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New wear resistant hypereutectic AlSi14Cu4FeCrMn alloys for high pressure die casting

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Introduction

The hypereutectic AlSi17Cu4Mg alloys are applied for castings where wear resistance plays a significant role. In addition, these alloys have low thermal expansion coefficients as well as good mechanical properties at room temperature and elevated temperatures, which make them interesting for high temperature applications. In the automotive field the hypereutectic AlSi17Cu4Mg alloys are used for example for climate compressor housings and for monolithic engine blocks.

The high wear resistance of these alloys is based upon the presence of primary silicon crystals, which are formed during solidification. The silicon particles with a hardness of up to 1148 HV provide the necessary wear resistance for the sliding pistons in compressor housings and engine blocks. Moreover, engine blocks made from hypereutectic Al-Si alloys have lower weight which leads to a reduced fuel consumption and thus lower CO_2 emission compared to hypoeutectic Al-Si blocks with cast iron liners [1].

Monolithic engine blocks in hypereutectic Al-Si alloys are exclusively produced by the low pressure die casting process, due to low turbulences during the filling of the die [2]. Although high pressure die casting is one of the most highly productive casting processes, the production of monolithic engine blocks by the high pressure die casting process is limited for the following reasons:

- The solidification starts with the precipitation of primary silicon at about 660 °C. The resulting high casting temperature and the abrasive effect of early precipitated Si-particles reduce the die life and the life of the shot chamber. In addition, high casting temperatures promote the absorption of hydrogen from atmospheric humidity or moist materials and the formation of oxides such as Al_2O_3 [3].
- The high latent heat of the primary silicon leads to low viscosity of the remaining melt and increases the risk of the melt spurting out of the die during the casting process [4, 5].

In order to overcome the limitations mentioned above and to adapt this alloy to the production of monolithic engine blocks in high pressure die casting as well as to improve their tribological properties the following innovative concept will be introduced. The silicon content in the hypereutectic Al-Si alloy will be reduced from 17 wt.-% to 14 wt.-% to allow a lower casting temperature. The addition of iron to the alloy compensates the reduced volume fraction of hard primary silicon particles and improves the tribological properties. This effect is based on the additional formation of the hard iron-containing α-$Al_{15}Fe_3Si_2$-phase. By adding elements such as Cr und Mn the formation of detrimental intermetallic β-Al_5FeSi platelets will be avoided.

State of the study

A uniform distribution of fine primary silicon particles within the aluminum matrix is the key for optimal characteristics for the cylinder block surface inside liners. In a conventional way, this can be achieved by adding phosphorous to the melt. Phosphorous reacts with aluminum in the melt to AlP, which acts as an effective heterogeneous nucleant for the silicon phase. Usually, in gravity die castings primary silicon particles can be reduced to a size of as small as 50 µm. However, by adding phosphorus to the melt the precipitation temperature of silicon particles increases. Moreover, in presence of iron in the melt phosphorus promotes the formation of intermetallic β-platelets [6]. Therefore, the addition of phosphorus to the melt has to be avoided.

Iron (Fe) is the most common detrimental impurity in aluminum casting alloys. The typical secondary Al-Si alloys usually contain iron levels ranging from 0,2 wt.-% - 0,8 wt.%. In high pressure die casting, iron is often added to prevent the molten Al alloy from soldering to the steel die.

Iron has very little solubility in the solid aluminum and leads to the formation of complex intermetallic phases of various types during solidification. The complex shapes of these intermetallic iron phases have a significant influence on the castability and moreover on the mechanical properties of the alloy. In Al-Si alloys the phases are Al_5FeSi, well known as β-phase, and α-Al_8Fe_2Si, usually known as sludge.

The β-Al_5FeSi phase is shaped as a very large and hard platelet and has detrimental effect on mechanical properties, particularly ductility. The scale of deterioration of mechanical properties depends on the volume fraction and the size of the platelets. Both parameters are a function of the iron content in the melt and the solidification conditions. It is well known that the cooling rate has an important influence on the length of the β-phase. Under normal casting conditions and moderate iron levels, β-phases can grow in the size range between 50 µm and 500 µm. In alloys with a small content of iron, which solidified with a very high cooling rate, the intermetallic particles have a size of typically 10 µm to 50 µm. Furthermore, the platelet-like morphology of the β-phase is expected to cause severe feeding difficulties during solidification and to increase the tendency of shrinkage porosity formation [7].

In order to avoid this detrimental effect of iron to castability and mechanical properties, the platelet-like morphology of β-phase should be transformed to a more compact, α-phase. Here, manganese is widely used as an alloying element to neutralize the effect of iron and to modify the β-platelets to intermetallic α-phase morphology. If Mn is present together with Si, the primary α-$Al_{15}(Fe,Mn)_3Si_2$-phase may appear as compact, star-like or dendritic or Chinese script crystals. All morphologies of the α-phase are less harmful to mechanical properties than the β-phase. However, the compact morphology of the α-phase is the best solution.

The combined addition of Mn and Cr to an Al-Si-Fe melt can also lead to precipitations of the α-phase which grow in a compact form. Here, iron is partially replaced through Mn and Cr forming α-$Al_{15}(Fe,Mn,Cr)_3Si_2$ phase. Because of its high micro-hardness of approx. 815 HV [8], the α-phase can in addition to the primary silicon serve as a wear resistant compound.

However, in Al-Si-melts the complex intermetallic α-$Al_{15}(Fe,Mn,Cr)_3Si_2$-particles have a high precipitation temperature and higher density than the melt and can sink as sludge on the bottom of the furnace reducing the effective capacity of the furnace.

The formation of sludge may also increase the die-soldering tendency of the alloy because of a decrease of Mn and Fe in the melt [9].

The sludge formation often occurs in industry and depends on two variables: chemical composition of the melt and furnace temperature. With increasing amounts of Fe, Mn and Cr the sludge formation temperature increases and can reach the temperature of the melt in the furnace. Thus, the amounts of the elements have to be restricted in the melt, that the precipitation temperature of the α-phase does not exceed the melt temperature. On the other hand, these elements are desired in the melt to get a high volume fraction of compact α-particles compensating the reduced volume fraction of Si-particles. Here, an optimum must be found.

Jorstad and Gobrecht studied the sludge phenomenon and defined a sludge factor (SF) for Al-Si-Cu alloys, which can be used to determine the critical ratio of Fe, Mn and Cr which can cause sludge formation [10,11]. This factor is calculated from the equation (1):

$$\text{Sludge Factor} = \text{Fe} + 2 \times \text{wt. \% Mn} + 3 \times \text{wt. \%Cr} \qquad (1)$$

A higher sludge factor promotes a higher sludge formation temperature which leads to increasing melting and casting temperatures with harmful consequences on the wear of the shot chamber and the die.

Development of a wear resistant AlSi-alloy for high pressure die casting

Investigation of sludge formation in the melt

Three alloys with sludge factors 1,6, 2 and 2,9 were prepared in an electrical resistance furnace. Their initial chemical composition is shown in in Table 1. All alloys are without phosphorus addition.

Table 1: Chemical composition of the alloys and their resulting sludge factor according to equation (1)

Alloy	wt.-% Si	wt.-% Cu	wt.-% Fe	wt.-% Mn	wt.-% Cr	S_f
1	14	4	0,9	0,2	0,1	1,6
2	14	4	1,2	0,1	0,2	2
3	14	4	1,8	0,1	0,3	2,8

The alloys were melted in a crucible and maintained over 30 minutes at 850°C getting a complete dissolution of all alloying elements and then cooled down to 680°C.

To determine the temperature of sludge formation the melt temperature was cooled down from 680°C in steps of 10°C and held at each temperature for 2 hours. During the holding time every 30 minutes samples from the melt surface were taken for chemical analysis. As the contents of Fe, Mn and Cr start to decrease at a certain temperature it is considered as the temperature of sludge formation. Experimental results of sludge formation temperatures for the new developed AlSi14Cu4FeMnCr alloys as well as for AlSi9Cu3(Fe) can be seen in Fig. 1.

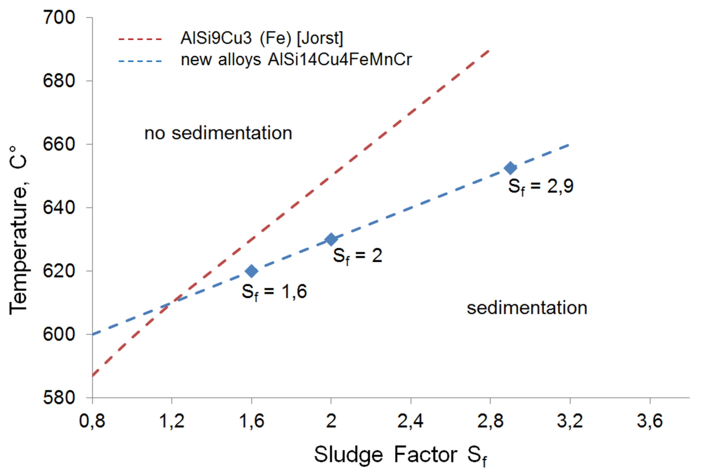

Fig. 1: Relationship between sludge formation temperature and sludge factor for AlSi9Cu3(Fe) [10] and AlSi14Cu4FeMnCr

According to [12], the temperature of the sludge formation shifts to lower values, when the Si content increases. It can be seen in Fig. 1 that the formation temperature of sludge of new alloys are situated to lower values compared to commercial AlSi9Cu3(Fe) alloy. Even, the alloy with a sludge factor of 2,9 and thus high volume fractions of α-phase has only a sludge formation temperature of 650 °C.

For microstructure analysis rod samples with a diameter of 10 mm were cast in gravity die casting. As a result it has been found that the sludge factor S_f of 2,9 promotes the highest volume fraction of hard α-AlFeSi phase.

In Fig. 2 the microstructure of a sample AlSi14Cu4Fe1,8Cr0,3Mn0,1 with S_f 2,9 is shown. It can be seen that both primary silicon and α-AlFeSi phases precipitate in a polyhedral shape. The detrimental β-AlFeSi phase appears in very low amounts.

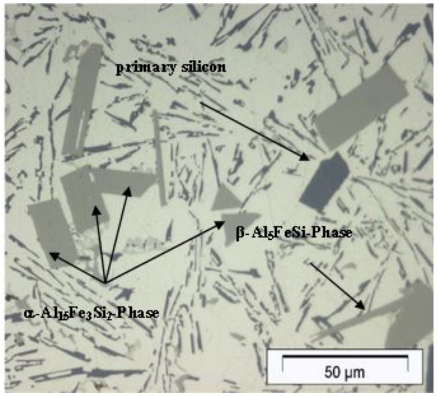

Fig. 2: Microstructure of gravity die cast AlSi14Cu4Fe1,8Cr0,3Mn0,1 alloy

Fraction of wear resistant primary silicon and α-AlFeSi phases

The results of the quantitative microstructure analysis in Table 2 show the volume fractions of both hard compounds of the new AlSi14Cu4Fe1,8Cr0,3Mn0,1. This corresponds to the volume fraction of primary silicon particles of the well-known hypereutectic AlSi17Cu4Mg alloy with about 8 % to 12 %. Furthermore, it can be seen, that even without the addition of phosphorus to the AlSi14Cu4Fe1,8Cr0,3Mn0,1 melt the size of silicon particles is lower than in conventional hypereutectic Al-Si-alloys. These facts make the new developed alloy AlSi14Cu4Fe1,8Cr0,3Mn0,1 very interesting for the production of monolithic engine blocks and other components with high pressure die casting.

Table 2: Quantitative analysis of both primary silicon and α-$Al_{15}Fe_3Si_2$ phases on gravity die casting samples of AlSi14Cu4Fe1,8Cr0,3Mn0,1

Gravity die casting			
Primary silicon phase		α-AlFeSi phase	
Average size, µm	Volume fraction, %	Average size, µm	Volume fraction, %
20	5	16	4

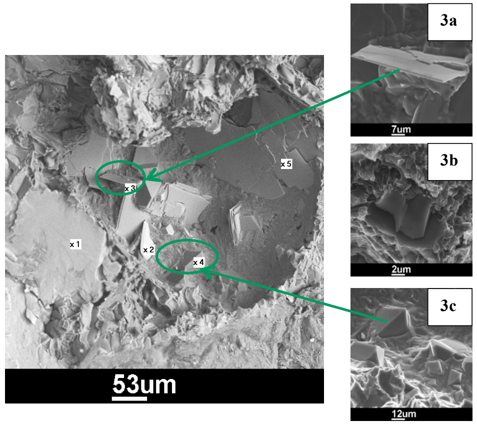

Fig. 3: SEM micrographs of fracture surface of gravity die casting specimens of AlSi14Cu4Fe1,8Cr0,3Mn0,1

Using SEM a fracture surface of specimen was investigated. The SEM images represent the α- and β- iron intermetallic phases and primary silicon particles in three dimensions within the eutectic matrix. In Fig. 3a the plate-like morphology of β-phase is shown. The primary silicon and α-AlFeSi phases are presented in Fig. 3b and 3c in compact polyhedral form.

Table 3: SEM-EDX analysis of iron containing α-$Al_{15}Fe_3Si_2$ and β-Al_5FeSi phases

Phase	Fe, wt.%	Mn, wt.%	Cr, wt.%
β	~ 50,0	~0,3	1,0
α	~15,0	~2,5	~6,0

The chemical compositions of iron containing intermetallic phases were determined by EDX method and show that the compact α-$Al_{15}Fe_3Si_2$ phase has a higher Mn- and Cr-content than platelet-like β-Al_5FeSi phase, Table 3. The iron content of β-Al_5FeSi phase is more than twice in comparison to iron content of α-$Al_{15}Fe_3Si_2$ phase.

In Table 4 mechanical properties of the new developed AlSi14Cu4Fe1,8Cr0,3Mn0,1 and a conventional AlSi17Cu4Mg, measured at room temperature, are compared.

Table 4: Mechanical properties of the new alloy AlSi14Cu4FeMnCr in comparison to AlSi17Cu4Mg, as cast, gravity die casting

Alloy	R_m, MPa	$R_{p0,2}$, MPa	A_5, %
AlSi17Cu4Mg *	180-235	170-225	$^{<}$1,0
New alloy AlSi14Cu4FeMnCr	197	176	0,3

* Characteristics from Rheinfelden Alloys, 2010

It can be seen that both alloys show comparable properties. However, the advantages of the new iron containing AlSi14Cu4Fe1,8Cr0,3Mn0,1 are in lower melting and casting temperatures as well as in reduced materials costs.

Experimental work in high pressure die casting (HPDC)

Based on the very promising results from the examinations done with gravity die casting, the following alloy compositions containing 0,2 and 0,3 chromium have been used for the following high pressure die casting tests. Table 5 shows the alloy compositions and casting temperatures used during the high pressure die casting experiments.

Table 5: Alloys, used for the HPDC experiments

version	alloy composition	casting temperatures
1	AlSi14Cu4Fe1,3Cr0,2	680 °C; 700 °C; 720 °C
2	AlSi14Cu4Fe1,8Cr0,3Mn0,1	680 °C; 700 °C; 720 °C
3	AlSi14Cu4Fe1,8Cr0,3Mn0,1Zn1	680 °C; 700 °C; 720 °C
4	AlSi14Cu4Fe1,8Cr0,3Mn0,1Zn3	680 °C; 700 °C; 720 °C

Two additional alloys with zinc contents were added as mostly all secondary aluminium alloys contain zinc in the range of 1 wt. % to 3 wt. %. According to [13], zinc in these aluminium alloys leads to the formation of intermetallic iron phases which are responsible for low mechanical properties. For this reason, it was of interest to also study the influence of zinc.

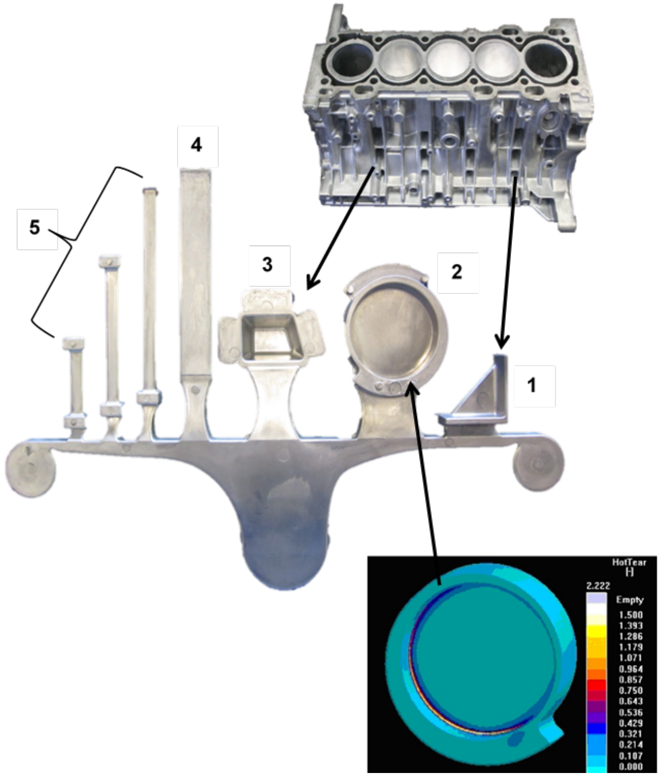

Fig. 4: High pressure die casting test geometry shows critical sections which appear in real life engine blocks. The disc shaped casting indicates

Fig. 4 shows the test casting used for the following investigations during processing all alloys described in Table 5 by high pressure die casting:

- hot tear formation
- soldering effects
- abrasive effect on the die
- Microstructure analysis
- mechanical properties
- Tribological properties

Out of geometry marked 1 in Fig. 4 the metallographic micrographs had been prepared. Geometries marked 2 and 5 were used to estimate the hot tear formation of the new alloy, geometry marked 4 for tensile tests and geometry marked 3 for measuring the soldering tendency. For visualizing the abrasive effect of the new iron containing alloys triangular shaped test geometry was introduced into the runner, Fig. 5. During processing alloys with hard intermetallic phases, a rounding of the sharp corners was expected.

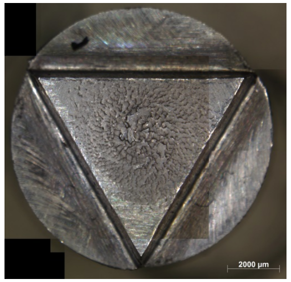

Fig. 5: Steel made test geometry for estimating abrasive effects during fill phase of hpdc mold

Results of high pressure die casting experiments

Casting temperature

First analyses of the micrographs of all tested alloys showed that lower pouring temperatures lead to a more uniform distribution of the primary silicon particles. Fig. 6a) depicts the micrograph of the alloy AlSi14Cu4Fe1,8Cr0,3Mn0,1, processed at 720 °C, Fig. 6b) processed at 680 °C. As a result all consecutive tests have been processed at a pouring temperature of 680 °C, [14].

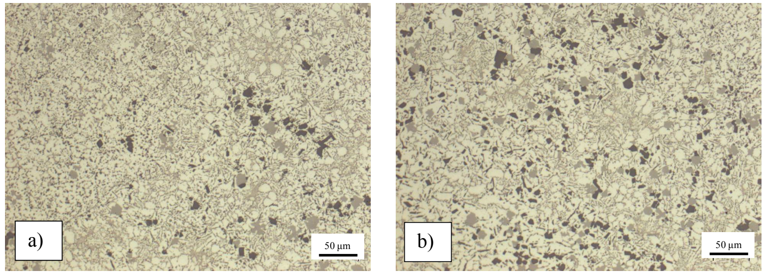

Fig. 6: a) AlSi14Cu4Fe1,8Cr0,3Mn0,1; cast at 720° b) AlSi14Cu4Fe1,8Cr0,3Mn0,1; cast at 680 °C

Hot Tear Formation

One of the critical issues in complex high pressure die casting parts besides shrinkage is the formation of hot tears. For this reason, the test tool, Fig. 4, was used to produce test samples with all alloys. For the examination of the hot tear formation, the geometries marked 2 and 5 were used. The simulation of the hot tear criteria was supplied by MAGMA and depicts the hot tear formation where the outer rib meets the bas plate. As the rib increases its wall thickness one can directly read the hot tear tendency of each alloy in length of millimeter.

However, the analysis of the cast samples produced with the new alloy did not show any cracks in this section indicating excellent castability in high pressure die casting.

Equivalent results were achieved by investigating the shrinkage bars, geometry marked 5 in Fig. 4 from the test castings. None of them showed any hot tears, verified by crack detection using a two component penetrant testing, Fig. 7.

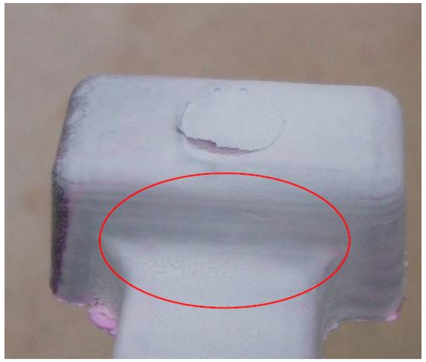

Fig. 7: Penetrant crack testing on an test casting out of the alloy AlSi14Cu4Fe1,8Cr0,3Mn0,1

Soldering effects of the tested alloys

The evaluation of the force, needed to eject the castings out of the die, shows a reduction of the values with increasing iron and zinc contents of the alloy, Fig. 8. Also must be mentioned that the ejecting force, gained from the actual examinations, compared to values from the alloy AlSi93Cu3 is about 30 times lower, [15].

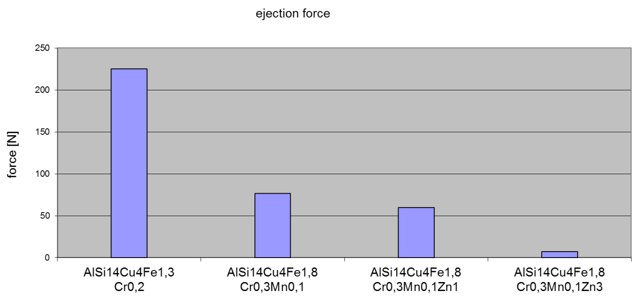

Fig. 8: Ejector force of the different test alloys

Abrasive effects on the die

Fig. 9a) shows an unused triangular shaped test pin made out of the tool steel X38CrMoV5. Fig. 9b) shows another test pin which was integrated in the runner of the die during all casting tests with the hypereutectic, iron containing alloys. The macroscopic comparison of both samples showed, that the sharp corners of the test pin had not been affected by abrasive intermetallics after the production of about 150 castings. Coming from that information, it can be assumed that the durability of high pressure die casting molds used for processing the new alloy is similar as the standard high pressure die casting alloy AlSi9Cu3 is processed.

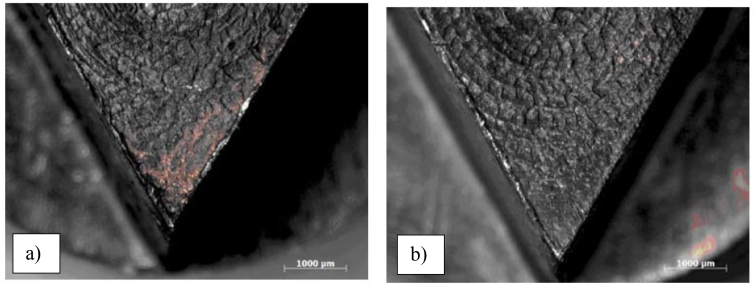

Fig. 9: Test geometry for displaying the abrasive effects of the various alloys made of X38CrMoV51: a) unused b) used during all hpdc tests in the runner of the mold

Microstructure analysis

Chemical composition of the iron phases

The EDX-analysis showed a strong correlation between chromium content and morphology of the precipitated iron containing phases. The block shaped α-AlFeSi phases showed increased Cr and Mn contents, while the plate shaped β-AlFeSi phases showed no Cr or Mn contents, Fig. 10.

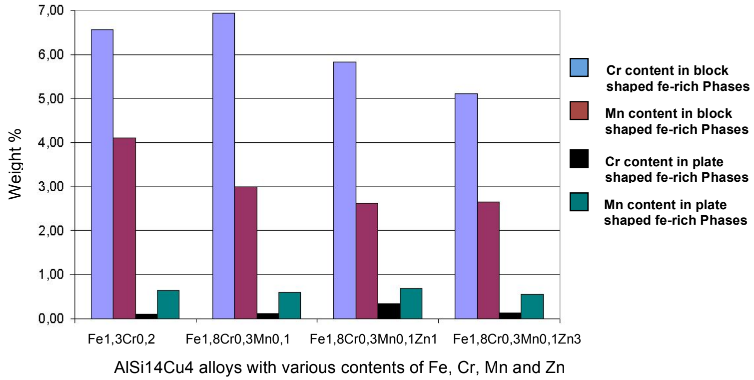

Fig. 10: Cr- and Mn-contents of different phases

Size of the precipitated iron phases

The block shaped α-AlFeSi phase precipitates in combination with the primary silicon phases have the task to increase wear resistance. Therefore, it is important that both phases evolve in similar size distribution.

The size of the block shaped α-AlFeSi phases in AlSi14Cu4Fe1,8Cr0,3Mn0,1 and in AlSi14Cu4Fe1,8Cr0,3Mn0,1Zn1 came closer to the size of the primary silicon in these alloys. The example is given in Fig. 11 which shows the microstructure of the AlSi14Cu4Fe1,8Cr0,3Mn0,1 alloy. In AlSi14Cu4Fe1,3Cr0,2 and AlSi14Cu4Fe1,8Cr0,3Mn0,1Zn3 the iron phases have been detected to be smaller than the primary silicon, represented in Fig. 12 with the alloy AlSi14Cu4Fe1,8Cr0,3Mn0,1Zn3.

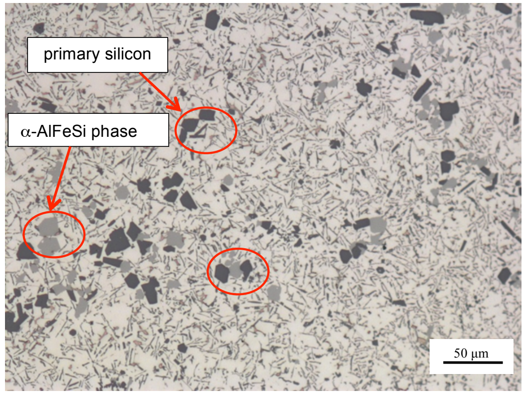

Fig. 11: Block shaped primary silicon and α-AlFeSi phases in AlSi14Cu4Fe1,8Cr0,3Mn0,1

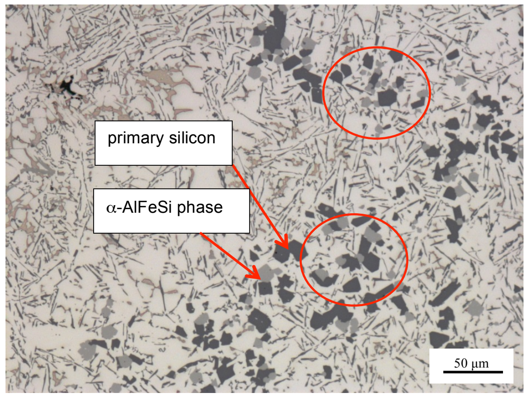

Fig.12: Block shaped primary silicon and α-AlFeSi phases in AlSi14Cu4Fe1,8Cr0,3Mn0,1Zn3

Eutectic structure

According to the modification scale by Chai [16], the eutectic structure is not refined or only partially refined. The highest degree of refinement of eutectic silicon showed the alloys AlSi14Cu4Fe1,3Cr0,2 and AlSi14Cu4Fe1,8Cr0,3Mn0,1Zn1 in thin wall thicknesses, Fig. 13.

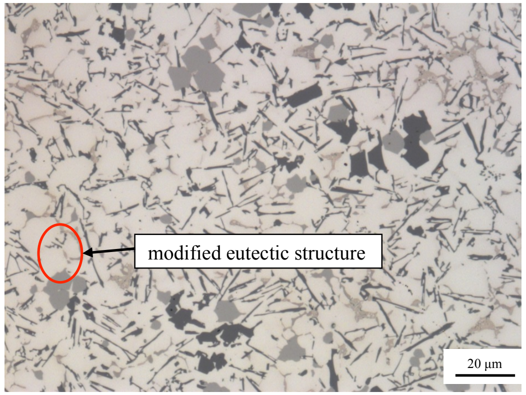

Fig. 13: Eutectic structure of AlSi14Cu4Fe1,8Cr0,3Mn0,1Zn1

Mechanical properties

Tensile tests have been carried out to investigate the mechanical properties of the alloys. As expected the results show decreasing elongation with increasing iron content. The values drop from 0,75% to 0,45%. The tensile strength does not change and reaches values of 250 MPa. Zinc contents increase the yield strength for approx. 25 MPa, Fig. 14.

Table 6 compares the mechanical properties of the standard high pressure die casting alloy AlSi9Cu3 and the new alloy AlSi14Cu4Fe1,8Cr0,3Mn0,1. The tensile strength and even the yield strength of the hypereutectic alloy reach higher values than the alloy AlSi9Cu3.

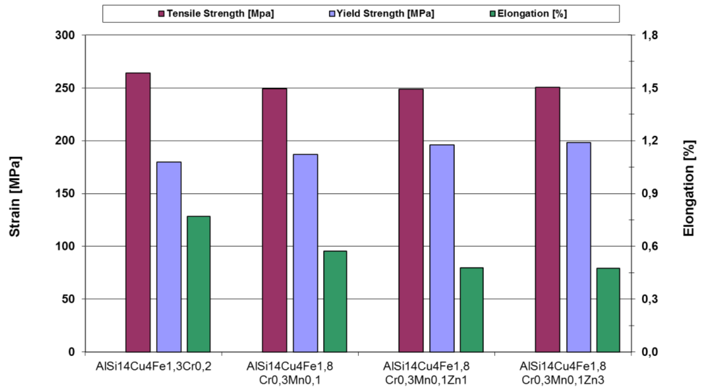

Fig. 14: Mechanical properties of the analyzed alloys

Table 6: Mechanical properties of the alloys AlSi9Cu3 and AlSi14Cu4Fe1,8Cr0,3Mn0,1Zn1

Alloy	$R_{p0,2}$ [MPa]	R_m [MPa]	Young's modulus [MPa]	A_5 [%]
AlSi9Cu3	170	240	$70\ 10^3$	0,7
AlSi14Cu4Fe1,8Cr0,3Mn0,1Zn1	196	249	$80\ 10^3$	0,5

Tribological properties

To analyze the wear resistance of the new alloy AlSi14Cu4Fe1,8Cr0,3Mn0,1 it was compared to the classic hypereutectic alloy AlSi17Cu4Mg, cast in high pressure die casting. In addition, samples from the alloy AlSi17Cu4Mg low pressure die casting were analyzed:

- AlSi14Cu4Fe1,8FeCr0,3Mn0,1 high pressure die casting test castings
- AlSi17Cu4Mg, high pressure die casting test castings
- AlSi17Cu4Mg, conventional low pressure die castings

The wear resistance tests have been performed using the disc cylinder method. The disc was made out of the various aluminum alloys and the cylinder material was cast iron simulating a piston ring, Fig. 15. The parameters for the tests have been:

- test load 20 N
- test frequency 100 Hz
- amplitude 0,5 mm
- test ends when reaching max. friction coefficient of >1 for more than 30s
- max. test duration 180 min

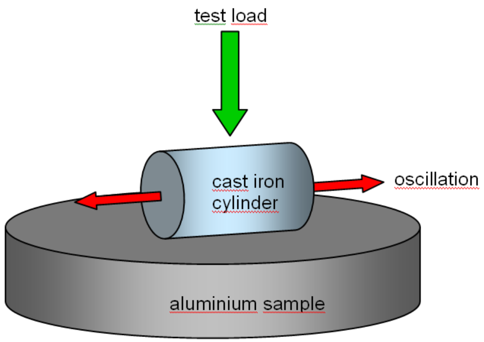

Fig. 15: Testing scheme for determining friction coefficients

The tests showed, that the AlSi14Cu4Fe1,8FeCr0,3Mn0,1 alloy which contained iron had the lowest friction coefficient compared to the other AlSi17Cu4Mg cast alloys, Fig. 16. The responsible metallurgical mechanism for this research result is not yet understood and is subject to further research.

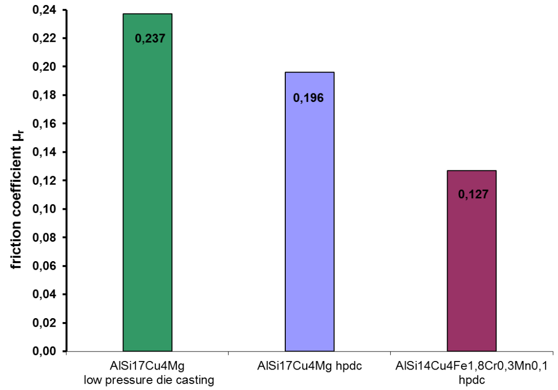

Fig. 16: Friction coefficients of different hypereutectic AlSi alloys

The test castings produced in high pressure die casting and in low pressure die casting out of AlSi17Cu4Mg failed after less than 10 minutes. The sample made out of the new AlSi14Cu4Fe1,8FeCr0,3Mn0,1 alloy failed after 135 minutes.

Summary

The results show that the newly developed alloy AlSi14Cu4Fe1,8FeCr0,3Mn0,1 combine excellent castability with extraordinary tribological properties. This is caused by the fact that the precipitated iron phases show similar size compared to the primary Silicon particles.

The mechanical properties are similar to conventional high pressure die casting alloys from which engine blocks are produced in series production.

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