

Dec. 7, 1971

H. JONES

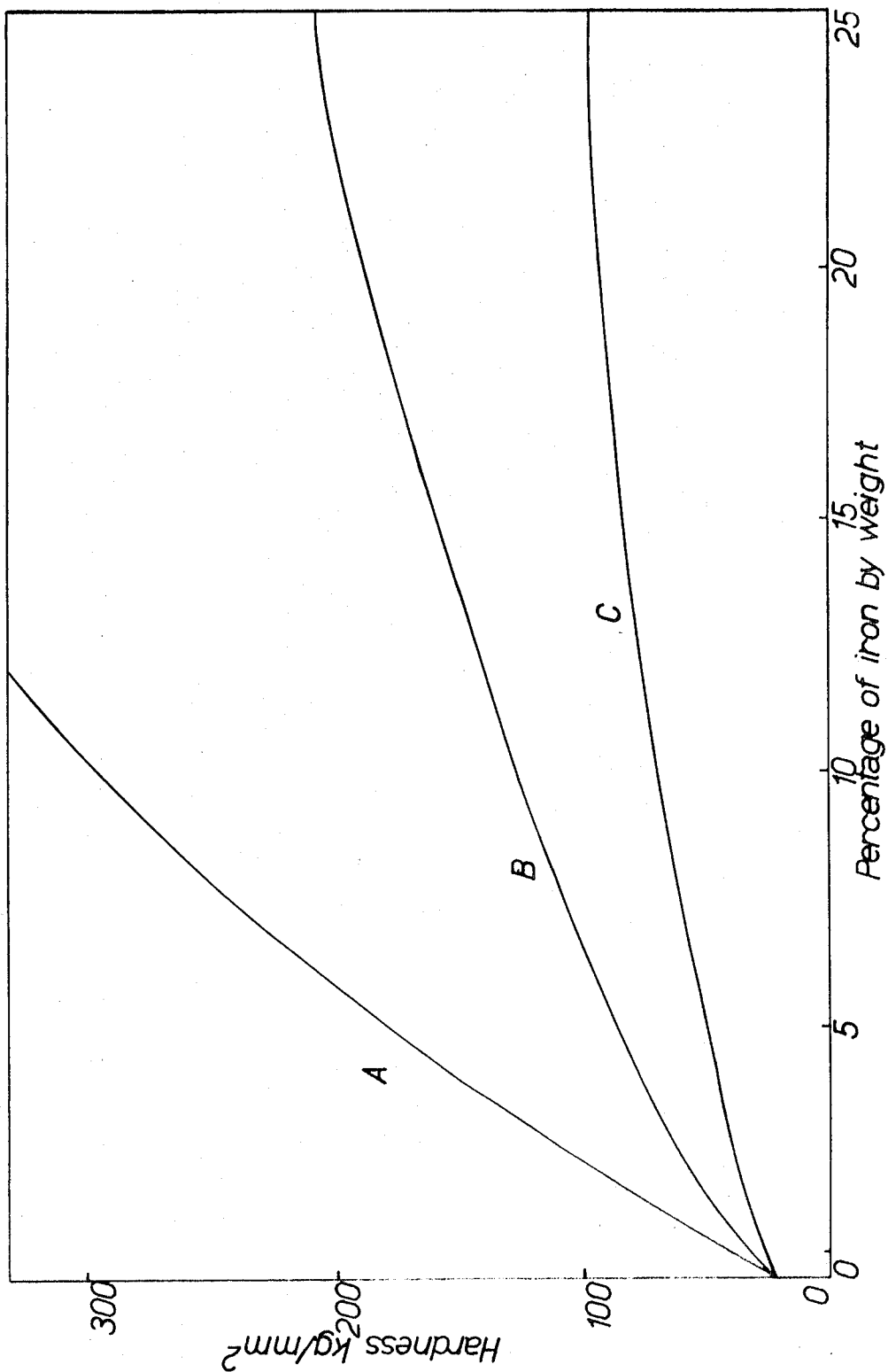
3,625,677

ALUMINIUM ALLOYS

Filed Dec. 26, 1968

2 Sheets-Sheet 1

FIG. 1



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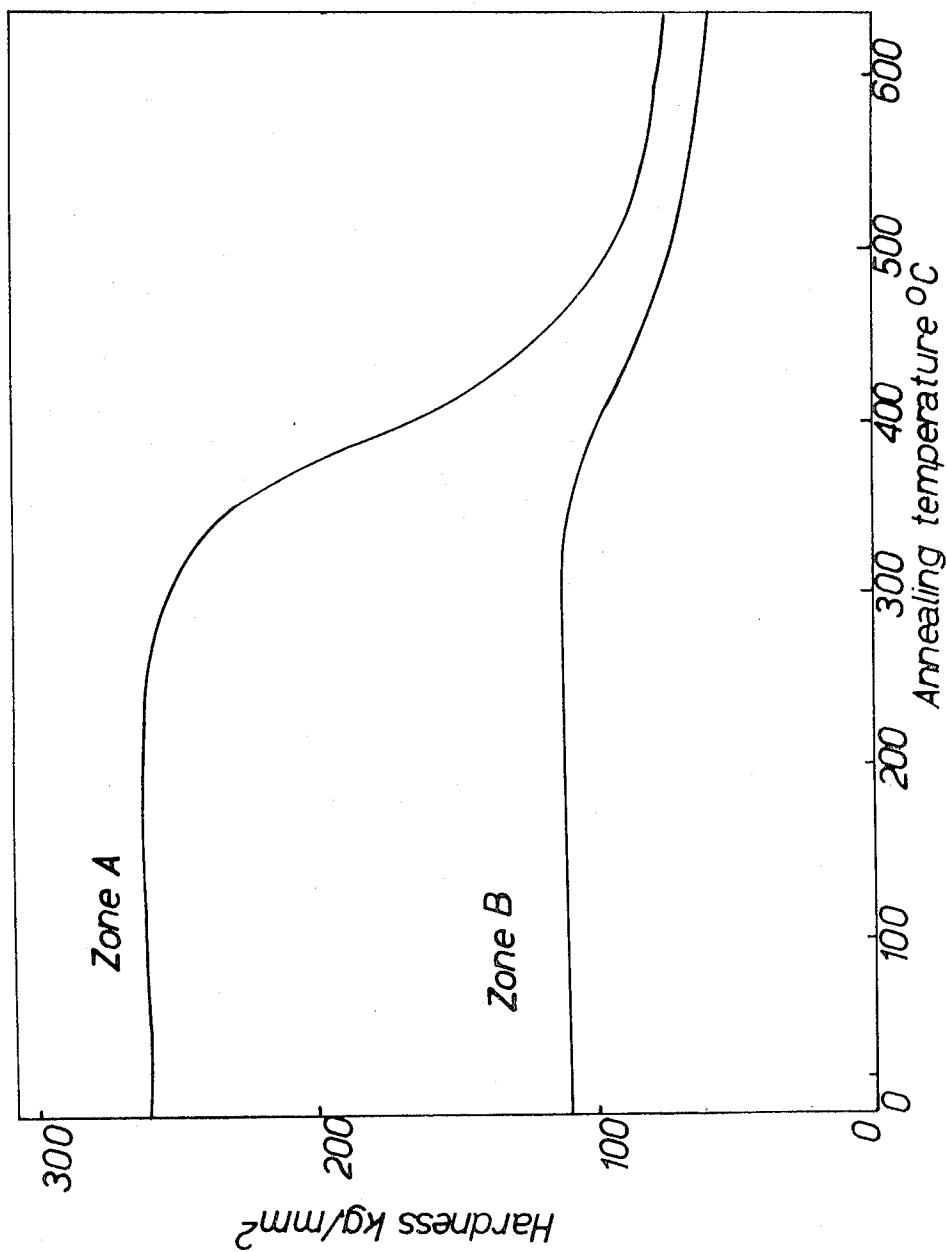
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ALUMINIUM ALLOYS

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FIG. 2



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ALUMINUM ALLOYS

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4 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a range of aluminium alloys, and methods of preparing them. The materials are primarily binary alloys in which the minor constituent is iron, although a third constituent may be present, or even more, apart from impurities, without departing from the scope of the invention and the second constituent may be elements other than iron but having a similar effect, as will be further explained later.

Previous research has covered a wide range of iron-aluminium alloys, both those with the iron predominating and those with the aluminium predominating. One alloy investigated has been that containing 7.6 weight percent of iron, the balance being aluminium. Towner has shown (Metal Progress, 1958, Vol. 73 (5), page 70 ff.) that certain aluminium-transition metal alloys, fabricated from atomised alloy powder can retain their strength up to 400° C., with ductility increasing with increasing temperature. The strength was dependent on the dispersion, on a sub-micron scale, of hard intermetallic particles derived from within each atomised drop. The enhanced stability, as compared with conventional precipitation-hardened aluminium alloys, was attributed to the low solubility and low diffusion coefficient of iron and certain other transition metals in aluminium, which inhibits coarsening of precipitated intermetallic particles, and to the characteristically high softening temperatures of aluminium-transition metal compounds in general. It was appreciated that the refinement of the inter-metallic dispersion was dependent upon a high cooling rate and rapid solidification achieved by the air quenching of the atomised particles.

Work has been done ("Aluminium" 31, Jahrg. 1955, No. 2, pages 51 to 55) on the rapid cooling of aluminium alloys, including aluminium/iron alloys over a range of 1 to 7% of iron but without finding any unexpected structures.

The aim of the present invention is to obtain a still further improvement in the properties of such aluminium alloys. According to the invention we propose to produce an aluminium-rich alloy of enhanced properties of aluminium with iron or another transition element by cooling extremely rapidly from the liquid phase, the cooling being at a rate which is on a different scale from that hitherto applied to such alloys. Our experiments have revealed that, provided the rate of cooling or solidification is kept above a critical value, the resulting structure is of totally different and readily distinguishable form from that obtained from normal rapid cooling.

The value of the minimum critical rate of cooling required in order to obtain the novel structure cannot be defined quantitatively, firstly because it is difficult to meas-

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ure the high cooling rates involved with any degree of accuracy and secondly because the critical value will, in any case depend on the nature of the transitional element constituent and on the proportion of it present. However, we can say with reasonable confidence that the cooling rate must exceed a value between 10^6 and 10^7 , degrees centigrade per second. The best way of ascertaining whether the desired rate has been attained is by examination and testing of the resulting material. The finer and harder grain structure formed in accordance with the invention is readily distinguishable under the microscope from the normal quenched material.

The required extremely rapid rate of cooling from the liquid phase can best be attained by employing the known technique of "splat" cooling, to be described later.

The invention will now be further described with reference to the accompanying drawings in which:

FIG. 1 is a graph showing the relationship between the hardness and the composition of the different structures obtained by rapid quenching and, for comparison, by chill casting.

FIG. 2 is a graph showing how the hardness varies with the annealing temperature for the different zones.

As indicated above, the heart of the invention lies in cooling specific materials at such an exceptionally high rate that a new and hitherto unobtained solid structure is obtained having desired properties. The materials are aluminium alloys containing predominantly aluminium with a limited percentage of a transition metal, i.e. a metal forming one of the transition elements in the Periodic Table, this metal further being characterised by having a very low solid solubility in aluminium. The first choice is iron, which has a maximum solid solubility in aluminium of about 0.05%. Cobalt and nickel may be used, and other possible metals include zirconium, niobium, molybdenum, tantalum and tungsten. The necessary exceptional rate of cooling can be achieved in one of a number of known ways, or by methods not yet known.

The chief known method by which the cooling rate can be achieved is that of "splat" cooling, in which the molten material is thrown in small quantities, of the order of a few milligrams at a time, at high velocity obliquely against a cold surface of good thermal conductivity. Such a process is described at pages 362 to 364 of volume 227 (April 1963) of the Transactions of Metallurgical Society of AIME. The method is further discussed and a modification disclosed at pages 1581, 1586 of volume 233 (August 1965) of the same publication. A shock-wave produced by gas pressure causing sudden rupturing of a diaphragm or the use of an explosive propels a slug of the molten material almost tangentially against a concave copper strip, so that the material impinging on the strip spreads along it in the form of a foil which is very thin (from less than one to fifty microns thick) and is rapidly cooled by conduction to the copper. By such a technique a cooling rate of up to 10^8 degrees centigrade per second is attainable. A continuous technique which is more practical for commercial use involves forcing the molten material by gas pressure downwards through a capillary orifice in the base of a stationary reservoir from which it falls into a small crucible which is rapidly spinning about a vertical axis. It is flung centrifugally from the rim of the crucible onto a surrounding cooled cylindrical copper wall, making impact while still liquid. The resulting flakes of rapidly solidified material forming on this wall fall

under gravity to be collected at the foot of the wall. Other continuous techniques to achieve the same result would include other methods of spraying liquid alloy on to a stationary or moving substrate. Conventional or plasma jet spraying could be used, in such a way as to ensure that solidification did not occur prior to impact with the substrate, which could be a rotating wheel or drum or a travelling belt and would normally be continuously cooled.

Another possible technique similar to the "splat" technique is that disclosed in British patent specification 1,067,657 (German B 81854 VIa/40b) in which the metal is suspended in a molten state and then suddenly dropped and flattened between two converging flat metal plates of high thermal conductivity.

Although these techniques are known in themselves they have not hitherto been used to obtain the new structure which forms the subject of the present invention and which is distinguished by a much greater degree of hardness than known materials of the same composition.

Another way of obtaining the desired structure by rapid cooling from the liquid phase is by the use of a laser beam or capacitance discharge from a pointed electrode to produce local melting of a very small region (for example a cubic millimetre) in the surface of a substantial body of the material. The heat is applied for only a brief period, of the order of a millisecond and on removal of the heat input the molten pool of material rapidly cools by conduction into the remainder of the body. Calculations and measurements indicate that a cooling rate higher than 10^6 degrees centigrade is obtainable in this way, but it is difficult to develop such a method into a continuous commercial process.

Both with the splat cooling technique and the liquid pool technique microscopic examination of etched sections taken in planes parallel to the direction of heat removal on cooling may reveal that some of the molten material has cooled at a fast enough rate to produce the desired structure and some has not. In general those parts of the molten body nearest to the cold surface will be more likely to show the desired structure than those which are more remote although the desired structure may occur locally at the exposed surface too. Thus in the splat cooling technique the foil may typically exhibit two main layers although one or other may be absent under particular conditions. These layers are readily distinguishable by etching a polished section with, for example, Keller's reagent, which, while leaving the areas with the desired structure relatively unattacked, darkens the other areas markedly. Neither structure is resolved completely by optical microscopy, the desired structure not at all. To ensure production of only the desired structure one would have to increase the rate of heat removal (a blast of argon or other inert gas immediately on impact may be found to help here) or alter the conditions to ensure the deposition of a thinner foil or deposition at a reduced rate. The splat technique would be expected to produce a considerable pressure pulse or shock wave within the molten drop on impact but it is not believed that this contributes to the formation of the desired structure.

The structure sought is, of course, a non-equilibrium structure and is distinguished from the structure obtainable by only moderately rapid cooling (also a non-equilibrium structure) not only by its limited response to etching but also by its enhanced properties, in particular its hardness: there is also a difference in X-ray powder pattern and electron microscopy reveals a much finer scale of structure. In a comparison of test samples of the two structures revealed by etching an alloy of aluminium with eight percent weight of iron it was found that whereas the structure obtained by orthodox quenching (which we call structure or zone B) had a mean hardness of about 100 kg./mm.² the desired structure or zone A had a mean hardness of 250 kg./mm.² i.e. more than twice times as great. The X-ray powder pattern of structure B

revealed the presence of a second phase which appears to be FeAl₃ whereas the pattern of structure A showed no such second phase but exhibited asymmetrical broadening or splitting of the reflections from the aluminium lattice which indicated up to a one percent reduction in the lattice parameter. Examination of thinned samples under the electron microscope showed the desired structure A to be basically dendritic with grain colonies having a diameter of the order of a micron and a dendrite arm spacing of around 300 angstrom units. In contrast, the less hard structure B, while having similarly sized grain colonies, had an interphase spacing about ten times as large.

The desired structure can be obtained over a range of alloy compositions. The main investigations so far have been done with aluminum containing 8 percent of iron. If the iron content is increased the hardness is increased. FIG. 1 is a graph showing how the hardness varies with the percentage of iron present in zone A, increasing steeply with increasing iron content. While the high degree of hardness obtained with high iron content represents an improvement in the properties sought the critical minimum cooling rate is increased and so for a given method of cooling and other conditions the yield of the desired structure A will be smaller. Iron contents as high as thirty percent may provide useful materials provided the necessary cooling technique can be improved to produce commercially worthwhile quantities.

Conversely, a reduction in the iron content below 8 percent means that the desired structure can be obtained with lower rates of cooling, or for a given rate of cooling the yield is higher, but at the same time the structure that is produced, even though having the desired characteristics, has them to a less marked degree.

In FIG. 1 we also show the hardness/iron content relationship for structure B and also at C for the structure obtained by chill casting between copper chills at a cooling rate of about 10^3 degrees centigrade per second. It is notable that the zone B is harder than this chill-cast structure by a factor of two and the zone A is harder by a factor of four, reflecting the effect of increasing the cooling rate.

Annealing studies indicate that the desired structure A, which is characterised by a very fine dendritic structure, displays hardness characteristics similar in form to precipitation hardened alloys but maintains its higher hardness to higher temperatures than would be possible with a precipitation hardened alloy with the same room temperature strength. The softer material B loses its strength above about 400° C. These hardness characteristics are illustrated in FIG. 2 which is a graph of room temperature hardness for both zones, measured after a one hour anneal at each temperature, plotted against this annealing temperature.

The material produced by the method described, preferably by the continuous centrifugal splat quenching method, can be collected and reduced to powder and then used to form useful articles by known powder metallurgy techniques.

A possible use for the invention directly without subsequent working may be for forming a hard skin on one or both faces of sheet or strip alloy material by flash-melting of the surface and thus forming a continuous skin or foil of the desired structure by rapid cooling into the remainder of the sheet.

It will be understood that the novel aluminum alloy structure A according to the invention cannot be defined precisely in terms of percentages or other qualitative limitations but at the same time it will be possible, by reference to the graphs and the other details given above, to determine whether a given material is or is not of the structure in question.

I claim:

1. A binary alloy product comprising from 0.05% to 8% by weight of iron, the balance being aluminium together with any impurities and which has been cooled from

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a liquidus alloy at a rate of at least 10^5 but not more than 10^8 degrees centigrade per second, the structure of said product being basically dendritic with grain colonies having a diameter of about a micron and a dendrite arm spacing of about 300 angstrom units.

2. The product according to claim 1 in which the structure has been obtained by cooling the liquidus alloy by splat cooling.

3. The product according to claim 1 in which the structure has been obtained by cooling a small volume of liquidus alloy produced by local melting within a larger body of the alloy.

4. The product according to claim 3 in which the prod-

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uct is in the form of a thin skin on a face of sheet aluminum alloy material.

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U.S. Cl. X.R.

75—0.5 R; 148—32