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[54] **METHOD OF PRODUCING A DISPERSION-STRENGTHENED ALUMINUM ALLOY ARTICLE**

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[30] **Foreign Application Priority Data**

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[51] **Int. Cl.** **B22f 3/24**

[58] **Field of Search** .... 29/527.5, 527.7, DIG. 39, 29/420.5; 164/46

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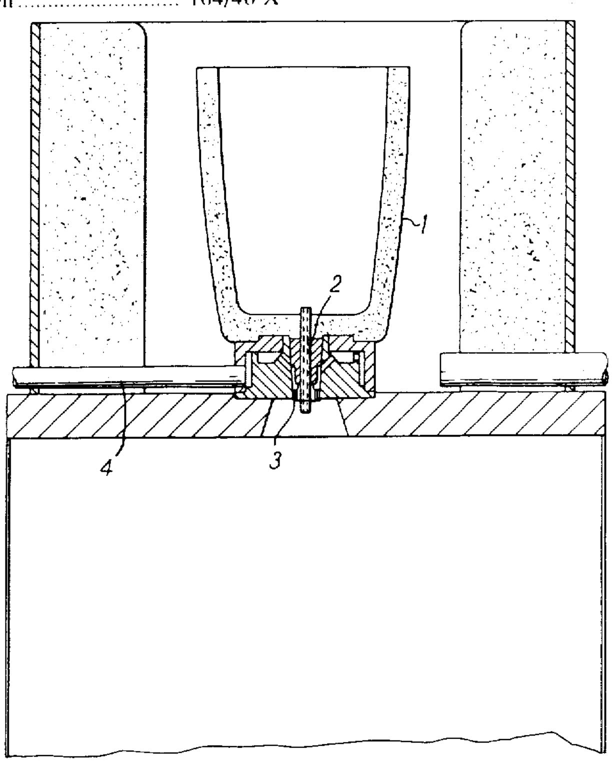
[57] **ABSTRACT**

Aluminium alloy articles of high strength and high resistance to temperature softening are produced by spraying droplets of selected aluminium alloy entrained in a stream of gas onto a substrate under such conditions that the metal droplets strike the substrate in a highly undercooled (supercooled) condition. On striking the substrate the undercooled liquid droplets flatten and are very rapidly chilled so that the alloying constituent is either maintained in supersaturated solid solution or is precipitated as a very fine precipitate. The deposit is consolidated by warm working. The selected aluminium alloy contains up to 25 percent of alloying constituent, which is in excess of the equilibrium solid solubility and has a low diffusion rate in aluminium. The preferred alloying constituents are one or more of Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb and Mo. Si may be added but is unsuitable by itself. Particularly satisfactory results are obtained with eutectic ternary alloys containing Ni or Si.

8 Claims, 3 Drawing Figures



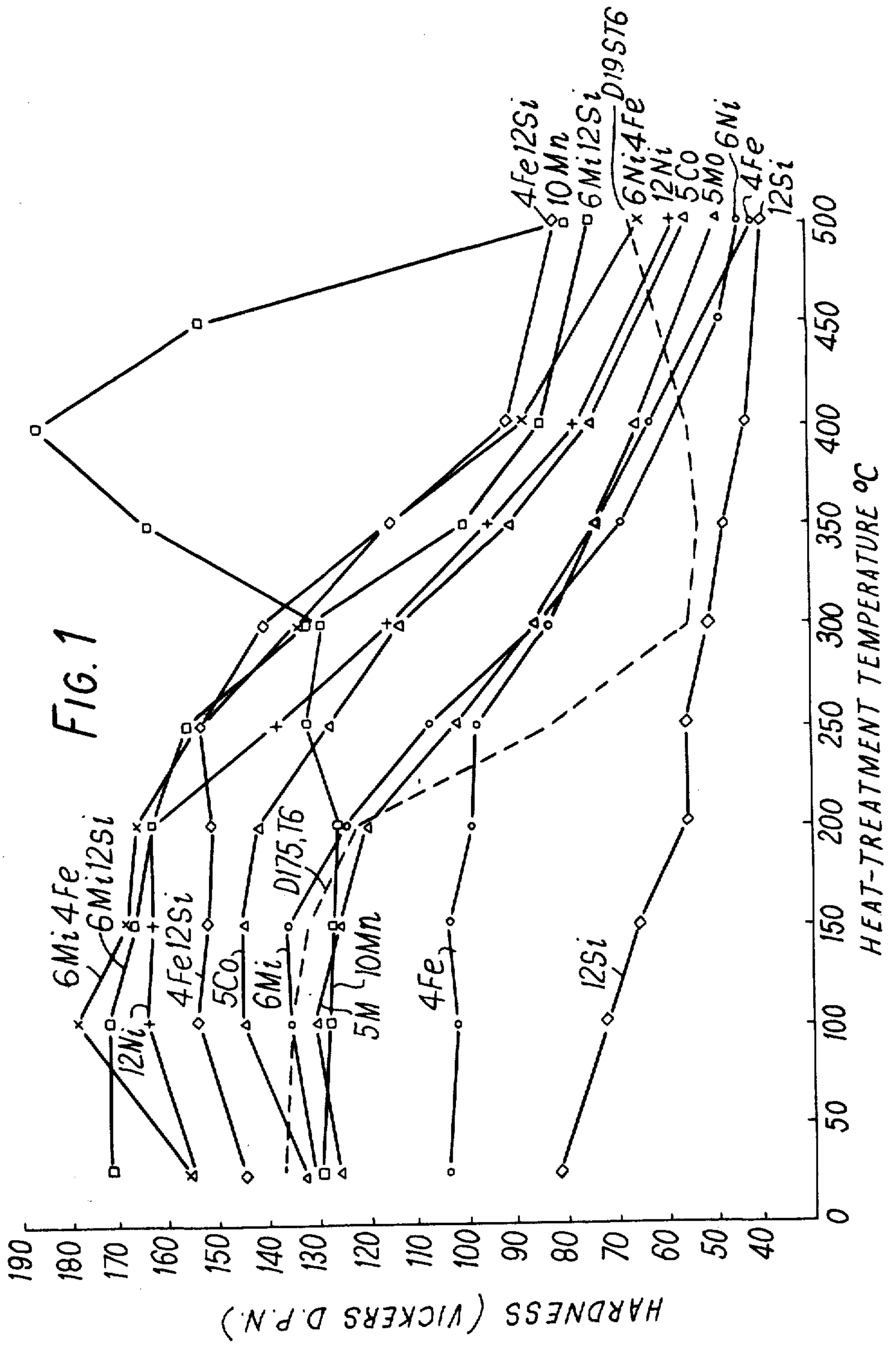

HARDNESS (VICKERS D.P.N.)
HEAT-TREATMENT TEMPERATURE °C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
0
50
100
150
200
250
300
350
400
450
500
6Ni4Fe
6Ni12Si
12Ni
4Fe12Si
5Co
6Ni
D175,T6
5M
10Mn
4Fe
12Si
10Mn
6Ni12Si
D19ST6
6Ni4Fe
12Ni
5Co
5Mo
6Ni
4Fe

FIG. 1

FIG. 2

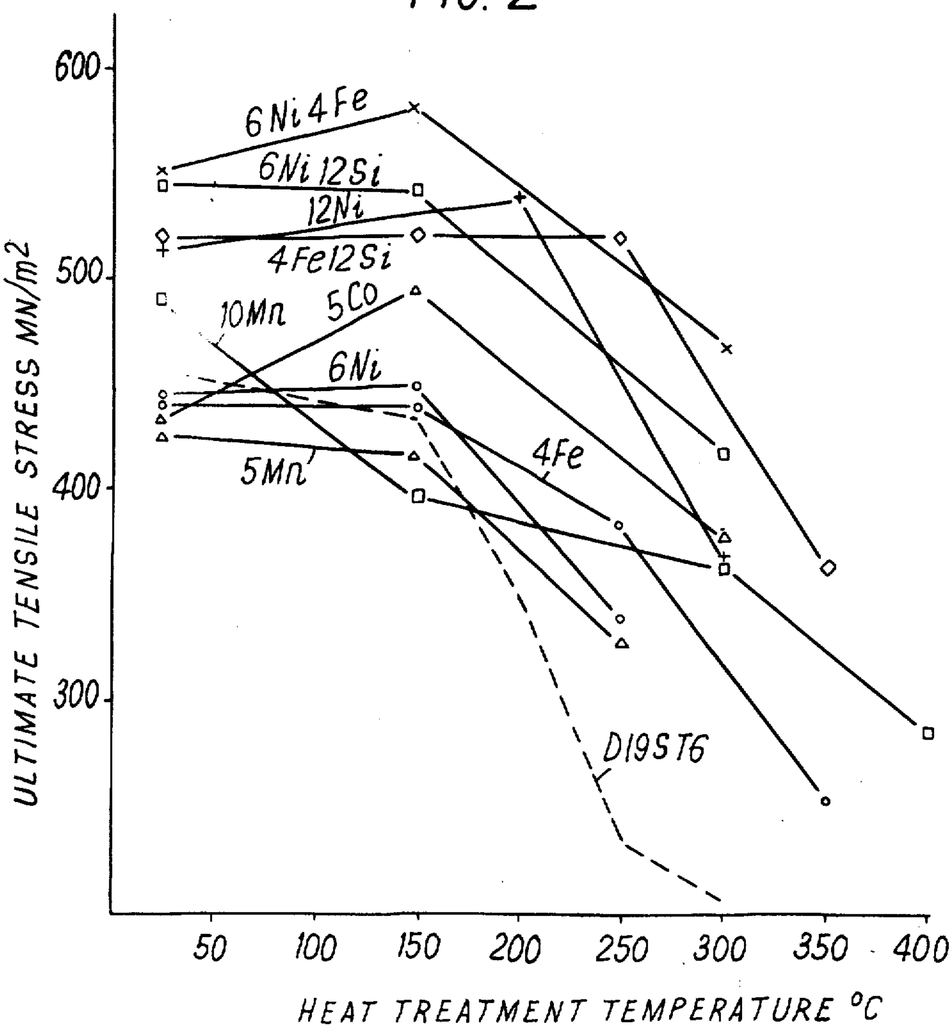
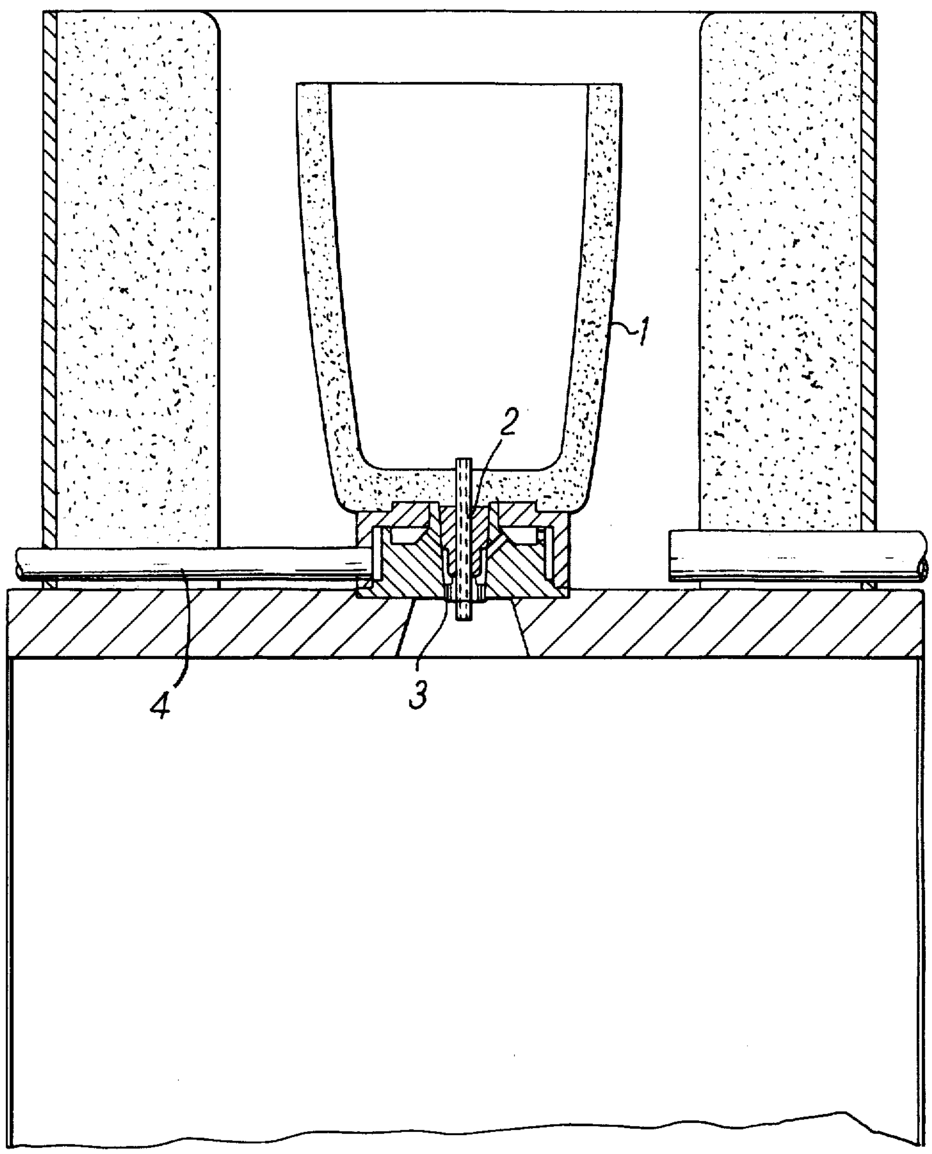

6Ni 4Fe
6Ni 12Si
12Ni
4Fe12Si
10Mn
5Co
6Ni
4Fe
5Mn
D19ST6
600
500
400
300
ULTIMATE TENSILE STRESS MN/m2
50
100
150
200
250
300
350
400
HEAT TREATMENT TEMPERATURE °C

FIG. 3



METHOD OF PRODUCING A DISPERSION-STRENGTHENED ALUMINUM ALLOY ARTICLE

The present invention relates to the production of high hot strength aluminium alloy articles. In the process of the present invention these articles are produced by employing a spray casting process which is operated to produce a deposit of aluminium alloy droplets in which the alloying constituent, which may be one or more metals, is maintained either in supersaturated solid solution or in the form of a precipitate of exceptionally fine particles. The mass of solidified droplets produced by the spray casting operation is then compacted to produce an article which may have high mechanical strength and resistance to temperature softening.

The spray-casting operation entails the atomisation and subsequent cooling of a stream of the molten alloy by high velocity jets of nitrogen or other suitable gas. In accordance with the present invention the atomised metal droplets are carried to a moving substrate where, upon impact, they become flattened and solidify almost instantaneously as a result of the initial gas cooling and secondary cooling from the substrate. The conditions for obtaining a supersaturated deposit or one containing a dispersion of fine ($< 1 \mu m$) particles are:

1. The alloy should be spray-cast above its liquidus temperature.
2. The initial melt temperature should be sufficiently low, and the gas velocity and flow rate should be such that the gas extracts enough heat to reduce the temperature of the metal droplets to below that at which solidification would normally commence.
3. The substrate should be sufficiently cool and should be able to absorb sufficient heat to contribute significantly towards cooling of the deposit.

If these conditions are satisfied then each droplet solidifies individually on deposition and the alloying additions, to be described, are largely retained in supersaturated solid solution or are dispersed as very fine ($<1 \mu m$) particles. The deposit that results from this operation is porous and of low strength and requires consolidation by hot working.

The object of the hot working (which may take the form of hot rolling, hot extrusion, hot pressing, hot forging or explosive forming) is as follows:

a. to heat porosity
b. to break down the original boundaries of the flattened droplets so as to weld them together
c. to cause some precipitation of very fine particles of the appropriate intermetallic phase (including metastable phases), the nature of which is dependent upon the alloy composition.

The effect of both (a) and (b) is to improve homogeneity and hence to improve ductility and strength. The effect of (c) is to produce a structure containing a very fine dispersion of very small intermetallic compound particles and it is this structure that determines the exceptional combination of properties, viz. high mechanical strength, high resistance to temperature softening and high elastic modulus.

The choice of alloying elements is determined by the need to achieve (a) maximum properties as previously defined, and (b) ease of spray-casting and consolidation.

According to the present invention a method of producing an aluminium alloy article having a high hot strength comprising establishing a substantially homogeneous body of molten metal comprising aluminium and 0.05 to 25 percent of alloying constitutent, the amount of said alloying constituent being in excess of the equilibrium solid solubility, the maximum value of the equilibrium solid solubility being 2 percent, said alloying constituent having a low diffusion rate in aluminium, establishing a stream of droplets of said molten metal in a stream of gas, preferably nitrogen or argon, or in some cases air, said droplets having an average diameter in the range of 50 μm to 1 mm, projecting said droplets against a substrate, undercooling said droplets of molten metal by at least 50°C during flight so that on striking the substrate they are very rapidly solidified to maintain said alloying constituent in supersaturated solid solution or in the form of particles of a size not greater than 1 μm in said aluminium, and compacting the mass of droplets by hot working at a temperature in the range of 200° to 500°C. Preferably the projection of the droplets is performed under such conditions that the droplets are undercooled by about 200°C. Under these conditions it is estimated that the individual droplets are chilled at a rate of at least 10^3 °C/sec. and indeed up to or even beyond 10^5 °C/sec. in their transition from the liquid state to the solid state on striking the substrate.

Preferably the droplets are projected against a substrate, which presents a surface moving relatively to the source of said droplets so as to form a strip of cohered solidified droplets on the substrate. The strip is then preferably separated from the substrate for compaction.

The alloying constituent is preferably constituted by one or more of the following elements Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb and Mo. It is preferred that at least one element should be present in approximately the amount required to form a eutectic with aluminium.

The alloying additions are chosen so as to have (1) very little solid solubility in aluminium and (2) very slow rates of diffusion in aluminium, up to at least 400°C. These requirements ensure that the precipitates, when formed, are stable and resistant to change at elevated temperatures. The alloying elements of interest are principally the transition metals Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb and Mo. The total addition of one or more of these metals is preferably 3–15 percent. The liquidus temperature of the resulting alloy should not exceed approximately 1,500°C; otherwise the amount of heat required to be extracted by the gas becomes excessive to ensure rapid solidification of the droplets on impact on the substrate.

In addition to the elements listed above, the presence of other alloying elements, especially silicon at about 12 wt% when added with one or more of the other elements provides for a strong alloy by making available increased numbers of siliconbearing intermetallic compound particles, even though silicon by itself is quite unsuitable because of its high rate of diffusion. For example, the addition of 12% Si to an Al-4% Fe alloy increases the strength by increasing the number of intermetallic particles.

Aluminium alloys of near eutectic composition, such as alloys containing 12% Si or 6% Ni are especially favourable alloys for spray-casting, because the liquidus temperature is relatively low. An alloy containing 5–7% Ni, preferably 5.5 – 6.5% Ni, with additions of one or more of the previously mentioned transition elements is particularly favourable. In consequence, the amount of heat needed to be extracted from the droplets by the gas to achieve undercooling is kept to a minimum. In addition, the contraction stresses during solidification appear to be low, since deposits of these alloys have less tendency to curl-up from the substrate during spray casting.

It has been observed that these desirable features (low liquidus temperature and flat deposit) are largely retained in ternary or higher order alloys that contain either 12% Si or 6% Ni even though the other elements, when present in binary alloys, cause difficulties by producing pronounced curling of the deposit.

It has already been proposed to produce aluminium alloy products of high strength by splat-casting, in which procedure metal droplets are subjected to rapid cooling by being projected against a chilled substrate. The metal particles are not subjected to any substantial degree of undercooling during flight, with the result that nearly the whole of the initial heat content of the droplets is absorbed by the substrate. In consequence, it is only possible to build up a thin deposit of droplets having a desirable fine precipitate of insoluble alloying constituents. Any attempt to build up a thicker layer of metal by splat-casting results in a relatively coarse precipitate. As a result splat-casting may only be employed to form a layer of particles which are continuously removed from the substrate and which are subsequently formed into products by powder metallurgy.

In contradistinction the method of the present invention allows the formation of a relatively thick deposit, for example up to 2 cms thickness, of droplets having a high content of alloying constituents in supersaturated solution or in the form of a very fine precipitate. However this can only be achieved by correct adjustment of the relation between the gas supply and the supply of molten metal to the spray jet so as to ensure that the metal droplets impinge on the substrate in a suitable undercooled (but still liquid) condition. If the metal droplet temperature is too high or striking the substrate, the droplets will not instantly solidify on impact and solidification will be delayed. This will be evidenced by a relatively coarse structure in the deposit.

On the other hand, if the droplets are subjected to excessive cooling by the gas a large number of generally spherical solidified droplets will be present in the deposit, indicating solidification before impact with the substrate. Such droplets exhibit a coarse structure as they have not undergone very rapid chilling at the transition from the liquid to the solid state. By contrast, droplets deposited under correct conditions appear flattened as a rsult of their impact with the substrate and are relatively free from coarse second phase particles and indeed may exhibit a virtually featureless structure.

Thus a visual inspection of the deposit under a microscope of suitable power will permit a determination of the correctness of the spraying conditions.

In a series of experiments designed to spray various molten aluminium alloys under the conditions already designated above, a series of binary and ternary alloys were sprayed onto a substrate, which was either air-cooled (A.C.) or water-cooled (W.C.). The loosely compacted strip formed by the spray casting process was then consolidated by warm-rolling at a temperature in the range of 250°–450°C. The consolidated strip was then further reduced by cold-rolling. The mechanical physical properties of the strip in the consolidated condition and in the cold-rolled condition were then measured. These, together with the temperature of the melt before spray casting and the warm-consolidation and cold-rolling conditions, are recorded in the following Table 1.

TABLE I

Alloy	Spray-casting			Fabrication					
				Roll-consolidation			Cold-rolling		
Composition	W.C. or A.C.	Melt temp. °C	Strip temp. °C	Original thickness mm	Final thickness mm	Total reduction %	No. of passes	Final thickness mm	Total reduction %
6.0% Ni	W.C.	750	250	10.25	1.73	83	7	0.47	73
			300	9.9	2.06	79	6	0.59	72
			350	10.5	2.13	80		0.55	74
			400	10.5	2.12	80	5	0.55	74
	A.C.	800	300	8.0	1.68	79		0.47	72
			350	7.6	1.67	78	6	0.44	74
			400	10.1	1.84	82		0.44	76
12.0% Ni	A.C.	920–1000	400	7.85	1.75	78	6	0.45	74
			450	7.30	1.77	76		0.45	75
5.4% Co	A.C.	1000	400	8.00	1.82	77	8	0.46	75
			450	8.25	1.81	78		0.46	74
5.2% Mn	W.C.	940	400	7.07	1.55	78	7	0.40	74
			450	7.35	1.36	81		0.36	73
5.3% Mn	A.C.	975	400	7.4	1.66	78	7	0.45	73
			450	7.4	1.66	78		0.44	73
6.0% Ni 3.5% Fe	W.C.	920–980	350	12.2	2.06	83	9	0.58	72
			400	11.90	2.11	82	6	0.56	73
6.8% Ni 5.2% Fe	A.C.	—	350	13.25	2.72	79	8	1.01	63

TABLE I – Continued

Alloy Composition	Spray-casting W.C. or A.C.	Spray-casting Melt temp. °C	Strip temp. °C	Fabrication: Roll-consolidation Original thickness mm	Roll-consolidation Final thickness mm	Roll-consolidation Total reduction %	Cold-rolling No. of passes	Cold-rolling Final thickness mm	Cold-rolling Total reduction %
6.3% Ni 12.0% Si	A.C.	750	350 400	10.63 10.55	2.29 2.12	78 80	7	— —	— —
4.2% Fe 13.8% Si	A.C.	870–900	350	10.1	2.18	78	7	0.93	58
5.9% Ni 2.0% Fe 0.8% Co	W.C.	950	400	10.25	2.82	73	6	0.77	73
6.4% Ni 1.9% Fe 2.0% Mn	A.C.	980	400	6.63	1.75	74	8	0.44	74
6.4% Ni 1.9% Fe 2.0% Mn	A.C.	980	450	7.00	1.65	76	8	0.40	76
6.2% Ni 2.2% Cr	W.C.	900	350	9.98	2.30	77	7	0.56	75
6.2% Ni 2.2% Cr	W.C.	900	400	10.25	2.50	76		0.61	76

Alloy Composition	Spray-casting W.C. or A.C.	Spray-casting Melt temp. °C	Tensile properties: Roll-consolidated condition 0.2% P.S. MN/m²	Roll-consolidated U.T.S. MN/m²	Roll-consolidated El. %	Cold-rolled condition 0.2% P.S. MN/m²	Cold-rolled U.T.S. MN/m²	Cold-rolled El. %
6.0% Ni	W.C.	750	401	447	11½	340	361	7½
			364	410	16½	408	444	10½
			352	404	15½	381	421	8½
			—	385	14½	378	423	9
	A.C.	800	377	441	12	400	444	7½
			367	419	12½	417	460	7½
			292	342	16½	343	400	6½
12.0% Ni	A.C.	920–1000	388 308	461 373	10½ 12½	440 361	517 445	7 7½
5.4% Co	A.C.	1000	413 391	451 419	9 12	404 371	438 414	11½ 13½
5.2% Mn	W.C.	940	332 305	358 339	13 12½	394 378	420 404	4½ 5
5.3% Mn	A.C.	975	333 295	360 325	13 16½	407 348	428 382	5 6
6.0% Ni 3.5% Fe	W.C.	920–980	518 445	558 508	4 7½	549 505	580 552	5½ 9
6.8% Ni 5.2% Fe	A.C.	—	—	—	—	352	417	4½
6.3% Ni 12.0% Si	A.C.	750	422 396	549 491	4 5	— —	— —	— —
4.2% Fe 13.8% Si	A.C.	870–900	387	479	7	428	520	7
5.9% Ni 2.0% Fe 0.8% Co	W.C.	950	498	528	4	490	558	8
6.4% Ni 1.9% Fe 2.0% Mn	A.C.	980	466	518	7	458	532	8
6.4% Ni 1.9% Fe 2.0% Mn	A.C.	980	354	448	10½	456	518	9
6.2% Ni 2.2% Cr	W.C.	900	453	536	10½	498	587	7
6.2% Ni 2.2% Cr	W.C.	900	404	474	12	472	550	7½

General observations relating to the effect of spray-casting and fabrication conditions on tensile properties can be made from Table 1:

a. Within the temperature range for adequate roll consolidation, strength increased with drop in roll-consolidation temperature. This was probably due to a combination of work-hardening and a minimum of coarsening of the precipitate.
b. Elongation tended to increase with rise in roll-consolidation temperature.
c. Cold-rolling the roll-consolidated material tended to increase its strength and decrease the elongation, the amount varying from alloy to alloy. There was in the case of 5.4% Co a slight apparent softening of the material on cold-rolling.

Although ternary alloys have been shown in the main to be preferable to binary alloys, it may be that small additions of many elements would be preferable to larger additions of a few, as in this way a larger total fraction of alloying elements can be added before the liquidus temperature becomes too high for successful spray-casting.

An important point concerning spray-cast alloys of the present invention is that they are suitable for being based on relatively impure aluminium metal. Any so-called impurities will be taken into solid solution during spray-casting and will add to the general strength of the fabricated material. This is demonstrated by the good properties of the spray-cast alloys containing iron and silicon, which are the two most common elements to be found in low purity aluminium.

In a further series of tests the effect of temperature on the hardness of spray-cast and consolidated alloy articles of the present invention was measured and compared with the effect of temperature on D19S alloy (corresponding to B.S. 1472: HF16), having the following composition: 2.5% Cu, 1.55% Mg, 1.1% Fe, 1.2% Ni and 0.06% Ti, the remainder commercial purity aluminium. The D19S alloy has the best resistance to temperature-softening of any normally employed, wrought commercial aluminium alloy.

In the accompanying FIGS. 1 and 2, the hardness and ultimate tensile stress of test pieces at room temperature, after being held at the indicated temperature for one week, is recorded. The test pieces were made by the spray-casting procedure as detailed above and are contrasted with the D19S alloy in the fully aged (T6) condition. They are also contrasted with a spray-cast, roll-consolidated Al-12% Si alloy (which does not fall within the scope of the invention). It is to be seen that the binary and ternary spray-cast, roll-consolidated alloys, based on the transition elements, the substantially more resistant to softening by exposure to temperatures in the 200°–400°C range for one week than is the known D19S alloy.

The properties shown in Table 1 and in FIGS. 1 and 2 do not necessarily represent the ultimate that might be achieved even for alloys with the same composition.

In the following Table 2 is set out the values for elastic modulus and density after roll-consolidation obtained for certain of the alloys shown in FIGS. 1 and 2 in contrast to D19S alloy.

TABLE 2

Alloy Composition %	Elastic Modulus GN/m^2	Density Mg/m^3
6 Ni	79	2.84
5 Co	78	2.86
5 Mn	87	2.80
4 Fe	79	2.78
12 Ni	87	3.02
6 Ni 4 Fe	87	2.92
4 Fe 12 Si	79	2.78
Conventionally prepared D19S alloy	79	2.78

One form of apparatus for carrying out the process of the invention is illustrated in FIG. 3 of the accompanying drawings.

The molten alloy, which is to be spray-deposited, is fed continuously to a crucible 1, having a delivery tube 2. The delivery tube 2 has a bore of 3 mms and is surrounded by an array of twelve gas nozzles 3, each 2 mms in diameter. Nitrogen is delivered to the nozzles 3 from a supply pipe 4 at a pressure of about 80 p.s.i. (about 5.6 atmospheres).

The substrate in the form of a steel strip was positioned at a distance of about 14 ins. (350 mms) from the delivery tube 2 and advanced at such a rate as to build up a deposit about 20 mms thickness. Under these conditions the droplet size of the metal (considered as a spherical droplet in flight) was about 180 microns and it is estimated to have been cooled from an initial temperature of 850°C by between 300° and 360°C before striking the substrate so as to result in undercooling by 110°–170°C. The chilling of the molten droplets by the nitrogen gas is mostly effected in the immediate vicinity of the delivery tube nozzle 2, where the gas is coolest and the difference in velocity between the gas and the molten metal is highest. With a given apparatus the particle size of the metal droplets and the extent of the undercooling can be varied by increase or decrease of the gas delivery pressure. As already stated, the correctness of the undercooling of the droplets can be judged by visual inspection of the deposit and appropriate corrections may be made as necessary to improve the deposit.

In order to demonstrate the importance of establishing the desired degree of undercooling during flight the alloy Al-Ni-6%-Fe-4% was sprayed under two different conditions (a) under the same conditions as in the foregoing examples, employing 18 cu.ft. of nitrogen per lb. of metal sprayed (1.1 m^3/Kg) and (b) 8–10 cu.ft. of nitrogen per lb. of metal sprayed (0.5–0.6 m^3/Kg). In the latter case it was estimated from examination of the structure of the deposit that the droplets had been subjected to little (if any) undercooling before striking the substrate because the deposit did not exhibit the appearance of a layer of solidified flattened droplets and, as a consequence of this lack of undercooling, the precipitate was coarse in character and the strength of the deposit after hot compaction and cold rolling was relatively poor as indicated in the following Table 3.

TABLE 3

Structure	Approx. gas/metal ratio cu.ft./lb.wt.	Tensile properties of rolled sheet 0.2% Proof Stress MN/m²	U.T.S. MN/m²	Elong. %
Good	18	550	583	5½
Bad	8–10	350	415	2

We claim:

1. A method of producing an aluminium alloy article having a high hot strength comprising establishing a substantially homogeneous body of molten metal comprising aluminium and 0.05 to 25 percent of alloying constituent, the amount of said alloying constituent being in excess of the equilibrium solid solubility, the maximum value of the equilibrium solid solubility being 2 percent, said alloying constituent having a low diffusion rate in aluminium, establishing a stream of droplets of said molten metal in a stream of unheated gas, said droplets having an average diameter in the range of 50 μm to 1 mm, projecting said droplets against a substrate, undercooling said droplets of molten metal by at least 50°C during flight so that on striking the substrate they are very rapidly solidified to maintain said alloying constituent in supersaturated solid solution or in the form of particles of a size not greater than 1 μm in said aluminium, and compacting the mass of droplets by hot working at a temperature in the range of 200° to 500°C.

2. A method according to claim **1** in which the droplets are undercooled by 110°–170°C.

3. A method according to claim **1** in which the alloy contains a total of 3–15% of transition metals Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb and Mo.

4. A method according to claim **3** in which the alloy contains up to 12% Si.

5. A method according to claim **1** in which the alloy is near eutectic composition for ease of spray casting.

6. A method according to claim **5** in which the alloy contains about 6% Ni or 12% Si.

7. A method according to claim **3** in which the alloy is a ternary alloy.

8. A method according to claim **7** in which the ternary alloy contains 5–7% Ni.

* * * * *