

Oct. 9, 1973

L. A. NEUMEIER ET AL

3,764,402

CREEP-RESISTANT, HIGH-STRENGTH Zn-Al AND Zn-Al-Mg ALLOYS

Filed Feb. 29, 1972

FIG. 1

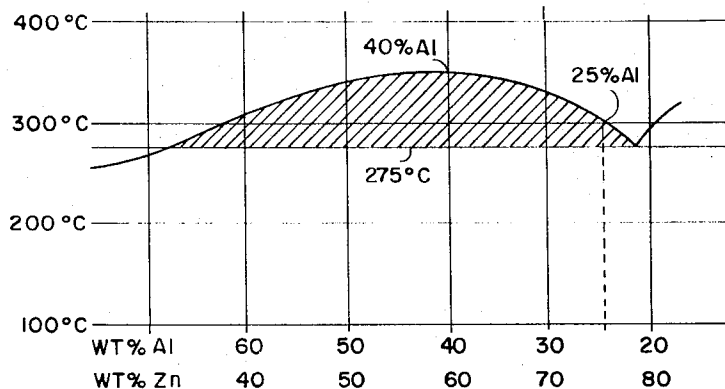
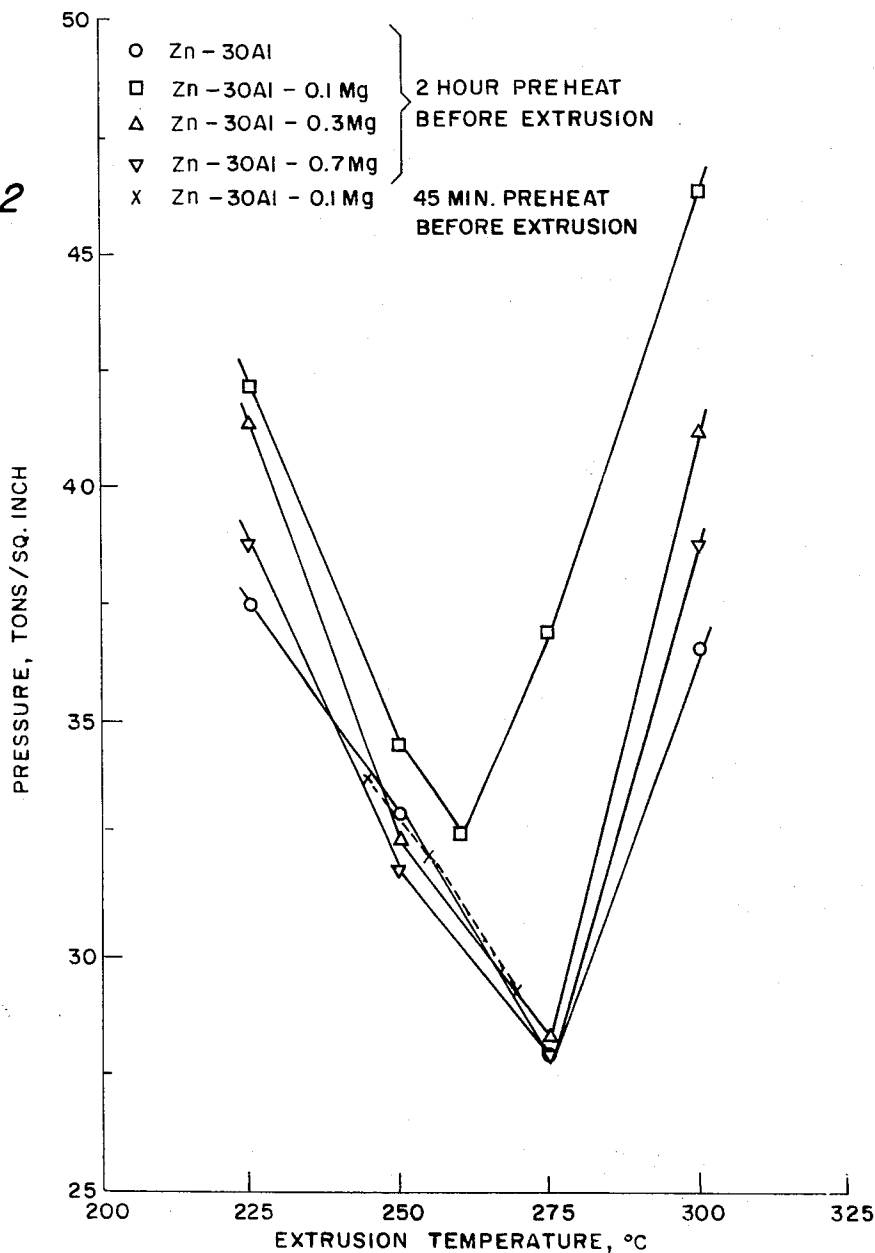


FIG. 2



1

3,764,402

## CREEP-RESISTANT, HIGH-STRENGTH Zn-Al AND Zn-Al-Mg ALLOYS

Leander A. Neumeier and John S. Risbeck, Rolla, Mo.,  
assignors to the United States of America as represented  
by the Secretary of the Interior

Filed Feb. 29, 1972, Ser. No. 230,397

Int. Cl. C22c 17/00; C22f 1/16

U.S. Cl. 148—12.7

9 Claims

### ABSTRACT OF THE DISCLOSURE

Metal form having good strength, creep-resistance, useful ductility is produced by heating ingot of zinc, 25–40 weight percent aluminum, and 0–0.7 weight percent magnesium at a temperature within the miscibility loop of the zinc-aluminum phase diagram; quenching; reheating to 225°–325° C. and forming at this temperature. For additional improvement, the form is solution-treated, quenched and heat stabilized.

This invention relates to preparing and fabricating zinc-base alloys.

Zinc-aluminum (Zn–Al) alloys of near eutectoid composition have been the subject of substantial interest. Much of this interest stems from the ability of these alloys to exhibit superplastic behavior (exaggerated ductility) when quenched from above the Zn–Al eutectoid temperature of 275° C., and then deformed not far below 275° C. However, poor tensile and creep strengths have been serious detriments to wider use of wrought zinc alloys.

We have now discovered that the combination of certain heating and forming temperatures for treatment of an alloy consisting essentially of zinc, 25–40 weight percent aluminum and 0 to 7 weight percent magnesium results in the fabrication of zinc-base alloys which exhibit useful ductility or excellent creep resistance or high strength or a combination of these properties. Broadly, the process comprises heat-treating (conditioning) the alloys at a temperature within the miscibility loop above the eutectoid temperature (275° C.) of the Zn–Al phase diagram which diagram is shown in "Constitution of Binary Alloys," Hansen and Anderko, page 149, McGraw-Hill 1958. Such conditioning is carried out for a time sufficient to essentially homogenize the phase structure throughout the piece. Thereafter the alloy is quenched, reheated to about 225–325° C., and formed at this temperature. The form is allowed to slowly cool (air-cool). As used throughout the specification and claims, the term "forming" or "formed" includes working.

To further enhance its properties, the form is reheated (solution-treated) at a temperature within the above described miscibility loop for a time sufficient to essentially homogenize the phase structure throughout the piece. Thereafter the piece is quenched and again reheated for the purposes of stabilizing or aging. These post-forming treatment steps are most suitable for magnesium-containing alloys.

In the case of magnesium-free alloys, solution treatment is carried out at a temperature of about 276–375° C., followed by quenching to 225–274° C., and heating at this latter temperature for a period to essentially transform the

2

high temperature phase structure which existed above 275° C.

It is therefore an object of the present invention to produce zinc-based alloys possessing such properties as useful ductility, high tensile strength or excellent creep resistance.

Another object is to produce such alloys having high tensile strength coinciding with excellent creep resistance and useful ductility.

A further object is to improve creep resistance and/or tensile strength of zinc-based forms.

A still further object is to reduce required forming pressures.

Other objects and advantages will be obvious from the following more detailed description of the invention taken in conjunction with the drawing in which:

FIG. 1 is a portion of the Zn–Al phase diagram; and FIG. 2 is a graph illustrating one of the properties of the product of the present invention.

In the practice of the present invention, the alloy of the desired composition is obtained by preparing a melt of the requisite ingredients, and casting ingots therefrom. The alloy is essentially composed of (a) zinc, (b) 25–40 weight percent aluminum, and (c) 0–0.7 weight percent magnesium, preferably 0.05–0.3 weight percent magnesium. If desired the ingots are machine cut or trimmed to a convenient handling size. Furthermore, although not essential, the ingots may be given a heat treatment for several hours above 275° C. for the purpose of chemical homogenization.

After final preparation of the ingot, which may include machining, chemical homogenizing, etc., the alloy is now ready for the special heat treatments and forming temperature steps of the process of the present invention. In the first of these steps the alloy is condition heat treated within the miscibility loop of the Zn–Al phase diagram. In other words, the heating temperature falls within the miscibility loop with regard to the Zn–Al composition of the piece being treated. FIG. 1 illustrates the miscibility loop (shaded area) of the Zn–Al phase diagram. As can be seen from the FIG. 1, the lower limit of the heat conditioning range is just above 275° C., while the upper limit is dependent upon the ratio of zinc to aluminum in the piece being heated; and the upper limit ranges from about 300° C. (25% aluminum) to about 350° C. (40% aluminum).

Such heat conditioning is carried on until the phase structure is essentially homogenized throughout the piece which usually requires ¼ hour or more. After the heating period, the alloy is rapidly quenched to about room temperature (e.g., 20–30° C.) with, for example, water.

Such preliminary treatment develops fine graded transformed structures in the alloy which favorably influence both subsequent forming and mechanical properties of the final product.

Next, the alloy is heated to a forming temperature of about 225°–325° C., preferably 250°–300° C., thereafter formed and subsequently allowed to slowly cool (air-cool) to room temperature. At a temperature within the range of 250°–275° C., the energy required for forming is considerably less than the energy required at forming temperatures either above 275° C. or below 250° C. This is

illustrated in FIG. 2 for zinc-30 percent aluminum alloys containing 0-0.7 percent magnesium.

Referring to the figure, the test rods were prepared in the following manner:

(a) Ingredients were melted in a clay-graphite crucible in air atmosphere;

(b) Melt was cast in carbon molds;

(c) Resultant ingots were chemically homogenized in air at 350° C. (not essential);

(d) Ingots were then cropped and scalped to produce extrusion billets about 2 inches in diameter;

creep resistance than those extruded below. Further, alloys with magnesium display much better creep resistance than magnesium-free alloys. For a relatively high stress of 12,000 p.s.i., the creep resistance of these Zn-Al-Mg alloys is very good.

Whether formed above or below the eutectoid temperature the form exhibits high tensile strength with useful ductility. Exemplary test results in this regard are shown in the following Table 2. Ductility is represented in this table by the ability of the test sample to be elongated or reduced in cross-sectional area.

TABLE 2

Tensile properties of Zn-30 percent Al and Zn-30 percent Al-Mg alloys as extruded at 250° or 300° C.<sup>1</sup>

Alloy	Extrusion temperature, ° C.	Tensile strength, p.s.i. <sup>2</sup>	Yield strength, p.s.i. <sup>3</sup>	Elongation, percent	Reduction in area, percent
Zn-30 percent Al.....	250	23,700	21,000	92	95
Do.....	300	30,600	27,700	32	53
Zn-30 percent Al-0.1 percent Mg.....	250	60,800	56,500	22	74
Do.....	300	59,400	56,000	9	16
Zn-30 percent Al-0.3 percent Mg.....	250	60,000	55,500	22	74
Do.....	300	62,400	57,700	11	53
Zn-30 percent Al-0.7 percent Mg.....	250	61,400	56,700	12	34
Do.....	300	63,800	58,600	11	31

<sup>1</sup> The rods (¾ inch diameter) were extruded as in Fig. 2; for tensile specimens, the rods were machine lathed to form a one inch section of reduced diameter (.16 inch); at room temperature the specimen shoulders were gripped in a tensile machine and the one inch reduced section was placed under load at a strain rate of 0.05 inch/inch/minute (constant cross-head movement).

<sup>2</sup> At maximum load.

<sup>3</sup> 0.2 percent offset method.

(e) Billets were conditioned at 300° C. for 2 hours, and water quenched to about room temperature;

(f) Conditioned billets were extruded to ¾ inch diameter at an extrusion speed (rod exit speed) of 2-3 feet/minute.

It can be seen from the figure that, whatever pre-forming heating procedure is employed on the alloys of the present invention, forming pressures markedly increase at above the eutectoid (275° C.) and below 250° C. With adjusted heating time before forming, magnesium-containing alloys can be as readily extruded as magnesium-free alloys.

Although forming temperatures above 275° C. require higher forming pressures in comparison to forming temperatures of 250°-275° C., magnesium-containing alloys formed at above 275° C. exhibit excellent creep resistance in the as-formed condition. Exemplary comparative test results are shown in Table 1. These and the following examples are for zinc-30 percent aluminum alloys containing 0-0.7 percent magnesium. In the tables, the lower the creep rate, the higher the creep resistance.

TABLE 1.—CREEP RATES IN THE AS-EXTRUDED CONDITION

Extrusion temperature, ° C.	Creep rate, percent/day	
	250	300
Alloy:		
Zn-30 percent Al g.....	503	9.94
Zn-30 percent Al-0.1 percent Mg.....	4.29	.00523
Zn-30 percent Al-0.3 percent Mg.....	5.43	.00583
Zn-30 percent Al-0.7 percent Mg.....	4.68	.0006

<sup>1</sup> The ¾ inch diameter rods were extruded as in FIG. 2; for creep specimens, the rods were machined to flat, 7-inch long slats, .08 inch in thickness, ¾ inch in width at the shoulders of each slat and having a width of 0.20 inch at a reduced two-inch gage section; the steady-state creep rates (percent elongation per day) were measured in the reduced section at 90°-13° F. under a stress of 12,000 p.s.i.

It can be seen from Table 1 that those alloys extruded above the eutectoid (275° C.) possess markedly better

In addition to showing the desirable properties of magnesium-containing alloys, Table 2 illustrates the low tensile strength and high ductility of magnesium-free alloys in the as-extruded condition of the process of the present invention.

Special post-forming heat treatments further improve the properties of the alloys of the present invention, particularly those formed below the eutectoid temperature. These procedures includes (a) heating (solution-treating) the form at a temperature within the miscibility loop for a period sufficient to essentially homogenize the phase structure throughout the piece, usually ¼ hour or more; (b) rapidly quenching (e.g., water-quenching) to about room temperature; (c) reheating (aging or stabilizing) to about 75° to 175° C., preferably about 100° to 125° C., for a time sufficient to essentially homogenize the phase structure throughout the piece, usually about ¼ to 2 hours; and (d) thereafter cooling (such as air-cooling) to room temperature. Such treatment significantly improves the creep resistance of magnesium-containing alloys which have been formed either above or below the eutectoid, and most particularly those formed below. In addition, such treatment significantly improves the tensile strength of magnesium-containing alloys which have been formed above the eutectoid temperature, and to a lesser extent those formed below. Ductility in both cases is somewhat decreased by the post-forming treatments. These results are exemplified in the following tables:

TABLE 3

Creep rates of Zn-30 percent Al and Zn-30 percent Al-Mg alloys extruded at 250° or 300° C., then solution-treated at 300° C. for 2 hrs, quenched, and aged at 100° C. for ¼ hr.

Extrusion temperature, ° C.	Creep rate, <sup>1</sup> percent/day	
	250	300
Alloy:		
Zn-30 percent Al.....	370	21.9
Zn-30 percent Al-0.1 percent Mg.....	0.0743	.00241
Zn-30 percent Al-0.3 percent Mg.....	.0657	.00239
Zn-30 percent Al-0.7 percent Mg.....	.0674	.00271

<sup>1</sup> See footnote at end of Table 1.

TABLE 4

Creep rates of Zn-30 percent Al and Zn-30 percent Al-Mg alloys extruded at 250° or 300° C., then solution-treated at 350° C. for 2 hrs, quenched and aged at 100° C. for ½ hr.

Extrusion temperature, ° C.	Creep rate, <sup>1</sup> percent/day	
	250	300
Alloy:		
Zn-30 percent Al.....		230
Zn-30 percent Al-0.1 percent Mg.....	0.00533	
Zn-30 percent Al-0.3 percent Mg.....		0.00370
Zn-30 percent Al-0.7 percent Mg.....		.00312

<sup>1</sup> See footnote at end of Table 1.

TABLE 5

Tensile properties<sup>1</sup> of Zn-30 percent Al and Zn-30 percent Al-Mg alloys extruded at 250° or 285° C., then solution-treated at 300° C., quenched, and aged at 100° C.

Alloy	Extrusion temperature, ° C.	Tensile strength, p.s.i.	Yield strength, p.s.i.	Elongation, percent	Reduction in area, percent
Zn-30 percent Al.....	250	26,500	22,700	72	95
Do.....	285	24,700	21,000	60	99
Zn-30 percent Al-0.1 percent Mg.....	250	67,600	62,100	11	45
Do.....	285	81,100	78,500	8	18
Zn-30 percent Al-0.3 percent Mg.....	250	68,000	61,900	16	43
Do.....	285	83,200	79,900	8	20
Zn-30 percent Al-0.7 percent Mg.....	250	69,900	65,000	7	11
Do.....	285	83,700	80,000	3	9

<sup>1</sup> See footnotes 1, 2, and 3 at end of Table 2.

<sup>2</sup> Alloys extruded at 250° C. were solution-treated for 3 hours and aged for ¼ hour.

<sup>3</sup> Alloys extruded at 285° C. were solution-treated for 2 hours and aged for 1 hour.

TABLE 6

Tensile properties<sup>1</sup> of Zn-30 percent Al and Zn-30 percent Al-Mg alloys extruded at 275° C., then solution-treated at 350° C. for 2 hr., quenched, and aged at 150° C. for ¼ hr.

Alloy	Percent			
	Tensile strength	Yield strength	Elongation	Reduction in area
Zn-30 percent Al.....	31,000	27,000	32	97
Zn-30 percent Al-0.1 percent Mg.....	73,200	66,900	0	7
Zn-30 percent Al-0.3 percent Mg.....	83,800	76,600	2	3
Zn-30 percent Al-0.7 percent Mg.....	79,300	71,400	2	6

<sup>1</sup> See footnotes at end of Table 2.

Referring first to Tables 3 and 4, it can be seen, in comparison to Table 1, that the post-forming heating procedure vastly reduces creep in magnesium-containing alloys extruded below the eutectoid (275° C.). With further regard to magnesium-containing alloys extruded below the eutectoid, a higher solution-treating temperature (350° C.) obtains the best results with regard to creep resistance, but as discussed later, not with regard to accompanying ductility.

Referring now to Tables 5 and 6, it can be seen, in comparison to Table 2, that for magnesium-containing alloys extruded at or above the eutectoid (275° C.), there is a substantial increase in tensile strength by post-forming treatment. However, as shown in Table 6, at a solution-treatment temperature of about 350° C., the increase in tensile strength is not accompanied with useful ductility. It can also be seen from these tables that after post-forming treatment, magnesium-containing alloys extruded below the eutectoid have considerably lower strength and higher ductility than those extruded above the eutectoid. Ductility is lowest in the alloy containing 0.7 percent magnesium. Magnesium-free alloys display high ductility and low strength before and after post-extrusion heat treatments.

For magnesium-free alloys formed above the eutectoid, there is an alternative post-forming heating procedure which increases tensile strength and vastly improves creep resistance although magnesium-free alloys so treated still do not possess the degree of creep resistance of magne-

sium-containing alloys. In this embodiment the form is heated (solution-treated) at about 276° to 375° C., preferably 325° to 350° C., for about ¼ hour or more, or long enough to essentially homogenize the elevated temperature structure throughout the piece, is cooled directly (without cooling below and reheating) to about 225° to 274° C., preferably about 250° C., and thereafter held at this latter temperature for about ¼ to 4 hours, or for a period needed to transform the high temperature structure that existed above 275° C.

Finally, it is cooled to room temperature. It should be stressed that this treatment is superior for magnesium-

free alloys but inferior to previous post-forming treatments for the magnesium-containing alloys. Test results exemplifying this procedure are shown in the following tables:

TABLE 7

Creep rates of Zn-30 percent Al and Zn-30 percent Al-Mg alloys extruded at 300° C., then solution-treated at 350° C. for 2 hr. and cooled directly to 250° C. and held 3 hr. for isothermal transformation

Alloy	Creep rate, <sup>1</sup> percent/day
Zn-30 percent Al.....	0.358
Zn-30 percent Al-0.1 percent Mg.....	.0176
Zn-30 percent Al-0.3 percent Mg.....	.0106
Zn-30 percent Al-0.7 percent Mg.....	.0255

<sup>1</sup> See footnote at end of Table 1.

TABLE 8

Tensile properties<sup>1</sup> of Zn-30 percent Al and Zn-30 percent Al-Mg alloys extruded at 300° C., then solution-treated at 350° C. for 2 hr. and cooled directly to 250° C. and held 3 hr. for isothermal transformation

Alloy	Percent			
	Tensile strength	Yield strength	Elongation	Reduction in area
Zn-30 percent Al.....	38,200	36,400	18	50
Zn-30 percent Al-0.1 percent Mg.....	52,800	50,900	7	21
Zn-30 percent Al-0.3 percent Mg.....	52,600	51,000	3	11
Zn-30 percent Al-0.7 percent Mg.....	55,400	53,500	6	02

<sup>1</sup> See footnotes 1, 2, and 3 at end of Table 2.

It can be seen from Tables 7 and 8 that not only are the strength and creep resistance of magnesium-free alloys improved by such post-extrusion treatment, but the magnesium-free alloys still exhibit substantially high ductility.

In the practice of the present invention in addition to extrusion, forming can be accomplished by rolling, forging etc. Generally, due to their properties, the magnesium-containing formed products of the present invention are not suitable for further forming steps at near room temperature.

All the heating steps of the invention can be carried out while the alloy is in contact with air, although other methods such as oil baths etc., could be employed.

7

In the practice of the present invention, to obtain useful ductility simultaneously with high strength and creep resistance, it is preferred to employ 0.05 to 0.3 percent magnesium in the alloy. Higher magnesium additions result in generally lower ductility although strength remains high. The presence of lower amounts of magnesium adjusts properties to higher ductilities at the expense of strength, which in some instances may be desired.

We claim:

1. A process for producing metal forms comprising:
  - (a) preparing an alloy consisting essentially of zinc, 25-40 weight percent aluminum and 0-0.7 weight percent magnesium;
  - (b) heat conditioning said alloy at a temperature within the miscibility loop of the zinc-aluminum phase diagram;
  - (c) rapidly quenching said alloy to about room temperature;
  - (d) reheating said quenched alloy to a temperature of about 225°-325° C.;
  - (e) forming said reheated alloy; and
  - (f) slowly cooling said form to about room temperature.
2. The process of claim 1 further including solution treating said form at a temperature within said miscibility loop to essentially homogenize phase structure; quenching; and aging at about 75° to 175° C. to homogenize and stabilize said phase structure throughout said form.
3. The process of claim 1 wherein said forming temperature is about 250°-300° C.
4. The process of claim 1 wherein said alloy contains

8

magnesium, and said forming temperature is above 275° C.

5. The process of claim 1 wherein said alloy contains 0.05-0.3 weight percent magnesium.

6. The process of claim 2 wherein said forming temperature is about 250°-300° C.

7. The process of claim 2 wherein said forming temperature is above 275° C., and said alloy contains magnesium.

8. The process of claim 2 wherein said alloy contains 0.05-0.3 weight percent magnesium.

9. The process of claim 2 wherein said aging temperature is about 100° to 125° C.

#### References Cited

##### UNITED STATES PATENTS

3,676,115	7/1972	Hare et al. ....	75-178 AM
1,945,288	1/1934	Morell .....	75-178 AM
2,008,529	7/1935	Werley .....	75-178 AM
3,420,717	1/1969	Fields et al. ....	148-11.5 R
3,632,454	3/1970	Marshall .....	148-11.5 R

##### FOREIGN PATENTS

4,822	12/1953	Germany .....	75-178
5,659	2/1954	Germany .....	75-178

CHARLES N. LOVELL, Primary Examiner

U.S. Cl. X.R.

30 148-2, 11.5 R