

1

3,706,605

SUPERPLASTIC LEAD ALLOYS

Dale E. Newbury, Shamokin, and Raymond David Prengaman, Coraopolis, Pa., assignors to St. Joe Minerals Corporation, New York, N.Y.

No Drawing. Filed Oct. 5, 1970, Ser. No. 78,177

Int. Cl. C22c 11/00, 11/02; C22f 1/12

U.S. Cl. 148—11.5 R

9 Claims

ABSTRACT OF THE DISCLOSURE

Superplastic lead alloys can be prepared by casting an age hardenable lead alloy; fully age hardening the casting; and thereafter severely working or deforming the fully age hardened casting by extruding it at a low exit surface temperature of from about 120° F. to about 250° F.

The present invention relates to superplastic lead alloys and to a process for their preparation.

Superplasticity in metals is the ability of the metal to undergo extensive elongation, e.g., at least 100% at room temperature, without necking, i.e., reduction in cross-section area, during deformation under stresses much lower than the normal yield point. In contrast thereto, with normal plasticity the metal will undergo an elongation of only 20% to 50% at room temperature and necking occurs rapidly. The low resistance to flow in the superplastic state offers advantages in metal processing by allowing extensive deformation before failure and reducing the amount of energy required for forming. As a result, the complexity of shapes that can be produced is increased, die fill is improved, the size and cost of forming equipment are reduced, equipment life is increased, die costs are lowered, and some of the low cost techniques normally associated with plastics, such as vacuum forming and blow molding, can be employed.

It is, therefore, the principal object of the present invention to provide superplastic lead alloys and a process for their production such that the lead alloys will have an elongation at room temperature of at least 100%.

The process of the present invention comprises casting an age hardenable lead alloy; fully age hardening the casting; and thereafter severely working or deforming the fully age hardened casting under controlled extrusion temperature conditions.

The lead alloys utilized in the process are age hardenable, i.e., the hardness of castings or billets thereof improves or increases with the passage of time at room or elevated temperatures. Representative of such age hardenable lead alloys are the lead-calcium binary alloys and the lead-calcium-tin ternary alloys. Suitable lead-calcium binary alloys are those containing from about 0.03% to about 0.5% by weight calcium, preferably from about 0.08% to about 0.1% by weight calcium, and the balance being substantially lead. Useful lead-calcium-tin ternary alloys are those containing from about 0.03% to about 0.5% by weight calcium, an amount up to about 1% by weight tin and the balance being substantially lead and usually those containing from about 0.08% to about 0.1% by weight calcium, from about 0.7 to about 1% by weight tin and the balance being substantially lead. Normal impurities can be present in the lead alloys.

The age hardenable lead alloys are cast as billets by conventional chill casting or continuous casting techniques well known to the art.

After casting, the lead alloy is permitted to remain at room temperature or is subjected to elevated temperatures until a fully age hardened condition is achieved, i.e., the hardness of the casting or billet does not change sig-

2

nificantly or remains steady with any further aging. The length of this aging treatment is dependent upon chemical composition and temperature of exposure. For example, a binary lead-calcium alloy containing 0.09% by weight calcium is fully age hardened after one day's exposure at room temperature (70° F.), since it thereupon has a relative hardness number of 63 which remains steady after further aging up to 28 days. A ternary lead-0.1% calcium-0.3% tin alloy requires approximately 60–90 days aging at room temperature to be fully age hardened, since it thereupon has a relative hardness number of about 50 which remains steady on further aging. A ternary lead-0.1% calcium-0.7% tin alloy also requires about 60–90 days aging at room temperature to be fully age hardened in view of the fact that it then has a relative hardness number of about 58 which remains steady on further aging. However, by aging the ternary lead-calcium-tin alloys at an elevated temperature, e.g., 400° F., they are fully age hardened in a shorter period, e.g., only about 5 hours. Thus an increase in temperature of aging accelerates age hardening. (The relative hardness values were obtained using a Rockwell hardness tester with a 1/8" diameter ball and a 60 kg. major load with a 10 kg. minor load applied for ten seconds.)

The fully age hardened casting is thereafter severely worked or deformed under controlled extrusion temperature conditions. Thus the extrusion temperature must be controlled to provide a low exit surface temperature of from about 120° F. to about 250° F., preferably from about 150° F. to about 250° F. or at about 200° F., because at lower or higher surface temperatures of the extrusion superplasticity is not achieved in that the percent elongation to failure of the extruded product at room temperature is less than 100%. The exit surface temperature of the extruded product can be controlled within the required range for inducing superplasticity by regulating or correlating the extrusion reduction ratio and the rate of extrusion or ram speed as illustrated hereinbelow. As either variable increases, the rate of deformation or working increases and the temperature increases. In general, the extrusion reduction ratio is between about 38:1 to about 133:1 and the extrusion ram speed is between about 1 to about 12 inches/minute, these variables being inversely correlated. The extrusion exit surface temperature can be further controlled within the required range while at the same time increasing productivity by water quenching or cooling the extrusions just as they leave the die face by water sprays surrounding the extruded product as also illustrated hereinafter.

The process and products of the invention will be illustrated further by the following typical examples thereof. In these examples, the age hardenable lead alloys were continuously cast in the conventional manner. The cast billets had a diameter of 3 3/8 inches and a length of 10 inches, were cut from the continuously cast logs and were scalped to remove the surface oxide layer. The castings or billets were fully aged-hardened by exposure to room temperature (70° F.) for from 1 to 90 days. The fully age hardened castings or billets were thereafter severely worked or deformed by extruding them into strips at various exit surface temperatures, ram speeds and reduction ratios, with or without water quenching or cooling. The temperatures of all extrusions were measured by means of a surface pyrometer. The extrusion temperature was defined as that in the "plateau region" of the temperature versus length curve, i.e., when the temperature of the extrusion stabilized after a period of time. The mechanical properties of ultimate tensile strength (UTS) in p.s.i. and percent elongation to failure [elongation (percent)] were evaluated at room temperature (70° F.) and at an elevated temperature (300° F.) to deter-

mine the effects of the above mentioned parameters on superplasticity.

EXAMPLES 1-6

These examples using a lead-calcium-tin ternary alloy age hardened for 90 days at room temperature before extrusion show the effect of exit surface temperature of the extrusion in achieving superplasticity, i.e., a percent elongation at room temperature of at least 100%.

TABLE I

The effect of Extrusion Temperature on the Mechanical Properties of Lead-0.08% Calcium-1% Tin Alloy Extrusions

Example No.	Extrusion exit surface temperature (° F.)	Extrusion ratio	Extrusion ram speed (in./min.)	Mechanical properties			
				70° F.		300° F.	
				UTS (p.s.i.)	Elongation (percent)	UTS (p.s.i.)	Elongation (percent)
1-----	215	38:1	1	4,700	115	1,900	500
2-----	225	54:1	1	4,800	120	1,800	450
3-----	290	38:1	2	6,000	80	2,800	310
4-----	290	54:1	2	6,500	80	2,700	230
5-----	300	38:1	4	6,000	70	2,300	250
6-----	325	54:1	4	6,300	70	2,300	300

From the above Table I it will be noted that there was a pronounced difference between the lead alloys having extrusion temperatures below about 250° F. and those which experienced higher temperatures. Below about 250° F. the extrusions exhibited superplastic behavior when tested at 300° F. and extensive elongation (at least 100%)

ram speed was increased, the rate of working increased which, in turn, caused the temperature to increase to an impermissible value above about 250° F. so that superplasticity was not achieved (comparative Examples 8-10, 13).

EXAMPLES 14-22

These examples using a lead-calcium-tin ternary alloy age hardened for 90 days at room temperature before ex-

trusion show the effect of water quenching or cooling in controlling the extrusion exit surface temperature to a value below about 250° F. so as to achieve superplasticity when the extrusion ratio and ram speed or rate of extrusion combined valves would otherwise result in non-superplasticity.

TABLE III

The Effect of Water Quenching on the Mechanical Properties of Lead-0.08% Calcium-1% Tin Alloy Extrusions

Example No.	Extrusion ratio	Extrusion ram speed (in./min.)	Cooling conditions	Extrusion exit surface temperature (° F.)	Elongation (percent)	
					70° F.	300° F.
14-----	38:1	1	No water----	215	115	495
15-----	133:1	1	do-----	220	130	500
16-----	38:1	2	do-----	290	80	310
17-----	38:1	2	Water-----	<150	105	400
18-----	38:1	4	No water----	300	70	250
19-----	38:1	4	Water-----	<150	105	350
20-----	133:1	4	do-----	150	100	360
21-----	38:1	12	do-----	150	100	350
22-----	133:1	4	No water----	375	65	220

at room temperature, while with extrusion temperatures above about 250° F. the lead alloys showed reduced elongation when tested at both room and elevated temperatures. In addition, the superplastic materials (Examples 1 and 2) exhibited greatly reduced strength while the non-superplastic materials (comparative Examples 3-6) approached the normal strength levels for extruded material of this composition.

EXAMPLES 7-13

These examples using a lead-calcium-tin ternary alloy age hardened for 90 days at room temperature before extrusion show the effect of extrusion ratio and ram speed or rate of extrusion in controlling the extrusion exit surface temperature to a value below about 250° F. so as to achieve superplasticity.

TABLE II

The Effect of Extrusion Variables on the Mechanical Properties of Lead 0.08% Calcium-1% Tin Alloy Extrusions

Example No.	Extrusion ram speed (in./min.)	Extrusion ratio	Extrusion exit surface temperature (° F.)	Elongation (percent)	
				70° F.	300° F.
7-----	1	38:1	215	115	500
8-----	2	38:1	290	80	310
9-----	4	38:1	300	70	250
10-----	24	38:1	375	70	200
11-----	1	54:1	225	120	450
12-----	1	133:1	220	130	500
13-----	4	133:1	375	65	220

As can be seen from the above Table II, a low extrusion ram speed of 1 inch/minute produced low extrusion temperatures below about 250° F. which resulted in high elongations of at least 100% at room temperature (70° F.) or superplasticity (Examples 7, 11, 12). As the

The data in the foregoing Table III show the production of superplastic lead alloys when the extrusion exit surface temperature is controlled to a value below about 250° F. by correlating extrusion ratio with ram speed (Examples 14, 15) or by not correlating extrusion ratio with ram speed and instead controlling extrusion exit surface temperature to a value below about 250° F. by means of water quenching or cooling (Examples 17, 19-21). When the extrusion exit surface temperature was not controlled to a value below about 250° F. by correlating extrusion ratio with ram speed, non-superplastic alloys resulted (comparative Examples 16, 18, 22). It will also be noted that by controlling extrusion exit surface temperature to a value below about 250° F. by means of water quenching, higher ram speeds or rate of extrusion and hence productivity of superplastic lead alloys becomes possible at the same extrusion ratio (Example 17 versus comparative Example 16; Examples 19 and 21 versus comparative Example 18; and Example 20 versus comparative Example 22). Furthermore, it will be observed that by controlling extrusion exit surface temperature to a value below about 250° F. by means of water quenching, higher extrusion ratios can be used at the same ram speed or rate of extrusion to produce superplastic lead alloys (Example 20 versus comparative Example 18).

EXAMPLES 23-32

These examples using a lead-calcium binary alloy and two lead-calcium-tin ternary alloys show the effects of chemical composition and age hardening period at room temperature upon achieving superplasticity. The extrusion ram speed was 1 inch/minute and the extrusion ratio

was 38:1 to control the extrusion exit surface temperature to a value below about 250° F.

TABLE IV

The Effect of Aging of Billets Before Extrusion on the Plasticity of Lead Alloy Extrusions

Example No.	Composition		Aging time	Mechanical properties at 70° F.	
	Percent calcium	Percent tin		UTS (p.s.i.)	Elongation (percent)
23	0.099	0	4 hours	4,400	160
24	0.099	0	1 day	4,400	155
25	0.099	0	16 days	4,600	155
26	0.099	0	35 days	4,700	155
27	0.107	0.30	1 day	5,050	85
28	0.107	0.30	16 days	4,750	110
29	0.107	0.30	35 days	4,800	130
30	0.110	0.67	1 day	5,750	65
31	0.110	0.67	16 days	5,600	90
32	0.110	0.67	35 days	5,600	100

It will be noted from the above Table IV that lead-calcium binary alloys require a shorter age hardening period than do the two lead-calcium-tin ternary alloys and the binary lead alloy was more superplastic than were the ternary lead alloys (Examples 23-26 versus Examples 28, 29, 32). The data further show that as the tin content of a lead-calcium-tin ternary alloy is increased, the period for age hardening prior to extrusion is also increased (Example 28 versus Example 32 and comparative Example 31).

Metallographic analysis showed that the superplastic lead alloys had a microstructure which consisted of a majority of micrograins, i.e., small, equiaxed, recrystallized grains of about 1-5 microns in diameter, whereas the non-superplastic lead alloys had a microstructure which was predominantly stringer grains, i.e., long thin grains formed by coalescence of micrograins or recrystallization textures in the extrusion direction.

While the process has been illustrated using lead-calcium binary alloys and lead-calcium-tin ternary alloys, it is equally applicable to other age hardenable lead alloys using one or more conventional lead alloying metals, such as lead alloyed with antimony, tellurium, barium, strontium, sodium and lithium.

It will be appreciated that various modifications and changes may be made in the process and products of the invention in addition to those noted above by those skilled in the art without departing from the essence of the invention and that therefore the invention is to be limited only within the scope of the appended claims.

What is claimed is:

1. A process for the preparation of superplastic lead alloys which comprises casting an age hardenable lead alloy; fully age hardening the casting; and severely working or deforming the fully aged hardened casting by ex-

truding it at a low exit surface temperature of from about 120° F. to about 250° F.

2. The process as defined by claim 1 wherein the exit about 150° F. to about 250° F.

3. The process as defined by claim 1 wherein the exit surface temperature of the extruded product is about 200° F.

4. The process as defined by claim 1 wherein the age hardenable lead alloy is a binary lead alloy consisting essentially of from about 0.03% to about 0.5% by weight of calcium and the balance substantially lead.

5. The process as defined by claim 4 wherein the age hardenable lead alloy is a binary lead alloy consisting essentially of from about 0.08% to about 0.1% by weight of calcium and the balance substantially lead.

6. The process as defined by claim 1 wherein the age hardenable lead alloy is a ternary lead alloy consisting essentially of from about 0.03% to about 0.5% by weight of calcium, an amount up to about 1% by weight of tin and the balance substantially lead.

7. The process as defined by claim 6 wherein the age hardenable lead alloy is a ternary lead alloy consisting of from about 0.08% to about 0.1% by weight of calcium, from about 0.7% to about 1% by weight of tin and the balance substantially lead.

8. Superplastic lead-calcium binary alloys produced by the process defined by claim 4 having an elongation at room temperature of at least 100% and having a microstructure which consists of a majority of micrograins.

9. Superplastic lead-calcium-tin ternary alloys produced by the process defined by claim 6 having an elongation at room temperature of at least 100% and having a microstructure which consists of a majority of micrograins.

References Cited

UNITED STATES PATENTS

1,880,746	10/1932	Bouton	148—12.7
2,159,124	5/1939	Betterton et al.	75—167
2,709,144	5/1955	Eckel	148—12.7
1,813,324	7/1931	Shoemaker	75—167
2,189,064	2/1940	Gillis et al.	148—12.7

OTHER REFERENCES

Hayden et al., Superplastic Metals, Scientific American, March, 1969, Vol. 220, No. 3, pp. 28-35.

Johnson, R. H., Metals and Materials and Metallurgical Reviews, Vol. 4, No. 9, September 1970, pp. 115, 121, and 124.

WAYLAND W. STALLARD, Primary Examiner

U.S. Cl. X.R.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,706,605 Dated December 19, 1972

Inventor(s) Dale E. Newbury and Raymond David Prengaman

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

Col. 2, line 29, "120°F." should be -- 120°F. --.
Col. 4, line 67, "compartive" should read -- comparative --.
Col. 6, following line 3, insert -- surface temperature
of the extruded product is from --; line 22, after
"consisting" insert -- essentially --.

Signed and sealed this 29th day of May 1973.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents