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# ACuZinc®: Improved Zinc Alloys for Die Casting Applications

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## **THE INFLUENCE OF COMPOSITION AND MICROSTRUCTURE ON THE STRENGTH OF ZINC ALLOYS**

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### **ABSTRACT**

Most commercial zinc alloys rely on aluminum additions for their strength. This study was undertaken to evaluate the influence of copper and aluminum additions on strength and microstructure. Mechanical properties were determined for several experimental Zn-Cu and Zn-Cu-Al alloys and some commercial zinc alloys, and correlated with microstructure. Strength, which increased with increasing (Cu + Al) content, was influenced by the type of primary phase present and the properties of the surrounding matrix. Insight was also obtained into the strengthening mechanisms operative in zinc alloys.

### **INTRODUCTION**

Zinc alloys have been used for structural and decorative applications for decades. Alloys such as Zamak 3 and 5 were developed in the 1920's to meet the demand for strong, stable die castings [1]. Subsequently, two other alloys, Zamak 2 and Kirksite were developed primarily for prototype tools and have been used extensively for this purpose. These hypoeutectic alloys contain about 4% aluminum with a trace of copper in Zamak 3, about 1% copper in Zamak 5 and about 3% copper in Zamak 2 and Kirksite. Solidification of these alloys begins with the formation of primary  $\eta$  phase dendrites which are then surrounded by the ( $\eta + \alpha$ ) eutectic [2]. The  $\eta$  phase has a hexagonal close-packed (HCP) crystal structure while  $\alpha$  is face-centered cubic (FCC).

The next significant development in zinc alloys occurred about 25 years ago [1] when a family of hypereutectic Zn-Al alloys, called ZA-5, ZA-8, ZA-12 and ZA-27, were developed; the 5, 8, 12 and 27 indicate the nominal weight percent aluminum. In addition, ZA-5, 8 and 12 contain about 1% copper and ZA-27 contains about 2% copper. Solidification of these alloys begins with the formation of primary  $\alpha$  phase dendrites which are then surrounded by the ( $\alpha + \eta$ ) eutectic. Although small amounts of copper are present, aluminum is thought to be the primary strengthening agent.

Most reported work on the Zn-Cu system [3] has dealt with the copper-rich end of the phase diagram, which includes various brasses. Very little has been reported on the zinc-rich region. Hence, this study was undertaken to explore the influence of copper on the microstructure, strength and strengthening mechanisms in pure zinc and zinc-aluminum alloys. Mechanical properties were determined for experimental Zn-Cu binary alloys with 0 to 12% copper, some ternary alloys with similar copper content and about 4% aluminum, and the above mentioned commercial alloys. Strength behavior was then correlated with alloy microstructure. In order to avoid possible errors in comparing published mechanical property data obtained by different investigators, test specimens of the commercial alloys were also made in this laboratory and tested under the same conditions as the experimental alloys.

Test specimens of the commercial alloys were obtained by melting purchased ingots of the alloy in an electric furnace, while specimens of the experimental alloys were made with 99.99% pure metals. The tension specimens had a 100 mm gauge length and were 9.5 mm in diameter. Compression specimens (50 mm long) were obtained from 22 mm diameter x 200 mm rods cast in a graphite mold and from risers from the tension test specimen castings.

## RESULTS AND DISCUSSION

Chemical composition, tension and compression properties of the Zamak, ZA, Zn-Cu, and Zn-Al-Cu alloys and Kirksite are listed in Table 1. The influence of composition and microstructure on alloy strength can be elucidated by grouping alloys by their primary phase (Table 2). With the exception of pure zinc and the Zn-Cu binary alloys with <2% copper, which consisted entirely of the  $\eta$  phase, all other alloys studied consisted of either  $\eta$ ,  $\epsilon$  or  $\alpha$  primary phase dendrites in a matrix of either the  $\eta$  phase, or a ( $\alpha + \eta$ ) binary, or a ( $\alpha + \epsilon + \eta$ ) ternary eutectic.

The UTS for alloys in these three groups are plotted in Figure 1 as a function of the sum of the atomic percent (Cu + Al). Plotting the data as a function of atomic percent rather than weight percent enabled evaluation of the combined influence of copper and aluminum by compensating for their density differences.

### $\eta$ - Phase

Zamak alloys have similar microstructures with primary  $\eta$  phase dendrites surrounded by a ( $\eta + \alpha$ ) eutectic. The average ultimate tensile strength (UTS) and total elongation ( $e_t$ ) of Zamak 3 were almost equal to that of Zamak 5. However, both tensile ( $YS_t$ ) and compressive yield strengths ( $YS_c$ ) of Zamak 3 were significantly lower than corresponding values for Zamak 5. Both alloys have similar aluminum content but Zamak 5 contains 1% more copper (Table 1). This results in the formation of a small volume of the ternary ( $\eta + \alpha + \epsilon$ ) eutectic. Hence, the ( $\eta + \alpha$ ) matrix is expected to contain some  $\epsilon$  which seems to increase yield but not tensile strength.

Comparable behavior was observed with Kirksite and Zamak 2. Both alloys have similar aluminum contents but Kirksite has slightly more copper. All mechanical properties of Kirksite were slightly higher than those for Zamak 2, again probably due to small amounts of  $\epsilon$  being present in the ( $\eta + \alpha$ ) matrix, as just discussed for Zamak 5.

Data for all alloys in the  $\eta$  phase group fell on a straight line in Figure 1. Tensile strength increased linearly with increasing atomic percent (Cu + Al) even though the group consisted of a diverse combination of materials, namely, a pure metal, two binary solid solutions and four commercial and one experimental ternary alloys. When <2% copper was added to pure zinc, a  $\eta$  solid solution was formed, the crystal structure remained the same as pure zinc, but strength was increased. When the amount of (Cu + Al) was increased beyond 2%, as in Zamak 3, the primary  $\eta$  dendrites were surrounded by a ( $\alpha + \eta$ ) matrix and strength increased because a fraction of the  $\eta$  phase was now strengthened by the  $\alpha$  phase. With a further increase in the amount of (Cu + Al), as in the remaining alloys in this group, the  $\eta$  phase was surrounded by a ( $\eta + \alpha$ ) matrix, a small fraction of which contained some  $\epsilon$ , and UTS increased further.

The common factor in this alloy group was the  $\eta$  phase and the observed linear behavior appeared to be a characteristic of the  $\eta$  phase. However, as the (Cu + Al) content was increased, the strength of the matrix surrounding the primary  $\eta$  dendrites also increased, and this also contributed to the UTS.

### $\alpha$ - Phase

In the ZA alloys,  $\alpha$  dendrites were surrounded by a ( $\alpha + \eta$ ) eutectic (Figure 1) and the volume fraction and size of the dendrites increased with increasing aluminum content. The UTS,  $YS_t$  and  $YS_c$  increased with increasing aluminum content while permanent set at 400 MPa decreased, consistent with the observed microstructure. However,  $YS_c$  was higher than the UTS of each alloy and  $e_t$  increased with increasing strength. The latter can be attributed to the increase in the  $\alpha$  phase with increasing aluminum content;  $\alpha$  being FCC is expected to be more ductile than the  $\eta$  phase which it displaces.

The line joining ZA-5 with ZA-8 and ZA-12 was found to be straight line and displaced below all preceding data suggesting that, for the same atomic percent (Cu + Al), alloys with a primary  $\epsilon$  phase were stronger than those with a primary  $\eta$  phase, which in turn were stronger than alloys with a primary  $\alpha$  phase.

This confirmed earlier results [5-6] that the  $\epsilon$  phase is harder, hence stronger, than the  $\eta$  phase.

#### $\epsilon$ - Phase

The  $YS_t$  and UTS of experimental Zn-Cu binary alloys increased with increasing copper content. The  $e_t$  of alloys with <2% copper was low; it more than doubled for alloys containing 5 and 7% copper and decreased with higher copper content. Pure zinc and alloys with <2% copper consisted entirely of the  $\eta$  phase. The other alloys consisted of primary  $\epsilon$  phase dendrites surrounded by a  $\eta$  matrix, and the volume fraction and size of these dendrites increased with increasing copper content.

The observed behavior suggested that the presence of  $\epsilon$  dendrites in a  $\eta$  matrix not only increased alloy strength but also ductility, making for a far tougher microstructure. This is quite unexpected because  $\eta$  and  $\epsilon$  are both HCP structures which traditionally have poor ductility. Yet,  $e_t$  increased with increasing  $\epsilon$  content. An explanation for this behavior is being sought. However, when copper content was increased further, the volume fraction  $\epsilon$  increased to the extent that the dendrites touched each other, increasing alloy strength but decreasing ductility.

The mechanical properties of the experimental ternary alloys with 0 to 13% copper and about 4% aluminum are listed also in Table 1. These alloys contained  $\epsilon$  dendrites which were surrounded by the  $(\alpha + \epsilon + \eta)$  ternary eutectic and some  $\eta$  phase. The volume fraction and size of the  $\epsilon$  dendrites increased with increasing copper content.

The  $\epsilon$  and  $\eta$  phases both have HCP crystal structures which generally have poor ductility. In these alloys the  $\epsilon$  phase appears to not only strengthen the  $\eta$  phase but also increase the ductility of the combined microstructure. The crystallographic implications of this unique strengthening mechanism are being evaluated.

This straight line is almost parallel to that for the binary Zn-Cu alloys and is displaced upwards. The similar slopes of the two lines appear to be the consequence of  $\epsilon$  phase dendrite strengthening in the two alloy groups. The upward displacement of the ternary alloy line can be attributed to the expected higher strength of the ternary eutectic matrix compared to the  $\eta$  matrix in the Zn-Cu binary alloys, suggesting that higher strength will result with a higher strength matrix.

For alloys with primary  $\eta$  or  $\epsilon$  phase dendrites, UTS appeared to be governed by the type of primary phase, and increased linearly with increasing atomic percent (Cu + Al). These data also indicated that matrix microstructure was altered and strength increased with increasing alloy content, suggesting that alloy strength can be increased by increasing the strength of the primary phase or that of the surrounding matrix. Research is in progress to explore this further.

Similar behavior can be observed for 0.2%  $YS_t$  as a function of atomic percent (Cu + Al) (Table 1). Once again, linear behavior was observed for the same alloy groups. However, the slopes of the two  $\epsilon$  phase groups were not similar as in the UTS plot and the slope for the higher strength  $\epsilon$  phase group was lower than that observed for the lower strength group (Table 3). Furthermore, the slope of the  $\epsilon$  phase group with an  $\eta$  matrix was close to that of the  $\eta$  phase group, suggesting that the force needed for yielding, or slip to occur, is similar in the two groups. Since the former group had an  $\eta$  matrix and the latter was essentially all  $\eta$ , this suggested that yield strength was controlled by  $\eta$ , and hence the matrix microstructure, while it was previously evident that tensile strength was governed by the type of primary dendrite phase.

### CONCLUSIONS

1. Tensile strength of the alloys studied is governed by the type of primary phase, while yield strength is controlled by the microstructure of the matrix surrounding the primary phase dendrites. Alloy strength can be increased by increasing the strength of the primary phase, and/or the strength of the surrounding matrix.

2. For alloys with either an  $\eta$  or  $\epsilon$  primary phase, tensile and yield strength increase linearly with increasing atomic percent (Cu + Al). Also, a higher strength matrix results in higher alloy strength.
3. For the same atomic percent (Cu + Al), alloys with a primary  $\epsilon$  phase are stronger than those with a primary  $\eta$  phase, which are in turn stronger than alloys with a primary  $\alpha$  phase. The crystallographic implications of this finding are being investigated.
4. In Zn-Cu binary alloys, both strength and ductility increase with increasing atomic percent copper. This is attributed to a unique strengthening mechanism where one hexagonal close packed (HCP) phase,  $\epsilon$ , strengthens another HCP phase,  $\eta$ . The mechanism is being evaluated.

## REFERENCES

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Table 1: COMPOSITION\* AND MECHANICAL PROPERTIES OF ALLOYS STUDIED

Alloy	Cu wt%	Al wt%	Cu+Al at%	Tension .2%YS MPa	UTS MPa	Compression elong %	.5% YS MPa	%perm Set at 400MPa
Zn	0.00	0.00	0.00	46.5	52.5			
0001**	1.10	0.10	1.37	79.7	86.7	1.4		
0002	2.01	0.10	2.31	97.7	108.1	1.4		
0005	4.90	0.10	5.27	152.3	194.3	2.9	194.5	>8%
0007	7.00	0.10	7.43	173.0	215.3	2.9	216.6	>8%
0012	11.30	0.10	11.82	216.5	247.0	1.2	242.5	11.1
Zamak 3	0.09	3.80	8.83	144.4	194.3	1.2	247.4	>8%
Zamak 5	1.00	3.30	8.65	175.1	197.4	0.8	280.8	5.5
Zamak 3	2.50	4.20	12.11	206.1	232.5	0.8	293.3	4.2
Kirksite	2.90	4.10	12.29	220.5	247.8	0.7	318.3	2.0
ZA 5	0.09	5.40	12.25	132.6	145.0	0.5	208.8	>8
ZA 8	1.00	8.20	18.77	217.7	242.7	0.7	372.5	2.0
ZA 12	0.80	11.20	24.18	260.0	295.8	1.0	402.3	1.0
ZA 27	2.30	26.40	48.49	374.2	418.6	1.5	455.6	0.2
0303**	3.30	4.70	13.97	228.6	273.2	0.7	308.5	3.3
0305	5.20	4.20	14.80	247.2	293.9	1.0	344.1	1.6
0307	7.20	3.70	15.74	280.2	319.2	0.8	349.9	1.3
0309	9.00	3.60	17.32	289.7	330.1	0.5	373.6	1.1
0310	10.00	3.80	18.75	281.2	330.3	1.3	378.4	1.1
0312	12.10	3.75	21.22	307.8	358.8	1.1		
0313	12.90	3.60	21.22	313.9	367.3	1.3		

\*\* All alloys contain about 0.05% Mg  
The first two digits correspond to Al wt% and the second two digits to Cu wt%.

TABLE 2: ALLOYS GROUPED BY PRIMARY PHASE

Group	Alloy	Primary Phase	Matrix
$\eta$ phase	Pure Zn	$\eta$	$\eta$
	Zn with <2% Cu	$\eta$	$\eta$
	Zamak 3	$\eta$	$\{\eta + \alpha\}$
	Zamak 2 & 5 & Kirksite 0303	$\eta$	$\{\eta + \alpha\} + \epsilon$
$\epsilon$ phase	0005	$\epsilon$	$\eta$
	0007		
	0012		
	0305	$\epsilon$	$(\alpha + \epsilon + \eta) + \eta$
	0307		$(\alpha + \epsilon + \eta)$
	0309		
	0311		
	0312		
	0313		
	$\alpha$ phase	ZA 5	$\alpha$
ZA 8			
ZA 12			
ZA 27			

TABLE 3: LINEAR REGRESSION OUTPUT FOR LINES SHOWN IN FIGURE 1 (UTS) AND ALSO FOR 0.2%YS FROM TABLE 1.

Group	UTS			YS		
	Slope	Ordinate MPa	R <sup>2</sup>	Slope	Ordinate MPa	R <sup>2</sup>
$\eta$	14.81	63.89	.99	12.41	57.45	.97
$\epsilon$ with $\eta$ matrix	7.92	154.11	.99	9.82	100.37	1.00
$\epsilon$ with $(\alpha + \epsilon + \eta)$ matrix	8.57	183.18	.99	5.81	189.47	.98

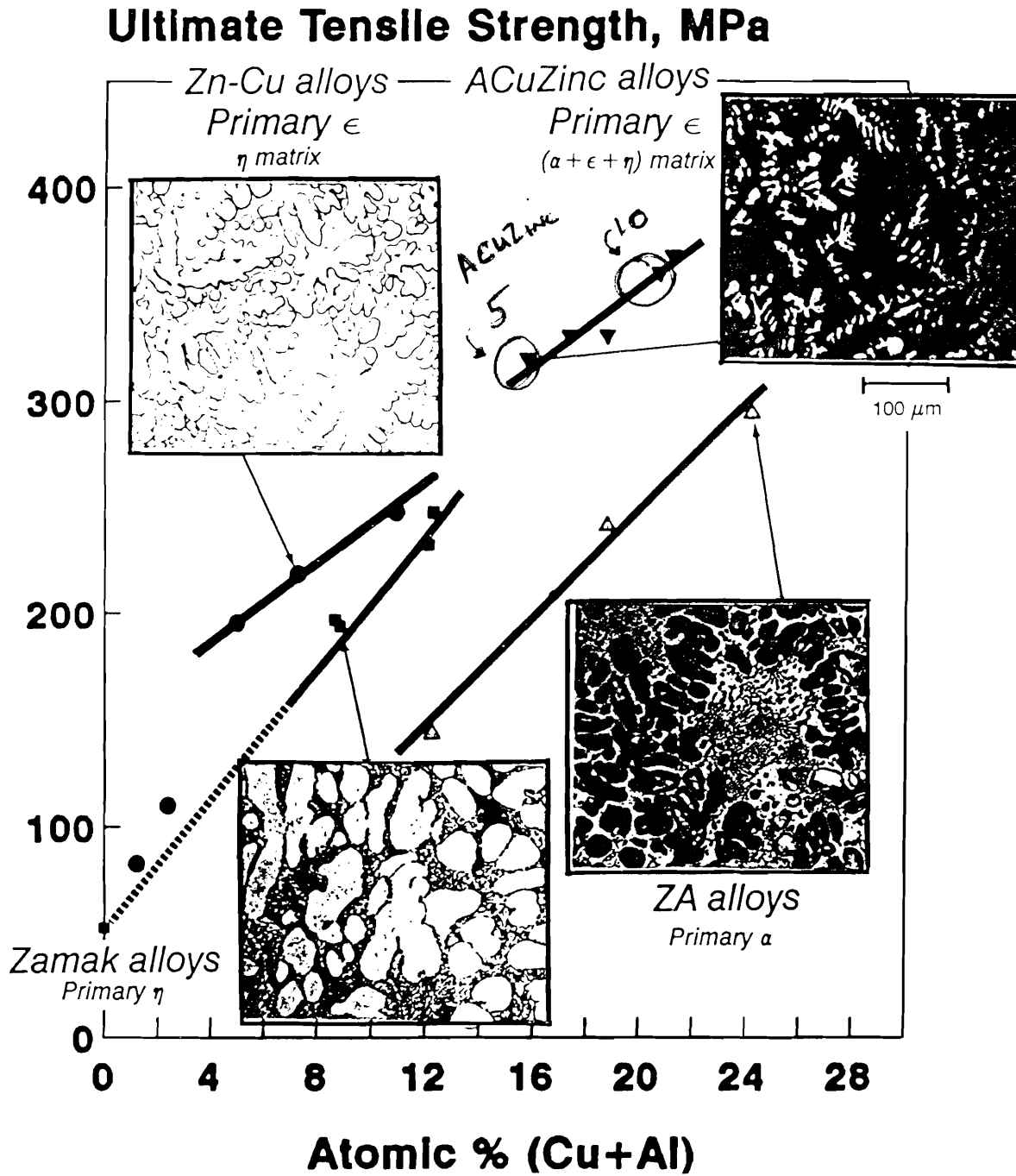


Figure 1. Variations of UTS as a function of atomic percent (Cu+ Al) for all alloys tested. Representative photomicrographs in the four groups studied are also included.