United States Patent [19]

Gervais et al.

[11] **3,793,091**

[45] **Feb. 19, 1974**

[54] **SUPERPLASTIC CONDITIONING OF TERNARY AND QUATERNARY ZINC-ALUMINUM ALLOYS**

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[73] Assignee: **Noranda Mines Limited,** Toronto, Canada

[22] Filed: **Dec. 7, 1971**

[21] Appl. No.: **205,616**

[30] **Foreign Application Priority Data**

Aug. 20, 1971 Canada 121,060

[52] **U.S. Cl.** ..... **148/11.5 R**

[51] **Int. Cl.** **C22f 1/16**

[58] **Field of Search** ..... 148/11.5 R

[56] **References Cited**

UNITED STATES PATENTS

3,676,115	7/1972	Hare et al.	148/11.5 R
3,632,454	1/1972	Marshall et al.	148/11.5 R
3,567,524	3/1971	Cook et al.	148/11.5 R
3,420,717	1/1969	Fields, Jr. et al.	148/11.5 R
3,340,101	9/1967	Fields, Jr. et al.	148/11.5 R

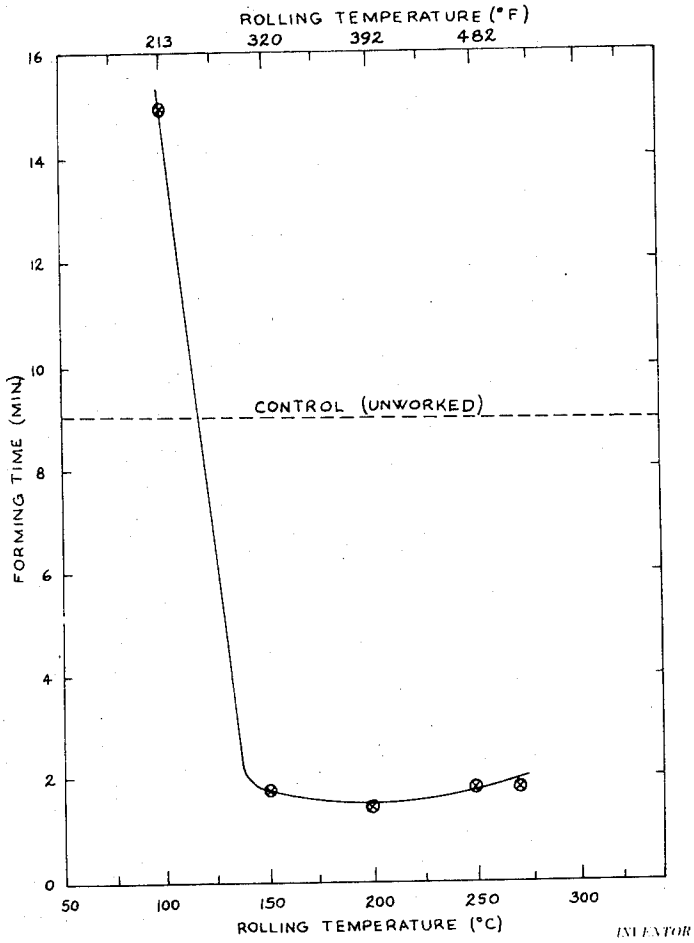
Primary Examiner—W. W. Stallard

Attorney, Agent, or Firm—Cooper, Dunham, Clark, Griffin & Moran

[57] **ABSTRACT**

Ternary and quaternary zinc-aluminum alloys are conditioned to exhibit superplastic behaviour by hot-working thereof at temperatures between about 205°C and the eutectoid temperature of the alloy. This conditioning may be preceded by homogenization and quenching of the alloy and followed by drawing of the alloy.

11 Claims, 3 Drawing Figures



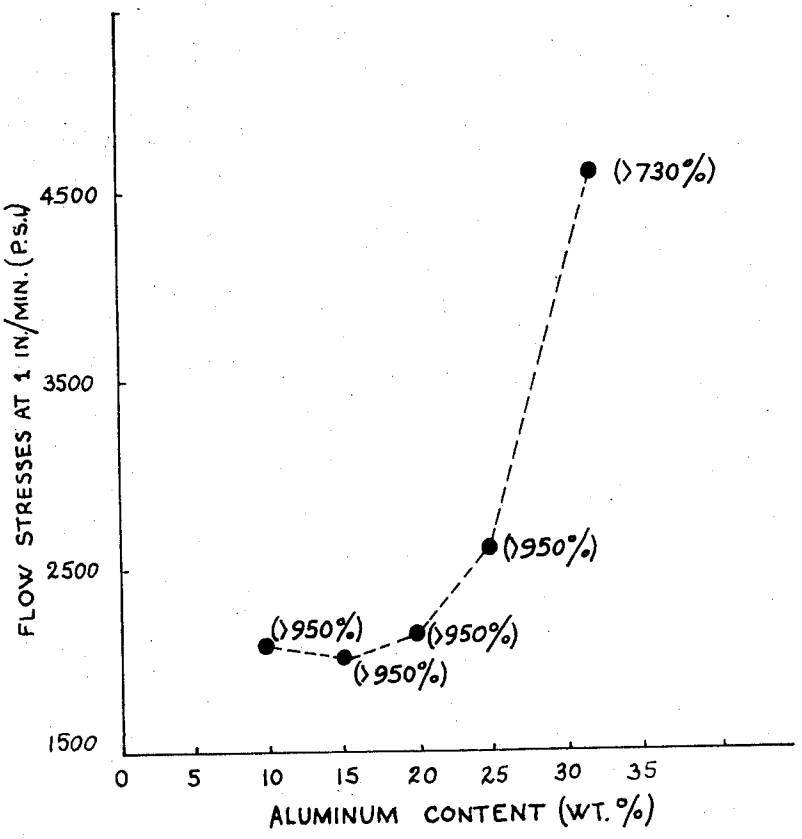

FLOW STRESSES AT 1 IN./MIN. (P.S.I.)
4500
3500
2500
1500
0
5
10
15
20
25
30
35
ALUMINUM CONTENT (WT. %)
(>730%)
(>950%)
(>950%)
(>950%)
(>950%)

FIG. 1

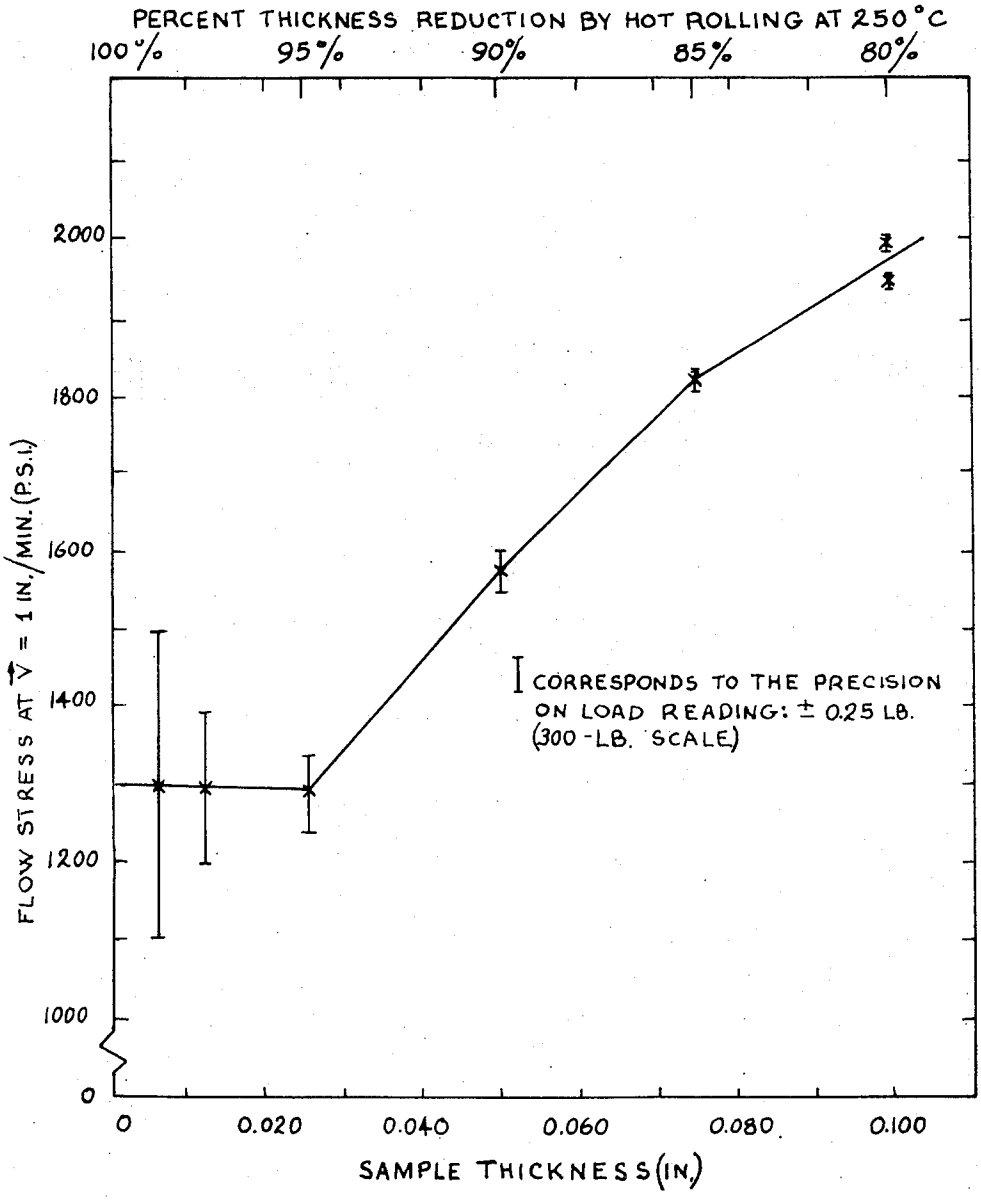

PERCENT THICKNESS REDUCTION BY HOT ROLLING AT 250°C
100%
95%
90%
85%
80%
2000
1800
1600
1400
1200
1000
0
FLOW STRESS AT $\dot{\bar{V}}$ = 1 IN./MIN. (P.S.I.)
CORRESPONDS TO THE PRECISION ON LOAD READING: ± 0.25 LB. (300-LB. SCALE)
0
0.020
0.040
0.060
0.080
0.100
SAMPLE THICKNESS (IN.)

FIG. 2

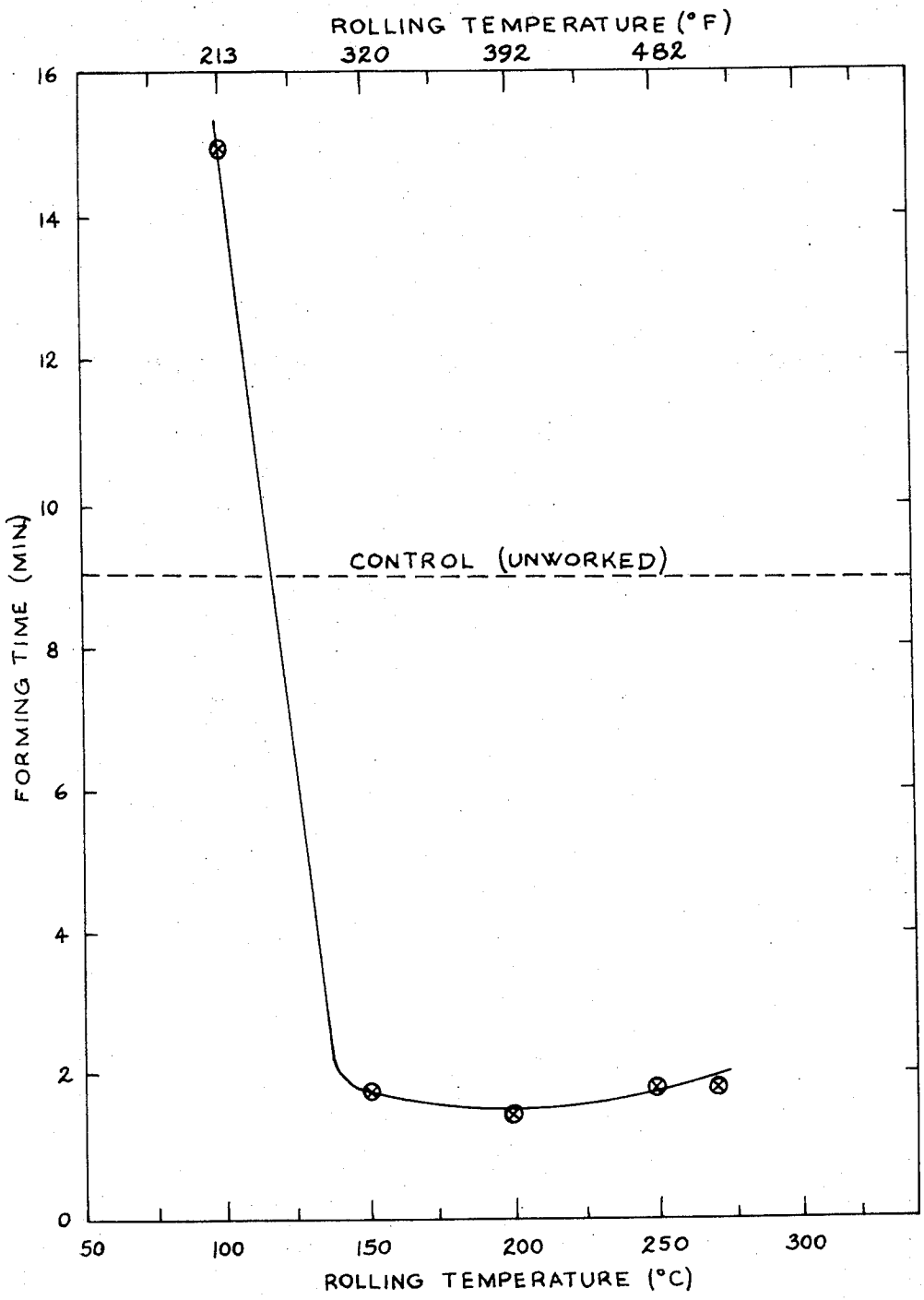

ROLLING TEMPERATURE (°F)
213
320
392
482
16
14
12
10
8
6
4
2
0
FORMING TIME (MIN.)
CONTROL (UNWORKED)
50
100
150
200
250
300
ROLLING TEMPERATURE (°C)

FIG. 3

SUPERPLASTIC CONDITIONING OF TERNARY AND QUATERNARY ZINC-ALUMINUM ALLOYS

This invention relates to a novel conditioning treatment of ternary and quaternary zinc-aluminum alloys which are conditionable to exhibit superplastic behaviour. More particularly, the invention provides a new method of conditioning ternary (Zn-Al-Cu or Zn-Al-Mg) and quaternary (Zn-Al-Cu-Mg) near eutectoid alloys so as to render them superplastic.

The superplasticity of near eutectoid binary zinc-aluminum alloys was discovered by Bochvar and Sviderskaia in 1945 (c.f. Bochvar, A.G., and Sviderskaia, Z.A., Superplasticity Phenomena in Zinc-Aluminum Alloys, Izv. Akad. Nauk SSSR, Otdel Tekh, Nauk, 9, 821 (1945)). Since then, this superplastic phenomenon has been the subject of numerous studies and several patents have recently issued on various aspects thereof, such as U.S. Pat. Nos. 3,340,101 and 3,420,717 of D.S. Fields, Jr. et al., issued Sept. 5, 1967 and Jan. 7, 1969 respectively, and U.S. Pat. Nos. 3,529,457 and 3,537,917 of R.D. Butler et al., issued Sept. 22, 1970 and Nov. 3, 1970 respectively. Superplastic alloys are characterized by an unusual relation between stress and strain rate; the maximum amount of deformation appears within a definite range of strain rates and temperatures. A piece of metal under tension normally brakes before it reaches 100 percent strain, but a superplastic alloy, properly conditioned, can be elongated to 1,000 or even 2,000 percent without breaking.

Generally, for an alloy to be superplastic, two conditions need to be fulfilled:

a. the production of a fine equiaxed grain structure;

b. the deformation of the alloy at a temperature close to half of its melting point as measured in degrees Kelvin.

The flow stress versus strain rate relationship has been used by most researchers studying the superplasticity of metals; from it they have derived the strain rate sensitivity index (m). Caculated m values greater than about 0.25 are considered to be characteristic of relatively large neck-free elongation and a measure of superplasticity.

The theoretically derived equation relating the steady state flow stress (σ^*) and the strain rate ($\dot{\epsilon}$) is,

$$\sigma^* = K\dot{\epsilon}^m$$

where

K = is the proportionality constant which is useful to characterize the tensile strength of the material, at unit strain rate.

According to the above equation, a log-log plot of σ^* versus $\dot{\epsilon}$ should give a straight line where m is the slope of the curve. Linear relationships are seldom found in the literature but rather a sinusoidal type of curve which is now considered typical of superplastic material; in such case "m" varies with the strain rate. The results obtained by the present applicants normally gave a linear relationship.

It is convenient for a rapid evaluation to use the flow stress and the total elongation obtained by doing a hot tensile test at a crosshead velocity ($\vec{V}$) of 1 in./min per inch of gauge length. The flow stress so obtained can be considered as a rough estimate of the value of "K". Since the sample elongates before reaching its flow stress, the true strain rate when the flow stress is measured is lower, hence the flow stress at a crosshead velocity of 1 in./min. is slightly smaller than the "K" value which are determined at $\dot{\epsilon} = 1$ in./in.. min. $^{-1}$.

Another method which can be used to evaluate the superplastic behaviour of sheet material is the free blowing test described by G.C. Cornfield and R.H. Johnson in The Forming of Superplastic Sheet Metal, Int. J. Mech. Sci. Permagon Press 1970, Vol. 12, pp. 479–490. This test consists in blowing sheet material through a circular orifice under constant gas pressure; the time required to blow a sheet to a given height, such as a hemisphere, and the material distribution give an estimate for anisotropy, strain rate sensitivity and flow stress.

Several methods have been described in the prior art whereby superplastic behaviour could be achieved in zinc-aluminum alloys. These methods were aimed at producing a very fine grain structure. Most of these methods refer to binary eutectoid or near eutectoid zinc-aluminum alloys containing about 78 percent zinc and 22 percent aluminum. When some of these methods were applied to selected ternary and quaternary alloys by the present applicant, they were found to be unsatisfactory. For example, an extruded quaternary alloy which was homogenized, water quenched and aged at room temperature for four months yielded a product with a very fine grain structure but which is not superplastic and the elongation whereof is less than 100 percent. It was therefore impossible to forecast the conditioning of ternary and quaternary zinc-aluminum alloys from the techniques described with relation to binary zinc-aluminum alloys of substantially eutectoid composition.

The novelty of the present invention resides in the finding that superplastic conditioning of ternary or quaternary zinc-aluminum alloys which are conditionable to exhibit superplastic behaviour can be carried out in an extremely simple and totally unobvious manner with regard to prior art by simple hot working of such alloys at a temperature between about 205°C and the eutectoid temperature of the alloys (about 275°C). The term "hot working" is well known in the art and includes, for example, operations such as hot extrusion and hot rolling. In addition, it was found that particularly satisfactory results are obtained where the alloy is homogenized and quenched prior to such conditioning by hot working between 205° and 275°C. This particular aspect of the invention is also quite surprising, especially for alloys containing magnesium, because for example, in the D.S. Fields et al U.S. Pat. No. 3,420,717 of Jan. 7, 1969, already mentioned above, it is specifically indicated that in the case of eutectoid binary alloys the conditioning should be effected by homogenization, quenching and thereafter working the stock at a temperature below 400°F (204°C) and that working above this temperature after quenching would increase the proportionality constant "K". It was therefore quite surpirsing to find that according to the present invention adequate results are obtained by homogenizing, quenching and then hot working the above mentioned alloys at a temperature above 400°F (204°C) and preferably as close as possible to the eutectoid temperature (275°C).

Finally, improved results are obtained when the alloy after either direct extrusion or extrusion preceded by homogenization and quenching is subjected to a draw-

ing operation such as rod drawing. Such drawing of the extruded product lowered the proportionality constant "K" (flow stress) of the extruded alloy.

The following examples illustrate the novel conditioning method without however being limitative.

EXAMPLE 1

A. A quaternary alloy having 22 percent aluminum, 1.4 percent copper and 0.05 percent magnesium, the rest being zinc apart from incidental impurities, was extruded at 250°C. Its strain rate sensitivity index "m3[and its proportionaltiy constant "K" were determined and it was found that this simple extrusion procedure developed fairly good superplastic properties.

B. The same alloy was cold drawn by 31 percent after extrusion at 250°C and again its strain rate sensitivity index "m" and its proportionality constant "K" were determined. It was established that in this way the proportionality constant "K" was lowered by about 10 percent.

C. The same alloy was homogenized by soaking it for 2 hours at 350°C and then ice water quenched prior to extrusion at 250°C and cold drawing by 31 percent. The strain rate sensitivity index "m" and the proportionaltiy constant "K" of such alloy were determined. It was found that in this way the proportionality constant was substantially reduced and that the strain rate sensitivity index was improved.

D. Finally, the same alloy was homogenized for 2 hours at 350°C and ice water quenched after extrusion and then aged four months at room temperature. The proportionality constant "K" was determined. This alloy was found to be not superplastic.

The following table I gives the results of the above tests and indicates the influence of the conditioning treatment according to the present invention on the strain rate sensitivity and on the proportionality constant of the alloy as determined by hot tensile testing at 250°C.

TABLE I

Influence of Conditioning Treatment on the Strain Rate Sensitivity

Alloy: Zn — 22%Al — 1.4%Cu — 0.05%Mg

$\vec{V}$ = 0.01 to 20 in./min.

Conditioning Treatment	Strain Rate Sensitivity Index "m"	Proportionality Constant "K" lb/in²-min.
Extruded at 250°C	0.45	3020
B. Extruded at 250°C – Drawn 31%	0.45	2780
C. Homogenized 2 hrs. at 350°C Ice Water Quenched – Extruded at 250°C –. Drawn 31%	0.52	1530
D. Extruded at 250°C Homogenized 2 hrs. at 350°C Ice Water Quenched and aged. 4 months at room temperature	Not Superplastic	11,000

It is interesting to note from the above Table that when the alloy is extruded at 250°C and then homogenized, ice water quenched and aged, which is a procedure similar to those disclosed in the prior art, no superplasticity is obtained. It was therefore highly unobvious that simple extrusion at 250°C or extrusion preceded by homogenization and water quenching would produce superplastic behaviour in ternary and quaternary alloys.

EXAMPLE 2

A. A quaternary alloy containing 22% Al, 1,0% Cu, 0.05% Mg, the rest being Zn apart from incidental impurities was used in the form of cast slbas of 0.5 in. thickness and rolled down at 250°C to 0.05 in. thickness, representing 90 percent of deformation by rolling. The flow stress value and the percent elongation were then determined. It was found that the so worked alloy developed fairly good superplastic properties.

B. The same alloy was similarly rolled at 350°C and its flow stress and percent elongation were determined. It was found that at this temperature the superplastic properties of the alloy had diminished.

C. The same alloy was homogenized for 2 hours by solution heat treatment at 350°C and then ice water quenched before being rolled as specified in (A) above. Its flow stress value and percent elongation were determined and were found to improve over those of simply rolled material.

D. Finally, the same alloy was rolled at 350°C to 90 percent reduction in thickness and then homogenized for 2 hours at 350°C and ice water quenched. Its flow stress and percent elongation were determined and were found to be deteriorated as compared with conditions (A), (B) and (C) above.

Table II herebelow summarizes the findings of this example.

TABLE II

Influence of Conditioning Treatment on the Flow Stress and Elongation at 250°C. ($\vec{V}$ = 1 in./min.)

Alloy: Zn — 22% Al — 1.0% Cu — 0.05% Mg

Conditioning Treatment	Flow Stress	% Elongation
A. Rolled at 250°C	4460	430
B. Rolled at 350°C	5220	340
C. Homogenized 2 hrs. at 350°C Ice Water Quenched Rolled 90% at 250°C	1590	460
D. Rolled 90% at 350°C Homogenized 2 hrs. at 350°C Ice Water Quenched	5380	320

The Table above shows that it is preferable to ice water quench the cast slab prior to rolling rather than after rolling.

EXAMPLE 3

A. A ternary alloy having 20% Al, 1% Cu, the remaining being Zn apart from incidental impurities, in the form of a cast slab 0.5 inch thick was rolled down at 250°C to 0.05 inch in thickness, representing 90 percent of deformation by rolling. It was found that this simple rolling produced superplastic behaviour in the alloy by determining at 1 in./min. the flow stress value and percent elongation thereof.

B. The same alloy was rolled at 350°C and it was found that its elongation properties worsened.

C. The same alloy was homogenized for 2 hours at 350°C and ice water quenched before being rolled at 250°C and it was found that its superplastic properties improved.

The following Table III summarizes the findings of this example.

TABLE III

Influence of Conditioning Treatment on the Flow Stress and Elongation at 250°C. ($\vec{V}$ = 1 in./min.)

Alloy: Zn — 20% Al — 1% Cu

Conditioning Treatment	Flow Stress	% Elongation
A. Rolled at 250°C	3180	>500
B. Rolled at 350°C	3150	375
C. Homogenized 2 hrs at 350°C Ice Water Quenched Rolled 90% at 250°C	1400	>500

EXAMPLE 4

The effect of varying the composition of quaternary alloys and particularly the magnesium content was studied. This effect on the flow stress and elongation (V = 1 in./min.) is summarized in the following Table.

TABLE IV

Effect of the alloy composition on the plasticity of zinc alloys *
($\vec{V}$ = 1 in./min.)
Hot Tensile Test Temperature: 250°C

Alloy No.	Alloy Composition Al	Cu	Mg	Flow Stress lb./in.²	% Elongation
124	24.4	5.13	0.013	2680	> 950
125	24.1	5.14	0.031	2580	> 950
126	25	5	0.05	2680	> 950
127	24.6	5.13	0.12	2790	> 920

* Semi-continuously cast, extruded at 250°C, extrusion ratio about 58:1, and cold drawn by 31%.

The results shown in this Table indicate that the magnesium in the range of 0.01 to 0.12 percent has practically no effect on the flow stress and the elongation.

EXAMPLE 5

The effect of composition on superplasticity indices of as extruded material testes at 250°C was determined.

The findings are summarized in the following Table V.

TABLE V

EFFECT OF COMPOSITION ON THE SUPERPLASTICITY INDICES AT 250°C OF AS-EXTRUDED * ALLOYS
$\vec{V}$ = 0.01 to 20 in./min.

Alloys	Strain Rate Sensitivity Index (m)	Proportionality Constant K (Psi)	Maximum Elongation, (%)
Effect of Mg on Alloys Containing Cu			
22% Al, 1.0% Cu	0.53	1640	950 (2,5,10,20)**
22% Al, 1.4% Cu, 0.05% Mg	0.45	3020	725 (10)
Effect of Cu on Alloys Containing Mg			
22% Al, 1.4% Cu, 0.05% Mg	0.45	3020	725 (10)
22% Al, 2.75% Cu, 0.06% Mg	0.44	2990	870 (5)
Effect of Al on Alloys Containing Cu			
22% Al, 1.0% Cu	0.53	1640	950 (2,4,10,20)
26% Al, 1.0% Cu	0.55	1860	500 (5)

* Semi-continuously cast, extruded at 250°C with an extrusion ratio of about 58/1
** The figures in parentheses indicate crosshead velocity

This Table shows the following:

a. Adding 0.05 Mg to a near eutectoid alloy containing approximately 1% Cu decreases the m value from 0.53 to 0.45 whereas K is almost doubled.

b. Increasing the copper content of a near eutectoid alloy containing 0.05 Mg from 1.4 to 2.75 percent does not significantly affect the superplasticity indices.

c. Increasing the aluminum from 22 to 26 percent in Zn-Al alloy containing 1% Cu does not significantly affect the superplasticity index but reduces the elongation at rupture.

Various embodiments of the present invention will now be further described with reference to the appended drawings in which:

FIG. 1 is a graphical representation showing the effect of the aluminum content on the flow stress and elongation of as extruded and drawn alloys;

FIG. 2 is a graphical plot showing the effect of the amount of rolling on the flow stress; and

FIG. 3 is a graph showing the effect of the rolling

temperature on blow forming time in minutes.

A quaternary zinc-aluminum alloy containing 5% Cu and 0.05% Mg was prepared with various amounts of aluminum content. The effect of this content on the flow stress and elongation at 250°C ($\vec{V} = 1$ in./min.) is illustrated in FIG. 1. The results indicate that the flow stress of the extruded and drawn (31 percent) material is rather insensitive to aluminum level in the range of 10 percent to 20 percent whereas it increases significantly between 25 percent and 33 percent aluminum. This finding is rather surprising and shows the merits of the simple conditioning method on alloys substantially different from the eutectoid composition.

The amount of rolling necessary to optimize the superplastic behaviour was also studied and is illustrated in FIG. 2. The alloy in this figure consisted of 22% Al, 1% Cu, 0.05% Mg the rest being Zn. This alloy was cast in the form of 0.5 inch thick slabs, homogenized 2 hours at 350°C, ice water quenched and then rolled at 250°C. FIG. 2 shows that for optimal superplastic properties a thickness reduction of about 95 percent is required. However, lesser reductions will also produce superplastic properties. The man of the art will have no difficulty in establishing the necessary reduction by hot working for each type of alloy or for the type of superplastic properties and behaviour required.

The effect of rolling temperature on bulging or forming time at 272°C is illustrated in FIG. 3 where the quaternary alloy of 22% Al, 1% Cu, 0.05 Mg, the rest being Zn, is studied. This alloy was first rolled at 316°C from 0.5 to 0.1 inch then homogenized for 1 hour at 316°C and ice water quenched. Rolling at various temperatures further reduced the thickness to 0.050 inch. The test consisted in blowing hemispheres under constant pressure and the time required to blow such hemispheres as a function of the rolling temperature is shown in FIG. 3. The results indicate an optimum rolling temperature between 150° and 270°C. It should be noted, however, that substantial rolling of the as cast alloy after solution heat treatment (homogenization) and water quenching is practically impossible at or below 150°C and difficult at 200°C. To obtain superplastic properties combined with ease of fabrication, the alloys must be rolled or cast at temperatures from about 205°C to the eutectoid temperature (approximately 275°C). The closer to the eutectoid temperature the better. Further, it should be noted that the improvement brought about by rolling the alloy below the eutectoid temperature is very significant. The control sample used for this experiment broke after 9 minutes of blowing and hence the control sample line on the graph is a conservative minimum. Thus, the improvement brought about by treating the alloy closer to the eutectoid temperature is of at least six times (from a minimum of nine minutes for the control sample to 1.5 minutes for the material hot worked at 250°C after ice water quenching from 316°C), which is a very significant and highly unobvious improvement.

It should, of course, be understood that the invention is not limited to the specifically described and exemplified embodiments and that many variations obvious to those skilled in the art can be made without departing from the spirit of the invention and the scope of the following claims. Thus, for example, any ternary or quaternary alloy containing zinc and aluminum which is conditionable to exhibit superplastic properties can be treated in accordance with the present invention although particularly suitable are near eutectoid ternary (Zn-Al-Cu or Zn-Al-Mg) and quaternary (Zn-Al-Cu-Mg) alloys. The degree of extrusion or hot working can also be easily adjusted by any man familiar with the art so as to achieve most appropriate superplastic behaviour. It will be realized that this particular invention provides probably the most economical way of supplying large tonnages of superplastic material and consequently is of great industrial importance.

We claim:

1. A method of conditioning ternary and quaternary zinc-aluminum alloys which are conditionable to exhibit superplastic behavior which comprises subjecting said alloy to homogenization heat treatment followed by quenching and hot working at a temperature between about 205°C. and the eutectoid temperature of the alloy to impart to said alloy superplastic behavior.

2. A method in accordance with claim 1 wherein said hot working is by hot extrusion.

3. A method in accordance with claim 1 wherein said hot working is by hot rolling.

4. A method in accordance with claim 1 wherein said alloys are drawn after hot extrusion.

5. A method in accordance with claim 1 wherein said alloys are selected from near eutectoid ternary Zn-Al-Cu and Zn-Al-Mg alloys and quaternary Zn-Al-Cu-Mg alloys.

6. A method in accordance with claim 1 wherein said alloys are hot worked by hot rolling up to a reduction in thickness of 80–95 percent.

7. A method in accordance with claim 1 wherein said alloys are hot worked at a temperature of about 250°C.

8. A method in accordance with claim 1 wherein said ternary and quaternary zinc-aluminum alloys contain magnesium in an amount less than 0.05 percent.

9. A method of conditioning ternary and quaternary zinc-aluminum alloys which are conditionable to exhibit superplastic behavior which comprises, without any associated or immediate prior heat treatment, subjecting said alloys to hot working at a temperature between about 205°C. and the eutectoid temperature of the alloy to impart to said alloys superplastic behavior.

10. A method in accordance with claim 9 wherein said alloys are selected from near eutectoid ternary Zn-Al-Cu and Zn-Al-Mg alloys and quaternary Zn-Al-Cu-Mg alloys.

11. A method in accordance with claim 9 wherein said alloys are hot worked by hot rolling up to a reduction in thickness of 80–95 percent.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,793,091 Dated February 19, 1974

Inventor(s) Edouard Gervais, Pierre Chollet, Robert Ranger

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 4 should read:

-- A method in accordance with claim 2 wherein said alloys are drawn after hot extrusion. --

Column 3, line 10, "m3[" should correctly read -- "m" --.

Signed and sealed this 22nd day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

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* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334