cr and $CrZn_{17}$ particles were found. Moser and Heldt (Ref 14) assessed the Zn-Cr system recently and suggested the existence of ζ-$CrZn_{13}$ based on the observation of Hartmann et al. (Ref 15). However, Hartmann et al. (Ref 15) were the only investigators who reported the existence of the ζ-$CrZn_{13}$ phase in the Zn-Cr system. As pointed out by Hansen (Ref 16), the Cr used in their experiment contained 1.5% Fe, and their finding "needs corroboration." It was found in the current study that when the Zn-Cr alloy was contaminated by Fe, $CrZn_{13}$ particles containing iron readily formed in the alloy.

A complete phase diagram for the Cr-Zn system is not available at present. Based on experimental results obtained in this study and on information available in the open literature, a schematic phase diagram for this system is shown in Fig. 5. The dashed lines indicate that the liquidus, solidus, and solvus lines in the diagram are estimates only.
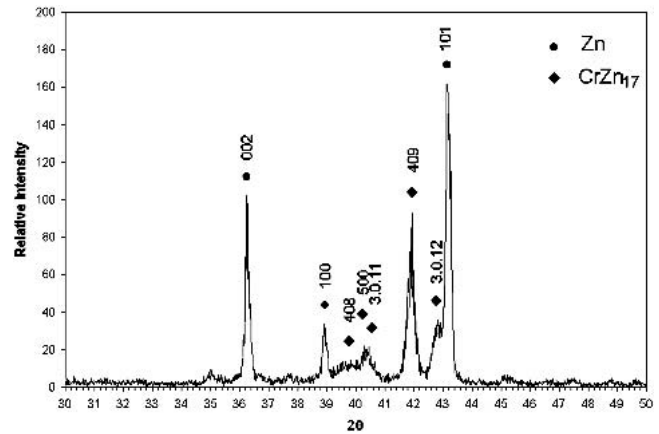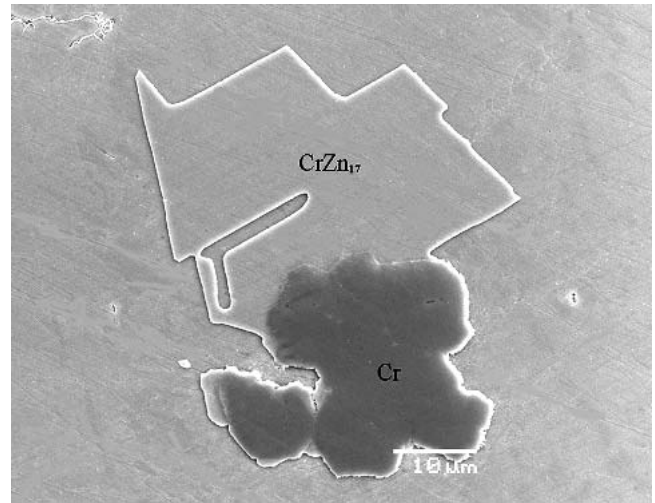

Fig. 4 A $CrZn_{17}$ particle coexists with the Cr-rich solid solution phase. Apparently, $CrZn_{17}$ is the only intermetallic compound in the Cr-Zn system.

Determination of Liquid Phase Boundary in Zn-Fe-Cr Alloy

To determine the liquid phase boundaries for the liquid-ζ-$FeZn_{13}$ two-phase region at galvanizing temperatures, two alloys containing 0.1% and 0.2% Cr, respectively, were prepared using the master alloy. The alloys were saturated with Fe by adding the Zn-Fe master alloy at the highest temperature of 470 °C. The bath temperature was then progressively lowered each day by increments of 10 °C. A melt sample was taken from the middle of the bath at each temperature to analyze the liquid composition. A second sample was taken from the bottom of the bath to characterize the intermetallic compounds in the alloys. The liquid compositions at different temperatures are listed in Table 2, together with the identities and compositions of the compounds coexisting with the liquid phase.

The data listed in Table 2 indicate that the Fe solubility decreases with an increase in the Cr content of the molten
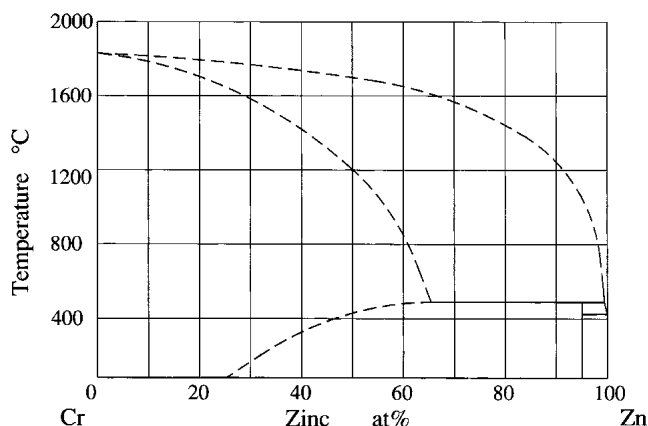
Fig. 5 The Cr-Zn binary phase diagram

Table 2   Compositions of the liquid phase and coexisting intermetallic compounds

Temperature °C	Liquid wt.%		Intermetallic compound at.%			
	Cr	Fe	Phase	Zn	Fe	Cr
472	0.103	0.041	ζ-FeZn$_{13}$	93.24	6.15	0.61
	0.197	0.036	ζ-FeZn$_{13}$	93.13	4.58	2.30
460	0.098	0.031	ζ-FeZn$_{13}$	93.30	5.96	0.73
	0.189	0.025	ζ-FeZn$_{13}$	93.25	4.20	2.54
450	0.097	0.023	ζ-FeZn$_{13}$	93.18	5.83	0.99
	0.180	0.019	ζ-FeZn$_{13}$	93.80	3.44	2.76
			θ-CrZn$_{17}$	94.62	2.05	3.33
442	0.097	0.018	ζ-FeZn$_{13}$	93.40	5.59	1.01
	0.161	0.011	ζ-FeZn$_{13}$	93.30	3.11	3.58
			θ-CrZn$_{17}$	94.05	2.73	3.21
430	0.093	0.012	ζ-FeZn$_{13}$	93.12	5.53	1.35
	0.142	0.007	θ-CrZn$_{17}$	94.11	2.43	3.46

Zn alloy. At a bath temperature higher than 460 °C, only one type of intermetallic compound, the ζ phase, existed in the alloys. At the intermediate temperatures of 450 and 442 °C, only the ζ phase was found in the Zn-0.1%Cr alloy. However, both the ζ phase and the θ-phase were found in the Zn-0.2%Cr alloy. This indicated that this alloy composition was located in the three-phase region. At the lowest temperature of 430 °C, only the ζ phase existed in the Zn-0.1%Cr alloy, and only the θ phase was found in the Zn-0.2%Cr alloy. These findings indicated that the invariant liquid composition corresponding to the liquid-ζ-θ three-phase equilibrium shifted significantly with temperature. The invariant was located at 0.18% Cr and 0.019% Fe at 450 °C, and at 0.161% Cr and 0.011% Fe at 440 °C. The Cr solubility limit in the ζ phase was inversely related to the temperature, being 3.58 at.% at 440 °C and lower than 2.30 at.% at 470 °C for the Zn-0.2%Cr alloy, and 1.35 at.% at 430 °C and 0.61 at.% at 470 °C for the Zn-0.1%Cr alloy. Apparently, the ζ phase possesses a relatively wide homogeneity range in the Zn-Fe-Cr system.

The liquid phase boundaries of the system at various temperatures were determined following the thermody-

namic model developed by Tang (Ref 17) in the study of the Zn-Fe-Mx system. The model relates the Fe solubility in the liquid to the solid solubility of the alloying element Mx in the ζ-FeZn$_{13}$ phase in the liquid-ζ two-phase region. In essence, the decrease in Fe solubility with increasing Cr content in the liquid is induced by the dissolution of Cr in the ζ phase. The solid solution results in a decrease in the free energy of formation of the ζ phase due to the entropy of mixing. For the convenience of readers, the equations describing the liquid phase boundary in the Zn-Fe-Mx system are listed below:

Fe solubility in liquid Zn, $[Fe]^o$, satisfies the following equation:

$$\ln [Fe]^o = 17.78 - 15{,}388/T$$

The Fe solubility in the liquid Zn-Fe-Mx alloy is given by:

$$[Fe] = [Fe]^o \exp \left[14(K X_\zeta X_{Mx} + X_\zeta \ln X_\zeta + X_{Mx} \ln X_{Mx})/X_\zeta \right]$$

with

$$X_{Mx} = \alpha X_{OMx}$$

where α and K are constants, X_{Mx} is the molar fraction of Mx in the ζ phase, and X_{OMx} is the Mx content of the liquid phase.

For most Zn-Fe-Mx systems, the solid solubility limit of the third element Mx in the ζ phase was rather limited, frequently less than 1 at.% (Ref 17). This is because the solubility limit of the third alloying element in the ζ-FeZn$_{13}$ phase is largely limited by the difference in the atomic sizes of Fe and Mx. When the solid solubility of Mx in the ζ-phase is low and insensitive to temperature change, the invariant liquid composition of the Zn-Fe-Mx system is also insensitive to temperature change. In this case, one set of constants, α and K, is enough for modeling the liquid-phase boundaries for the entire temperature range that is relevant to galvanizing production. However, in the current study, the size of a Cr atom is similar to that of an Fe atom; the Fe and Cr atoms are almost interchangeable in the ζ phase. The Cr solubility limit in the ζ-FeZn$_{13}$ phase is high and changes noticeably with temperature. The invariant liquid composition for the three-phase equilibrium also changes noticeably with temperature. As a result, one set of constants α and K is no longer enough for modeling the liquid phase boundary for the entire temperature range under study. A new set of constants is required for every temperature increment of 10 °C. The segments of the liquid-phase boundary, where the ζ phase is the equilibrium phase, are shown in Fig. 6 for four temperatures: 472, 460, 450, and 442 °C. Experimentally measured Fe solubility data at these temperatures are superimposed on the curves. It can be seen that all experimental data fall in the immediate vicinity of the curves. The complete liquid phase boundary at 450 °C is shown in Fig. 7 with the three-phase region also outlined. The liquid-phase boundary of the liquid-θ two-phase region was determined using a similar approach, which was detailed earlier.
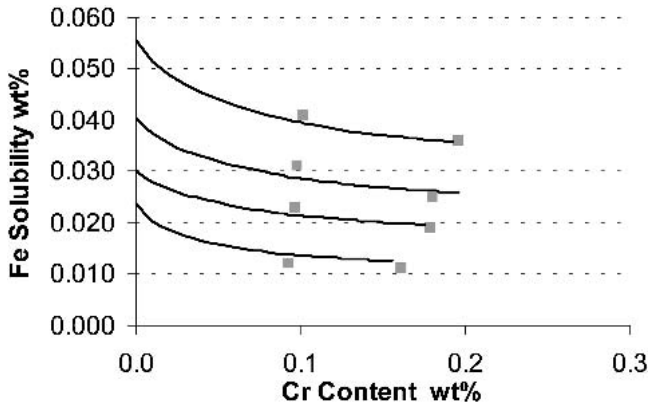
Fig. 6 Fe solubility as a function of the Cr content of the Zn alloy at four temperatures (from top to bottom): 472, 460, 450, and 442 °C
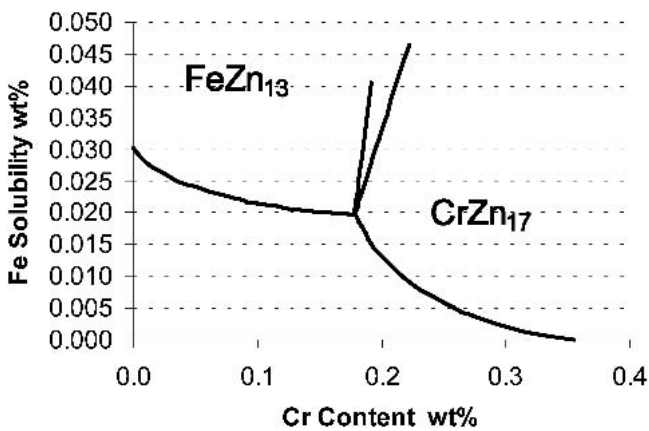

Fig. 7 The Zn-rich corner of the Zn-Fe-Cr ternary system at 450 °C. There are two intermetallic compounds that are in equilibrium with the liquid phase: the ternary extensions of the ζ-FeZn$_{13}$ phase and θ-CrZn$_{17}$ phase

Conclusions

The Zn-rich corner of the Zn-Fe-Cr ternary system was studied at temperatures that are relevant to galvanizing operations. The following conclusions can be drawn:

- The Cr solubility in molten Zn was largely overestimated by previous researchers.
- The θ-CrZn$_{17}$ phase is the only intermetallic compound in the Zn-Cr system.
- In the Zn-rich corner of the Zn-Fe-Cr system, the liquid is in equilibrium with the ζ-FeZn$_{13}$ phase and/or the θ-CrZn$_{17}$ phase.
- The solubility limit of Cr in the ζ-FeZn$_{13}$ phase changes significantly with temperature; the invariant liquid composition of the (liquid-ζ-θ) three-phase equilibrium also changes significantly with temperature.

References

1. M.S. Brunnock, R.D. Jones, D.T. Llewellyn, and G.A. Jenkins, *Ironmaking Steelmaking,* Vol 23 (No. 2), 1996, p 171-176
2. B. Gay, A. Piccinin, and M. Dubois, Corrosion Resistance of Stainless Steel in a GA/GI Galvanizing Bath, *Proceedings Galvatech'01,* Verlag Stahleisen GmbH, Düsseldorf, Germany, 2001, p 262-269
3. M. Nakagawa, J. Sakai, T. Ohkouchi, and H. Ohkoshi, Corrosion, Friction and Wear Proprties of Various Materials in Molten Zinc, *Tetsu to Hagane,* Vol 81 (No. 10), 1995, p 989-994
4. V. Lampe, H. Roos, and M. Svensson, The Attack of Molten Zn on Steels, *Werkst. Korros.,* Vol 28, 1977, p 226-232
5. B. Gay and S. Claessens, Zinc Alloy and Process for Hot-Dip Galvannealing of Steel, International Patent WO 2004/020684 A1
6. N.-Y. Tang and X.P. Su, Update on 450°C Isothermal Section of the Zn-Fe-Al System, *Metall. Mater. Trans. A,* Vol 33A (No. 5), 2002, p 1559-1561
7. X.P. Su and N.-Y. Tang, The Zinc-Rich Corner of the Zn-Fe-Ni-Si Quaternary System at 450°C, *J. Phase Equilibria,* Vol 23 (No. 5), 2002, p 424-431
8. N.-Y. Tang, X.P. Su, and J.M. Toguri, Experimental Study and Thermodynamic Assessment of the Zn-Fe-Ni System, *Calphad,* Vol 25 (No. 2), 2001, p 267-277
9. V. Raghavan, Ternary and Higher Order Iron Phase Diagram Updates, *J. Phase Equilibria,* Vol 24 (No. 6), 2003, p 543
10. T. Heumann, Contribution to the Knowledge of Zinc-Chromium System, *Z. Metallkde.,* Vol 39, 1948, p 45-52 (in German)
11. P. Chiotti and S.J.S. Parry, "Selective Oxidation and Reduction Reactions," Rep. IS-193, U.S. Atomic Energy Commission, 1960, p 78-85
12. J.B Knighton and L.F. Dorsey, "The Solubility of Chromium in Liquid Zinc," Report ANL-7575, U.S. Atomic Energy Commission, 1969, p 22-24
13. A.R. Harding and G.V. Raynor, The Constitution of the Aluminum-Chromium-Zinc Alloy at Low Chromium Contents, *J. Inst. Met.,* Vol 80, 1952, p 446
14. Z. Moser and L.A. Heldt, The Cr-Zn (Chromium-Zinc) System, *J. Phase Equilibria,* Vol 13 (No. 2), 1992, p 172-176
15. H. Hartmann, W. Hofmann, and D. Müller, Contribution to the Knowledge of Zinc-Chromium System, *Abhandl. Braunschweig. Wiss. Ges.,* Vol 7, 1955, 100-106 (in German)
16. M. Hansen, *Constitution of Binary Alloys,* McGraw-Hill, 1958, p 572
17. N.-Y. Tang, Determination of Liquid Phase Boundaries in Zn-Fe-Mx Systems, *J. Phase Equilibria,* Vol 21 (No. 1), 2000, p 70-77