

MASS OF METAL ALLOY FOR FORMING IN THE SEMI-SOLID
STATE

Field of the invention

This invention relates to the field of forming metal alloys in the semi-solid state, i.e. at a temperature between the solidus and liquidus of the alloy, with thixotropic properties in this semi-solid state. This forming in the semi-solid state may be done by "rheoforming", a process in which liquid metal is produced by casting an arbitrarily shaped mass of semi-solid metal alloy under special conditions, and immediately forming it by forging, drawing or die casting, derived from die casting.

It may also be done by "thixoforming", a more industrially widespread process, in which a partly finished solid product is prepared, for example a billet, this partly finished product (or a piece taken from the partly finished product) is heated to the semi-solid state and is shaped by drawing, forging or die casting.

State of the art

Forming of metal alloys in the semi-solid state developed starting from the discovery made by Pr. FLEMINGS's team at MIT at the beginning of the 1970s, that a metal cast under some specific conditions and heated to the semi-solid state, has an apparent viscosity that depends on the time and the shear rate. This viscosity may thus vary from 10^9 Pa.s at rest, so that it can be handled like a solid, to 1 Pa.s at high shear, so that it can be injected into a mold like a viscous liquid.

In order to have these properties, the metal must be solidified with a particular structure, namely either globular that can be obtained either by

mechanical stirring as in Pr. FLEMINGS's first patents, or by electromagnetic stirring, for example as described in patent ITT-ALUMAX US 4434837 and US 4457355, or patents ALUMINIUM PECHINEY EP 0351327 and
5 EP 0439981 or a very refined equiaxial dendritic structure enabling globularization when reheating in the semi-solid state, which is obtained by adding a grain refiner to the alloy and specific casting conditions.

10 The article written by M.P. KENNEY et al. in volume 15 "Casting" of the Metals Handbook, 9th edition, 1989 published by the American Society of Materials, p. 327-338 entitled "Semisolid Metal Casting and Forging" presents a fairly complete summary of this technique
15 which is applicable to ferrous and non-ferrous alloys such as alloys of Zn, Mg, Cu and Ti and Ni or Co based superalloys, but which has developed commercially mainly for casting aluminum alloys.

The main advantages of forming in the semi-solid
20 state are related to the ease of handling of alloys that behave like solids and can thus be manipulated using automatic carousel type installations, to the low injection pressure due to the quasi-liquid behavior under high shear, the thermal gain since it is not
25 necessary to heat to complete fusion, and finally the quality of parts obtained without producing shrink holes or segregation, and with the possibility of making thin walls with laminar filling.

These advantages are particularly marked when the
30 viscosity at high shear is lower, i.e. as the behavior becomes closer to the behavior of a liquid, while behaving like a solid when at rest.

Furthermore, since the beginning of the commercial development of thixotropic alloys, suppliers have taken
35 steps to keep the porosity of the metal due to gases as

low as possible in the same way as for conventional high quality alloys, since porosity is presumed to reduce the metallurgical soundness of the parts manufactured. Thus, the article in the Metals Handbook mentioned above indicates that porosity due to gases is very infrequent in products obtained by forging in the semi-solid state, that it is caused by excessive attack speeds creating excessive turbulence of the metal flow thus trapping the mold atmosphere, and that it can be eliminated by reducing this speed. This clearly shows that this porosity is undesirable.

The metal gassing level may be estimated on the liquid metal by a measurement of the density called d_{80} . It consists of taking a small quantity of liquid metal using a goblet, placing it under a vacuum bell where it will slowly solidify at a residual pressure of 80 hPa, and measuring its density using precision weighing scales. This density is higher when the liquid metal contains less gas.

In the case of aluminum alloys, specifications for thixotropic billets recommend minimum values of the density d_{80} ; for example, for an alloy with 7% silicon and 0.6% magnesium, the value of $d_{80} > 2.60$ is fixed for a theoretical density of 2.67, giving a porosity of the sample solidified at 80 hPa defined by the ratio $(d_{th} - d_{80})/d_{th} < 2.62\%$.

Purpose of the invention

The present inventors observed that unexpectedly, in the case of semi-solid forming, a failure to respect this specification, i.e. if the degassing level is higher, not only failed to produce the disadvantages expected on the metallurgical soundness of the parts manufactured, but also resulted in a very significant reduction in the apparent viscosity of the slug heated



again to the semi-solid state under high-shear, on the contrary improving the quality of forged or die cast parts, which are free of all porosity even after subsequent heat treatment. Furthermore, the elongation
5 of finished parts is increased without reducing the ultimate strength and the yield stress, and the dispersion of elongations is significantly reduced.

Thus, the purpose of the invention is a mass of metal alloy for forming in the semi-solid state cast
10 from liquid metal in which the gassing level measured by the 80 hPa low pressure solidification test, is such that the porosity $a = (d_{th} - d_{80}) / d_{th}$ is between 3 and 50%, and preferably between 4 and 25%. In the case of rheoforming, this metal mass is cast in the semi-solid
15 state and is immediately formed to obtain the finished part. In the case of thixoforming, it is cast in the solid state in the form of a partly finished product, for example a forging blank or a drawing billet, or a billet that will be cut into cylindrical slugs for die
20 casting.

Another purpose of the invention is a mass of metal alloy for forming in the semi-solid state, which has to be cooled in ambient air from a temperature corresponding to a liquid fraction ratio of between 30
25 and 70%, down to room temperature, has a porosity p measured by image analysis at mid-distance between the center of gravity and its external surface of between 2 and 20%, and preferably between 3 and 8%.

In the case of rheoforming, the mass is obtained
30 directly in the semi-solid state from casting. In the case of thixoforming, the metal mass is derived from the solid partly finished product obtained from casting (blank, billet or slug), heated again to the semi-solid state up to a temperature corresponding to a liquid
35 fraction rate of between 30 and 70%. The heating time

used for the measurement of the porosity p is t (in minutes) $= 2.56 (V/S)^2$, where V/S is the ratio of the volume of the mass of alloy to its external surface area, measured in cm. In the frequent case in which
5 the mass is cylindrical, $t = 0.16 D^2$, where D is the cylinder diameter in cm.

The invention is particularly applicable to aluminum alloys, and especially to AlSi alloys containing 3 to 30% of Si, and possibly other additives
10 such as copper or magnesium.

Description of the invention

The thixotropic metal according to the invention is manufactured in the normal way (apart from particular
15 measures to obtain the controlled porosity), for example for thixoforming billets, by vertical die casting with pseudotoric stirring using three-phase linear motors with sliding fields according to the process described in patents EP 0351327 and EP 0439981.
20 But the metal masses may also be manufactured by mechanical stirring during solidification by the use of static mixers-stirrers, or by other electromagnetic stirring methods like those described in US patents 4434837 and US 4457355. They can also be made without
25 stirring from a metal containing a grain refiner (for example TiB_2 for aluminum alloys) with particular casting conditions, for example as described in WO patent application 96//32519.

Conventional liquid metal treatment methods
30 (filtration, ladle with rotary injector) may be used to ensure freedom from inclusions and a uniform structure of the cast metal.

To obtain the controlled porosity according to the invention, a determined quantity of a soluble gas is
35 introduced into the liquid metal in the bath using a

gas that will not react chemically with it, to obtain a fine and uniform dispersion of the gas bubbles. The best gas for this purpose is hydrogen, that could be mixed with a neutral gas such as nitrogen or argon.

5 Fluxes based on hydrated salts could also be used as a hydrogen source.

Another means of introducing hydrogen would be to use the processing ladle, which is usually positioned between the holding furnace and the casting site, for
10 example the ladle could be equipped with a gas injector with a rotating nozzle such as the ALPUR® ladle sold by the PECHINEY RHENALU company. In this case, a certain proportion of hydrogen will be mixed with the neutral gas instead of injecting a pure neutral gas
15 such as argon or nitrogen. A static gas bubble through device could also be used. Metal gassing may be facilitated by maintaining a pressure exceeding atmospheric pressure during the treatment.

The gas or the gas mix will preferably be injected
20 continuously, in order to keep the gassing level as constant as possible while casting the billets.

The liquid metal gassing level may be evaluated by measuring the density d_{80} described above. In the case of an aluminum alloy with 7% of Si and 0.6% of Mg for
25 which the theoretical density in the absence of any porosity is 2.67, the supplier specification gives a $d_{80} > 2.60$ which corresponds to a porosity $a = (2.67 - 2.60)/2.67 = 2.62\%$. To obtain properties according to the invention, this value should be greater than 3% and
30 preferably 4%, and it is only above 50% that harmful porosities may appear in the forged or die cast part. However, it is preferable to remain below 25%.

The porosity of a mass of alloy to be used for forming in the semi-solid state may also be measured on
35 a sample cooled by convection of ambient air starting

from the forming temperature, corresponding to a liquid fraction content of between 30 and 70%, and preferably close to 50%, down to room temperature. In the case of thixoforming, the solid partly finished product must preferably be heated again to the forming temperature for a nominal period $t = 2.56(V/S)^2$, where t is expressed in minutes, V is the volume of the metal mass in cm^3 and S is its external surface area in cm^2 . In the case most frequently encountered in industry in which the initial partly finished product is a slug cut out from a cylindrical billet of diameter D , the formula is written $t = 0.16 D^2$ when D is expressed in cm, or $t = D^2$ when D is expressed in inches which is normal practice in industry for aluminum alloys.

p is measured using an image analysis method that consists of taking samples at about half-way between the geometric center of the alloy mass and its external surface, i.e. in the case of a cylindrically shaped mass such as a slug cut out from a billet, at mid-height and mid-radius, and then carrying out an image analysis on the micrographies made on a polished surface without chemical etching of the sample. White parts represent globules, grey parts the eutectic, and black parts the porosities. The resolution must be such that pores $> 10 \mu\text{m}$ are included. The measurement is repeated on at least 25 fields of the sample distributed around 360° , until the average of the surface fraction stabilize.

Note that viscosity reduction properties start to appear as soon as the porosity exceeds 2%, and at about 20% porosities start to appear in forged or die cast parts. These values are real gassing porosities in the metal at the stage of its industrial use for drawing, forging or die casting.

The main result related to use of the metal according to the invention is the spectacular drop in the apparent viscosity of the metal mass in the semi-solid state, all other parameters and particularly the microstructure being similar.

The rheological test that measures this apparent viscosity is a penetration test that consists of measuring the resistance to deformation F of the metal mass in the semi-solid state, compressed by a tool at constant speed at the end of a determined length. The ratio of this force F to a constant threshold force F_s is determined for a conventional value of metal loss by exudation equal to 8%, the metal loss being an indicator of the temperature and therefore the liquid fraction content for a given material.

A reduction of more than 40% in the F/F_s ratio is observed in the case of AlSi aluminum alloys. Despite the increase in porosity, it is also observed that the metallurgical soundness of forged or die cast parts is at least as good as with degassed metal, and the mechanical characteristics are at least equivalent, the elongation even being increased without any reduction in the strength. Furthermore, this elongation is better controlled since statistical dispersion is significantly lower.

Furthermore, welding tests using TIG and MIG processes have verified that the use of an alloy treated according to the invention does not cause any porosity in the weld itself, or in the heated area, so that welded parts can be manufactured with this type of alloy.

Example

An aluminum alloy A-S7G0.6 (357 according to the Aluminum Association designation) was made with 7%

silicon and 0.6% magnesium modified with strontium with a theoretical density of 2.67. Before casting, the alloy was treated in an ALPUR® ladle with a rotating injection nozzle. Part of the alloy was treated with
5 pure argon, and two other parts were treated with argon to which 10% (by volume) of hydrogen was added at two different flows. The assembly was cast in the form of 76 mm diameter 3 m long billets by applying electromagnetic stirring using three-phase linear
10 motors with sliding fields according to PECHINEY Patent EP 0439981.

The alloy treated with pure argon has a density d_{80} of 2.64 corresponding to a porosity a of 1.2%, whereas the alloy treated with the argon-hydrogen mixture with
15 a lower flow has a density d_{80} of 2.52, corresponding to a porosity a of 5.6%, and the alloy treated with a higher flow has a density d_{80} of 2.23, and a porosity a of 16.5%.

Ten 110 mm high slugs were taken from a billet of
20 alloy treated with pure argon, and ten slugs were taken from each alloy billet treated with the argon-hydrogen mix at the two flows, each slug corresponding to the quantity of metal necessary for die casting of a standard part. The slugs were heated to a temperature
25 of 578°C for 9 minutes in an induction furnace to reach a liquid fraction content of 50%.

Rheology tests carried out on these slugs gave an average value of the F/Fs ratio of 8% metal loss equal to 0.355 for metal treated with argon and 0.20 for
30 metal treated with the argon hydrogen mix at low flow and 0.15 for metal treated with the mix at higher flow, which represents a very large reduction in the apparent viscosity.

On slugs made from the same billets, heated again
35 under the same conditions as above and cooled in air to

room temperature, the porosity p (in %) was measured by image analysis. Observations were made at mid-height of the slug on areas of 110 mm^2 centered on the center line of the slug at mid-radius, and at 10 mm from the edge, respectively. For each area examined, 3 groups of 8 measurements each offset by an angle of 120° were measured, in order to eliminate the bias due to possible segregation. The images of the micrographies obtained were analyzed using KONTRON's IBAS analysis software with a resolution less than $10 \text{ }\mu\text{m}$, the porosities corresponding to the black parts. The results were as follows:

P	10 mm from the edge	mid-radius	axis
without H_2	1.9	1.8	1.7
low H_2	4.1	4.4	4.8
high H_2	4.5	6.2	7.1

10 slugs of each of the first two types of billets (without H_2 and low H_2 flow) were heated again under the same conditions as before and injected under pressure in the form of tensile test pieces of diameter 19 mm, the final injection pressure being 100 MPa. The mechanical characteristics (ultimate strength R_m (in MPa), conventional yield stress at 0.2% elongation $R_{0.2}$ (in MPa) and elongation at rupture A (in %)) of test pieces with a diameter of 13.8 mm and an initial length between marks of 70 mm machined starting from cast blanks, were measured according to standards NF EN 10002-1 and NF A 57102. The results were as follows:

Ar treated alloy

Test piece	R_m	$R_{0.2}$	A
1	350	299	10.0
2	352	306	8.7
3	349	301	10.3
4	354	309	8.9
5	340	301	3.6
6	355	304	8.7
7	347	313	2.9
8	340	307	2.4
9	353	306	8.1
10	351	302	8.7
Average	349.1	303.8	7.2
Standard deviation			2.87

Ar + H₂ treated alloy

Test piece	R_m	$R_{0.2}$	A
1	351	309	6.1
2	346	300	8.6
3	351	305	10.0
4	346	293	10.7
5	358	318	7.0
6	351	304	8.7
7	348	301	8.3
8	350	304	7.7
9	350	303	11.0
10	351	304	9.7
Average	350.2	304.1	8.8
Standard deviation			1.51

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Note that with samples made of alloy treated with hydrogen, the average of R_m and $R_{0.2}$ is very slightly higher and the average elongation is significantly higher. Furthermore, the dispersion of elongations measured by the standard deviation is very much reduced.

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MIG and TIG welding tests were carried out in order to verify the weldability of the alloy treated with hydrogen. Tensile testing pieces identical to those used for the measurement of mechanical characteristics
5 were welded onto flats made from 6061 alloy plates. A micrographic observation of welded joints showed that the porosity of the weld at the thermally affected area of the alloy treated with hydrogen was not different from the porosity of the weld obtained on the
10 ungassified alloy. The weld quality was very good in both cases and in this respect satisfied class 1 in French standard NF 89-220.

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CLAIMS

1. Mass of metal alloy for forming in the semi-solid state, characterized in that after having been cooled in ambient air starting from a temperature corresponding to a liquid fraction of between 30 and 70%, down to room temperature, its porosity p measured by image analysis half way between the center of gravity and its external surface, is between 2 and 20%.
2. Mass according to claim 1, characterized in that the porosity p is between 3 and 8%.
3. Mass according to one of claims 1 or 2, characterized in that the alloy is an aluminum alloy.
4. Mass of metal alloy according to any one of claims 1 to 3, characterized in that it is output from a solid partly finished product and that for the measurement of the porosity p , this partly finished product is heated to the semi-solid state at a temperature such that its liquid fraction is between 30 and 70%, for a time t (in min) such that $t = 2.56 (V/S)^2$, where V and S are the volume and surface area of the mass respectively, expressed in cm^3 and cm^2 .
5. Mass according to claim 4, characterized in that it is a cylindrical slug of diameter D and that the heating time is $t = 0.16 D^2$, where D is expressed in cm.
6. Mass of metal alloy to be used for forming in the semi-solid state, characterized in that it is cast from liquid metal for which the gassing level as measured by the solidification test at 80 hPa, is such that the porosity of the sample $a = (d_{th} - d_{80})/d_{th}$ is between 3 and 50%.
7. Mass according to claim 6, characterized in that the porosity is between 4 and 25%.



8. Mass according to one of claims 6 or 7, characterized in that the metal alloy is an aluminum alloy.

9. Mass according to one of claims 6 to 8, characterized in that it is a billet to be used for thixoforming.

10. Process for controlled gassing of a metal alloy mass according to any one of claims 1 to 9 including manufacturing of a metal alloy, treatment of this alloy in the liquid state in order to introduce a soluble gas into the liquid alloy in a fine and uniform manner, the gas not reacting chemically with it, and casting of this alloy in the form of a mass with a microstructure resulting in thixotropic properties in the semi-solid state.

11. Process according to claim 10, characterized in that the gas is hydrogen.

12. Process according to claim 11, characterized in that the gas is mixed with a neutral gas such as argon or nitrogen.

13. Process according to one of claims 10 to 12, characterized in that the liquid alloy is subjected to a pressure exceeding atmospheric pressure.

14. Process according to one of claims 10 to 13, characterized in that the gas or the gas mix is introduced into the liquid alloy by a static bubble through device.

15. Process according to one of claims 10 to 13, characterized in that the gas or gaseous mix is introduced into the liquid alloy by a processing ladle fitted with a gas injector with a rotating nozzle.

16. Process according to one of claims 10 to 12, characterized in that the gas is added into the liquid alloy using a flow including a hydrated salt.

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17. Process according to any one of claims 10 to 16, characterized in that the cast mass is a billet.

18. Process according to claim 17, characterized in that the billet is stirred as it is cast, providing it
5 with a globular solidification structure.

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