An alloy having a composition which falls within an area enclosed with straight lines drawn to connect Point A (89.8% Al, 9.7% Si and 0.5% Mg), Point B (78.6% Al, 14.1% Si and 7.3% Mg), Point C (78.5% Al, 16.6% Si and 4.9% Mg) and Point D (86.3% Al, 13.2% Si and 0.5% Mg) in the phase diagram of a ternary alloy of Al-Si-Mg system is subjected to intense hot-working. This treatment converts the alloy into a superplastic alloy having Si and Mg content uniformly distributed in the form of particles of a very small grain size throughout a mother phase of Al. The superplasticity of this alloy is further enhanced by incorporating therein a very small amount of at least one member selected from the group consisting of titanium, phosphorus and boron.
ALUMINUM-SILICON-MAGNESIUM TERNARY SUPERPLASTIC ALLOY AND METHOD FOR MANUFACTURE THEREOF

This invention relates to a superplastic ternary alloy of Al-Si-Mg system and to a method for the manufacture thereof.

Metals generally have low degrees of plasticity. The term "superplastic alloy" as used in the present invention means an alloy of the type possessed of a high level of plasticity, unlike the said low plasticity found in ordinary metals, in a fixed range of temperatures not exceeding the melting point thereof.

It has long been known that a eutectoid alloy composed of 78 percent zinc and 22 percent aluminum shows superplasticity. At Imperial Smelting Corporation of England, the manufacture of automobile bodies and refrigerator linings by effective use of the superplasticity of this alloy is approaching perfection for actual operation. This company has given the products thus manufactured a trademark "Prestal."

Further, U.S. Pat. No. 3,340,101 discloses superplastic alloy combinations of 20% Al and 80% Zn, 67% Al and 33% Cu, 88.3% Al and 11.7% Si, and 62% Cu and 38% Zn respectively.

The phase diagrams of these superplastic alloys indicate that the alloys have eutectoid alloy composition or eutectics alloy composition and they are invariably binary alloys.

The superplastic alloys heretofore known are, as mentioned, invariably of binary composition, and these alloys are limited to combinations of specific metal elements. Thus, the uses found for these alloys are limited to within a fixed range in which the properties of these specific alloys can be utilized to advantage. Thus, these alloys do not have high utility value. It is, therefore, only logical to conclude that an epochal advance will be achieved in the manufacture of various products if only alloys of high utility value can be made to acquire superplasticity.

The main object of this invention is to provide a ternary superplastic alloy of Al-Si-Mg system which has high strength, high corrosion resistance and high wear resistance and, therefore, is suitable for a wide range of advantageous uses.

Another object of this invention is to provide a method for the manufacture of the said ternary superplastic alloy of Al-Si-Mg system.

FIG. 1 is a ternary phase diagram of Al-Si-Mg alloy and illustrates the alloy composition according to the present invention.

FIG. 2 illustrates a typical model representing a photomicrographic view of the alloy according to the present invention.

The alloy of the present invention has a composition which falls within the area enclosed with straight lines drawn to connect Point A (89.8% Al, 9.7% Si and 0.5% Mg), Point B (78.6% Al, 14.1% Si, 7.3% Mg), Point C (78.5% Al, 16.6% Si, 4.9% Mg) and Point D (86.3% Al, 13.2% Si, 0.5% Mg) shown in the phase diagram of the ternary system of FIG. 1. The alloy has a composition such that the precipitated phases of Si and MgSi are distributed in the form of particles of a very small grain size throughout the mother phase of Al. In the diagram, E₁ denotes the eutectic point and the curve drawn to connect E₁ and E₂ represents the eutectic line.

The structure of the alloy according to this invention is described in further detail. FIG. 2 illustrates, in the form of a model, a photomicrographic view of the structure of a typical ternary superplastic eutectic alloy composed of 80.5% Al, 14.6% Si and 4.9% Mg according to the present invention. In this diagram, the blank area represents Al crystal grains, the area indicated by slant lines represents primary crystals of Si, and the solid black area represents precipitated crystals of MgSi respectively. The average particle diameter of Al crystal grains is 5μ or under and that of Si and Mg, Si is 2 to 3μ. As metallurgical structure, the alloy of this invention has a microtriple structure in which the two precipitated phases of Si and MgSi are uniformly distributed in the form of particles of a very small grain size throughout the mother phase of Al.

The said superplastic alloy is improved further in terms of fineness of alloy elements and of plasticity when it incorporates therein one or more members selected from the group consisting of 0.01 - 0.20 percent by weight of Ti, 0.005 - 0.03 percent by weight of B and 0.01 - 0.05 percent by weight of P each based on the weight of the alloy.

Now, an explanation is given as to why the composition of the alloy of this invention is limited to the aforementioned range. In this range of alloy composition, the minimum Si content is fixed at 9.7 percent and the minimum Mg content at 0.5 percent. If the Si and Mg contents are lower than their respective minimum levels just mentioned, then the resultant alloy fails to assume a desired fine structure and, therefore, does not acquire superplasticity. The upper limits of Si content and Mg content are fixed at 16.6 and 7.3 percent respectively. When their contents exceed these respective upper limits, the resultant alloy shows an increased degree of brittleness.

P, Ti and B are incorporated for the purpose of improving the alloy in terms of fineness of alloy elements. When the amounts of these substances fail to reach the lower limits of the aforementioned weight ranges, their incorporation fails to produce the effect aimed at. When their amounts exceed the upper limits, however, the excess amounts are wasted without producing any effect. Such excess use rather has a disadvantage that the elution of primary crystals is increased and the alloy acquires a heterogeneous structure.

The fact that the alloy of the present invention assumes superplasticity in a fixed temperature range below its melting point can logically be explained by the following postulate: The alloy of this invention, as previously described, has a triple structure wherein countless minute crystal grains and finely precipitated grains are uniformly distributed throughout the system. Consequently, there exist fine phase boundaries within the structure. These boundaries easily shift their position under stress at elevated temperatures. This easy shifting in position of boundaries enables the alloy of this invention to acquire superplasticity.

Now the method for the manufacture of the alloy of this invention is described.

As the first step, an Al ingot is fused at about 800°C, Then, Si and Mg are added in the form of mother alloy to the fused Al each in a required amount. Where P, Ti or B is further added thereto for the purpose mentioned previously, the addition is made last. The resultant fused mixture is retained in the fused condition until the added elements have been uniformly distributed.
throughout the Al phase. The fused alloy is then cast in molds. This casting is for example, started at a temperature 60°C above the melting point of the alloy.

The alloy acquires a finer texture ideal for superplastic alloy when it is cooled quickly during casting. The method which utilizes water-cooled casting molds, the water-cooled continuous casting method which is adopted popularly and other similar methods are suitable for the purpose of quick cooling of the alloy. The ingot thus obtained has a structure in which Si and Mg₄Si are uniformly distributed. If P, B or Ti has been incorporated, then the ingot has such additive element likewise distributed uniformly therein. The superplasticity which the alloy exhibits in its unmodified state is, however, not outstanding.

The alloy is then subjected to intense hot-working, in the range of from 300°C to 500°C. The object of this intense hot-working resides in breaking the alloy texture produced in consequence of casting and further breaking up primary crystals of Al and precipitated crystals of Si and Mg₄Si so as to complete a structure having all these particles distributed uniformly in still finer grain sizes.

This intense hot-working can be accomplished by such methods as hot extrusion, hot rolling, hot swaging and hot forging. These methods may be used in combination. For example, the ingot may be converted into slabs by extrusion and the slabs may be stretched by rolling. Through research, the inventors have ascertained that the operations of hot extrusion hot swaging and hot rolling, if used for the method of this invention, must satisfy the following requirements.

As to hot extrusion and hot swaging, the extrusion ratio and swaging ratio i.e., the ratio of the cross-sectional area of billet before extrusion or swaging to the cross-sectional area of billet after extrusion or swaging, should be at least 3 : 1.

As to hot rolling, the reduction ratio, P, should be 50 percent or over. Here, P is defined as follows.

\[ P = \left( t - t' \right) \times 100 \]

wherein, \( t \) is the thickness of alloy before rolling and \( t' \) the thickness of alloy after rolling.

The superplastic alloy of the present invention can be obtained by the preceding treatment. The superplasticity of the alloy thus obtained can be improved further by subjecting this alloy to annealing, quenching and aging treatments in the order mentioned. To be specific, the alloy obtained in consequence of the intense hot-working is annealed at about 520°C for one hour to 10 hours, then quenched at 0°C to 20°C and finally aged to have the superplasticity further enhanced.

These treatments enable the alloy to acquire a still finer texture and more desirable superplastic property.

As is clear from FIG. 1, the alloy of the present invention has a composition which approximates a eutectic alloy composition. It is, therefore, necessary that both intense hot-working and annealing treatment should be carried out at temperatures not exceeding the melting point of the composition in question. The alloy elements are further reduced in grain size and then recrystallized when these treatments are performed at such temperatures. Consequently, countless minute crystal grains and finely precipitated grains are uniformly distributed throughout the alloy system. Finally, the alloy acquires a triple structure of the type mentioned previously to exhibit superplasticity.

The utility value of the alloy of the method of this invention is described.

The superplastic alloy of this invention exhibits its superplastic property at temperatures in the range between the melting point of the alloy and about 80°C below the melting point. Within this temperature range, this alloy molded in the shape of a plate, for example, can be formed to any desired complex shape.

Since the superplastic alloy of this invention contains Si and Mg, it enjoys high levels of strength, corrosion resistance and wear resistance. The alloy, therefore, is suitable for the production of materials for which these properties are indispensable. A wide range of uses are found for this superplastic alloy. For example, automobile bodies, refrigerator linings and other articles of similarly complicated shapes can readily be manufactured by subjecting plates or sheets of the said superplastic alloy to deep drawing at about 500°C, to bulging or some other treatment. Machine parts of complicate shapes can also be manufactured by hot pressing or hot forging treatment.

The following preferred embodiments are illustrative of the present invention and are not to be construed as limitative in any way.

**EXAMPLE 1**

The results of the present example are shown in Table 1. Runs No. 1 through No. 7 inclusive pertain to superplastic alloys according to this invention and Runs No. 8 through No. 12 inclusive pertain to alloys lacking superplastic property and used for the purpose of comparison.

First, specimen alloys were prepared. Test pieces were obtained from these specimen alloys and from alloys produced by subjecting such specimen alloys first to intense hot-working indicated in Table 1 and subsequently to annealing treatment. The test pieces were tested for their ultimate tensile strength and elongation on a tensile tester operated at an elevated temperature.

Preparation of specimen alloy: Al was fused at 800°C and required amounts of Si and Mg were added thereto in the form of mother alloy. In the case of specimens for Runs No. 5 through No. 7, Ti and B were added in required amounts. The fused mixtures were held at 800°C for a fixed length of time so as to allow these additive elements to be distributed uniformly. By continuous casting, billets 7 inches in diameter were produced from the fused mixtures. These billets were found to have a structure which comprised ternary eutectic crystals about 5 μ in grain size, primary crystals of Mg₂Si or Si and Mg₄Si and primary crystals of alpha-crystalline Al about 20 μ in grain size.

Hot extrusion: Billets 7 inches in diameter were hot extruded to a diameter of 40 mm. The extrusion ratio is found by calculation to have been 18.6 : 1.

Hot swaging: Rods 20 mm in diameter were obtained from billets 7 inches in diameter by mechanical treatment and then reduced to a diameter of 10 mm by swaging treatment, with test temperature fixed at 300°C.

Hot rolling: Slabs 20 mm in thickness were cut from the aforementioned billets and then rolled to a thick-
5

ness of 6mm. The reduction ratio is found by calculation to have been 70 percent.

Tensile test at elevated temperature: Test pieces each 25 mm in gauge length and 5 mm in diameter at parallel portion were prepared and tested for ultimate strength and elongation, with temperature fixed at 520°C and strain rate at 1 mm/min.

Table 1 indicates that the elongation increased and the superplasticity evidently increased with the elevation of temperature. The elongation was 200 percent at

Referring to Table 1, the specimens No. 1 through No. 7 inclusive exhibited superplasticity with elongation invariably exceeding 200 percent. The specimens No. 2 through No. 4 and No. 9 had one same composition but involved different type of forming treatments and heat treatments from one another. The specimen No. 9 which had undergone no other treatment than casting exhibited a relatively low degree of superplasticity with elongation at 170 percent. The specimen No. 2 which had additionally undergone an extrusion treatment showed an elongation exceeding 200 percent. When such extruded specimen was subjected to heat treatment, it underwent recrystallization to bring forth further size reduction of phase boundaries and improvement of superplastic property. The specimen No. 4 which was obtained by rolling showed a higher level of superplastic property than the specimen No. 3 which was obtained by extrusion.

The specimens No. 5, No. 6 and No. 7 were obtained by incorporating Ti, Ti and B, and Ti, B and P, respectively into the specimen No. 2. The effect of the incorporation of these additive elements is evident when the results obtained for these specimens are compared with those for the specimen No. 3 which was obtained under entirely the same conditions except for the addition of such elements. The specimens No. 8 through No. 12 were alloys obtained by methods other than the method of this invention. None of them exhibited superplasticity.

Example 2

The present example is intended to show the relationship between temperature and superplastic property as determined by using the specimen No. 3 of Table 1 as an example.

The specimen No. 3 had a melting point 558°C. Test pieces were tested for elongation (%) and ultimate tensile strength (kg/mm²), with temperature varied in the range of 440°C and 520°C. The results are shown in Table 2 below.

Table 2

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>520</th>
<th>500</th>
<th>480</th>
<th>460</th>
<th>440</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate tensile strength (kg/mm²)</td>
<td>0.22</td>
<td>0.46</td>
<td>0.67</td>
<td>1.20</td>
<td>1.44</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>460</td>
<td>348</td>
<td>356</td>
<td>214</td>
<td>200</td>
</tr>
</tbody>
</table>

440°C. No superplastic property was recognized at temperatures below 440°C.

We claim:

1. A superplastic alloy consisting of a composition falling within an area enclosed with straight lines drawn to connect Point A (89.8% Al, 9.7% Si, 0.5% Mg), Point B (78.6% Al, 14.1% Si, 7.3% Mg), Point C (78.5% Al, 16.6% Si, 4.9% Mg) and Point D (86.3% Al, 13.2% Si, 0.5% Mg) in a phase diagram of the ternary alloy Al-Si-Mg system, said alloy having a microtriplx structure wherein two precipitated phases composed of primary crystals of Si and precipitated crystals of Mg₃Si each having an average particle diameter of 2-3 μ and uniformly distributed throughout the mother phase of aluminum composed of aluminum crystals having an average particle diameter of up to 5μ.

2. A superplastic alloy comprising a basal alloy of a composition falling within an area enclosed with straight lines drawn to connect Point A (89.8% Al, 9.7% Si, 0.5% Mg), Point B (78.6% Al, 14.1% Si, 7.3% Mg), Point C (78.5% Al, 16.6% Si, 4.9% Mg) and Point D (86.3% Al, 13.2% Si, 0.5% Mg) in a phase diagram of the ternary alloy Al-Si-Mg system and at least one member selected from the group consisting of 0.01-0.20 percent by weight of Ti, 0.005-0.03 percent by weight of B and 0.01-0.05 percent by weight of P each based on the weight of the said basal alloy, said superplastic alloy having a microtriplx structure wherein two precipitated phases composed of primary crystals of Si and precipitated crystals of Mg₃Si each having an average particle diameter of 2-3μ, and one member selected from the group consisting of Ti, B and P are uniformly distributed throughout the phase of aluminum composed of aluminum crystals having an average particle diameter of up to 5μ.

3. A method for the manufacture of a superplastic
alloy consisting of a composition falling within an area enclosed with straight lines drawn to connect Point A (89.8% Al, 9.7% Si, 0.5% Mg), Point B (78.6% Al, 14.1% Si, 7.3% Mg), Point C (78.5% Al, 16.6% Si, 4.9% Mg) and Point D (86.3% Al, 13.2% Si, 0.5% Mg) in a phase diagram of the ternary alloy Al-Si-Mg system, said alloy having a microtriplex structure wherein two precipitated phases composed of primary crystals of Si and precipitated crystals of MgSi each having an average particle diameter of 2-3\(\mu\)m are uniformly distributed throughout the mother phase of aluminum composed of aluminum crystals having an average particle diameter up to 5\(\mu\)m, which method comprises rapidly cooling and casting an alloy having a composition falling within an area enclosed with straight lines drawn to connect Point A (89.8% Al, 9.7% Si, 0.5% Mg), Point B (78.6% Al, 14.1% Si, 7.3% Mg), Point C (78.5% Al, 16.6% Si, 4.9% Mg) and Point D (86.3% Al, 13.2% Si, 0.5% Mg) in the phase diagram of the ternary alloy Al-Si-Mg system, and subjecting the resultant alloy to intense hot-working.

4. The method as set forth in claim 3, wherein the intense hot-working comprises one or more operations selected from the group consisting of extrusion, rolling, swaging and forging.

5. The method as set forth in claim 3, further comprising quenching, annealing, and thereafter, aging the alloy.

6. The method as set forth in claim 5, wherein the intense hot-working comprises one or more operations selected from the group consisting of extrusion, rolling, swaging and forging.

7. A method for the manufacture of a superplastic alloy comprising a basal alloy of a composition falling within an area enclosed with straight lines drawn to connect Point A (89.8% Al, 9.7% Si, 0.5% Mg), Point B (78.6% Al, 14.1% Si, 7.3% Mg), Point C (78.5% Al, 16.6% Si, 4.9% Mg) and Point D (86.3% Al, 13.2% Si, 0.5% Mg) in a phase diagram of the ternary alloy Al-Si-Mg system and at least one member selected from the group consisting of 0.01-0.20 percent by weight of Ti, 0.005-0.03 percent by weight of B and 0.01-0.05 percent by weight of P each based on the weight of the said basal alloy, said alloy having a microtriplex structure wherein two precipitated phases composed of primary crystals of Si and precipitated crystals of MgSi each having an average particle diameter of 2-3\(\mu\)m and one member selected from the group consisting of Ti, B and P are uniformly distributed throughout the mother phase of aluminum composed of aluminum crystals whose average particle diameter of up to 5\(\mu\)m, which method comprises rapidly cooling and casting an alloy having a composition falling within an area enclosed with straight lines drawn to connect Point A (89.8% Al, 9.7% Si, 0.5% Mg), Point B (78.6% Al, 14.1% Si, 7.3% Mg), Point C (78.5% Al, 16.6% Si, 4.9% Mg) and Point D (86.3% Al, 13.2% Si, 0.5% Mg) in the phase diagram of the ternary alloy Al-Si-Mg system, and at least one member selected from the group consisting of 0.01-0.20 percent by weight of Ti, 0.005-0.03 percent by weight of B and 0.01-0.05 percent by weight of P each based on the weight of the said basal alloy, and subjecting the resultant alloy to intense hot-working.

8. The method as set forth in claim 7, wherein the intense hot-working comprises one or more operations selected from the group consisting of extrusion, rolling, swaging and forging.

9. The method as set forth in claim 7, further comprising quenching, annealing, and thereafter, aging the alloy.

10. The method as set forth in claim 9, wherein the intense hot-working comprising one or more operations selected from the group consisting of extrusion, rolling, swaging and forging.