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(54) **Aluminum die casting alloy**

(57) Aluminum die casting alloy comprising 4 to 6 %
by weight nickel, 0.1 to 0.3 % by weight zirconium, 0.3
to 0.4 % by weight vanadium, optionally up to 5 % by
weight manganese, optionally up to 2 % by weight iron,
optionally up to 1 % by weight titanium, optionally up to
2 % by weight hafnium, optionally up to 2 % by weight
magnesium, optionally up to 1 % by weight chromium,

optionally up to 1 % by weight molybdenum, optionally
up to 0.5 % by weight silicon, optionally up to 0.5 % by
weight copper, optionally up to 0.5 % by weight zinc, and
aluminum as the remainder with impurities due to pro-
duction total max. 1 % by weight.

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Description

Casting Alloy," Metals Forum, Vol. 28, pp. 533-538, 2004.

FIELD OF THE INVENTION

[0001] The present invention relates to aluminum alloys that can be processed by conventional high pressure die casting and are dispersion-strengthened, age-hardenable, and have useful mechanical properties at temperatures up to at least 300°C.

BACKGROUND OF THE INVENTION

[0002] Aluminum alloys are one of the most important groups of light materials employed in the automotive industry, mainly because of their high specific strength. Most of the traditional aluminum casting alloys are based on the aluminum-silicon eutectic system because of its excellent casting characteristics. Unfortunately the solidus in this system does not exceed 550°C, and consequently the maximum working temperature of aluminum-silicon alloys is limited to about 200°C. In addition, the major alloying elements in traditional aluminum-based alloys (i.e., zinc, magnesium, and copper) have high diffusivity in the aluminum solid solution. Therefore, while these elements enhance the room temperature strength of the alloy, they compromise the alloy's thermal stability. For example, aluminum alloys based on the Al-Zn-Mg, the Al-Cu-Mg, and the Al-Li systems are able to achieve very high tensile strength (up to about 700 MPa); however their mechanical properties rapidly degrade when they are used at high temperature. In many applications, stability of mechanical properties at high temperature - not high strength - is the primary need. Therefore traditional aluminum alloys are not useful in such applications, and there is a need for a light-weight, thermally-stable material.

PRIOR ART

[0003] Attempts have been made in the prior art to provide aluminum casting alloys with enhanced thermal stability. Notable among these attempts are those that utilize the aluminum-nickel system with minor additions of zirconium. The following journal articles represent these attempts:

N.A. Belov, "Structure and Strength of Cast Alloys of the System Aluminum- Nickel- Zirconium," Metall., No. 10, pp. 19- 22, 1993.

N.A. Belov, "Principles of Optimizing the Structure of Creep-Resisting Casting Aluminum Alloys using Transition Metals," Journal of Advanced Materials, Vol. 1, No. 4, pp. 321-329, 1994.

N.A. Belov, V.S. Zolotarevsky, S. Goto, A.N. Alabin, V.V. Istomin-Kastrovsky, and V.I. Mishin, "Effect of Zirconium on Liquidus and Hardening of Al-6%Ni

[0004] The preceding journal articles teach that an optimum structure for an aluminum alloy that exhibits stability at high temperature can be produced on the basis of a eutectic composition consisting of an aluminum solid solution (α -aluminum) phase that is alloyed with at least 0.6 % by weight zirconium; and a second phase that has high creep strength, namely nickel tri- aluminide (Al_3Ni) .

[0005] The preceding journal articles also teach that objects made from these alloys are obtained by melting the carefully weighed solid alloy ingredients (aluminum, aluminum nickel master alloy, and aluminum zirconium master alloy) at about 900°C. This relatively high melting temperature is necessary in order to dissolve the high zirconium content (≥ 0.6 % by weight zirconium) into aluminum and obtain a homogeneous aluminum-nickel-zirconium melt. In addition, the preceding journal articles teach that the aluminum-nickel-zirconium melt must be cooled at a cooling rate that is faster than 10°C/second in order to solidify it and retain a homogeneous super saturated solid solution of zirconium in α -aluminum at room temperature. Furthermore, the preceding journal articles teach that as the material cools from the melt temperature, it may be shaped into the desired object form by casting it in a mold. Said mold must permit the material to cool from the melt temperature to room temperature at a rate that exceeds 10°C/second. Finally, the preceding journal articles teach that the cast solid object may be aged at a temperature between 350°C and 450°C in order to precipitate fine zirconium tri-aluminide (Al_3Zr) particles that harden the alloy.

[0006] When properly processed, the alloys represented in the preceding journal articles have better mechanical properties at elevated temperature than traditional aluminum casting alloys. However, hardening will not occur in the alloys represented in the preceding journal articles unless the zirconium content of the alloy is in excess of 0.4 % by weight, and significant hardening will not occur unless the zirconium content of the alloy is at least 0.6 % by weight. Smaller amounts of zirconium will not result in a volume of second phase particles (in this case Al_3Zr) that is sufficient to induce significant hardening of the α -aluminum solid solution. Fig. 1 depicts the amount of solid present in the melt as a function of temperature for an alloy of the prior art. The Figure shows that the alloy is completely molten only at temperatures above 850°C. Such high melt temperature does not allow the alloys represented in the preceding journal articles to be processed into shaped objects by conventional high pressure die casting since the temperature of the melt that may be introduced into the shot sleeve of a traditional high pressure die casting machine should not exceed 750°C.

[0007] A high cooling rate - in excess of 10°C/second - is necessary for retaining 0.6 % by weight zirconium in solid solution in α -aluminum at room temperature. With

the exception of high pressure die casting, such a fast cooling rate cannot be attained in most objects that are cast by conventional casting processes. Accordingly, with the exception of casting very small objects in graphite or copper molds, the alloys represented in the preceding journal articles cannot be processed into shaped objects by conventional casting processes.

DISCLOSURE OF THE INVENTION

[0008] This invention relates to a class of aluminum alloys which (i) are dispersion-strengthened, (ii) can be age-hardened for improved mechanical properties, and (iii) can be processed by conventional high pressure die casting to produce shaped articles that have useful mechanical properties at temperatures up to at least 300°C.

[0009] It is an object of the present invention to provide light-weight, wear-resistant, and corrosion-resistant materials that are castable via the conventional high pressure die casting process and that are thermally-stable up to at least 300°C.

[0010] The foregoing object is achieved according to the invention by an aluminum die casting alloy comprising 4 to 6 % by weight nickel,

0.1 to 0.3 % by weight zirconium,

0.3 to 0.4 % by weight vanadium,

optionally up to 5 % by weight manganese,

optionally up to 2 % by weight iron,

optionally up to 1 % by weight titanium,

optionally up to 2 % by weight hafnium,

optionally up to 2 % by weight magnesium,

optionally up to 1 % by weight chromium,

optionally up to 1 % by weight molybdenum,

optionally up to 0.5 % by weight silicon,

optionally up to 0.5 % by weight copper,

optionally up to 0.5 % by weight zinc,

and aluminum as the remainder with impurities due to production total max. 1 % by weight.

[0011] The alloys of the present invention have the general chemical composition: aluminum- nickel- zirconium- vanadium and their chemical composition is optimized such that their liquidus temperature is less than 750°C.

[0012] Upon solidification from the melt, nickel and aluminum form a eutectic structure comprised of a solid solution of nickel in aluminum (referred to as the α - aluminum phase) and a second phase comprised of nickel tri-aluminide (Al_3Ni). Alloys with a eutectic component in their microstructure have a narrower solidification range, and therefore are less prone to hot tearing, than alloys without a eutectic component in their microstructure. The Al_3Ni phase is in the form of thin rods whose diameter is in the range of 300 to 500 nanometers. If cooling from the melt temperature to room temperature is performed fast enough (i.e., at a rate that exceeds 10°C/ second), then also dissolved in the α - aluminum phase will be zirconium and vanadium. Upon subsequent controlled thermal aging of the solid alloy, zirconium and vanadium com-

bine with aluminum via a solid- state reaction to form a strengthening precipitate phase of the chemical composition $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$. The sub- micron size meta- stable $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ particles have the L1_2 cubic crystal structure and are uniformly distributed in the α - aluminum solid solution.

[0013] The alloys of the present invention may also include up to 5 % by weight manganese and up to 2 % by weight iron. In addition to forming metal aluminides, which can further strengthen the alloy, iron and manganese are useful ingredients in high pressure die casting alloys as they tend to mitigate soldering of the alloy to the die components.

[0014] The alloys of the present invention may also include up to 2 % by weight magnesium, up to 2 % by weight hafnium, up to 1 % by weight titanium, up to 1 % by weight molybdenum, up to 1 % by weight chromium, up to 0.5 % by weight silicon, up to 0.5 % by weight copper and up to 0.5 % by weight zinc. The alloys of the present invention preferably include substantially uniformly dispersed particles of $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$, where x is a fraction of unity that depends on the ratio of Zr : V in the alloy, the particles having an equivalent diameter of less than about 50 nm and preferably less than about 30 nm.

[0015] The alloys of the present invention preferably include particles of Al_3Ni having an equivalent diameter of less than about 500 nm, preferably less than about 300 nm, particularly less than about 100 nm.

[0016] The alloys of the present invention may include substantially uniformly dispersed particles of manganese aluminide having an equivalent diameter of less than about 50 nm and preferably less than about 30 nm.

[0017] The alloys of the present invention may include substantially uniformly dispersed particles of iron aluminide having an equivalent diameter of less than about 50 nm and preferably less than about 30 nm.

[0018] A feature of the alloys of the present invention which distinguishes them from prior art aluminum alloys which contain nickel and zirconium but without vanadium (described in the journal articles by N.A. Belov) is that the alloys of the present invention have a much lower liquidus temperature (typically less than 750°C as opposed to more than 850°C for the prior art alloys). The lower liquidus temperature permits the alloys of the present invention to be processed into shaped objects by conventional high pressure die casting whereas the alloys of the prior art cannot be processed into shaped objects by conventional high pressure die casting and are thus limited to the casting of small objects in graphite molds.

[0019] Another feature of the alloys of the present invention which distinguishes them from the prior art aluminum alloys containing nickel and zirconium but without vanadium is that the precipitation hardening particles in the alloys of the present invention are $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ particles (compared to Al_3Zr particles in the alloys of the prior art). Because of the smaller size of the vanadium atom (0.132 nm) compared to the zirconium atom (0.159 nm), the

$\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ lattice has a lattice parameter that is smaller than that of the Al_3Zr lattice and which more closely matches the lattice parameter of the α -aluminum matrix. For this reason, aluminum-nickel alloys that are hardened with $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ precipitates are more thermally stable than aluminum-nickel alloys that are hardened with Al_3Zr precipitates.

[0020] The foregoing and other features and advantages of the present invention will become more apparent from the following detailed description and accompanying drawings.

DESCRIPTION OF THE DRAWINGS

[0021]

Figure 1 is a computer-generated solidification path for aluminum - 6 % by weight nickel - 0.6 % by weight zirconium alloy;

Figure 2 is a computer-generated solidification path for aluminum - 6 % by weight nickel - 0.1 % by weight zirconium - 0.4 % by weight vanadium alloy.

DETAILED DESCRIPTION OF THE INVENTION

[0022] Dispersion strengthening of aluminum alloys relies on the creation of dispersed particles in the alloy's matrix. This strengthening mechanism is typified by alloys based on the aluminum- nickel system. Hypo- eutectic and eutectic aluminum- nickel alloys solidify in a structure that contains a fine dispersion of nickel tri- aluminide (Al_3Ni) particles in a matrix comprised of a solid solution of nickel in aluminum (α - aluminum) . Since nickel tri- aluminide is essentially insoluble in aluminum up to about 855°C, aluminum- nickel alloys are more stable at elevated temperatures than aluminum- silicon alloys. However, aluminum- nickel binary alloys do not possess adequate mechanical properties for most automotive applications as their room temperature tensile yield strength does not exceed 80 MPa; and therefore additional strengthening of these alloys is necessary.

[0023] Precipitation strengthening is a well-known mechanism of strengthening aluminum alloys as typified by alloys based on the aluminum-copper system. In these alloys precipitation of copper aluminide particles in an α -aluminum matrix is thermally controlled in order to produce effective strengthening of the alloy matrix.

[0024] The present invention combines characteristics of both types of the hardening mechanisms previously described in order to obtain aluminum alloys with sufficient elevated temperature mechanical strength for most automotive applications. The alloys of the present invention contain a fine dispersion of creep- resistant nickel tri- aluminide particles and a strengthening precipitate that is based on zirconium and vanadium, namely $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$.

[0025] In the prior art alloys, which contain nickel and zirconium but without vanadium (described in the journal articles by N.A. Belov), a strengthening phase with the chemical composition Al_3Zr is formed. In the invention alloy, the strengthening phase is also based on the Al_3Zr structure but with vanadium atoms substituting for some of the zirconium atoms. The accurate representation of the strengthening phase in the invention alloy is thus $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ with x being a fraction of unity whose magnitude depends on the ratio of zirconium to vanadium. The role that vanadium plays in the invention alloy is important in allowing the alloy to be processed into articles by high pressure die casting. The extent of strengthening induced by a precipitate is related to both the volume fraction of the precipitate and the size of the precipitate particles. A large volume fraction of small size particles is essential for strengthening. The prior art alloys employ a minimum 0.6% by weight zirconium in order to create about 0.83% by volume of the Al_3Zr strengthening phase. This amount is shown to be sufficient for significant strengthening of the alloy. However, examination of Fig. 1 shows that the liquidus temperature of an alloy with 0.6% zirconium is over 850°C. This relatively high melt temperature is prohibitive for conventional high pressure die casting, and therefore alloys of the prior art cannot be mass produced by high pressure die casting operations. A preferred version of the invention alloy employs only 0.1% by weight zirconium and 0.4% by weight vanadium. This mixture creates about 0.84% by volume of the $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ strengthening phase. The main benefit of employing vanadium in the invention alloy is that the liquidus temperature of the invention alloy is only about 730°C-see Fig. 2, which permits the use of conventional high pressure die casting in manufacturing shaped articles with the invention alloy.

[0026] A broad description of the invention material after optimum processing is that it is an α - aluminum (a very dilute solid solution of nickel in aluminum) matrix which contains about 0.8- 1.0% by volume of a uniformly distributed strengthening phase that is based on zirconium and vanadium and that has a structure represented by the chemical formula $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$, and about 1- 10% by volume nickel tri- aluminide particles uniformly dispersed in the alloy matrix. In a material of this invention that has been processed to have maximum strength, the $\text{Al}_3\text{Zr}_x\text{V}_{1-x}$ strengthening particles are meta- stable, have the L_{12} cubic structure, are coherent with the α - aluminum matrix, and have an average diameter of less than about 25 nm.

[0027] The production of such a structure requires: (1) fast cooling from the melt temperature, and (2) controlled thermal aging of the solidified article.

[0028] Fast cooling from the melt temperature is necessary to ensure that zirconium and vanadium are retained in solution in the α -aluminum matrix at room temperature; i.e., at room temperature the alloy contains the Al_3Ni eutectic phase and a second phase that is a super saturated solid solution of zirconium and vanadium in α -

aluminum. For the invention alloy, a cooling rate that exceeds 10°C / second is necessary to obtain a super saturated solid solution of zirconium and vanadium in α -aluminum. One of the advantages of the invention alloy over prior art alloys is that it is designed so that it can be processed into shaped articles by conventional high pressure die casting wherein the molten alloy at about 750°C is introduced directly into the shot sleeve of the die casting machine. It is then injected under high pressure into a steel die; the pressure is maintained on the alloy until solidification is complete, and then the solidified article is ejected. It is known that cooling rates in conventional high pressure die casting operations typically exceed 10°C/second. Therefore the casting process which shapes the article also provides the quenching that is necessary for obtaining a homogeneous super saturated solid solution of the strengthening elements (zirconium and vanadium) in α -aluminum.

[0029] Controlled thermal aging of solidified cast articles made with the invention alloy is necessary in order to precipitate the meta-stable $L1_2$ cubic $Al_3Zr_xV_{1-x}$ strengthening particles in the α -aluminum solid solution. This may be accomplished by an optimized thermal aging schedule. One such schedule includes holding the solidified cast article at a temperature between 250°C and 350°C for between two and six hours followed by holding it at a temperature between 350°C and 450°C for between two and six hours. A preferred thermal aging schedule includes holding the solidified cast article at 350°C for three hours followed by holding it at 450°C for an additional 3 hours. Simultaneous with precipitating the $Al_3Zr_xV_{1-x}$ strengthening particles in the α -aluminum solid solution, the prescribed thermal aging schedule fragments and changes the shape of the Al_3Ni eutectic rods into submicron size particles. This fragmentation and globularization of the Al_3Ni eutectic rods enhances the overall ductility of the cast article.

[0030] Although this invention has been shown and described with respect to detailed embodiments thereof, it will be understood by those skilled in the art that various changes in form and detail thereof may be made without departing from the spirit and scope of the claimed invention.

Claims

1. Aluminum die casting alloy comprising
 - 4 to 6 % by weight nickel,
 - 0.1 to 0.3 % by weight zirconium,
 - 0.3 to 0.4 % by weight vanadium,
 - optionally up to 5 % by weight manganese,
 - optionally up to 2 % by weight iron,
 - optionally up to 1 % by weight titanium,
 - optionally up to 2 % by weight hafnium,
 - optionally up to 2 % by weight magnesium,
 - optionally up to 1 % by weight chromium,
 - optionally up to 1 % by weight molybdenum,

optionally up to 0.5 % by weight silicon,
optionally up to 0.5 % by weight copper,
optionally up to 0.5 % by weight zinc,
and aluminum as the remainder with impurities due to production total max. 1 % by weight.

2. Aluminum die casting alloy according to claim 1, including substantially uniformly dispersed particles of $Al_3Zr_xV_{1-x}$, where x is a fraction of unity that depends on the ratio of Zr : V in the alloy, the particles having an equivalent diameter of less than about 50 nm and preferably less than about 30 nm.
3. Aluminum die casting alloy according to claim 1, including particles of Al_3Ni having an equivalent diameter of less than about 500 nm, preferably less than about 300 nm particularly less than about 100 nm.
4. Aluminum die casting alloy according to claim 1, including substantially uniformly dispersed particles of manganese aluminide having an equivalent diameter of less than about 50 nm and preferably less than about 30 nm.
5. Aluminum die casting alloy according to claim 1, including substantially uniformly dispersed particles of iron aluminide having an equivalent diameter of less than about 50 nm and preferably less than about 30 nm.
6. Die-cast component made from an aluminum alloy according to any one of claims 1 to 5.
7. Method of producing a die-cast component made from an aluminum alloy according to any one of claims 1 to 5, wherein the alloy is age-hardened by holding the solidified die-cast component at a temperature of 250°C to 350°C for 2 to 6 hours followed by holding it at a temperature of 350°C to 450°C for 2 to 6 hours.

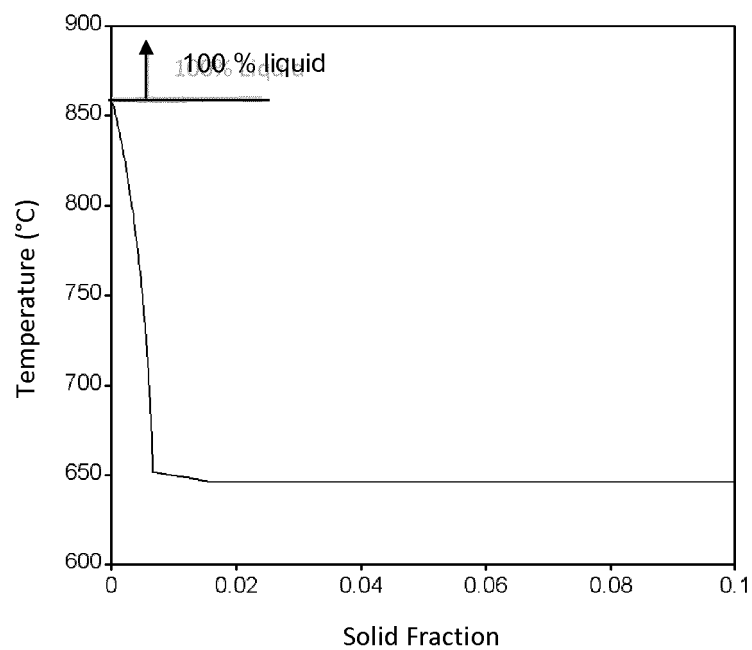


Fig. 1

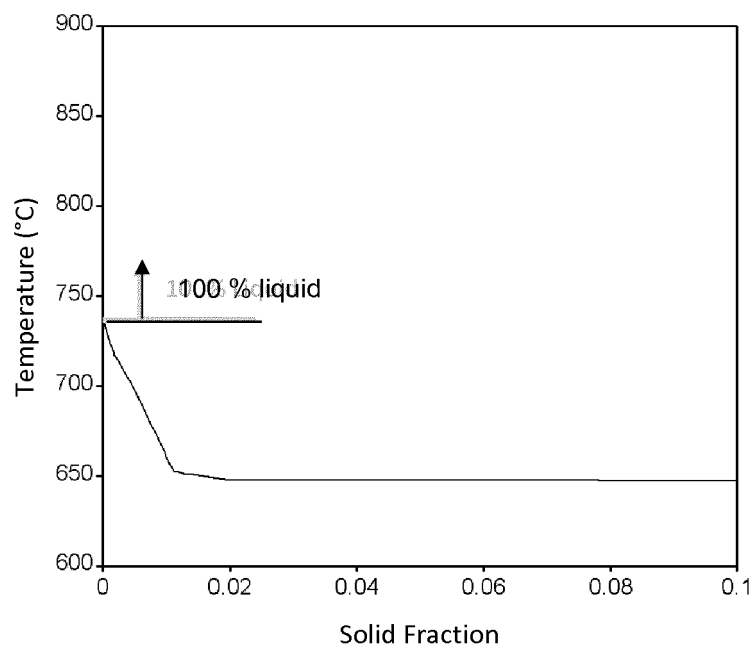


Fig. 2



EUROPEAN SEARCH REPORT

Application Number
EP 13 17 6662

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	JP 63- 219 543 A (SHOWA ALUM CORP) 13 September 1988 (1988-09-13) * abstract; table 1 * -----	1-7	INV. C22C21/00 C22F1/04
			TECHNICAL FIELDS SEARCHED (IPC)
			C22C C22F
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 10 September 2013	Examiner González Junquera, J
<p>CATEGORY OF CITED DOCUMENTS</p> <p>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</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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10-09-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 63-219543 A	13-09-1988	-----	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

- **N.A. BELOV.** Structure and Strength of Cast Alloys of the System Aluminum-Nickel-Zirconium. *Metall-ov.*, 1993, 19-22 [0003]
- **N.A. BELOV.** Principles of Optimizing the Structure of Creep-Resisting Casting Aluminum Alloys using Transition Metals. *Journal of Advanced Materials*, 1994, vol. 1 (4), 321-329 [0003]
- **N.A. BELOV ; V.S. ZOLOTOREVSKY ; S. GOTO ; A.N. ALABIN ; V.V. ISTOMIN-KASTROVSKY ; V.I. MISHIN.** Effect of Zirconium on Liquidus and Hardening of Al-6%Ni Casting Alloy. *Metals Forum*, 2004, vol. 28, 533-538 [0003]