Proceedings of the 12th International Conference on
Aluminium Alloys, September 5-9, 2010, Yokohama, Japan

pp. 1319-1323

Substitution of Nickel by Combined Addition of Cobalt and Zirconium in Alloy A 332

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The piston alloy A 332 shows an optimum combination of mechanical and casting properties and an attractive cost-performance ratio whereas nickel being the most expensive alloying element. The goal of alloy development at Clausthal University of Technology was therefore to replace Ni by a combined addition of Co and Zr. Thermo-Calc simulations of intermetallic phases were carried out investigating the effects of the Ni substitution. To evaluate the simulations intermetallic phases were observed under optical microscope and SEM. Volume fractions of intermetallic phases and size and morphology of the primary Silicon were analyzed by the use of image analysis software. The mechanical properties of the alloys were determined in tensile tests at room temperature, 250°C and 350°C. The tensile specimens were tested in both as-cast and pre-aged condition. The effect on the castability was characterized by determining the fluidity, shrinkage and hot crack sensitivity.

The standard alloy containing nickel and an optimized alloy with cobalt and zirconium were compared. The pre-aged (250°C/100h) optimized alloy exhibits at 250°C a yield strength of 115 MPa and a tensile strength of 171 MPa. At 350°C the pre-aged (350°C/100h) optimized variant displays a yield strength of 57 MPa and a tensile strength of 85 MPa. The favorable castability of the standard alloy is not affected by the substitution of nickel.

These results prove that a heat-resistant, thermally stable alloy was developed which is superior to the standard alloy concerning technological and economical aspects. The expensive alloying element nickel was successfully substituted by cobalt and zirconium.

Keywords: *casting, piston, alloy-development, creep*

1. Introduction

The need for innovative, high quality cast materials increased rapidly along the development of more efficient combustion engines as the increased efficiency results in a rise of the working temperatures and pressures combined with the tendency in development to reduce the weight of the engine. Worsening international competition and the strong price pressure that the foundries have been exposed to, especially during the last decade, proved to be a further driving force for the development of innovative cast alloys.

Beginning in the 40s of the last century foundries used mainly Al-Si-Cu-alloys for the production of pistons and crankcases. This type of alloy contains Si in a range between 5 and 17 % Si and Cu in the range of 1 to 4 % as well as additional alloying elements like Mg, Mn, Fe, Ti, Ce, Cr and Ni. These alloys exhibit a high specific strength combined with a good processability [8].

2. Piston Alloy Development

As shown in Table 1 a lot of new alloys have been developed that meet the requirements mentioned above. Among these alloys the alloy AlCu5Ni1,5CoSbZr [6] exhibits excellent mechanical properties at room temperature and at elevated service temperature by reaching a yield strength of 140 MPa at 250°C. Besides the poor castability and the strong sensitivity to corrosive attacks the relatively high price due to the high amount of expensive alloying elements limits the wide application of this cast alloy. Compared to this alloy the piston alloy AlSi12CuNiMg shows a higher level of mechanical properties at room temperature but lower strength at temperatures exceeding 250°C. Compared to all alloys mentioned in Table 1 the alloy AlSi12CuNiMg exhibits an optimum combination of castability and mechanical properties as well as an attractive cost-performance-ratio. The most expensive alloying element in this aluminium alloy is nickel. If this element can be replaced by the use of cheaper components combined with an increase in the mechanical properties this would mean a great improvement of its technological and economic competitiveness. Cobalt and Zirconium are both well suited for this purpose as both increase the high-temperature strength and creep resistance [5, 6, 7].

Table 1: Mechanical properties of established high-temperature aluminium alloys according to [8]

Index	Temperature	AlSi6Cu4 T6	AlSi9Cu3 T6	AlSi12CuNiMg T6	AlSi17Cu4Mg T6	AlCu5Ni1,5CoSbZr T6
Rm/MPa	20°C	220	210	300	270	250
	250°C	120	110	112	100	210
$Rp_{0,2}$/MPa	20°C	180	150	280	260	210
	250°C	90	80	83	90	140
A_5/%	20°C	<1	<1	<1	<1	1
	250°C	11	4.5	10	4	12

3 Experimental Details

Using the design of experiments (DoE) software Modde 7.0 it was possible to find the optimum combination of the alloying elements Co and Zr in the base alloy AlSi12,6Cu1Mg1 requiring a limited number of experiments. Thermo-Calc-Simulations were carried out to predict the phases that might occur during solidification. The test melts were prepared under standard atmosphere using an electric resistance furnace. The alloys were cast into a test bar permanent mould made of steel which was preheated up to 250°C according to the German Standard DIN 29 531 at a casting temperature of 740°C. The standard alloy AlSi12CuNiMg is also used for cylinder heads which are highly complex components. Therefore the castability of the new piston alloy is of great importance which was tested by determining the fluidity by the spiral test and the shrinkage sensitivity by using the TATUR permanent mould with subsequent determination of the fraction of macro and micro shrinkages, respectively. Specimens were cast into a permanent mould to evaluate the generation of hot cracks during the solidification of Al-alloys, STERN permanent mould. Using the test bars tensile specimen as well as metallographic samples were fabricated. Prior to the final mechanical processing the test samples were partially aged for 100 h at the tensile testing temperature 250°C and 350°C, respectively. For an evaluation of the Thermo-Calc-calculation the metallographic samples were investigated under light and scanning electron microscope and the results of these investigations were compared to the results of the simulations. The following tensile tests were executed at room temperature, 250°C and 350°C. The results of this procedure described below show a comparison between the standard alloy AlSi12,6Cu1Ni1Mg1 and the best candidate alloy from the optimization AlSi12,6Cu1Mg1CoZr.

4 Results

The intermetallic phases according to thermodynamic simulation combined with the temperatures of their first appearance are presented in Tables 2 and 3. Thermo-Calc calculations predict the existence of the binary Al_9Co_2 phase in the microstructure of the new piston alloy as well as the existence of the iron containing phases α (AlFeSiMn) and β (AlFeSi) which is harmful to the mechanical properties of this alloy due to their needle like nature. According to simulation both phases will be found in the reference alloy as well as in the candidate alloy for industrial tests. The crystallisation temperatures of the eutectic are shifted upwards so that no modification is expected which confirms the experimental results given in [5] showing no effect on the morphology of the α (Al) – Si – eutectic by the addition of Co and Zr.

Table 2: Intermetallics in reference alloy

T/°C	Phase
<589,8	Liq
589,8	α(AlMnFeSi)
568,6	Si
567,7	α(Al)
561,5	β(AlFeSi)
547,5	Al_3Ni
544,0	Mg_2Si

Table 3: Intermetallics in candidate alloy

T/°C	Phase
>735,9	Liq
735,9	Si_2Zr
626,3	Al_9Co_2
583,1	α(AlMnFeSi)
570,4	Si
570	α(Al)
564,6	β(AlFeSi)
549,8	Mg_2Si

During the investigations of the metallographic samples the microstructure of the new alloy was analysed and compared to the microstructure of the reference alloy. Both microstructures show single small crystals of primary Si whose size does not exceed 30 µm and which are embedded in a matrix of α (Al) – Si – eutectic. A modifying effect by the addition of Co and Zr was not observed. Phases bearing iron occur mainly as α-(AlFeSiMn)-phases what can be explained by a very low Fe/Mn-ratio and the high cooling rate of 30°C/s in the permanent mould which benefits the solidification of α (AlFeSiMn)-phases [4]. In the microstructure of the reference alloy the nickel containing phases Al_3Ni and AlCuFeSiNi were observed while they could not be observed in the new piston alloy, of course. In [4] is reported an improvement of the wear resistance of AlSi12CuNiMg with increasing Ni-content attributed to the coarsening of the latter mentioned phases which should be proved by further investigations. The measurement of the secondary dendrite arm spacing revealed a slight difference between the dendrite arm spacing of the reference alloy, 23 µm, and the SDAS of the new piston alloy, 20 µm. In general a lot of phases in the new alloy exhibited a finer morphology which might be attributed to the missing Ni, because an increasing Ni-content leads to a coarsening microstructure [4]. Furthermore the refining impact of Zr on the microstructure, as described in [5], must be considered. A striking feature of the microstructure of the new alloy is the existence of a Mn-containing AlMnFe-phases that could not be observed in the standard alloy what is attributed to the stabilizing effect of Co on Mn-containing phases. The new piston alloy contains a small amount of Zr which is too small to form AlZrSi-needles according to literature [3, 5]. But single needles with a maximum length of 20 µm can be found in the microstructure of AlSi12,6Cu1Mg1CoZr. This length is not critical for the mechanical properties.

A fraction of the Co in the alloy is dissolved in the Chinese script α-(AlFeSiMn)-phases and it also participates to form the globular intermetallic phase AlSiCuMnCo to be found very often in the microstructure of the new alloy. Compared to the thermodynamic simulation there are more phases in the real microstructure which is attributed to equilibrium conditions during the simulation and the limitations of REM/EDX-measurements. Futhermore, the solubility of various elements in different phases is not sufficiently taken into account. Contrary to the simulation the formation of the binary plate-like Al_9Co_2-phase can not be confirmed.

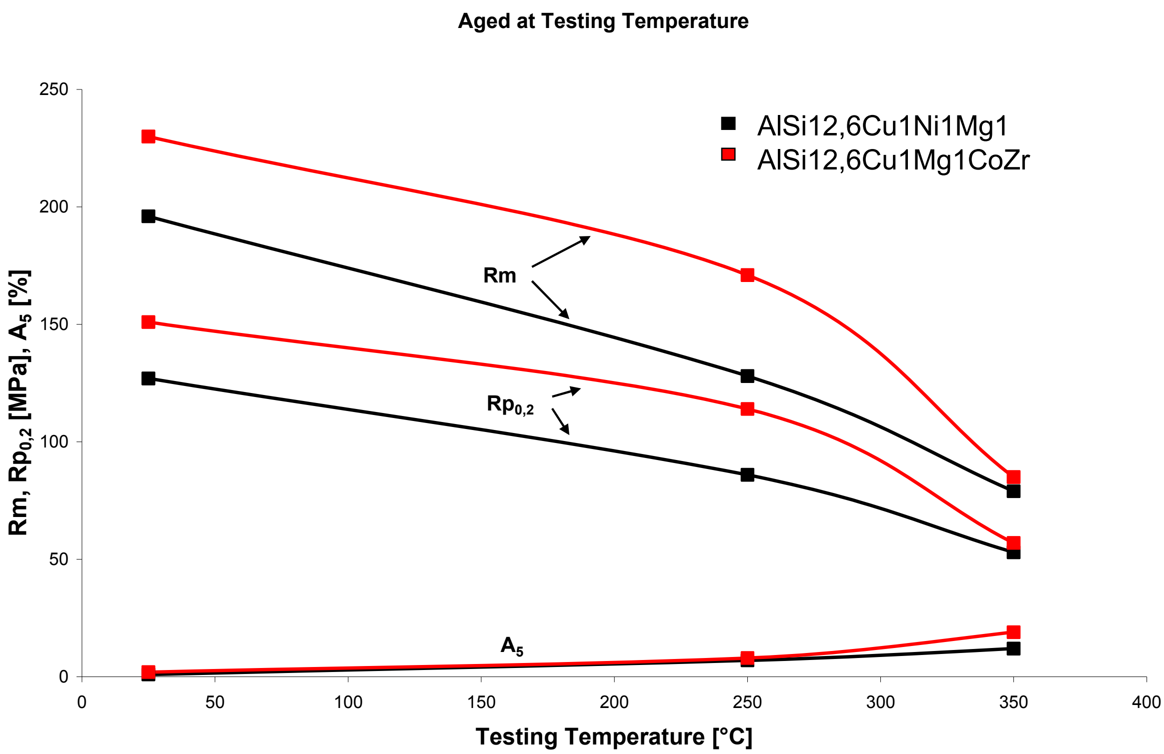

Fig. 1: Mechanical properties of tested alloys as a function of temperature

Figure 1 shows the mechanical properties of the alloys as a function of testing temperature. The piston alloy containing Co and Zr shows superior mechanical properties especially at the service temperature of modern pistons and cylinder heads which is 250°C according to literature [4]. It exceeds the yield strength of the standard alloy about 25 % when reaching 115 MPa after preageing at testing temperature for 100 h. This is attributed to the formation of Al_3Zr which is stabilized by cobalt-addition [6, 7]. Additional to the higher strength at every testing temperature the candidate alloy shows a better elongation at fracture arising with increasing temperature which might be explained by a finer microstructure of the candidate alloy.

An excellent castability is of great importance for later industrial application. That is why the castability was also investigated, Figure 2. The decrease in flow length lies within the measuring accuracy. The measured values for micro- and macro-shrinkages lie in a typical range for the alloy AlSi12CuNiMg. The eutectic solidification of both alloys does not generate any hot cracks. The results prove that the nickel-substitution has no negative influence on the favorable casting properties of the standard alloy.

5. Summary

A series of experiments was conducted to increase the technological and economic competitiveness of the standard piston alloy AlSi12CuNiMg. The expensive alloying element Ni was substituted by a combined addition of low contents of Co and Zr. The best candidate alloy AlSi12,6Cu1Mg1CoZr was compared to the standard piston alloy AlSi12,6Cu1Ni1Mg1 with the following results:
(1) The substitution of Ni by Co and Zr does not influence the morphology of the α (Al) – Si – eutectic. It slightly reduces the SDAS and morphology of some phases, stabilize the Mn-containing phases and creates several Zr- and Co-containing phases including Al_3Zr, AlZrSi and AlMnSiCuCo.
(2) The mechanical properties at elevated temperatures are significantly improved compared to the reference alloy.
(3) The castability, investigated as flow length, fraction of macro- and micro-shrinkages and the hot crack sensitivity are not negatively affected by the Ni-substitution.

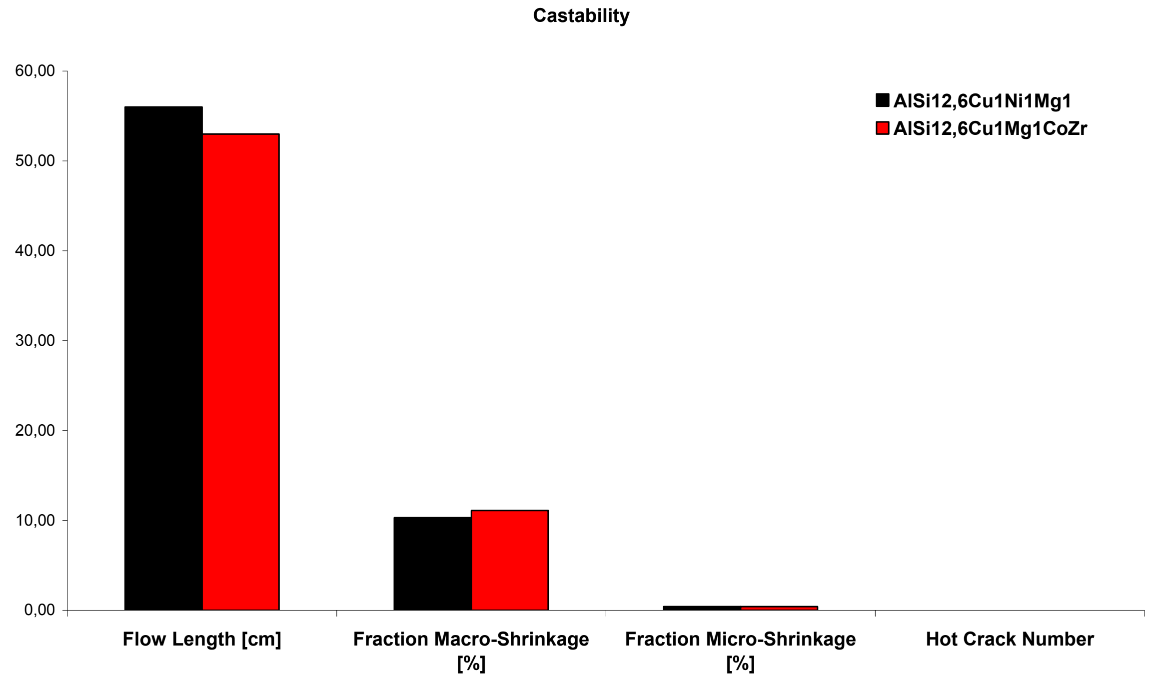

Fig. 2: Castability of tested alloys

References

[1] E. Brunhuber.:Gießerei-Praxis 3 (1974)39-47
[2] J. Korrita, A. Franek and S. Halacek: Aluminium 6 (1969)352-355
[3] E. di Russo: The Atlas of Microstructures of Aluminium Casting Alloy, (Edimet Spa., Brescia, 1993)95-135
[4] H.W. Rockenschaub, R. Gschwandtner, A. Holzinger, I. Topic and J. Mikota: Giesserei-Praxis 1 (2008)13-25
[5] L.F. Mondolfo: Aluminium Alloys, Structure and Properties (Butterworths Group, London, 1976)
[6] S. Klan: Beitrag zur Evolution von Aluminium-Gusslegierungen für warmfeste Anwendungen (phd-thesis, Freiberg, 2004) pp. 1-37
[7] K.E. Knipling, D.C.Dunand and D.N.Seidman, Z.Metallk. 97 (2006)246-265
[8] C. Reeb, H. Zak, B. Tonn: Aluminium Alloys-Their Physical and Mechanical Properties Vol.1,Ed.by J.Hirsch,B.Skrotzki and G.Gottstein (WILEY-VCH, Weinheim, 2008)121-126