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CASTINGS OF MAGNESIUM-ALUMINUM-ZINC ALLOYS

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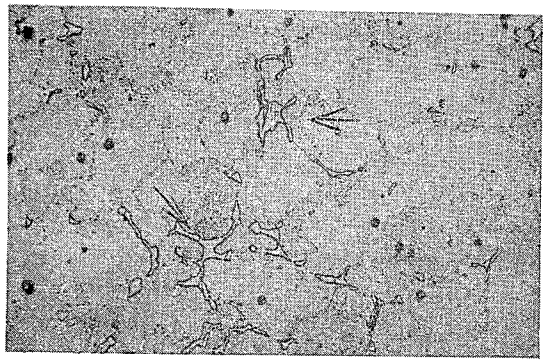


Fig. 1

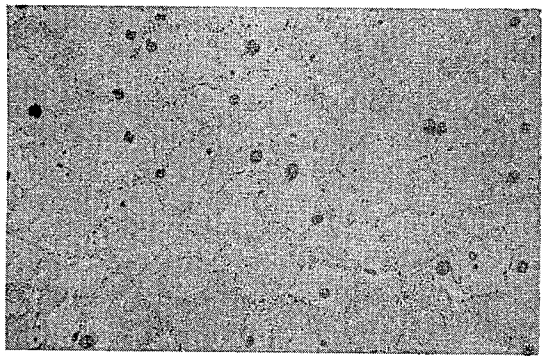


Fig. 2

INVENTOR:

KARL ERNST MANN

By Burgess, Dinklage & Sprung

ATTORNEYS

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3,291,656 CASTINGS OF MAGNESIUM-ALUMINUM-ZINC ALLOYS

Karl Ernst Mann, Meinerzhagen, Westphalia, Germany, assignor to Otto Fuchs, Meinerzhagen, Westphalia, Germany, a corporation of Germany

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13 Claims. (Cl. 148—161)

This invention relates to new and useful improvements in castings of magnesium-aluminum-zinc alloys.

In an article published in "Metal Industry" (1960) under the title "Magnesium Casting Alloys," the authors give a review over alloys used since the first development of magnesium casting materials to the present. They differentiate four groups.

Group one enumerates the oldest magnesium casting alloys with appreciable contents of aluminum and zinc which conventionally contain additionally a few tenths percent of manganese. Among the alloys in this group which are of interest today are especially those designated "AZ91" (9.5 to 10.5% aluminum, 0.2 to 0.6% zinc, 0.2 to 0.5% manganese, balance magnesium with maximum 0.2% silicium, and maximum 0.15% copper) and "AZ92" (8.3 to 9.7% aluminum, 1.7 to 2.3% zinc, 0.10% manganese, balance magnesium with a maximum of 0.3% silicium, 0.05% copper, and 0.01% nickel).

The second group contains the high strength magnesium-zirconium alloys with appreciable contents of zinc. Modified alloys of this type additionally contain small amounts of metals of the rare earths or thorium.

The third group enumerates magnesium-zirconium alloys which are creep-proof even at higher temperatures and contain appreciable alloy additions of metals of the rare earths or thorium.

The fourth group comprises magnesium-zirconium alloys which have been only developed in recent years and which contain additions of metals of the rare earths and silver.

Without considering the alloys of group three, a comparison of the strength values of the heat-treated alloys in the other groups shows superiority of the alloys of groups two and four as against the alloys of group one. The zirconium containing alloys, however, are more difficult to handle in casting operations and they are appreciably more expensive, particularly when they additionally contain metals of the rare earths and silver, than are magnesium-aluminum-zinc alloys, and for this reason, they have been unable to replace the latter in many fields of use.

One object of the invention comprises high strength MgAlZn alloys not containing zirconium or rare earths; other objects will be apparent from the following description.

In accordance with the invention heat-treated castings of magnesium-aluminum-zinc alloys may be produced having strength characteristics and especially yield strength values which not only equal those of castings of the said magnesium-zirconium alloys with contents of zinc or metals of the rare earths and silver but actually surpass the same in that they have a tensile strength (σ_B) in the order of magnitude of at least 30 kp./mm.^{2} and up to 35 kp./mm.^{2} or even higher, a yield strength ($\sigma_{0.2}$) on the order of magnitude of at least about 19 kp./mm.^{2} and up to 25 kp./mm.^{2} or higher and an elongation (δ_5) of an order of magnitude of at least about 3% and up to about 7%.

Castings, including heat-treated castings of magnesium-aluminum-zinc alloys contain a specific non-dissolved

phase of an intermetallic compound $Mg_xAl_yZn_z$ of relatively coarse grained structure which separates during the casting operation and is easily microscopically identifiable. Conventional solution heat treatments as they have been hitherto applied to magnesium-aluminum-zinc alloy castings do not completely remove this separated intermetallic compound. These conventional heat treatments involve heating to temperatures maximum about 410° C., whereby it is conventionally necessary to heat in stages usually beginning at about 380° C. for periods sufficient to avoid eutectic melting before the final heating temperature is applied.

The invention is based upon the discovery that the presence of this non-dissolved intermetallic compound phase interferes with the strength characteristics of the alloys containing the same. In the past such non-dissolved compound was not removable even with extended and/or severe heat treatment.

It has been, however, surprisingly found that if the alloys are kept within a certain specific narrow component range which is substantially about of the following order of composition: 8.3 to 8.7% aluminum, 1.4 to 1.6% zinc, 0 to 0.3% manganese, 0 to 0.7% copper, and the balance magnesium; this non-dissolved intermetallic phase can be removed by subjecting castings of these alloys, after they have undergone the conventional preheating in stages, to a heating at temperatures about from 415° to 425° C. and preferably about from 418° to 422° C., followed by quenching. Unexpectedly, the resulting castings which are substantially free from the individually identifiable non-dissolved intermetallic $Mg_xAl_yZn_z$ phase, ordinarily present in magnesium-aluminum-zinc alloy castings, possess, upon suitable artificial aging, the highly advantageous strength values above set forth and which have never been heretofore obtained for alloys of the type usable in accordance with the invention.

The heat treatment in accordance with the invention comprises a solution heat treatment of the castings, preheated in stages betwen 380° and 410° C., in the conventional manner, to temperatures about from 415° to 425° C. and preferably about from 418° to 422° C., a quenching of the thusly solution heat-treated castings, preferably to temperatures between about 20° C. and about 120° C., and thereafter an artificial aging of the castings preferably at temperatures between about 170° C. and about 190° C., the heating of the castings above 415° C. being maintained for a time sufficient to show for the castings substantial freedom from the originally present intermetallic compound $Mg_xAl_yZn_z$, the freedom from said intermetallic compound being sufficient to impart to the artificially aged product minimum strength values in tensile strength (σ_B) of at least 30 kp./mm.^{2}, in yield strength ($\sigma_{0.2}$) of at least 19 kp./mm.^{2}, and an elongation (δ_5) of at least 3%.

All of the heat treatments including the quenching are carried out in conventional, well known manner using conventional, well known equipment. Duration and temperature of the artificial aging may be carried out as is conventional. It is a preferred embodiment to age the solution heat treated and quenched castings in accordance with the invention at temperatures between about 170° C. and about 190° C.

Within conventional practice as applied to the invention, it is of advantage for best results to conduct the solution heat treatment at increasing temperature stages and most advantageously first maintaining the castings for a time at a temperature of or near 380° C., thereafter for a time at at least one intermediate temperature for example at about 400° C. and finally in accordance with the invention at the highest temperature preferably at about 420° C. maintaining the castings thereat at a sufficient length of

time to obtain the substantial freedom of the compound $Mg_xAl_yZn_z$ adequate for the obtaining of the minimum strength values above set forth after the following quenching and aging.

Good results have thus been obtained, for instance by heating the castings at least about 5 to 8 hours at 380° C., at least about 5 to 8 hours at or near 400° C., and at least 8 hours at or near 420° C., followed by quenching to a temperature between 20° C. and 120° C. and an artificial aging at a temperature between 175 to 185° C. for a period of time of about 8 to 20 hours and preferably 10 to 15 hours.

The quenching of the castings from their highest treatment or homogenization temperature of about 420° C. is best effected for high strength values by using a liquid medium, such as water or oil. Quenching may be, however, also conducted by the use of air or other suitable gas as is conventional practice.

When using a heat treatment in accordance with the invention in which the quenching step is carried out by the use of a liquid medium, it is sometimes observed with castings having adjacent heavier and appreciably thinner cross-sections that quenching fractures occur within these areas or that such fractures occur in castings of particularly complicated forms.

In accordance with a further preferred embodiment of the invention, it has been found that the tendency for such fractures may be substantially eliminated without interfering practically with the high strength values of the castings in accordance with the invention by avoiding a direct quenching from the highest solution heat treatment temperature and by first subjecting the castings to a preliminary cooling from its highest solution heat treatment temperature and preferably within the same oven by at the most 40° C. and preferably by about 30° C. and to continue this cooling under conditions and for a time sufficient to obtain substantially complete temperature equilibrium throughout the castings. Thus, when the highest temperature has been about 420° C., a cooling is first effected to about 380° to 395° C. and preferably to about 390° C., maintaining in each case the temperature to which cooling is to be effected such as for example from 15 to 120 minutes to give the desired temperature equilibrium within the casting. The thusly cooled casting is then subjected to the quenching in a liquid medium. Even though the quenching step has been rendered thus less severe by the pre-cooling and even if thereafter the quenching is effected under still milder conditions in that the quenching medium, such as water or oil, is at a higher temperature than 20° C., above mentioned, and has, for instance, a temperature up to about 120° C., the herein mentioned strength values, i.e. σ_B=30–35kp./mm.^{2}, $\sigma_{0.2}$=19–25kp./mm.^{2}, δ_5=3 to 7%, are still obtained.

The temperature to which the castings in accordance with the invention may be pre-cooled or from which the quenching is effected may, however, not be appreciably less than about 380° C. inasmuch as the intermetallic compound $Mg_xAl_yZn_z$ already separates or precipitates at about 370° C. whereby the strength values of the castings thereafter quenched and artificially aged may be reduced to below the minimum values herein specified for the alloys in accordance with the invention.

It is surprising that the hereinabove stated minimum strength values in accordance with the invention are still obtainable with a substantially complete homogenization at about 420° C. even though the castings are then not quenched in a liquid medium but in air. Even though the strength values of castings obtained in this manner are somewhat lower than those obtained with quenching in a liquid medium, such as water or oil, they are nevertheless still higher than is the case for the conventionally heat-treated castings of the alloy type MgAlZn.

For the purpose of obtaining good strength characteristics melts of magnesium alloys of the type MgAlZn have been conventionally subjected to any conventional grain refining treatment. Such a grain refining treatment is here exemplified by the use of hexachlorethane. Though a small copper content of the alloys, such as of about 0.5% copper will also effect a refining of the cast grain, that effect is somewhat less than that obtainable with, for example hexachlorethane treatment of substantially copper-free alloys. Within a further embodiment of the invention, it has been found, however, that if the alloys do possess such a copper content, the same will effect a fining of the casting separated intermetallic compound $Mg_xAl_yZn_z$ to such an extent that the homogenization, i.e. effective removal of said compounds within the scope of this invention, can be accelerated. As applied within the scope of this invention, such copper content will then produce the same improved results as will, for instance a treatment with hexachlorethane. Thus, when using castings with, for instance, 0.5% copper and subjecting the same to the same heat treatment in accordance with the invention as herein set forth at least the same strength values are obtained as for a casting subjected to the identical treatment but embodying a copper-free alloy and subjected to a conventional grain refining treatment with, for instance, hexachlorethane.

It has been found that when subjecting an alloy constituted in accordance with the invention and containing about 0.5% copper, to a grain refining treatment with, for instance, hexachlorethane, the resulting casting will have an appreciably coarser grain than that of the same untreated copper containing alloy product. It is of advantage, therefore, to use either substantially copper-free alloys or alloys containing only up to about 0.1% copper for a grain refining treatment with, for instance, hexachlorethane or to use melts with about 0.5% copper without subjecting the same to a grain refining treatment.

The time required for the homogenization, i.e., the solution heat-treatment in accordance with the invention, may vary to a certain extent inasmuch as the obtaining of high strength values depends upon the effective solution of the intermetallic compound $Mg_xAl_yZn_z$, the relative greater or lesser coarseness or amount of which, as separated in the casting, is dependent upon the particular casting method. Important is that the solution heat treatment of the castings is carried out at final temperatures about from 415° to 425° C., for a period of time sufficient to assure the above specified minimum strength values after quenching and artificially aging the solution heat treated castings as herein set forth.

It is understood that by the conventional preheating in stages those components are substantially removed which could cause eutectic melting. The preheating in stages for the removal of the melting components which could cause eutectic melting include the substantially continuous and relatively slow heating from about 380° C. to the final heat treating temperature.

The following examples are furnished by way of illustration and not of limitation:

Example 1

The melt of a magnesium alloy with 8.5% aluminum, 1.5% zinc, and 0.2% manganese was subjected in conventional manner at 750° C. to a grain refining treatment with hexachlorethane (2 parts by weight hexachlorethane to 1,000 parts by weight of melt) whereupon the melt was permanent mould cast.

The castings were then heated in a conventional oven with revolving of circulating hot air by maintaining the same at first for 14 hours at about 380° C., then with increase of the temperature for about 10 hours at about 400° C., and finally with a further increase in temperature for 16 hours at about 420° C. The castings were then quenched from about 420° C. in water of about room temperature and were thereafter artificially aged

for about 10 hours at about 180° C. Thereafter the castings show the following strength values:

Tensile strength (σ_B)	kp./mm.^{2}	33.0
Yield strength ($\sigma_{0.2}$)	kp./mm.^{2}	24.0
Elongation (δ_5)	percent	3

Example 2

A melt of a magnesium alloy with 8.5% aluminum, 1.5% zinc, 0.5% copper, and 0.2% manganese was permanent mould cast at a temperature of about 750° C. without a preceding grain refining treatment.

The castings were then heated in the same air circulation oven described in Example 1 for 14 hours at about 380° C., for about 10 hours at about 400° C., and for about 16 hours at about 420° C., whereupon they were quenched from the 420° C. temperature in water of room temperature. The quenched castings were thereafter artificially aged for 10 hours at about 180° C.

The castings show the following strength values:

Tensile strength (σ_B)	kp./mm.^{2}	33.5
Yield strength ($\sigma_{0.2}$)	kp./mm.^{2}	24.5
Elongation (δ_5)	percent	4.5

Example 3

A melt of a magnesium alloy with 8.4% aluminum, 1.45% zinc, and 0.18% manganese was subjected at 750° C. to the same grain refining treatment set forth in Example 1 whereupon the melt was, for a short period of time, heated to 800° C., and then sand cast at about 750° C.

The castings were then treated in the same air circulation oven described in connection with the preceding examples by heating the same at first for about 8 hours at 380° C., then for about 15 hours at about 400° C., and finally for about 8 hours at 420° C., whereupon the castings were quenched in water of room temperature from the 420° C. After a then following aging for about 12 hours at about 180° C., the castings showed the following strength values:

Tensile strength (σ_B)	kp./mm.^{2}	35.0
Yield strength ($\sigma_{0.2}$)	kp./mm.^{2}	22.3
Elongation (δ_5)	percent	4.5

Example 4

Sand castings from the same melt obtained as set forth in accordance with Example 3 were initially heated as set forth in said Example 3 using the same temperatures and time intervals. The heated castings were then, however, first pre-cooled from 420° C. in the same air circulating oven, reducing the temperature of the oven to 380° C., and maintaining said temperature for about 2 hours, i.e., until the castings had obtained temperature equilibrium throughout over the whole cross-section at the temperature of 380° C. Thereafter the pre-cooled castings were quenched in water of room temperature from the 380° C. temperature and were then aged for about 12 hours at about 180° C. The castings then show the following strength values:

Tensile strength (σ_B)	kp./mm.^{2}	34.1
Yield strength ($\sigma_{0.2}$)	kp./mm.^{2}	21.9
Elongation (δ_5)	percent	4.5

Example 5

The heat treatment of the sand casting in accordance with Example 4 was modified in that the cast parts pre-cooled to 380° C. were not quenched in water of room temperature but rather in water of 100° C. whereby the following strength values were obtained:

Tensile strength (σ_B)	kp./mm.^{2}	30.9
Yield strength ($\sigma_{0.2}$)	kp./mm.^{2}	21.3
Elongation (δ_5)	percent	4.0

Example 6

Sand castings from the same melt as described in accordance with Example 3 were initially heated for about 8 hours at about 380° C., for about 15 hours at about 400° C., and for about 16 hours at about 420° C. whereupon they were quenched in air of room temperature and were finally aged for about 13 hours at about 180° C. The resulting castings show the following strength values:

Tensile strength (σ_B)	kp./mm.^{2}	30.0
Yield strength ($\sigma_{0.2}$)	kp./mm.^{2}	21.2
Elongation (δ_5)	percent	3.0

The strength values of the heat-treated castings obtained in accordance with the invention and composed of the specific narrow range magnesium-aluminum-zinc alloys herein specified are unexpected and surprising. This is especially so in view of the fact that these values are not obtainable except for the specific combination of the particular alloy and range of components herein specified and the particular conditions of full heat treatment herein set forth. As above pointed out, it has not been previously recognized that by substantially eliminating the casting separated intermetallic compound $Mg_xAl_yZn_z$ ordinarily present in heat-treated castings of magnesium alloys of similar composition to those covered in the instant invention and treated in accordance with conventional heat treating procedures, a very appreciable increase in strength characteristics was obtainable. The extent to which the specific combination of materials and composition and thus the substantial removal of the intermetallic compound $Mg_xAl_yZn_z$ is critical is evident from the following further examples:

Example 7

In accordance with a USA-Norm published in "Metals Handbook," 8th edition, 1961, vol. 1, page 1099, Table IV, castings of the magnesium alloy AZ92 with 8.3 to 9.7% aluminum, 1.6 to 2.4% zinc, and at least 0.10% manganese are subjected to a heat treatment consisting in heating the castings for 20 hours at 404° C., thereafter quenching the same in air and finally aging them for 14 hours at 216° C.

When taking, for example, the alloy composition in accordance with the invention, as illustrated in Examples 3–6 above and which corresponds substantially to an above identified magnesium AZ92 alloy, and subjecting the same to the heating, quenching, and aging specified for said magnesium AZ92 alloy, the following strength values are obtained:

Tensile strength (σ_B)	kp./mm.^{2}	22.3
Yield strength ($\sigma_{0.2}$)	kp./mm.^{2}	17.9
Elongation (δ_5)	percent	1.5

These values do not reach the minimum values obtainable even under adverse conditions in accordance with the invention. In comparison with the values obtained when proceeding in accordance with the invention as set forth in Examples 3–6, the superior results are clearly evident.

Even if the experiment, using the treating conditions specified in said USA-Norm are modified by quenching from 404° C. temperature not in air but in water of 20° C., the strength values are not sufficiently improved. These values are as follows:

Tensile strength (σ_B)	kp./mm.^{2}	25.0
Yield strength ($\sigma_{0.2}$)	kp./mm.^{2}	18.4
Elongation (δ_5)	percent	2.7

Example 8

In accordance with another published report in "A Series of 5 Educational Lectures on Magnesium Presented to Members of the A.S.M. during the 27th National Metal Congress and Exposition, Cleveland, February 4 to 8, 1946, page 78" (copyright 1946 by Amer-

ican Society for Metals, Cleveland, Ohio) a similar magnesium alloy composition identified by the trademark "Dowmetal C" and consisting of 8.3 to 9.7% aluminum, 1.7 to 2.3% zinc and at least 0.10% manganese was heat treated by heating the castings in a period of 2 hours from a temperature of 260° C. to a temperature of 404° C. and maintaining the latter temperature for a further 18 hours, thereafter quenching the same in air and finally aging the same for 10 hours at 216° C.

When taking castings of melts represented by the above Examples 3–6 and subjecting the same to the solution heat treatment, quenching, and aging just described in connection with said "Dowmetal C," the following strength values are obtained:

Tensile strength (σ_B)	kp./mm.^{2}	25.8
Yield strength ($\sigma_{0.2}$)	kp./mm.^{2}	18.9
Elongation (δ_5)	percent	2.0

Again comparison with the values obtained in accordance with the invention and proceeding as specified in Examples 3–6 shows the superior results residing in the product obtained when proceeding in accordance with the invention.

When repeating the experiment using the solution heat treating, quenching, and aging procedure specified in this example, except that in lieu of air quenching, there is practiced quenching in water at room temperature, no appreciable and significant increase in strength values is obtained.

Example 9

Using the same castings and solution heat treatment as specified in Example 8, but continuing the solution heat treatment in accordance with the invention for a further 16 hours at about 420° C., quenching in water and aging for about 13 hours at about 180° C., the following strength values are obtained:

Tensile strength (σ_B)	kp./mm.^{2}	34.2
Yield strength ($\sigma_{0.2}$)	kp./mm.^{2}	23.3
Elongation (δ_5)	percent	3.3

Thus, the additional heating for about 16 hours at about 420° C. substantially dissolved or homogenized the casting separated intermetallic compound to a sufficient extent to give the high strength values in accordance with the invention.

For the conventional preheating below 415° C. by which the removal of low melting components is obtained, it is desirable to have at least one and preferably at least two lower temperature heating stages for the solution heat treatment before the ultimate final highest heating temperature in accordance with the invention is applied. The duration and specific temperatures for the lower stage heating will, to some extent, determine the duration for the highest temperature heating stage in accordance with the invention. Inasmuch as it may be desirable to confine the duration of the heating at the highest temperature as much as possible, it may be of advantage to accordingly select the lowest and/or intermediate temperature stage or stages to a duration that good results are still obtainable in accordance with the invention while yet holding the highest temperature stage of the solution heating to a minimum of duration. These values may be readily determined empirically by subjecting a few test pieces of castings to a few test runs involving initial heating at various temperatures and/or durations using substantially fixed quenching and aging treatments and physically inspecting the resulting products by microscopic examination of etched and polished cuts obtained in conventional manner, thereby permitting to select that combination of initial solution heat treatment below 415° C. and final solution heat treatment above 415° C. in accordance with the invention, which is economically or otherwise the most advantageous while yet resulting in that removal of the intermetallic casting separated compound $Mg_xAl_yZn_z$ giving at least the minimum or higher strength values obtainable in accordance with the invention after the subsequent quenching and aging.

A typical exemplification of the casting derived intermetallic compound $Mg_xAl_yZn_z$ ordinarily present in castings as cast or heat treated in accordance with conventional methods is illustrated by the accompanying photomicrograph, FIG. 1 having a magnification of 160 and in which the arrows point to some of the readily identifiable separations from the otherwise substantially uniform structure of the alloy matrix. This photomicrograph is that of a sectional cut conventionally etched and polished of the alloy of Example 8 heat treated in conventional manner. The areas appearing as black spots in the photomicrograph represent manganese and are of no importance.

The photomicrograph represented in the accompanying drawing as FIG. 2 and having a magnification of 160 shows an etched and polished cut of the same alloy treated in Example 8 but subjected to the final heat treating conditions at 420° C. in accordance with the invention as set forth in Example 9. The relatively coarse deposits of intermetallic compound ordinarily present in the conventionally treated product as exemplified by the photomicrograph of FIG. 1 are completely absent in the sample represented by the photomicrograph of FIG. 2.

I claim:

1. A heat treated casting of a magnesium alloy of the type MgAlZn consisting by weight substantially of 8.3 to 8.7% aluminum, 1.4 to 1.6% zinc, 0 to 0.3% manganese, 0 to 0.7% copper, and the balance magnesium and having substantially the following order of magnitude minimum strength values:

Tensile strength	kp./mm.^{2}	30
Yield strength	kp./mm.^{2}	19
Elongation	percent	3

2. A casting according to claim 1 in which said casting is substantially free from separately identifiable intermetallic compound between magnesium, aluminum, and zinc.

3. In the method of preparing heat treated castings of a magnesium alloy of the type MgAlZn which method includes a solution heat treatment about from 380° C. to below 415° C., quenching, and artificially aging, the improvement which comprises selecting an alloy substantially consisting by weight of 8.3 to 8.7% aluminum, 1.4 to 1.6% zinc, 0 to 0.3% manganese, 0 to 0.7% copper and the balance magnesium and subjecting the same after said solution heat treatment below 415° C. and prior to quenching to a further solution heat treatment at a temperature of the order of about 415° C. to 425° C. for a time sufficient to obtain for the finished casting substantially the following order of magnitude minimum strength values:

Tensile strength	kp./mm.^{2}	30
Yield strength	kp./mm.^{2}	19
Elongation	percent	3

4. The improvement in accordance with claim 3 in which said further solution heat treatment is carried out at a temperature from about 418° C. to 422° C.

5. The improvement according to claim 3 in which the quenching is carried out to a temperature from about 20° C. to 120° C. and in which the aging of the quenched castings is effected at from about 170° C. to about 190° C.

6. The improvement according to claim 5 in which the quenching material is a liquid quenching agent.

7. The improvement according to claim 5 in which the quenching agent is a gaseous quenching agent.

8. The improvement according to claim 3 in which the solution heat treatment below 415° C. is carried out for at least about 5 to 8 hours at about 380° C. followed by at least about 5 to 8 hours at about 400° C. and in which said solution heat treatment of at least 415° C.

is carried out for at least 8 hours at about 418° to 422° C., in which the quenching is carried out to a temperature from about 20° C. to about 120° C. and in which the aging is effected at from about 170° C. to about 190° C.

9. The improvement according to claim **8** in which said aging is carried out from about 8 to 20 hours at about 175° to 185° C.

10. The improvement according to claim **3** in which the quenching is preceded by a pre-cooling of the castings from the final solution heat treatment temperature to a temperature within the range from about 380° C. to about 395° C. to give the solution heat treated castings a substantially uniform temperature and in which the quenching is effected from said last mentioned temperature.

11. The improvement according to claim **10** in which the quenching material is a liquid quenching agent of the type of water and oil.

12. The improvement according to claim **10** in which the quenching material is a gaseous quenching agent.

13. The improvement according to claim **10** in which the aging of the quenched castings is effected at from about 170° C. to about 190° C.

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DAVID L. RECK, *Primary Examiner.*

C. N. LOVELL, *Assistant Examiner.*