PRIMARY CRYSTALLISATION OF INTERMETALLIC COMPOUNDS IN THE Al-Ni-Fe-Mn-Si SYSTEM IN RELATION TO FOUNDRY ALLOYS BASED ON AN ALUMINIUM-NICKEL EUTECTIC

N.A. Belov[1], A.N. Alabin[1], I.A.Matveeva[2], A.V. Sannikov[1]

[1]The National University of Science and Technology Moscow Institute of Steel and Alloys, 4 Leninskiy prospect str., 119049, Moscow, Russia

[2]UC RUSAL, 13/1 Nikoloyamskaya str., 109240, Moscow, Russia

Keywords: Al-Ni-Fe-Mn-Si system, phase composition, liquidus, primary crystals, intermetallic phases, eutectic

Abstract

We have calculated liquidus projections in the typical sections of the Al-Ni-Fe-Mn-Si system up to: 9% Ni, 3% Fe, 3% Mn, and 3% Si (%wt). We have identified concentrations of elements enabling primary crystallisation of the Al_3Ni, Al_9FeNi, Al_3Fe, $Al_6(Fe,Mn)$, and $Al_{15}(Fe,Mn)_3Si_2$ intermetallic phases. We have demonstrated close agreement of the experimental data and calculated data. Primary crystals of two phases - Al_9FeNi and $Al_6(Fe,Mn)$ will most likely form during casting to metal moulds in the area of nickalyn compositions. Primary crystallisation of the Al_3Ni and $Al_{15}(Fe,Mn)_3Si_2$ phases is possible only at higher Ni and Si concentrations respectively, while formation of the Al_3Fe phase requires slow solidification achieved through casting to expendable moulds.

Introduction

Aluminium alloys based on a nickel-containing eutectic (nickalyns) and doped solely with transition metals according to the principles stated in ref. [1] have an improved combination of foundry and mechanical properties (including those at higher temperatures) as compared to Al-Si alloys of 3xx series, ref. [2, 3]. The most balanced complex of properties has been implemented in the $AlNi_4Mn_2$ alloy containing 4% Ni, ref. [4, 5]. However, this nickalyn with all nickel contained in an $(Al)+Al_3Ni$ eutectic (where (Al) - an aluminium solid solution) should be considered as a model composition, since it supposes low Fe content, i.e. its production requires high-purity aluminium. The key shortcomings of the $AlNi4Mn2$ alloy have been eliminated in a new product developed at the Casting Processes Technology Chair of the MISiS National University of Science & Technology: thinly doped nickalyn - $AlNi2FeMn$ alloy based on the Al-Ni-Fe-Mn system, ref. [6]. Ni content in this alloy is decreased roughly twice, while iron is not an impurity, but an alloying component, since the primary structural constituent is an $(Al)+Al_9FeNi$ eutectic. For the reasons of reinforcement of the aluminium matrix, this alloy also contains Zr and Mn additives which evolve as dispersoids during annealing. If zirconium does not form other phases in addition to Al_3Zr, manganese may be distributed between several phases, but this process requires a special analysis. Hence, it follows that the Al-Ni-Fe-Mn-Si system is basic for the $AlNi2FeMn$ alloy (allowing for an inevitable impurity of silicon). This five-component system in respect to the considered alloy group may contain seven intermetallic phases: Al_3Ni, Al_3Fe, $Al_6(Fe,Mn)$, Al_9FeNi, Al_8Fe_2Si, $Al_{15}(Fe,Mn)_3Si_2$, and Al_5FeSi, ref. [7]. At certain concentrations, they may evolve as primary crystals.

Primary crystals of intermetallic compounds are undesirable in the structure of nickalyns, since their rough morphology has an adverse effect on mechanical properties, ref. [5]. This implies the need for identification of concentration limits at which these crystals form. In order to solve this task, it is reasonable to use dedicated software products, such as Thermo-Calc software. It allows calculating multicomponent systems including aluminium-based systems, which is described in the monograph, ref. [7].

The following tasks have been set for this research activity:
1) To calculate concentrations of elements in the Al-Ni-Fe-Mn-Si system, making primary crystallisation of intermetallic phases using the Thermo-Calc software (TTAl5 base) possible.
2) To select experimental alloys based on the calculation and to compare the experimental data with the calculated data.

Calculation of typical liquidus sections in the Al-Ni-Fe-Mn-Si system

The range of concentrations for calculation of primary crystallisation has been selected based on a qualitative analysis of the multicomponent diagrams for the Al-Ni-Fe-Mn-Si system in respect to nickalyns: 0-9% Ni, 0-3% Fe, 0-3% Mn, 0-3% Si (%wt), ref. [7-12].

The combined effect of iron and nickel at 0.5% Mn is shown in Fig.1a. It follows from this figure that location of primary crystallisation fields of intermetallic phases in this quaternary system which is quite similar to location of respective fields in the Al-Ni-Fe system, ref. [5, 7, 8, 10].
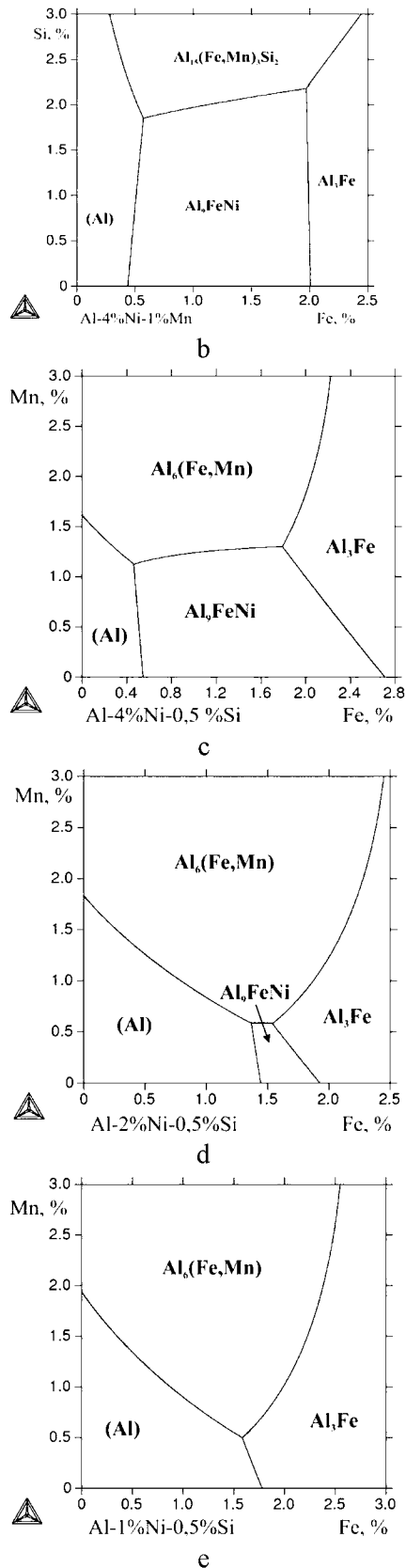

a

b

c

d

e

f
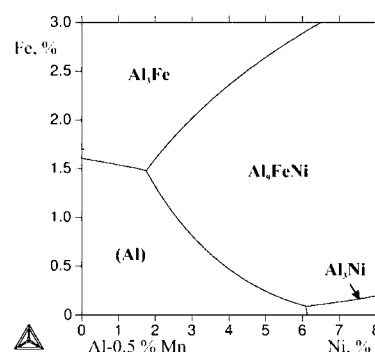
Fig.1. Projections of liquidus surface in sections of Al-Ni-Mn-Fe-Si system: a) at 4% Ni and 0.2% Fe; b) at 4% Ni and 1% Mn; c) at 4% Ni and 0.5% Si; d) at 2% Ni and 0.5% Si; e) at 1% Ni and 0.5% Si; f) at 1% Ni and 1% Mn.

It follows from the section at 0.5% Ni that only two phases may primarily crystallise in the considered range in addition to (Al): $Al_6(Fe,Mn)$ and Al_3Fe.

It is known that the silicon may be present in four phases of alloys in the Al-Ni-Fe-Mn-Si system, but only one of them $(Al_{15}(Fe,Mn)_3Si_2)$ may primarily crystallise in the considered range of concentrations. In particular, the section at 2% Ni and 0.2% Fe shows that Si content should exceed 1.5% (Fig.4a). At lower Si content, the excess of manganese should result in formation of $Al_6(Fe,Mn)$ primary crystals. At low Mn content, the formation limit of $Al_{15}(Fe,Mn)_3Si_2$ primary crystals shifts towards increase of Si content (over 3% Si).

To summarise the calculation results, we can notice a complex effect of composition both on the size of the primary crystallisation area of an aluminium solid solution and on the intermetallic component type which may form in the structure as primary crystals.

Experimental methodologies

We have prepared five alloys for the experimental study where the following intermetallic phases should primarily crystallise according to the calculation: Al_3Ni, Al_9FeNi, Al_3Fe, $Al_6(Fe,Mn)$, and $Al_{15}(Fe,Mn)_3Si_2$. We have prepared the alloys in a resistance furnace of SHOL 0.02 type based on on aluminium wire rod waste (99.7% purity) and in a graphite/fire clay crucible at 850°C. The main doping components have been added using the following charge materials: Al-20%Ni, Al-10%Mn, Al-10%Fe master alloys, as well as Al-12%Si alloy. Slabs 15x30x180 mm in size have been cast using a graphite mould. Chemical composition of the alloys according to the spectral analysis data has been made using an emission spectrometer of ARL 4460 type is shown in Table 1.

Table 1. Chemical composition of the experimental alloys

#	Concentration, %wt				
	Ni	Mn	Fe	Si	Al
1	7.95	<0.01	0.11	0.10	Basis
2	3.63	0.02	1.30	0.09	Basis
3	0.55	0.49	1.96	0.09	Basis

4	1.84	1.92	0.99	0.11	Basis
5	1.83	2.17	0.34	1.87	Basis

Microstructure of the cast specimens has been studied using an optical microscope and a scanning electron microscope: Axio Observer MAT and JSM-6610LV respectively. The JSM-6610LV microscope equipped with an energy-dispersive attachment - Oxford Instruments INCA SDD X-MAX microanalyser and INCA Energy software have been also used to identify composition of the primary intermetallic compounds.

We have studied the polished sections cut from central parts of the slabs. The polished sections have been prepared using first mechanical polishing and then electrolytic polishing. The latter has been carried out at 12V voltage in the bath containing 6 parts of ethyl alcohol, 1 part of perchloric acid, and 1 part of glycerine.

Experimental results and discussion

Temperature ranges supposing formation of the primary intermetallic compounds have been estimated in the Thermo-Calc software using the Sheil-Gulliver model through calculation of total solids (Q_S) - temperature functions (Fig.2). The calculation results are shown in Table 2. This table indicates that temperature ranges are from 11°C to 36°C, while weight fractions of the primary intermetallic compounds are from 1.5 to 4.9%.
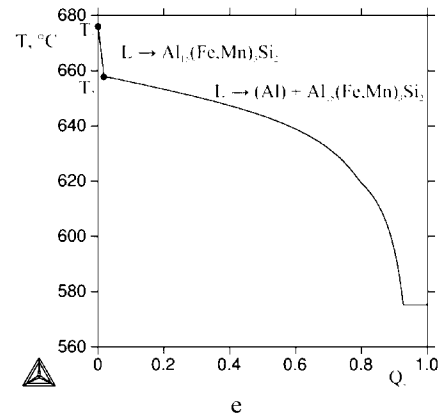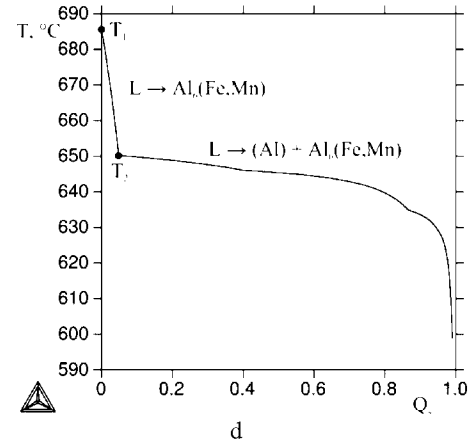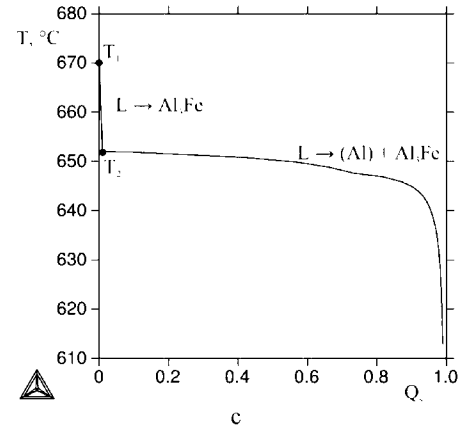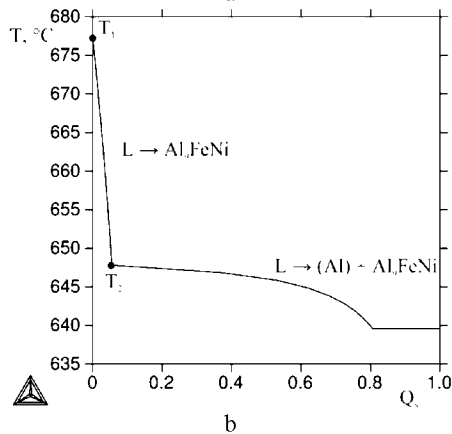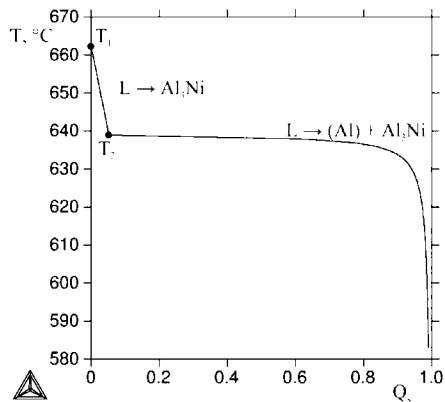

a

b

c

d

e

Fig.2. Calculated total solids (Q_S) - temperature functions at non-equilibrium crystallisation of experimental alloys: a) alloy #1; b) alloy #2; c) alloy #3; d) alloy #4; e) alloy #5 (for compositions of alloys refer to Table 1).

To make sure that the conditions are close to those of equilibrium, the weighted quantities of alloys (apprx. 50 g) were melted and kept at the temperature that was 10^0 centigrade higher than that at the beginning of crystallization (Al) – please see Figure 2. After this, the weighted quantities of alloys, still placed in a crucible, were quenched in water, in order to provide the conditions close to equilibrium (at the temperature of holding). Microstructure of all prepared alloys against the eutectic background contains distinct primary crystals, size of which may be tens and even hundreds of microns (Fig.3). Their identification by morphological features was not absolutely reliable; therefore, we

191

had made a microprobe analysis. Its results are shown in Figs.4, 5 and are discussed below.
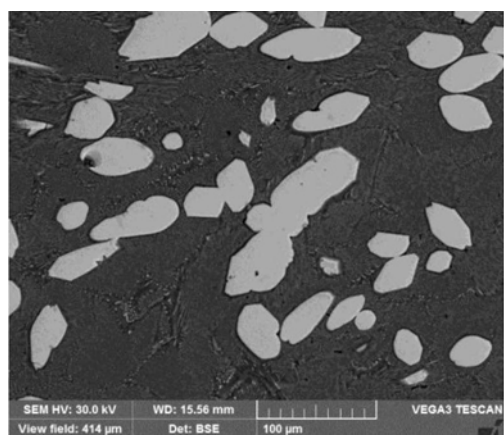
Al_3Ni intermetallic compound (Fig.4) primarily crystallises in alloy #1 with low Ni, Fe, Si contents in full conformity with Fig.2a. Primary crystals of only iron-containing phases are found in other alloys.

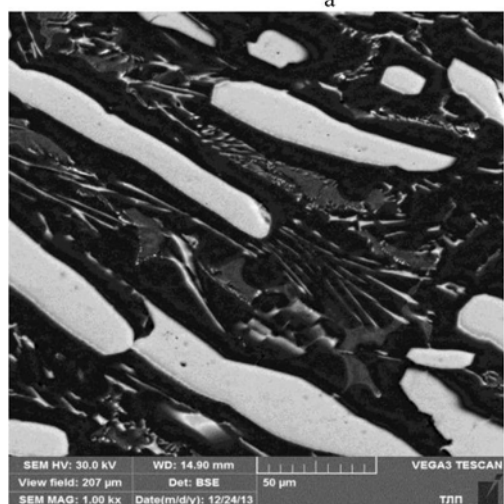Table 2. Calculated crystallisation parameters of intermetallic phases[1]

	Phases	T_1, °C	T_2, °C	ΔT, °C	Q, %wt
1	Al_3Ni	662.6	651.5	11.1	2.46
2	Al_9FeNi	677.6	648.0	29.6	1.50
3	Al_3Fe	670.6	652.2	18.4	3.54
4	$Al_6(Fe,Mn)$	686.2	650.3	35.9	4.86
5[2]	$Al_{15}(Fe,Mn)_3Si_2$	676.3	658.1	18.2	2.00

[1]T_1, T_2, ΔT - crystallisation beginning, end, and range for the respective intermetallic phases, Q - weight fractions of intermetallic phases
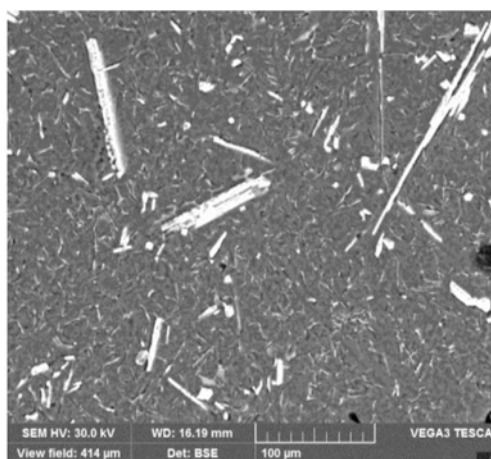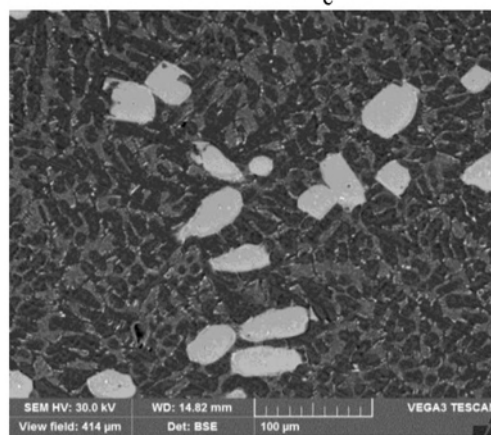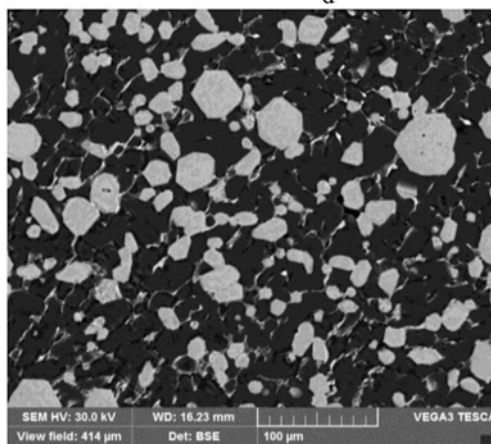[2]Calculated using the COST2 database

Fig.3. Microstructure of experimental alloys with primary intermetallic phases, scanning electron microscope: a) alloy #1; b) alloy #2; c) alloy #3; d) alloy #4; e) alloy #5 (for compositions of alloys refer to Table 1).
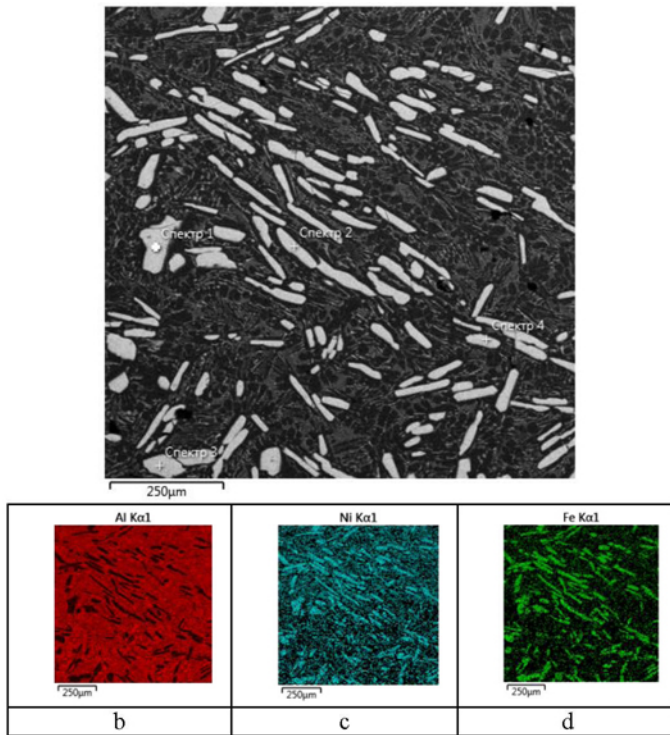
192

Fig.4. Primary crystals of Al_3Ni phase in alloy #1 (Table 1):
a) microstructure, scanning electron microscope,
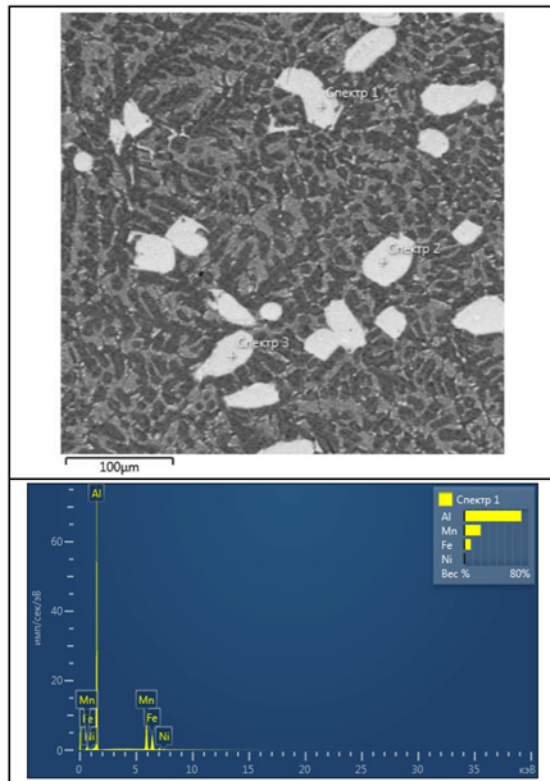b), c), d) distribution of elements Al, Ni, Fe

Fig.5. Primary crystals of Al_9FeNi phase in alloy #2 (Table 1):
a) microstructure, scanning electron microscope, b) distribution of elements in crystal
Analysis of alloy #2, composition of which certainly falls within the primary crystallisation area of the Al_9FeNi phase (Fig.1a,

Fig.3b), shows presence of that particular phase (Fig.5) in this alloy. According to the calculation the Al_3Fe intermetallic compound is also present in the alloy #3. Analysis of the composition of primary crystals in the alloy #4 confirms that this is the $Al_6(Fe,Mn)$ phase (Fig.5) which is consistent with the calculation (Fig.1, Fig.3d). Chemical analysis of primary crystals in alloy #5 also corresponds to the calculated data (Fig.2e) which demonstrate formation of the $Al_{15}(Fe,Mn)_3Si_2$ phase.

Conclusions

1) Using the Thermo-Calc software (TTAl5 base), we have plotted liquidus projections in the typical sections of the Al-Ni-Fe-Mn-Si system up to: 9% Ni, 3% Fe, 3% Mn, and 3% Si (%wt). We have identified concentrations of elements in this system, enabling primary crystallisation of the Al_3Ni, Al_9FeNi, Al_3Fe, $Al_6(Fe,Mn)$, and $Al_{15}(Fe,Mn)_3Si_2$ intermetallic phases.
2) Based on the calculation results, we have selected and prepared the experimental alloys. Using the method of microprobe analysis of primary crystals, we have demonstrated close agreement of the experimental data and calculated data.
3) Primary crystals of two phases - Al_9FeNi and $Al_6(Fe,Mn)$ will most likely form during casting to metal moulds in the area of nickalyn compositions. Primary crystallisation of the Al_3Ni and $Al_{15}(Fe,Mn)_3Si_2$ phases is possible only at higher Ni and Si concentrations respectively, while formation of the Al_3Fe phase requires slow solidification achieved through casting to expendable moulds.

Acknowledgment

References

1. N. Belov. Principles of Optimising the Structure of Creep-Resisting Casting Aluminium Alloys Using Transition Metals. Journal of Advanced Materials, 1994 1 (4), p.321-329.
2. N. Belov, V. Zolotarevskiy. Aluminium-nickel eutectic based foundry alloys (nickalyns) as a possible alternative to silumins. Non-Ferrous Metals, 2003, #2, p.99-105.
3. N. Belov, A. Alabin. Advanced aluminium alloys with increased heat resistance for the valve industry as a possible alternative to steel and cast iron. Valve Industry, 2010, #2, p.
4. N. Belov. Aluminium-based foundry alloy. Russian Patent #2001145, Bulletin #37-38 dated October 15th, 1993 (MISiS).
5. V. Zolotarevskiy, N. Belov. Metallurgy of foundry aluminium alloys. - Moscow: MISiS, 2005, 376 p.
6. N. Belov, V. Belov, A. Alabin, S. Mishurov. AlNi2FeMn heat-resistant foundry aluminium alloy. Russian Patent Application #2010144164, Publication #10.05.2012, Bulletin #13.
7. N. Belov. Phase composition of commercial and advanced aluminium alloys. - Moscow: MISiS Publishing House, 2010, 511 p.
8. L. Mondolfo. Structure and properties of alloys / Translated from English - Moscow: Metallurgy, 1979 - 640 p.
9. Aluminium. Properties and physical metallurgy: Reference book. U. Anthony, F. Eliot, M. Ball / Edited by J. Hatch. Translated from English. Moscow, Metallurgy, 1989, 324 p.
10. Lijun Zhang, Jiong Wang, Yong Du, Rongxiang Hu, Philip Nash, Xiao-Gang Lu and Chao Jiang. Thermodynamic properties

of the Al-Fe-Ni system acquired via a hybrid approach combining calorimetry, first-principles and CALPHAD. Acta Materialia, 2009, v.57, p 5324-5341.

11. A. Richter, C.-L. Chen, R. Smith, E. McGee, R.C. Thomson, S.D. Kenny. Hot stage nanoindentation in multi-component Al-Ni-Si alloys: Experiment and simulation. Materials Science and Engineering A, 2008, v.494, p.367-379.

12. Yong Du, Shuhong Liu , Lijun Zhang, Honghui Xu, Dongdong Zhao, Aijun Wang, Liangcai Zhou. An overview on phase equilibria and thermodynamic modeling in multicomponent Al alloys: Focusing on the Al-Cu-Fe-Mg-Mn-Ni-Si-Zn system. CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry, 2011, v.35, p.427-445.