

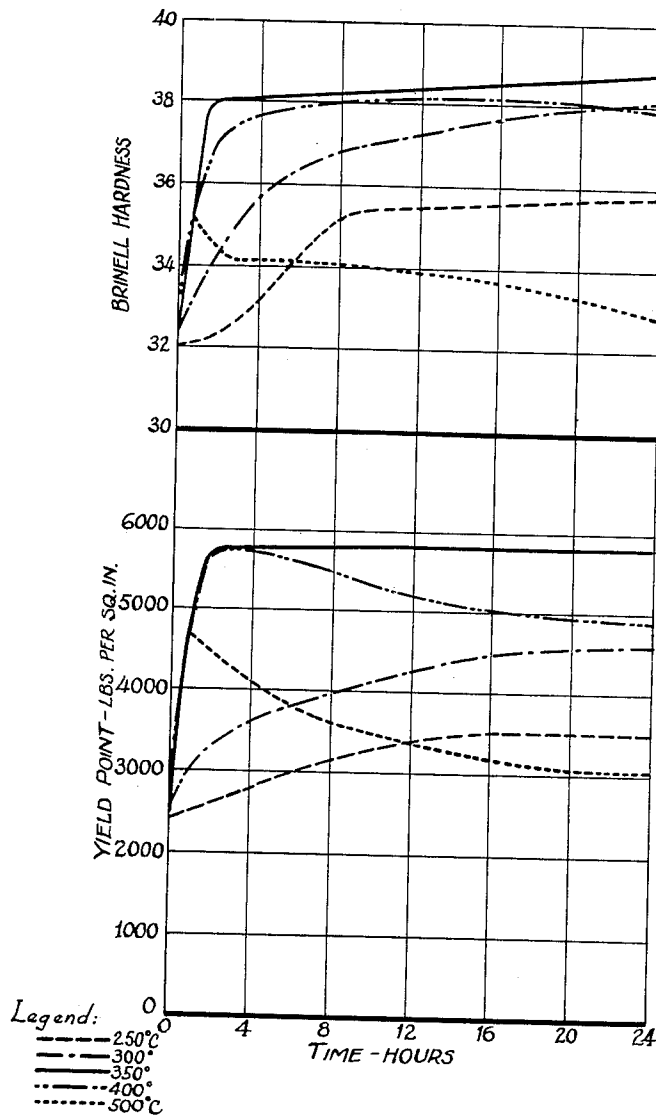
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HEAT TREATING MAGNESIUM BASE ALLOYS

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## HEAT TREATING MAGNESIUM BASE ALLOYS

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The present invention, relating as indicated, to the treatment of light metal alloys, has more particular regard to the treatment of alloys in which magnesium is the predominant constituent. The specific alloys involved are magnesium-manganese alloys wherein the manganese may be the only metal alloyed with magnesium or may be only one of the metals alloyed therewith. It is known that articles made from magnesium alloys, wherein the magnesium constitutes 80 per cent and upwards of the total, possess valuable characteristics when in the form of cast articles or the like. The corrosion resistance of binary magnesium-manganese alloys is the best that has been obtained with magnesium alloys, and moreover the workability of this alloy makes it highly desirable for many uses. The binary magnesium-manganese alloys in cast form, however, have a relatively low yield point and a somewhat lower hardness than most of the commercial magnesium alloys. These disadvantages have to a certain extent limited the commercial use of the alloys in question. At this time it was known that castings made from magnesium-manganese alloys contained manganese in solid solution. If some of this manganese were present in solid solution in excess of its equilibrium solubility, it appeared to us that part or all of such excess might be precipitated by heat treating, and advantageously affect the properties of the alloy article treated. Accordingly, we heat treated some high percentage manganese alloys for 24 hours at various temperatures, for example 150° and 200° C., according to the conventional precipitation practice for heat treating magnesium-aluminum and magnesium-zinc alloys. Hardness and yield point tests on the alloys heat treated at 150° and 200° C. showed that there was apparently no precipitation of manganese at these temperatures, there being no property change at 150° C. and the improvement made, if any, at 200° C. was within the limits of experimental error. We have, however, found that manganese can be precipitated and that the temperature for its precipitation in magnesium-manganese alloys is unexpectedly high, in fact it is even above the maximum solution heat treatment temperature for binary magnesium-zinc alloys. We have further discovered that a magnesium alloy containing not only manganese in solid solution in excess of its equilibrium solubility, but another metal capable of going into solution, may be heat treated so as to simultaneously precipitate the manganese and cause the other metal to pass into solution. As a result of the foregoing discoveries, it is no longer necessary to be limited to having the manganese present in the casting or like article in solution in excess of its equilibrium solubility, but much better properties can be obtained by precipitating

part or all of such excess manganese by a suitable heat treatment.

Having regard to the accomplishment of the foregoing and related ends, the invention, then, consists of the steps and product hereinafter fully described and particularly pointed out in the claims, the annexed drawing and the following description setting forth but several of the various ways in which the principle of the invention may be used.

In said annexed drawing:—

The figure is a diagram illustrating the changes in yield point and hardness of a binary magnesium-manganese alloy during heat treatment at different temperatures over varying periods of time according to our method or process.

As indicated above, the present improved process has to do with light metal alloys in which magnesium is the predominant ingredient. The alloy must furthermore have manganese present in solid solution in excess of its equilibrium solubility at normal temperatures, i. e., in excess of about 0.5 per cent. In addition to manganese, the alloy may contain other metals, part of which may or may not be capable of being dissolved in the alloy or otherwise changed in state by solution heat treatment at the precipitation heat treatment temperature for manganese. The placing of such material in solution in the alloy or otherwise changing its state simultaneously with the precipitation of manganese therein is accordingly one phase of the present invention. What we accomplish by our present improved process is to regulate the length of time and temperature of heat treatment of such an alloy so that the desired amount of precipitation of manganese as such takes place with resulting increase in hardness and yield point, and, where other ingredients are also present that are capable of beneficial change of state at the temperature range involved, the temperature and duration of heat treatment can be so regulated that both beneficial effects are simultaneously obtained. While in the drawing we have illustrated the effect of precipitation heat treatment on a binary magnesium-manganese alloy, it will be understood that the process may be advantageously applied to more complex magnesium alloys having manganese present in solid solution in excess of its equilibrium solubility, and that part of the other constituents may be simultaneously changed in state, during the precipitation of manganese, to affect the properties of the alloy.

The principle involved in this regulated heat treatment is very well illustrated by such magnesium-manganese alloys. Thus referring to the figure, which deals with the precipitation heat treatment of a binary magnesium-1.4% manganese alloy (contains 1.4% manganese) at different temperatures for periods of time up to 24

hours, it will be seen that the yield point and Brinell hardness of the alloy at any given temperature of heat treatment tend to follow in general a somewhat parallel change. In other words, the rate of increase or decrease in hardness is quite closely followed by a corresponding increase or decrease in yield point. Referring more particularly to the yield point and hardness curves for the precipitation heat treatment at 250° C., it will be seen that the hardness increases fairly rapidly for approximately 8 hours and then increases very slowly up to 24 hours. The yield point, on the other hand, increases at a uniform rate up to about 16 hours, at which point further heating at the same temperature has practically no effect. In order to avoid any confusion as to what is meant by the term "yield point" in connection with magnesium alloys, it is to be noted that it is commonly defined as the load at which the stress-strain curve has deviated 0.1% elongation from the true modulus line (Young's Modulus for magnesium alloys is 6,500,000 pounds per sq. in.) and the term "yield point" as used herein is to be understood to conform to that definition. Referring next to the curves representing precipitation heat treatment at 300° C., it is to be noted that the yield point and hardness attained at the end of 24 hours is much higher than was the case where 250° C. was employed, and that there was very little change in the yield point after 16 hours had elapsed. However, during the first 16 hours the yield point had increased from 2500 to 4500 pounds per sq. in., in other words, the yield point had almost doubled. The Brinell hardness also was much higher than in the case of the 250° C. treatment for the same time. The 350° C. precipitation heat treatment, on the other hand, shows that the hardness and the yield point came up quickly and reached a condition of substantially uniform high properties at the end of 2 hours. Further heating at the same temperature had practically no effect on the yield point and but very slight hardening effect. Now referring to the 400° C. curves, it will be seen that the hardness and yield point rise to a maximum point in about 2 to 4 hours, following which the hardness remains substantially constant. The yield point, however, gradually falls back which indicates that the best temperature for precipitation heat treatment of these alloys has been passed. At this point it is well to note that at low temperatures of precipitation heat treatment indications are that the maximum properties possible to attain by heat treating such an alloy can be obtained only after long periods of time. On the other hand, at temperatures approximating 350° C. the maximum properties attainable are quickly reached and upon further heating there is substantially no change in the yield point and hardness of the alloy. When higher temperatures, for instance 400° C. and above, are employed, the hardness and yield point quickly rise to a maximum lower than that at 350° C. and then tend to decrease. This condition is more and more noticeable as the temperature at which the heat treating takes place is raised. Referring more particularly to the 500° C. curve, as compared with the 400° C. curve, the entire curve will be seen to rise to a maximum quickly and then fall away so that at the end of 24 hours the properties are but little better than those present in the casting before heat treatment. Theoretically, the cause for this is that for each temperature of heat treatment there is a definite size to which the particles of manganese precipitated can coalesce. Where the heat treating temperature is increased to a point above the optimum, the size to which the particles can grow is relatively large, in fact, so large that part or all of the advantages of the precipitation heat treatment may be lost. In this connection, it is to be noted that apparently the precipitated particles are elemental manganese and not a magnesium-manganese compound. It is to be understood, of course, that this is only an attempt to explain what happens during the heat treatment and we accordingly do not wish to be limited thereby. By reference to the curves, it is to be noted that a satisfactory range of operation for precipitation heat treatment of the alloys in question will be from 250° to 500° C. At the lower temperature the treatment will, of course, have to be carried out for a relatively long time to reach the desired properties, while at 500° C. the heat treatment period should be short in order to avoid loss in properties. A more desirable range for operation is between 300° and 400° C., while the preferred temperature to be used is approximately 350° C. For example, the heat treatment of a magnesium-1.4% manganese alloy for 2 hours at 350° C. raised its yield point from 2500 to 6200 pounds per sq. in. and simultaneously increased its Brinell hardness from 32 to 38. These improvements in properties together with the high corrosion resistance of the alloy make it highly desirable for extensive commercial use. The heat treating period, however, can go as high as 40 hours or more for all except the high temperatures whereat loss of properties occurs if the heat treatment is carried out for too long a time. On the other hand, a heat treating period as low as one hour can be used satisfactorily to increase the properties of these alloys except for the low temperatures of heat treatment where the improvement would be slight. The range of time for the heat treatment that will meet most requirements will be from 1 to 16 hours, while the preferred time of the optimum temperature of 350° C. will be approximately 2 to 4 hours. Heat treatment at temperatures and times outside of these ranges where beneficial results of the type described are attained are to be considered as falling within the scope of the present invention.

From the above it is to be noted that the general principle involved is that a magnesium alloy containing manganese in solid solution in excess of its equilibrium solubility at ordinary temperatures can be given a precipitation heat treatment to improve its yield point and hardness. This precipitation of manganese is substantiated by microstructural changes and by an increase in electrical conductivity. The same condition holds whether manganese is the only metal alloyed with magnesium or whether it is only one of several present in the alloy so long as it is present in solid solution in excess of its equilibrium solubility. The precipitation of manganese is not limited to the treatment of castings to obtain beneficial results but may be used with wrought metal or the metal may be given the precipitation heat treatment and then worked if desired. At this point it is well to state that where a given magnesium alloy is heat treated so as to increase its hardness, the yield point of that alloy in general increases at somewhat the same rate. Accordingly, in the following examples dealing with magnesium-cadmium-manganese alloys and magnesium-copper-manganese alloys, hardness alone will be given since this is a sat-

isfactory indicator for showing not only increase in hardness, but increase in yield point. An alloy consisting of magnesium-3% cadmium-1.4% manganese and having an initial Brinell hardness of 34 in the "as cast" state was heated for 24 hours at 350° C. which increased its hardness to 40. Since cadmium is perfectly soluble in magnesium and has substantially no effect upon the hardness and yield point of the binary alloy when heat treated, it is to be seen that the improvement in properties of the alloy was due to the precipitation of manganese even though another metal perfectly soluble in the magnesium was present. This was further borne out by heat treating a magnesium-10% cadmium-1.2% manganese alloy for 24 hours at 350° C. which raised the Brinell hardness from 34 to 41. On the other hand, copper is almost insoluble in magnesium. Tests on alloys containing this metal indicated that the same principle held with them as it did for the binary magnesium-manganese alloys. For instance, a magnesium-1% copper-1.5% manganese alloy having a Brinell hardness of 37 in the "as cast" condition was heat treated 24 hours at 350° C. which increased its hardness to 40. In general copper tends to spheroidize or globularize upon heat treatment, which condition, if anything, tends to soften the alloy slightly rather than harden it. Accordingly, the hardening effect due to the precipitation of the manganese may have been even greater than was indicated, because of the possibility that it had to overcome the softening tendency due to the spheroidizing of the copper during the heat treatment.

A still different situation arises where a metal is alloyed with magnesium and manganese that can be placed in solution at the same temperature that the precipitation of manganese takes place. One such metal is zinc which forms an eutectic with magnesium having a melting point of 344° C. In order to set forth clearly the situation involved, reference is made to the following table which is based on the average results of a number of tests, the same as the curves and all other examples given herein.

| Property                      | Mg-1.5% Mn |                                       | Mg-3.5% Zn |                                  | Mg-3% Zn-1.5% Mn |                                 |
|-------------------------------|------------|---------------------------------------|------------|----------------------------------|------------------|---------------------------------|
|                               | As cast    | Precipitation H.T. 24 hrs. at 300° C. | As cast    | Solution H.T. 16 hrs. at 320° C. | As cast          | Heat treated 24 hrs. at 320° C. |
| Tensile strength, lb./sq. in. | 19,000     | 19,000                                | 27,000     | 28,000                           | 26,000           | 26,000                          |
| Yield point, lb./sq. in.      | 3,200      | 6,400                                 | 5,800      | 6,200                            | 5,500            | 7,800                           |
| Brinell hardness              | 34         | 44                                    | 42         | 42                               | 37               | 42                              |

Referring to the magnesium-1.5% manganese alloy in the "as cast" and heat treated condition, it will be noted that the yield point was doubled by heat treating it for 24 hours at 300° C. The Brinell hardness at the same time increased from 34 to 44. These properties are very important where relatively high strength commercial alloys are desired. It is further to be noted that the precipitation took place at 300° C. which will give a lower yield point than would the same period of heat treatment at 350° C., as shown by comparison of the 300° and 350° C. yield point curves on Fig. 1. Referring now to the magnesium-3.5% zinc alloy, as shown in the above table, it will be seen that the solution heat treatment

of this alloy for a period of 16 hours at 320° C. had no effect on hardness and a very small effect on yield point. This shows that, if an alloy containing magnesium, zinc, and manganese, having approximately the same amount of zinc as shown in the binary alloy, were heat treated below 344° C. practically no effect on properties could be expected from the zinc. With this in mind reference is now made to the magnesium-3% zinc-1.5% manganese alloy, as shown in the above table. The heat treatment of this alloy for 24 hours at 320° C. increased the yield point from 5500 to 7800 and at the same time increased the Brinell hardness of the alloy from 37 to 42. It is thus to be seen that the precipitation of the manganese not only hardened the alloy, but had a decided effect on increasing its yield point. The hardness and yield point of the thus heat treated magnesium-zinc-manganese alloy can be further increased in appreciable amount by further heat treating at a temperature of approximately 150° to 200° C. for 8 hours or more to precipitate part or all of the zinc held in solid solution in excess of its equilibrium solubility. This shows that the precipitation of manganese can be simultaneously accomplished to advantage with the solution heat treatment of another metal in the alloy where such other metal is capable of solution heat treatment at the precipitation temperatures for manganese. It will accordingly be seen that the results of heat treatment of the magnesium-zinc-manganese alloy also bear out our discovery that, where manganese is present in solid solution in excess of its equilibrium solubility, part or all of that excess can be precipitated regardless of whether the manganese is the only ingredient alloyed with magnesium or whether other ingredients are also present.

Binary magnesium-manganese alloys present the greatest resistance to corrosion of any magnesium alloy known at this time, and the use of manganese as an ingredient in magnesium alloys containing other metal or metals also aids in increasing their resistance to corrosion. However, the relatively low yield point and Brinell hardness has heretofore acted to prevent the more general commercial use of the binary magnesium-manganese alloys. Accordingly, casting alloys having good properties, such as Dowmetal "E", which is a magnesium-6% aluminum-20% manganese alloy, have been commonly used for miscellaneous commercial work in spite of their lower corrosion resistance. According to our present invention the binary magnesium-manganese alloys can be given a precipitation heat treatment which will raise their yield point and Brinell hardness to a point closely approaching that of the now commonly used casting alloys, and at the same time such heat treated alloy will have a better corrosion resistance than any magnesium alloy now in commercial use. The comparative properties of these alloys are set forth in the following table:—

|                           | Dowmetal "E" as cast | Mg-1.5% Mn prec. H.T. 24 hrs. at 300° C. |
|---------------------------|----------------------|------------------------------------------|
| Yield point.....          | 7,800                | 6,400                                    |
| Brinell hardness.....     | 47                   | 44                                       |
| Corrosion resistance..... | Good.                | The best.                                |

From the above table and comments, it is to be noted that we have not only devised an entirely new method and procedure for heat treating al-

loys containing manganese in solid solution in excess of 0.5 per cent of manganese in solid solution, comprising subjecting such alloy to a heat treatment at a temperature between 250° and 500° C.

5 alloy.

While we have described our invention as starting with an "as cast" magnesium alloy containing manganese in solid solution in excess of its solid solubility, we do not wish to be limited to the precipitation heat treatment of castings in the "as cast" form, since such castings or articles made therefrom in some cases may be better prepared for the precipitation heat treatment by giving them a solution heat treatment at a temperature above the precipitation heat treatment range, but below the melting point of the alloy. The alloy should preferably contain approximately one-half of one per cent manganese or more, whereas best results are obtained when the alloy contains more than one per cent of manganese. While we have described the precipitation heat treatment as being carried out by heating the article to the desired precipitation temperature and holding it there until the precipitation is partially or wholly completed, we do not wish to be limited to that exact procedure since the cooling of the casting after pouring or after solution heat treatment can be artificially retarded in a suitable furnace or the like so as to give sufficient time for the precipitation to take place, and such procedure is to be considered as one phase of the present invention.

Other forms may be employed embodying the features of our invention instead of those explained, change being made in the method and form of construction, provided the elements or steps stated by any of the following claims or the equivalent of such stated elements or steps be employed, whether produced by our preferred method or by others embodying steps equivalent to those stated in the following claims.

We therefore particularly point out and distinctly claim as our invention:—

1. The process of improving the properties of a magnesium-manganese alloy in which magnesium largely predominates and which contains in

2. The process of improving the properties of a magnesium-manganese alloy in which magnesium largely predominates and which contains in excess of 0.5 per cent of manganese in solid solution, comprising maintaining such alloy at a temperature between 300° and 400° C., for from two to four hours.

3. The process of heat treating a magnesium base alloy having a manganese content of more than 0.5 per cent in solid solution and also containing a minor proportion of at least one additional metallic constituent from the group consisting of cadmium, copper and zinc, which comprises maintaining such alloy at a temperature above 250° C. but below the melting point of the most fusible constituent thereof for a period of time to cause precipitation of manganese.

4. The process of heat treating a magnesium base alloy having a manganese content of more than 0.5 per cent in solid solution and also containing a minor proportion of zinc capable of going into solid solution in the alloy, which comprises maintaining the alloy at a temperature above 250° C. but below the melting point of the zinc-containing eutectic for a period of time to cause precipitation of manganese and solution of zinc.

5. The process of heat treating a magnesium base alloy having a permanent manganese content of more than 0.5 per cent in solid solution and also containing a minor proportion of zinc capable of going into solid solution in the alloy, which comprises maintaining the alloy at a temperature above 250° C. but below the melting point of the zinc-containing eutectic for a period of time to cause precipitation of manganese and solution of zinc, and then further heat treating by maintaining the alloy at a temperature between approximately 150° and 200° C. for a period of time to cause precipitation of zinc.

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