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(54) **MANUFACTURING OF HIGH STRENGTH AND HEAT RESISTANT ALUMINIUM ALLOYS STRENGTHENED BY DUAL PRECIPITATES**

(57) The present invention the Manufacturing of High Strength and Heat Resistant Aluminium Alloys Strengthened by Dual Precipitates relates to a high-strength and heat resistant aluminium alloy and a method for producing the same. The alloys possess 2.0-5.0 mass.% Mn; 0.001-2.0 mass.% Cr; 2.0-5.0 mass.% Cr + Mn; 0.001-0.5 mass.% V; 2.0-4.5 mass.% Cu; 0.001-0.9 mass.% Be; 0.05-0.5 mass.% Sc; and comprising of at least one element out of Zr, Y, Ti, Hf and Nb with a content of 0.001-0.4 mass.%; the balance being Al and inevitable

impurities up to 0.5 mass.%. The alloys are cast with a cooling rate exceeding 100 K s<sup>-1</sup>. The alloys can be plastically deformed before aging. Afterwards, they are aged at a first ageing temperature for a first predetermined time. Then they are subjected to the second ageing treatment at a second temperature for a second predetermined time to obtain a combination of icosahedral and L<sub>12</sub> precipitates. The alloys can be aged at a third ageing temperature for a third predetermined ageing time after being quenched from the second ageing temperature.

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**Description****The technical field of the invention**

5 [0001] The invention belongs to the area of non-ferrous metallurgy, more specifically to the casting and heat treatment of aluminium alloys.

**Description of the background art**

10 [0002] The aluminium and aluminium alloys are characterized by low densities, high specific strengths (strength divided by density), and competitive corrosion resistance. Aluminium parts can be produced economically using versatile manufacturing technologies. By using standard strengthening mechanisms limiting values of tensile strengths between 550 MPa and 600 MPa can be achieved in wrought alloys, but with reduced elongation (around 10 %). In Al-Si casting alloys alloyed with different alloying additions (e.g. AlSi12CuNiMg) tensile strengths up to 400 MPa can be attained, and the  
15 elongation is around 5 %.

[0003] Most of the high-strength aluminium alloys are precipitation hardened. The most typical heat treatment is designed by T6. The T6 heat treatment consists of solution treatment at temperatures above the alloy's solvus temperature. This treatment results in homogenising the alloy and transferring the precipitates-forming alloying elements from different intermetallic phases into an Al-rich solid solution. Alloy is then quenched. The cooling rate is to be sufficient to  
20 retain almost all dissolved alloying elements in the solid solution. During natural ageing (at room temperature) or artificial ageing (at elevated temperatures, typically below 200 °C), the alloying elements start to precipitate from the solid solution. The precipitates strengthen the aluminium alloy.

[0004] Heat treatment T5 is an alternative to T6. When this treatment is applied, the alloy is directly heated from temperature to the temperature of artificial ageing without solution treatment. The prerequisite for this is, for example  
25 by casting, that sufficiently high-cooling rates are achieved, which retain a high content of alloying elements in the solid solution. Precipitates are formed during direct ageing.

[0005] In both T5 and T6 treated alloys, precipitates strengthen the matrix at lower temperatures. At temperatures approaching 200 °C, precipitates start to coarsen and dissolve, and mechanical properties start to drop rapidly.

[0006] For advanced applications, aluminium alloys should be manufactured in different shapes, having an appropriate  
30 combination of low density, high-strength at room temperature, heat resistance, and competitive price. There have been several solutions in the scientific literature and patents to the above-stated problem, which have been applied in the industrial practice, and are relevant to the current topic.

[0007] High-strength and heat-resistant precipitation hardening alloys without Sc, lose their heat resistance at temperatures slightly above 200 °C because the precipitates become coarser or even dissolve themselves. Precipitation-  
35 hardened alloys with Sc have higher heat resistance, but are more expensive because of Sc. The content of Sc in these alloys is rather high. Because of scarcity of Sc, it is not possible to produce alloys in higher amounts. The alloys, strengthened only by quasicrystals, can be produced by rapid solidification, therefore their use is rather limited.

**a) High-strength and/or heat-resistant heat-treatable aluminium alloys without Sc**

40 [0008] High-strength aluminium alloys are based mainly on heat-treatable alloys from the systems Al-Cu (series AA2xxx), Al-Si-Mg (series AA6xxx), Al-Li and Al-Zn-Mg (series AA7xxx). The alloys are produced by different techniques (casting, powder metallurgy, forming), and then heat treated mainly by T6 and T5 heat treatments. Increased heat resistance is achieved by the addition of Mn, Cr, Zr, Nb, Hf or V, which can form different types of precipitates that are  
45 less soluble in the aluminium matrix, and can remain in the alloy at elevated temperatures.

[0009] The patent WO 2002063059 A1 discloses a two-stage ageing process of an article made from an alloy comprising at least aluminium and copper. The patent WO 2008003503 A2 discloses the method of manufacturing of AA2xxx alloys for manufacturing aluminium wrought products in relatively thick gauges. In both alloys, different **Al-Cu precipitates** are  
50 formed during manufacturing that cannot withstand temperatures above 200 °C.

[0010] The patent US 5759302 A describes the compositions of Al-Cu and Al-Zn-Mg alloys, alloyed with Mn, Cr or Zr, and heat treating procedures to obtain **dispersoids from the systems Al-Mn, Al-Cr or Al-Zr** that can contribute to increased fracture toughness, fatigue resistance and formability.

[0011] The patent US 20170051383 A1 determines the composition of the alloys and parameters of the three-step ageing process to obtain dual precipitates in the aluminium matrix that can provide the application of the said alloys for  
55 high-temperature applications. The alloy is alloyed **with Cu and Zr, and also with Nb, Hf or V**.

[0012] The patent US 5226983 A discloses the Al-Zr-Li-X alloys that are produced by rapid solidification. The alloy is then subjected to multiple ageing treatments after solution treatment. The microstructure of the alloy is composed of aluminium matrix and **Al<sub>3</sub>(Zr, Li) precipitates**.

[0013] The patent WO 2011122958 A1 optimises the Al-Mg-Si-Cu alloy for high-temperature stability. It defines the chemical compositions of the alloy. The aim is to obtain an **L-phase** as a dominant precipitate type about its number density in the over-aged state.

[0014] The patent US 6074498 A defines Al-Cu-Li-Sc alloys, which are subjected to a dual ageing treatment. The purpose is to attain an array of fine T1 phase precipitates within the aluminium grain, leaving a substantially T1 phase precipitate-free zone along the grain boundaries, and an array of coarse  $\theta'$  and  $\delta'$  phase precipitates throughout the grains with little or no  $\theta'$  and  $\delta'$  phase-free zones.

*b) High-strength and heat-resistant Al-alloys, containing Sc and L<sub>12</sub> precipitates*

[0015] L<sub>12</sub>-precipitates have an ordered cubic crystal structure with a general formula Al<sub>3</sub>X, where X presents one or more elements, the most important are Sc, Zr, and Y. The L<sub>12</sub>-precipitates are coherent with Al-rich solid solution. They are formed during heat treatment, and are rather stable at elevated temperatures. Table 1 gives a list of patents for Al-alloy containing L<sub>12</sub>-precipitates. The patents disclose the composition, manufacturing procedures, e.g. casting, rapid solidification, rolling, welding, extrusion, as well as their heat treatment of aluminium alloys.

[0016] The patent US 6248453 B1 discloses the aluminium alloys with Sc, Er, Lu, Yb, Tm and U, and also with at least one element selected from the group consisting of Mg, Ag, Zn, Li, Cu. The alloy produced with the said composition and rapid solidification comprises of Al-matrix and Al<sub>3</sub>X precipitates with the L<sub>12</sub>-structure.

[0017] There are several patents with the title "High strength L12 aluminium alloys" (see Table 1). The patents disclose several basic compositions of the alloys, with the addition of at least one of scandium, erbium, thulium, ytterbium, and lutetium; and at least one of gadolinium, yttrium, zirconium, titanium, hafnium, and niobium. One of the stated possible composition is Al-(1-8)Cu-(0.2-4)Mg-(0.1-0.5)Sc-(0.05-1.0)Zr (US 7909947). In other patents, different basic alloys are proposed [in US 8002912 B2, the base alloy is Al-(4-25)Ni-(0,1-15)Tm (transition metal), and in US 7871477 B2, the base alloy is Al-(3-6)Mg-(0,5-3)Li]. In all cases, the microstructure after heat treatment composes of Al-rich matrix and Al<sub>3</sub>X precipitates with L<sub>12</sub>-structure.

[0018] The patent US 5620652 A discloses the aluminium alloys containing scandium with zirconium additions that can be used for recreational products, ground transportation, marine and aerospace structures. No details of heat treatment are given. It can be supposed that they predominantly consist of Al-rich matrix and Al<sub>3</sub>X precipitates with L<sub>12</sub>-structures.

[0019] The patent US 20100143185 A1 discloses a method for producing high-strength aluminium alloy powder containing L<sub>12</sub> intermetallic dispersoids. The powder is produced by melt atomization. The patented compositions of alloys cause the formation of L<sub>12</sub>-precipitates in the powder, which are uniformly distributed in Al-rich matrix.

[0020] **Belov et al.** [1] developed an Al-Cu-Mn-Zr-Sc alloy, which does not require solution treatment and quenching for obtaining high-strength. This alloy contains L<sub>12</sub> precipitates, but do not have icosahedral quasicrystalline precipitates. Instead of IQC-precipitates, Al<sub>20</sub>Mn<sub>3</sub>Cu<sub>2</sub> precipitates formed. Their disadvantage is that they are in the form of rods. In addition, their number density is much lower than the density of icosahedral precipitates with spherical morphology.

[1] N.A. Belov, A.N. Alabin, I.A. Matveeva, Optimization of phase composition of Al-Cu-Mn-Zr-Sc alloys for rolled products without requirement for solution treatment and quenching, J. Alloy. Compd., 583 (2014) 206-213.

Table 1: List of patents for Al-alloys containing L<sub>12</sub> precipitates

EP 2598664 B1	HIGH TEMPERATURE SCANDIUM-CONTAINING ALUMINIUM ALLOY WITH IMPROVED EXTRUDABILITY
US7811395, US7871477, US7909947, US8002912, US20090260722, US20090260723, US20090263273	High strength L12 aluminum alloys
US7875131	L12 strengthened amorphous aluminum alloys
US7875133, US20090260724, US20090260725, US20110041963, US7883590	Heat treatable L12 aluminum alloys
US7879162	High strength aluminum alloys with L12 precipitates
US8017072	Dispersion strengthened L12 aluminum alloys
US8409373	L12 aluminum alloys with bimodal and trimodal distribution
US8409496	Superplastic forming high strength L12 aluminum alloys

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5	EP 2598664 B1	HIGH TEMPERATURE SCANDIUM-CONTAINING ALUMINIUM ALLOY WITH IMPROVED EXTRUDABILITY
	US8409497	Hot and cold rolling high strength L12 aluminum alloys
	US8728389	Fabrication of L12 aluminum alloy tanks and other vessels by roll forming, spin forming, and friction stir welding
10	US8778098	Method for producing high strength aluminum alloy powder containing L12 intermetallic dispersoids
	US8778099	Conversion process for heat treatable L12 aluminum alloys
15	US9127334	Direct forging and rolling of L12 aluminum alloys for armor applications
	US9194027	Method of forming high strength aluminum alloy parts containing L12 intermetallic dispersoids by ring rolling
20	US9611522	Spray deposition of L12 aluminum alloys
	US20090263266	L12 strengthened amorphous aluminum alloys
	US20110044844	Hot compaction and extrusion of I12 aluminum alloys
25	US20110052932	Fabrication of I12 aluminum alloy tanks and other vessels by roll forming, spin forming, and friction stir welding
	US20110061494	Superplastic forming high strength 112 aluminum alloys
	US20110064599	Direct extrusion of shapes with 112 aluminum alloys
30	US20110085932	Method of forming high strength aluminum alloy parts containing I12 intermetallic dispersoids by ring rolling
	US20110088510	Hot and cold rolling high strength L12 aluminum alloys
	US20110091346	Forging deformation of L12 aluminum alloys

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c) Quasicrystal-strengthened Al-alloys

[0021] Quasicrystals are crystals having long-range order, but **without periodicity**. This is the main difference with periodic crystals. Aluminium quasicrystal-strengthened alloys possess periodic aluminium-rich matrix, in which a quasicrystalline phase is dispersed. The quasicrystalline phase can form during rapid solidification and casting, or it is added to aluminium by methods typical for manufacturing composites. For the production of composites, the quasicrystalline particles can be added to an aluminium melt; parts are then obtained by casting. Alternatively, the quasicrystalline powder is added to aluminium powder, and products are produced via powder metallurgical routes.

[0022] The patent US 5593515 A discloses the manufacturing of alloy with a general formula  $Al_{bal} Q_a M_b X_c T_d$ , wherein Q represents at least one element selected from the group consisting of Mn, Cr, V, Mo and W; M represents at least one element chosen from the group consisting of Co, Ni, Cu and Fe; X represents at least one element selected from rare earth elements including Y or Mm; T represents at least one element selected from the group consisting of Ti, Zr and Hf; and a, b, c and d represent the following atomic percentages:  $1 \leq a \leq 7$ ,  $0 > b > 5$ ,  $0 > c \leq 5$  and  $0 > d \leq 2$ . The alloy of this invention is said to be excellent in the hardness and strength at both room temperature and a high temperature, and also in thermal resistance and ductility. The products can be of a rapidly solidified alloy, a heat-treated alloy obtained by heat-treating a rapidly solidified alloy, and a compacted and consolidated alloy material obtained by compacting and consolidating a rapidly solidified alloy.

[0023] The patent US 5419789 A discloses the aluminium-based alloy which consists Al and 0.1 to 25 atomic % of at least two transition metal elements and has a structure in which at least quasicrystals are homogeneously dispersed in a matrix composed of Al or a supersaturated Al solid solution. The alloy is in the form of a rapidly solidified material, a heat treated material of the rapidly solidified material, or a compacted and consolidated material formed from the rapidly solidified material.

[0024] Schurack et al. [2, 3] wanted to achieve improved properties of aluminium alloys applying quasicrystal-strength-

ening. Alloys were produced by melt spinning, mechanical alloying and conventional casting. They reported that mechanical alloying of stable AlCuFe-quasicrystals and aluminium powders did not give required combination of strength and ductility. However, Ce-addition to Al-Mn-alloys improved the quasicrystal forming ability, presumably due to stabilisation of the icosahedral melt structure. This procedure allowed the direct formation of icosahedral quasicrystals while cooling the melt. The milled and extruded melt-spun ribbons of the alloy  $Al_{92}Mn_6Ce_2$  attained strength of approximately 800 MPa and elongation ~25 %, but the conventionally cast rods had strength around 500 MPa and elongation ~20 %.

[0025] Song et al. [4] found out that the addition of Be sharply reduced the critical cooling rate for formation of quasicrystals during solidification and the required Mn-content in Al-Mn alloys. They established that quasicrystals formed at conventional casting methods as well (e.g. die casting). However, in their alloys were always present additional intermetallic phases, which reduce mechanical properties. Improved version of their alloys was prepared by Rozman et al. [5].

[2] F. Schurack, J. Eckert, L. Schultz: Synthesis and mechanical properties of cast quasicrystal-reinforced Al-alloys, *Acta materialia*, 49 (2001) 1351-1361

[3] F. Schurack, J. Eckert, L. Schultz: Synthesis and mechanical properties of quasicrystalline Al-based composites, *Quasicrystals, Structure and Physical Properties*, Wiley-VCH GmbH & Co. KgaA, Weinheim, 2003, 551-569

[4] G.S. Song, E. Fleury, S.H. Kim, W.T. Kim, D.H. Kim: Enhancement of the quasicrystal-forming ability in Al-based alloys by Be-addition, *Journal of Alloys and Compounds*, 342 (2002) 251 - 255

[5] N. Rozman, J. Medved, F. Zupanic, Microstructural evolution in Al-Mn-Cu-(Be) alloys, *Philos. Mag.*, 91 (2011) 4230-4246.

#### d) *Quasicrystalline precipitates in Al-alloys*

[0026] Kim et al. [6] found decagonal quasicrystalline precipitates in as-rapidly solidified and annealed commercial AISI 2024 aluminium alloy containing 2 wt% Li. The decagonal quasicrystalline phase precipitated from the solid solution at 400 °C. Zhang et al. [7, 8] studied the annealing of supersaturated solid solutions in some rapidly solidified Al-transition metal alloys using transmission electron microscopy. They found that icosahedral quasicrystalline precipitates formed in the Al-matrix in the binary systems Al-Cr and Al-Fe, and also in the systems Al-V, Al-Cr and Al-Mo, when they were alloyed by a small amount of Fe.

[0027] Zupanic et al. [9] discovered icosahedral precipitates in an Al-Mn-Be-Cu that was cast into a copper mould, after 24 h of annealing at 300 °C. The kinetics and mechanisms of precipitation at 300 °C were studied by Boncina and Zupanic [10].

[0028] There also exists a patent regarding quasicrystalline precipitates (US 5632826). However, it is related to the iron-based alloy and is inapplicable to the current invention.

[6] D.H. Kim, K. Chattopadhyay, B. Cantor, QUASI-CRYSTALLINE AND RELATED CRYSTALLINE PHASES IN A RAPIDLY SOLIDIFIED 2024-2LI ALUMINUM-ALLOY, *Acta Metallurgica Et Materialia*, 39 (1991) 859-875.

[7] X.D. Zhang, Y.J. Bi, M.H. Loretto, STRUCTURE AND STABILITY OF THE PRECIPITATES IN MELT SPUN TERNARY AL-TRANSITION-METAL ALLOYS, *Acta Metallurgica Et Materialia*, 41 (1993) 849-853.

[8] X.D. Zhang, M.H. Loretto, Stability and decomposition mechanisms of supersaturated solid solutions in rapidly solidified aluminium transition metal alloys, *Materials Science and Technology*, 12 (1996) 19-24.

[9] ZUPANIĆ, Franc, WANG, Di, GSPAN, Cristian, BONČINA, Tonica. Precipitates in a quasicrystal-strengthened Al-Mn-Be-Cu alloy. *Materials characterization*, ISSN 1044-5803. [Print ed.], Aug. 2015, vol. 106, str. 93-99. <http://www.sciencedirect.com/science/article/pii/S1044580315001606>, doi: 10.1016/j.matchar.2015.05.013.

[10] BONČINA, Tonica, ZUPANIĆ, Franc. In situ TEM study of precipitation in a quasicrystal-strengthened Al-alloy. *Archives of metallurgy and materials*, ISSN 1733-3490, 2017, vol. 62, iss. 1, str. 5-9. [http://www.imim.pl/files/archiwum/Vol1\\_2017/01.pdf](http://www.imim.pl/files/archiwum/Vol1_2017/01.pdf), doi: 10.1515/amm-2017-0001.

#### Description of a new solution

[0029] The invention **Manufacturing of High Strength and Heat Resistant Aluminium Alloys Strengthened by Dual Precipitates** is a method for manufacturing of high strength and temperature resistant Al-alloys that are strengthened by quasicrystalline and L12 precipitates. Al-alloys produced in this way are convenient, but not limited, for the application in the automobile and aerospace industries, as well as in the construction and building.

[0030] The required properties can be obtained by an appropriate combination of alloy's chemical composition, solidification of the melt by casting methods, in which the cooling rate in the liquid exceeds 100 K/s just before the beginning of the solidification, and two- or three stage heat treatment. Before heat treatment, the casting products can be cold or warm plastically deformed by any forming technology.

**[0031]** The invented heat-treatable aluminium alloy having a high strength and heat resistance, comprising

Mn: 2.0-5.0 mass.%;

Cr: 0.001-2.0 mass.%;

Cr + Mn: 2.0-5.0 mass.%;

V: 0.001-0.5 mass.%;

Cu: 2.0-4.5 mass.%;

Be: 0.001-0.9 mass.%;

Sc: 0.05-0.5 mass.%; and comprising of at least one element out of

Zr: 0.001-0.4 mass.%;

Y: 0.001-0.4 mass.%;

Ti: 0.001-0.4 mass.%;

Hf: 0.001-0.4 mass.% and

Nb: 0.001-0.4 mass.%;

the balance being Al and inevitable impurities up to 0.5 mass.%.

**[0032]** The alloy with the invented composition provides Al-rich matrix containing predominantly icosahedral quasicrystalline and  $L_{12}$  precipitates after appropriate casting and heat treatment. The alloying elements Mn, Cr and V are necessary to obtain quasicrystalline phase during solidification. The elements Cr and V can cause during heat treatment the formation of Cr- and V-rich shells around cores of the IQC-precipitates that are rich in Mn. A small amount of Be enables the formation of icosahedral quasicrystalline phase by casting when cooling rates exceed 100 K/s, and it also promotes the formation of quasicrystalline precipitates during heat treatment. The elements scandium and X element group (yttrium, zirconium, titanium, hafnium, and niobium) are essential for the formation of  $L_{12}$  precipitates, having an ordered crystal structure. The combination of Sr with any of the X-elements provide the creation of the so-called core-shell  $Al_3(Sr, X)$  precipitates. In these precipitates, the scandium is predominantly in the cores, while the X-elements (yttrium, zirconium, titanium, hafnium, and niobium) are in their shells. The presence of Cu allows the formation of Cu-rich precipitates ( $\Theta''$  or  $\Theta'$ ) in the matrix, between quasicrystalline and  $L_{12}$  precipitates during the third, low-temperature heat treatment. It also causes the in-situ conversion of the quasicrystalline phase to the T-phase ( $Al_{20}Mn_3Cu_2$ ) at higher temperatures during service.

**[0033]** The alloy can be produced in the liquid state by melting in induction or other furnaces, preferably under a vacuum or protective atmosphere to prevent loss of some alloying elements, hydrogenation of the melt and formation of oxides. As a charge, technically pure aluminium and commercial master alloys (e.g. AlCu50, AlY10) can be used.

**[0034]** Transformation to the solid state should be done by any casting technique, by which a **cooling rate exceeds 100 K/s**. These methods encompass but are not limited to casting into permanent moulds, gravitational casting, high-pressure die-casting, centrifugal casting, continuous casting, single-roll and dual-roll casting. Adequate cooling rates firstly provide the formation of quasicrystalline phase within grain boundaries and at the grain boundaries than prevent grain growth during further heat treatments. Secondly, a sufficient amount of alloying elements is preserved in the Al-rich solid solution, which enables precipitation of different types of precipitates during further heat treatment (a modified T5 heat treatment).

**[0035]** The invented alloy has a reasonable ductility so the castings can be plastically deformed before heat treatment by any forming process. The plastic deformation can increase the alloy's homogeneity, induce fragmentation of phases formed during solidification, and can also speed up the precipitation processes during ageing. This step is optional.

**[0036]** Heat treatment consists of two or three steps of artificial ageing, which represent a modified T5 heat treatment.

**[0037]** The aim of ageing at a first ageing temperature for a first predetermined time is to obtain an exceptionally high density of icosahedral quasicrystalline precipitates. A quasicrystal represents a state of matter, in which atoms are regularly arranged in space, but are not periodic. An icosahedral quasicrystal is quasiperiodic in three dimensions - in space. It also has a very high symmetry. Hence, it can often grow in the spherical form which is advantageous in comparison to plate-like or needle-like growth of many other phases in aluminium alloys. The quasiperiodicity allows excellent matching of icosahedral quasicrystal with the aluminium matrix. Therefore, the interface energy between the matrix and icosahedral precipitates is very low. The low interface energy enables homogeneous nucleation of IQC-precipitates, which are formed in very high number density. For example, the size of IQC-particles can be 10-15 nm, and the interparticle distances are 30-40 nm. The mobility of Mn atoms determines the size and interparticle distances between IQC-precipitates. For this reason, temperatures between 260 °C and 340 °C are required, and the ageing times are between 2 hours and 90 hours. The quasicrystalline precipitates contain aluminium and manganese predominantly. During the first ageing treatment also cuboidal  $Al_3Sc$ -precipitates can form in between IQC-precipitates. Their sizes are below 10 nm. The microstructure after first ageing treatment consists of a mixture of nanoscale quasicrystalline and  $L_{12}$  precipitates in the Al-rich solid solution.

**[0038]** The goal of the second ageing is to make the microstructure more stable when exposed to higher temperatures during service. The second ageing temperature should be higher than the first ageing temperature. The second ageing is to be carried out in the temperature range between 350 °C and 490 °C, and the duration from 15 minutes up to 10

hours. During the second ageing, the quasicrystalline precipitates that formed during first ageing stem continue to grow, the size becomes greater, and they also coarsen. During the coarsening the number density of IQC-precipitates decreases. When an alloy contains Cr and V, a Cr- and V-shell form around the Mn-rich core. Since the diffusivities of Cr- and V- are much smaller than that of manganese, the shell retards the coarsening of the IQC-precipitates during exposure of the alloy to higher temperatures. L<sub>12</sub> precipitates, rich in scandium (e.g. Al<sub>3</sub>Sc) will continue to grow. During this stage, the elements X (Zr, Y, Ti, Hf, Nb) will form a shell around Sc-rich L<sub>12</sub> precipitates. They have smaller diffusivities than Sc. Thus, the shell rich in X-elements will make harder the coarsening of L<sub>12</sub>-precipitates. The microstructure after the second ageing consists of the core-shell icosahedral precipitates, with the sizes 20-50 nm, and the core-shell L<sub>12</sub>-precipitates, with the sizes 10-20 nm, that are uniformly distributed between IQC-precipitates. This microstructure is very stable up to the temperatures close to the temperature of the second ageing treatment (maximum 450 °C).

**[0039]** The third ageing treatment is optional. Its aim is to cause precipitation of Cu-rich precipitates from the Al-matrix in the spaces between the icosahedral and L<sub>12</sub> precipitates. It is required that the alloy is quenched from the second ageing temperature, and then heated to a third ageing temperature, which is between 120 °C and 195 °C. The third ageing time is between 2 hours and 16 hours. The content of Cu in IQC- and L<sub>12</sub>-precipitates is minimal. Therefore, copper remains in the solid solution at the temperature of the second ageing. By quenching, it stays in the solid solution. After heating to the third ageing temperature, it precipitates in the form of Cu-rich precipitates; θ' and θ". By this treatment, the strength of the alloy at a low temperature is increased. However, the heat resistance is not changed because the Cu-rich precipitates dissolve when the alloy is heated to a temperature above 200 °C.

**[0040]** The important advantage of this method is that different shapes of castings and the desired as-cast microstructure that allows the successful heat treatment can be obtained by typical casting methods in aluminium foundries. The contents of alloying elements are rather low. Thus, the cast parts can be plastically deformed, if necessary, due to their ductility. The quantities of alloying elements, especially those with higher prices (e.g. scandium), are low. Thus the cost per unit of property is very low. This is important in comparison with scandium alloyed aluminium alloys (e.g. patent EP 2598664 B1). The IQC- and L<sub>12</sub>-precipitates are coherent with the Al-matrix, thus can be formed in much higher number densities than dispersoids. Thus, there are many more possibilities to tune the properties of the alloy by heat treatment and plastic deformation.

#### **Example of the invention Manufacturing of High Strength and Harder Aluminium Alloy Strengthened by Dual Precipitates**

**[0041]** The chemical composition of the alloy was:

mass. % Mn	mass. % Be	mass. % Cu	mass. % Zr	mass. % Sc	mass. % Y	mass. % Si	mass. % Fe	mass. % Al
3.29	0.36	3.57	0.11	0.51	0.12	0.21	0.16	remain

**[0042]** The alloy was produced by melting technically pure aluminium (Al 99.5), and master alloys AlMn10, AlBe5.5, AlCu50, AlZr10, AlSc2 and AlY10 in an electric resistant furnace. The alloy melt was homogenized at 750 °C and cast into a copper mould having cylindrical parts with diameters of 2.5, 4, 6 and 10 mm (the hardness in the as-cast condition was 100-120 HV 1).

**[0043]** Thereafter, some samples were plastically deformed at room temperature for 50 %. The hardness of deformed samples increased to 140-150 HV 1.

**[0044]** Samples were heat treated in an electrical resistance furnace in air. The first ageing temperature was 300 °C, and the first ageing time was 30 hours. After the first ageing, the hardness of the cast and aged samples was 120-130 HV 1, and the hardness of the cast, deformed and aged samples was 130-140 HV 1.

**[0045]** The samples were aged for the second time in an electrical resistance furnace in air. The second ageing temperature was 400 °C and the second ageing time was 1 hour. After the second ageing, the hardness of the cast, deformed and twice aged samples was 100-110 HV 1, and the hardness of the cast, deformed and twice aged samples was 110-120 HV 1.

**[0046]** The samples were quenched in water from the second ageing temperature. Then they were aged for the third time in an electrical resistance furnace in air. The third ageing temperature was 170 °C and the third ageing time was 5 hours. After the third ageing, the hardness of the cast and three times aged samples was 120-130 HV 1, and the hardness of the cast, deformed and three times aged samples was 130-140 HV 1.

## Claims

1. Manufacturing of High Strength and Heat Resistant Aluminium Alloys Strengthened by Dual Precipitates, in which the alloys

**are characterized**

**by** the following chemical composition:

Mn: 2.0-5.0 mass.%;

Cr: 0.001-2.0 mass.%;

Cr + Mn: 2.0-5.0 mass.%;

V: 0.001-0.5 mass.%;

Cu: 2.0-4.5 mass.%;

Be: 0.001-0.9 mass.%;

Sc: 0.05-0.5 mass.%; and comprising of at least one element out of

Zr: 0.001-0.4 mass.%;

Y: 0.001-0.4 mass.%;

Ti: 0.001-0.4 mass.%;

Hf: 0.001-0.4 mass.% and

Nb: 0.001-0.4 mass.%;

the balance being Al and inevitable impurities up to 0.5 mass.%.

2. High Strength and Heat Resistant Aluminium Alloys Strengthened by Dual Precipitates of Claim 1

**are characterized by**

the manufacturing by a casting technique, which may comprise any method facilitating a cooling rate in the liquid before beginning of solidification higher than  $100 \text{ K s}^{-1}$ ,

wherein the casting technique can involve but is not limited to gravitational casting into permanent moulds, high-pressure die-casting, centrifugal casting, single-roll casting, dual-roll casting and continuous casting;

where the cast products can be deformed by plastic deformation, wherein the plastic deformation method can involve but is not limited to rolling, pressing, forging, extrusion, bending, stretching, drawing and deep drawing.

3. High Strength and Heat Resistant Aluminium Alloys Strengthened by Dual Precipitates of Claim 1 produced by a method defined by Claim 2

**are characterized by**

heat-treatment according to a two-step-ageing treatment,

wherein the first ageing at the first ageing temperature takes place between  $260 \text{ }^\circ\text{C}$  and  $340 \text{ }^\circ\text{C}$ , and the first ageing time is between 2 hours and 90 hours, where the microstructure after first ageing treatment consists of quasicrystalline and  $L_{12}$  precipitates in the Al-rich solid solution;

wherein the second ageing temperature is between  $350 \text{ }^\circ\text{C}$  and  $490 \text{ }^\circ\text{C}$ , and the second ageing time is between 15 minutes and 10 hours; and the microstructure after second ageing consists of stabilised, slightly coarser icosahedral precipitates, and core-shell  $L_{12}$  precipitates.

4. High Strength and Heat Resistant Aluminium Alloys Strengthened by Dual Precipitates of Claim 1 produced by a method defined by Claim 2, and heat-treated according to Claim 3;

**are characterized by that**

the alloy is quenched from the second ageing temperature in water or similar cooling medium at room temperature; and thereafter aged at a third ageing temperature for a third ageing time; where the third ageing temperature is between  $120 \text{ }^\circ\text{C}$  and  $195 \text{ }^\circ\text{C}$ , and the third ageing time is between 2 hours and 16 hours; where Cu-rich precipitates are formed in the Al-matrix in the spaces between icosahedral and  $L_{12}$  precipitates to enhance a high-strength of the alloy at room temperature.



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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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