Ageing of Zink Alloys

Goal of the research was the investigation of the material properties of zinc alloys under natural and artificial ageing to find a correlation between artificial and natural ageing. As zinc die castings are produced under a variety of production conditions it was necessary to produce test castings using different parameters under extremely controlled conditions.

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1 Introduction

Hot chamber die casting is a highly productive production technology for zinc parts of highest quality. Main customers are manufactures of cars, furniture and other mechanical parts. Although zinc alloys have a rather high density of 6.7 g/cm^3 they are used in automotive applications due to their high mechanical properties, thin wall thicknesses and their plating properties. Zinc parts can be recycled 100 %.

The low melting temperature of 390 °C leads to an increased creep rate. In addition, zinc alloys loose mechanical properties over time due to ageing effects. The natural ageing is typically compensated by artificial ageing. The parts are tested typically between -35 °C and +85 °C as these are the temperatures used in automotive applications.

Until today only few statistical reliable data have been published on these temper-ate ranges.

2 State of the knowledge

2.1 Chemical composition of the die casting alloys

The chemical composition of the zinc alloys influences the fluidity, the mechanical properties, the feeding properties and the structure. For most of the parts ZP0410 (Z410) with 4 wt % aluminum and 1 wt % copper is used. Besides the alloys ZP0430 (Z430) and ZP0400 (Z400) are used. All of these alloys are hyper eutectic alloys with small amounts of Pb, Cd, Sn, Fe, Ni and Si. The melting temperatures are below 400 °C.

The phase diagram of aluminum-zinc (**Figure 1**) shows an extremely low solubility of zinc in aluminum and vice versa.

Copper which is typically used between 0.3 and 3 wt % increases the solubility of aluminum in zinc (**Figure 2**) and therefore increases the strengthening effect.

2.2 Zinc die casting alloys

Worldwide only four alloys are used which are described in the European Norm EN12844.
Table 1 shows the alloy elements in these alloys. In row 3 of this table the measured composition of the alloys used in this research are shown.

2.3 Advantages of zinc alloys

A big advantage of zinc alloys is the low melting temperature below 400 °C. As a result cooling and cycle times are very short. In addition the life of die casting dies lies in the range of one million and more shots exceeding the values for aluminum by the factor of ten.

As an disadvantage the creep already starts at room temperature at loads exceeding 50 MPa. The very high mechanical properties diminish within one year and also measured data of parts change.

2.4 Usage of Zinc

In 2007 more than 11 million tons of zinc have been used worldwide, most of it for corrosion protection, zinc die castings and alloying of copper (**Figure 3**).

The usage of zinc in automotive application increases and a passenger car already includes more than 10 kg of zinc [5].

2.5 Literature

Until today there are few data available for ageing of zinc alloys most of them deal with measure changes (**Figure 4**). In [6] describes the solubility of Al in Zn and the eutectoid phase change of the β-phase into β´-Phase. The addition of copper increases the solubility of Al. The measure changes describe [8, 9], especially Z430 contracts more than Z400 or Z 410 [8, 10]. To get around the measure changes the automotive industry suggests to heat treat the parts at 105 °C for 24 hours.

Zinc alloys change also their mechanical properties with time [11, 12]. A comparison between artificial and natural ageing is given in [13]. An improved creep resistance is based on the copper rich ε-phase, however the production conditions under which the specimens have been produced are not available in the literature [14, 15].

Ageing processes:
Basically all alloys undergo ageing as the solubility in the liquid phase differs from the solid phase. Zinc alloys age already at room temperature as diffusion at room temperature is relatively high due to the low melting point of zinc (**Figure 5**).

2.6 Creep processes

Creep is plastic deformation under load caused by atom movements without concentration differences. Creep is also evident at pure metals. A typical creep curve is depicted in Figure 6.

Technical important is the phase of stationary creep. The creep rate is a function of the mechanical load and the temperature and the diffusion [1] provides the following equation:

$$\dot{\varepsilon}_s = A \cdot \left(\frac{\sigma}{G}\right)^n \cdot e^{-\frac{Q}{k \cdot T}} \qquad (1)$$

A coefficient of creep in 1/s (%/h)
σ ...
G shear modulus in MPa
k ....
n ...
T temperature
Q ...

For the most materials creep is related to the liquidus temperature T_l:

$0.6 < T/T_l < 1$	fast creep
$0.3\text{-}0.4 < T/T_l < 0.6$	slow creep
$0 < T/T_l < 0.3$	no creep

Comparison Al and Zn:
The low melting point of Zn of 420 °C (693 K) causes slow creep at 0 °C which increases at room temperature. Figure 7 shows the differences between temperature and creep for Al and Zn.

Creep is proportional to the mechanical load when the diffusion is only caused along grain boundaries. Then equation (2) describes the creep rate:

$$\dot{\varepsilon}_s = A \cdot \left(\frac{\sigma}{G}\right) \cdot e^{-\frac{Q}{k \cdot T}} \qquad (2)$$

3 Experiments

3.1 Experimental program

The experiments have been carried out for ZP0400, ZP0410 and ZP0430 according to DIN EN 12844.

To analyze the mechanical properties die cast plates have been cast with thicknesses of 0.8 mm, 1.5 mm and 3 mm using a hot chamber die casting machine Type DAW 80 by Frech.

From these plates probes have been machined for the tensile test according to DIN 50125. A variety of casting parameters have been used to cover all different die cast parts.

Sensors for pressures and temperatures within the machine and within the die have been used to control the process during test part production.

The following material properties have been investigated using as cast probes, artificially aged probes and naturally aged probes:

- yield strength, tensile strength, elongation and Young's modulus;
- at testing temperatures;
- -35 °C, RT (room temperature) and +85 °C;
- creep rate at RT and 85 °C;
- fatigue data at RT;
- density;
- hardness;
- creep behavior.

Process parameters have been varied (Figure 8):
- wall thickness: 0.8 mm, 1.5 mm and 3.0 mm;
- gate velocity: 25 m/s, 40 m/s and 55 m/s;
- die temperatures: 120 °C, 160 °C and 200 °C.

The influence of the natural ageing has been tested after 3 and 6 weeks, 3 and 6 months and after 1 year. After 2 years a last measurement will be conducted.

The artificial ageing was carried out using a 24 hour tempering at 65 °C, 85 °C and 105 °C.

DOE:
To reduce the amount of run DOE was used using Design-Expert 7 by Stat-Ease. The design of the plan included center point conditions 1.5 mm wall thicknesses, 160 °C die temperature and 40 m/s gate velocity.

3.2 Die casting machine Frech DAW 80

A newly updated hot chamber machine with 200 tons locking force has been used to produce the test specimen.
Measure data were piston velocity, pressure, internal die pressure and temperature (Figures 9 and 10).

Plate size was 50 mm by 150 mm with the volumes, showed in Table 2. Piston diameter was d_K = 60 mm; the gate area was 0.41 cm². The piston velocities and the resulting fill times are shown in Tables 3 and 4. The solidification time is calculated after Chworinoffs equation (Table 5). After production the plates were frozen to -20 °C (Figure 11).

3.3 Ageing

Artificial ageing:
Five specimens have been aged at +65 °C, +85 °C and +105 °C for 24 hours.

Natural Ageing:
Natural Ageing was performed at room temperature in a climate controlled room where also the measuring took place (Figure 12).

3.4 Mechanical data

3.4.1 Tensile testing

Test equipment:
The tensile test machine is a 100 kN Universal „Schenck“ with modern computerized control (Figure 13). The specimens have been tested under as cast conditions, naturally aged condition and artificially aged condition under three test temperatures.

The tests at +85 °C and -35 °C are executed in a climate chamber. The cooling of the probes is performed using CO_2-gas. Control was done using a thermocouple.

Stress-strain diagram:
More than 3000 specimen have been tested. For each probe the stress-strain-diagram is available indicating the test conditions and the production conditions (Figure 14).

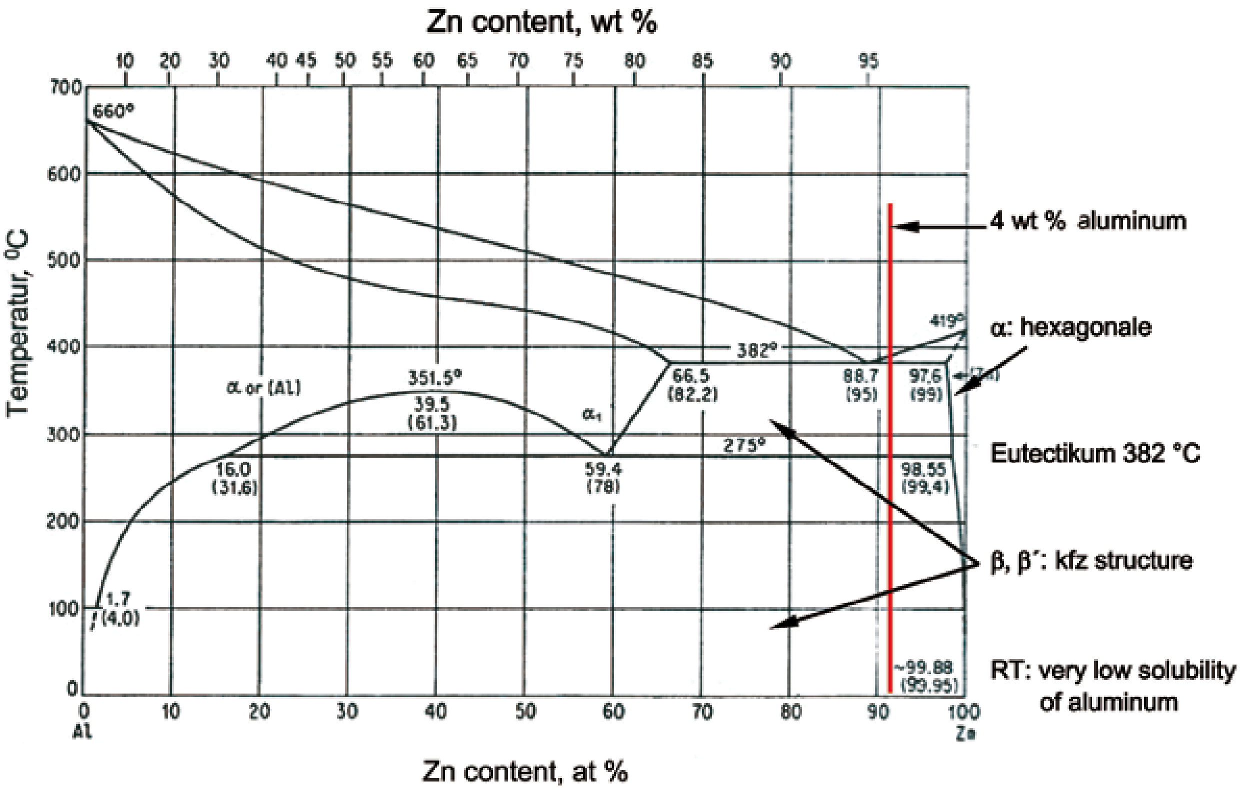

Figure 1: Phase diagram zinc – aluminum [1]

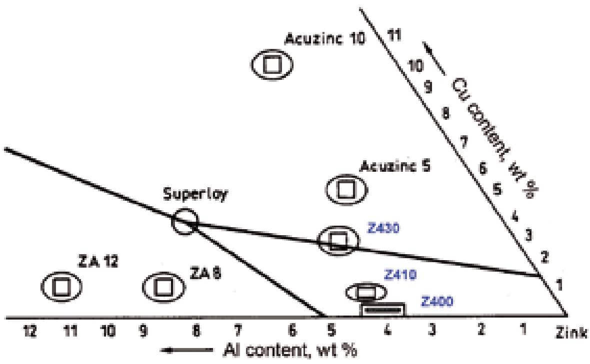

Figure 2: Ternary system Zn – Al – Cu and positions of zinc die casting alloys [2]

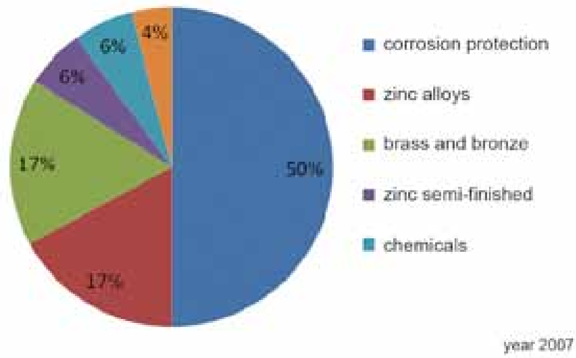

Figure 3: Usage of zinc [4]

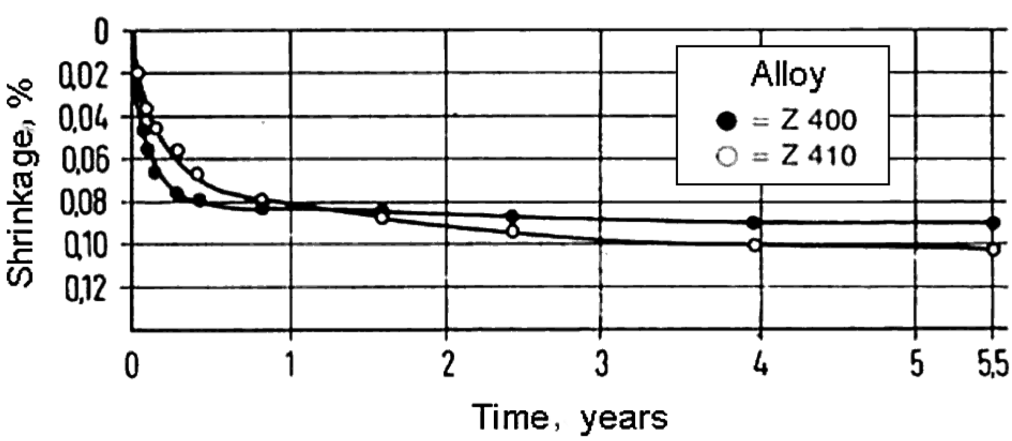

Figure 4: Dimensional stability of zinc die casting parts at room temperature (ageing time: 5.5 years; die temperature: 180 °C; quenching: air) [7]

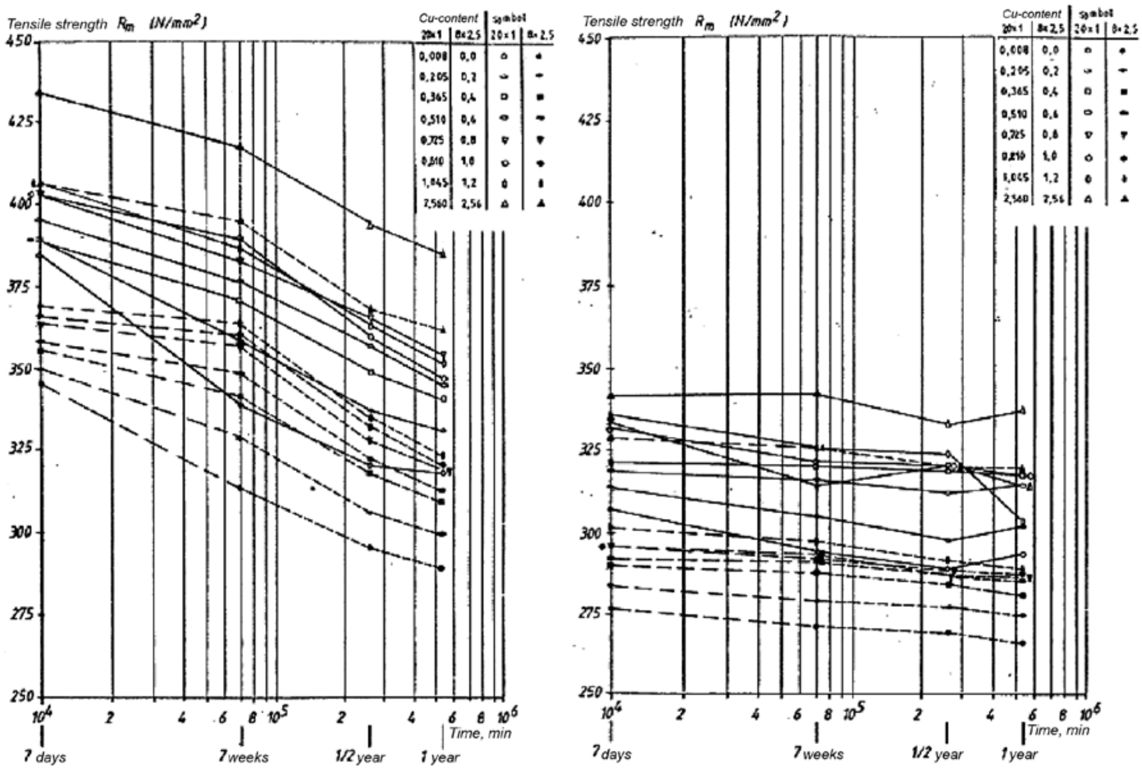

Figure 5: Natural ageing (left) and artificial ageing (right) as a function of copper content

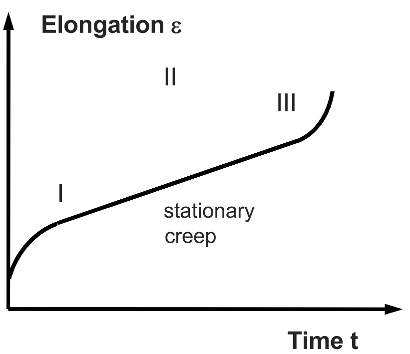

Figure 6: Typical creep curve

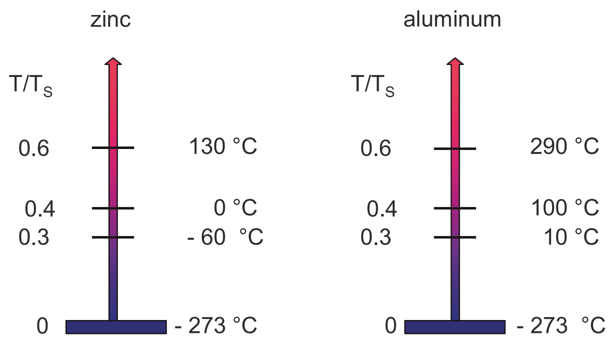

Figure 7: Homologue temperature for zinc and aluminum

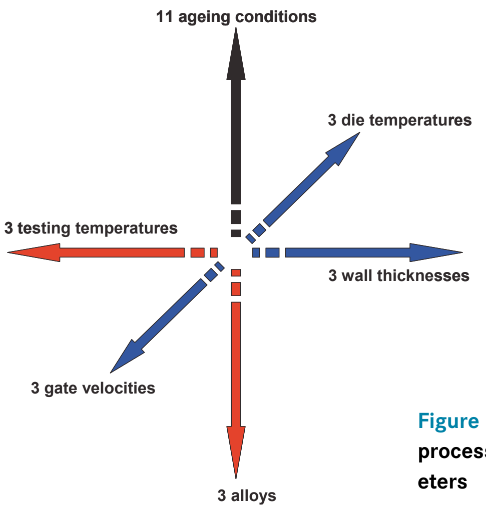

Figure 8: Varied process parameters

Figure 9: Position of the thermocouple 2 mm under the surface

Figure 10: Position of the ejector pins with load sensors

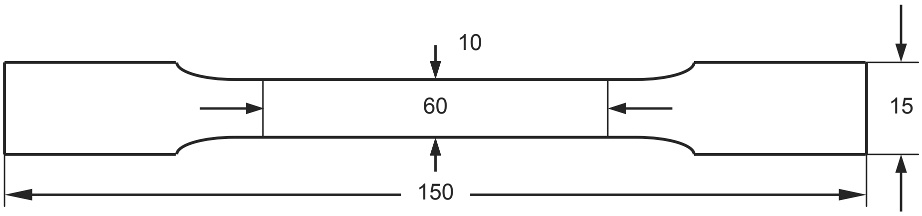

Figure 11: Geometry of the specimens for static tensile tests

Figure 12: Boxes for the specimens for natural ageing (23 °C, room air conditioned)

Figure 13: Upgraded tensile testing machine

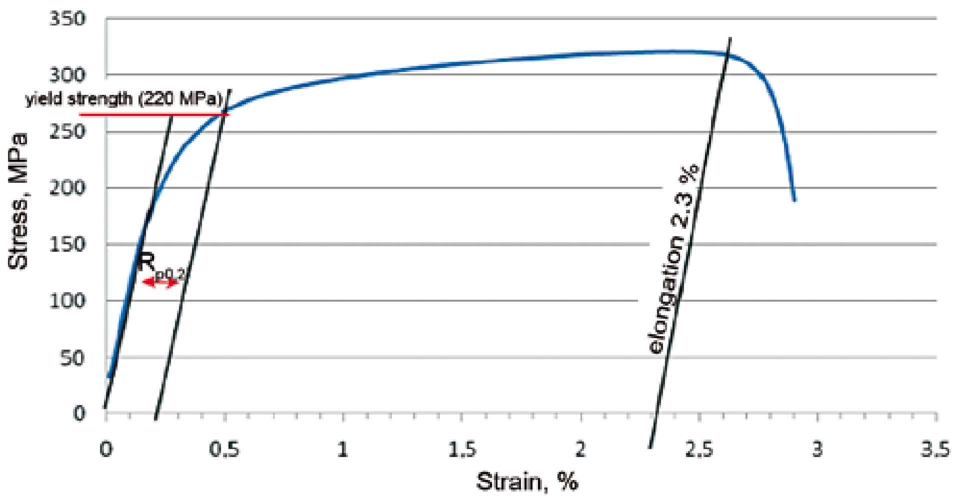

Figure 14: Stress-strain-curve run 23 (3 mm; 160 °C; 40 m/s) measured in as cast condition at RT (23 °C)

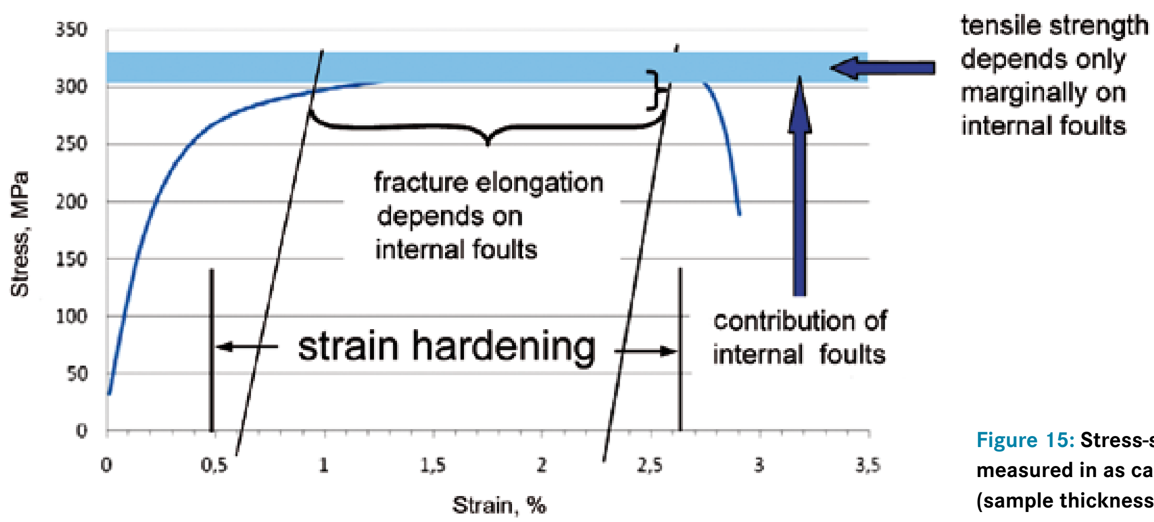

Figure 15: Stress-strain-curve measured in as cast condition (sample thickness 3 mm)

Table 1: Specification of zinc die casting alloys after EN12844 [3]

Content of chemical elements, wt %		Alloy ZP3 ZP0400 ZnAl4	ZP5 ZP0410 ZnAl4Cu1	ZP2 ZP0430 ZnAl4Cu3	ZP8 ZP0810 ZnAlCu1
Aluminum	max	4.3	4.3	4.3	8.8
	min	3.7	3.7	3.7	8
Copper	max	0.1	1.2	3.3	1.3
	min		0.7	2.7	0.8
Magnesium	max	0.05	0.05	0.05	0.03
	min	0.025	0.025	0.025	0.015
Lead	max	0.005	0.005	0.005	0.006
Cadmium	max	0.005	0.005	0.005	0.006
Tin	max	0.002	0.002	0.002	0.003
Iron	max	0.05	0.05	0.05	0.06
Nickel	max	0.02	0.02	0.02	0.02
Silicon	max	0.03	0.03	0.03	0.045
Zinc		rest	rest	rest	rest

Table 2: Volume of the different parts

Thickness, mm	Volume V_{Part}, cm^3
0.8	6.0
1.5	11.25
3.0	22.5

Table 3: Gate velocities for the three parts

Thickness, mm	Gate velocity, m/s	Piston velocity, m/s
0.8	25	0.36
1.5	40	0.58
3.0	55	0.79

As Zn alloys show no yield strength data are provided for the elongation of 0,2%.

Porosity influences the elongation properties which lead to a high variation of the elongation data between 2% and 12% (Figure 15). The tensile strength data show a standard variation of only 5%. The ageing behavior can therefore be checked using the tensile test data. Using a test temperature of -35 °C the tensile strength and the yield strength increase by 5%. The elongation data are lower (Figure 16). At +85 °C the stress-strain-curve shows data depicted in Figure 17. The data are 20% lower compared to room temperature. Elongation is in the range of 20%.

Young's modulus:
The data for Young's modulus is calculated out of the stress strain curves using software. The ageing shows no influence on the Young's modulus, neither do the production conditions. The main influence is the test temperature (Table 6).

Tensile strength R_m and yield strength $R_{p0,2}$:
Both tensile strength and yield strength depend on the production data. Highest values achieve thin specimens as cast and low die temperature at -35 °C testing temperature (Figure 18).

The influence of wall thickness, die temperature and gate velocity is linear according to the Design Expert. The largest impact has the wall thickness, followed by the die temperature and the gate velocity. The influence of the testing temperature on the measured mechanical data is not linear (Figure 19).

Artificial ageing leads to mechanical properties corresponding to a one year natural ageing. The Figures 20 and 21 are shown the influence of the wall thickness and the die temperature on the mechanical properties after artificial ageing (105 °C, 24 hours).

3.4.2 Static testing Z400 and Z430

Elongation at fracture:
The elongation data show a wide band of values. The data measured at -35 °C (ca. 1% to 2%) are the lowest, the highest data are at +85 °C (ca. 20% to 25%) (Table 7).

3.4.3 Creep testing

The creep testing equipment is shown in Figure 22 and is performed as a function of time and temperature according to DIN 50118. The system allows the measurement of changes in specimen's length within a resolution of 1 µm up to 20% of the original length.

Results of Creep testing:
For the creep tests stresses between 40 MPa and 100 MPa have been used at room temperature. At testing temperature of +85 °C stresses between 12 MPa und 50 MPa have been applied to the specimen.

With these data stress exponent and activation energy can be calculated. Specimen as cast and artificially aged at 120 °C over 15 hours and over ageing of 150 °C and 15 hours have been tested 1000 hours (Figures 23 to 25).

The primary creep is strong and ends at 2% creep. Then the cross section of the specimen decreases which again increases the stress load and the creep rate increases (Figure 24). If the stress in the cross section was constant the creep rate would then decrease up to 10% of elongation.

Some specimens have been averaged at 150 °C for 15 hours. These probes show a creep rate which is 5 time higher than the artificially aged probes (120 °C for 15 hours).
All tests follow the creep based on self diffusion. For all measurements with Z 410 the exponent n had a value of 4.1 when 0.5% to 1% creep elongation was archived and the activa-

tion energy was 94 kJ/mol. According to this finding the creep rate can be calculated between 0 °C and 100 °C and stresses between 10 MPa and 100 MPa using the following equation:

$$\dot{\varepsilon}_s = A \cdot \sigma^n \cdot e^{-\frac{94\ kJ}{R \cdot T \cdot mol \cdot K}} \quad (3)$$

R ...

The activation energy leads to an increase of the creep rate of 25 °C to 85 °C by the factor of 700 (**Figure 26**).

If one accepts a creep rate of 1 % per year as a limit as a result you can read the maximal allowable stresses as a function of temperature as depicted in (**Figure 27**).

Creep rate of Z400 and Z430:
Figure 28 shows the creep data of the three alloys in comparison. The copper content influences the creep by a factor of 4, between Z410 and Z430 is only a small difference.

Out of Figure 26 and Figure 28 one can extract the parameters for secondary creep according to equation (1) in **Table 8.**

Table 4: Calculated filling time

Thickness, mm	Filling time, m/s		
	v_A = 25 m/s	v_A = 40 m/s	v_A = 55 m/s
0.8	5.9	3.7	2.7
1.5	11.1	6.9	5.0
3.0	22.1	13.7	10.1

Table 5: Calculated solidification time

Thickness, mm	Solidification time, ms		
	T_F = 120 °C	T_F = 160 °C	T_F = 200 °C
0.8	16	19	23
1.5	57	68	83
3.0	228	270	330

Table 6: Young's modulus as function of testing temperature and ageing conditions

Ageing condition	Young's modulus, GPa		
	T = +23 °C	T = +85 °C	T = -35 °C
As cast condition	90 ± 8	82 ± 8	92 ± 8
1 year natural ageing	88 ± 8	78 ± 8	90 ± 8

Table 7: Fracture elongation as a function of testing temperature and ageing

Alloy / ageing condition	Fracture elongation, %		
Z400	T = +23 °C	T = +85 °C	T = -35 °C
as cast	5.0 ± 3.0	20 ± 8	2.0 ± 1.0
2 month natural ageing	9.0 ± 5.0		
artificial ageing 105 °C/24 h	10 ± 5	25 ± 5	2.0 ± 1.0

Alloy / ageing condition	Fracture elongation, %		
Z410	T = +23 °C	T = +85 °C	T = -35 °C
as cast	2.7 ± 1.0	22.7 ± 8.6	1.5 ± 0.4
1 year natural ageing	5.5 ± 1.7	22.6 ± 6.8	2.0 ± 0.5

Alloy / ageing condition	Fracture elongation, %		
Z430	+23 °C	+85 °C	-35 °C
as cast	3.0 ± 1.0	15 ± 8	1.1 ± 0.5
4 month natural ageing	5.0 ± 1.5		
artificial ageing 105 °C/24 h	4.6 ± 1.5	24 ± 8	1.7 ± 0.9

3.4.4 Fatique testing

Fatique testing equipment:
For fatigue testing a resonance testing machine by Russenberger & Müller, type Mikroton 654 with maximal 20 kN load has been used **Figure 29**. The test frequency was 150 Hz. The specimen is shown in **Figure 30**.

The tests have been conducted at R = -1 (tension-compression) and R = 0 (tension). As small probes up to 2 mm break under compression for the probes with 0.8 mm and 1.5 mm only tension has been tested. The data vary extremely heavily with internal defects, much more than the static data. Therefore all specimens have been X-rayed before testing.

Results of the fatigue tests:
The zinc alloy does not show a sharp edge between time strength and permanent strength. For 10 million cycles one can assume 85 MPa, after artificial ageing the value drops down to 80 MPa (**Figure 31**).

For Z400 the lower tensile data lead to a smaller decline of the slope and the higher ductility leads to a higher permanent time value.

The sensitivity for combination of static and dynamic loads can be calculated from values at R = -1 and R = 0 and has the value of 0.45 (**Figure 32**).

3.4.5 Hardness

Hardness has been tested for all specimen and all ageing conditions. The values for as cast probes are in the range of

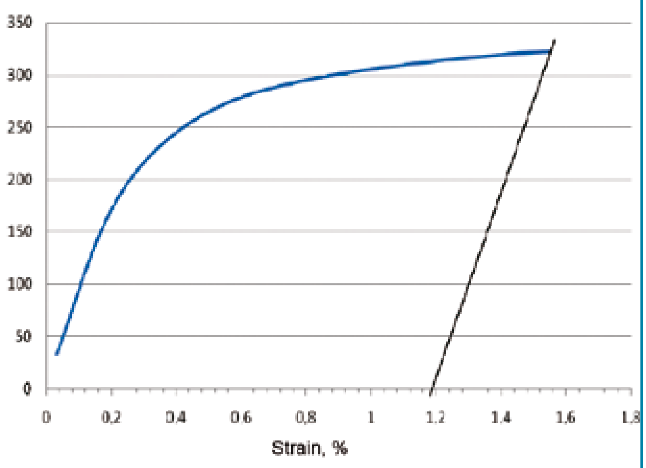

Figure 16: **Stress-strain-curve run 26 (3 mm; 200 °C; 55 m/s) measured in as cast condition at -35 °C**

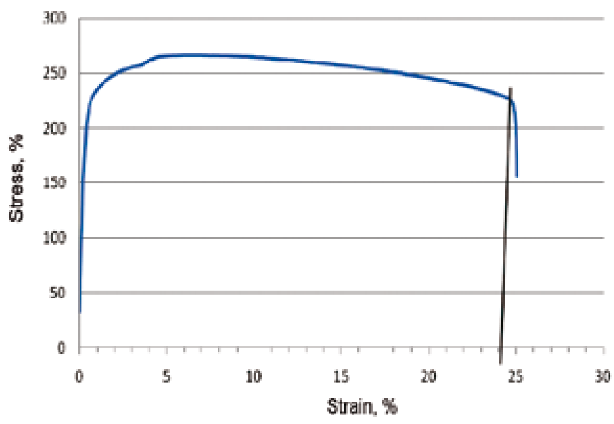

Figure 17: **Stress-strain-curve run 26 (3 mm; 200 °C; 55 m/s) measured in as cast condition at 85 °C**

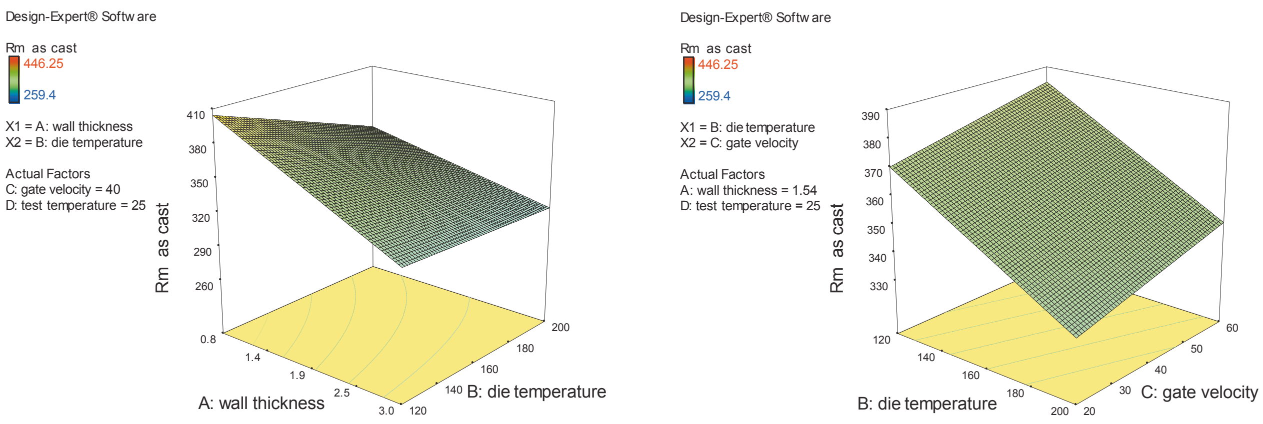

Figure 18: **Tensile strength as a function of wall thickness and die temperature (left) and as a function of die temperature and gate velocity (right) as cast condition**

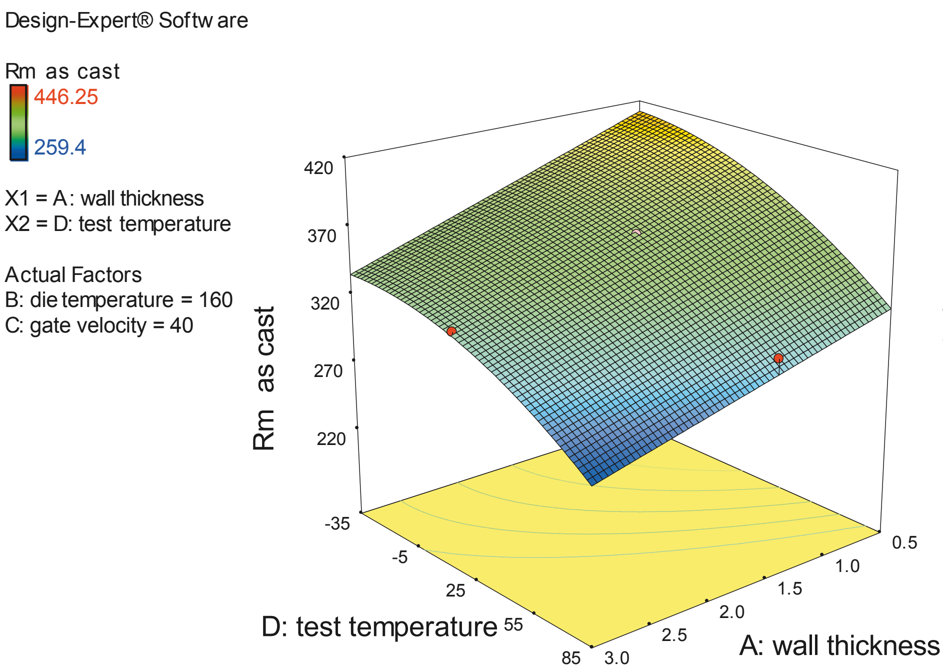

Figure 19: **Tensile strength as a function of wall thickness and test temperature as cast condition**

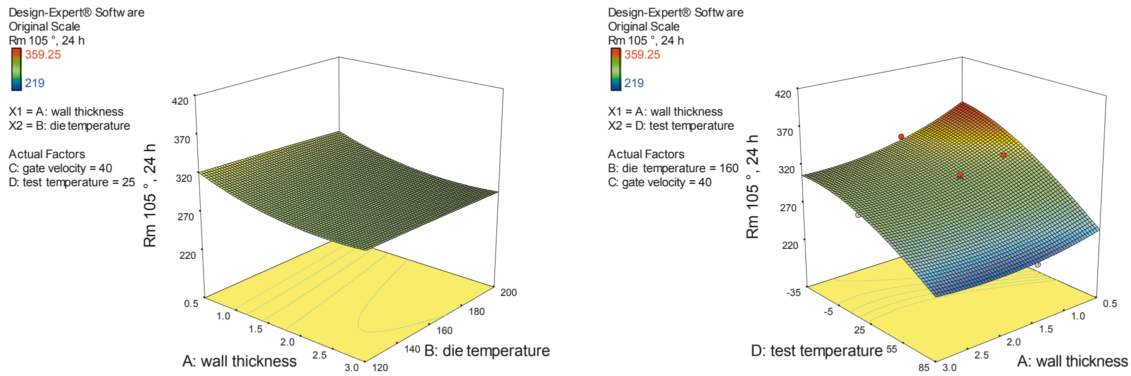

Figure 20: **Tensile strength as a function of wall thickness and die temperature (left) and as a function of testing temperature and wall thickness (right) artificially aged at 105 °C for 24 hours**

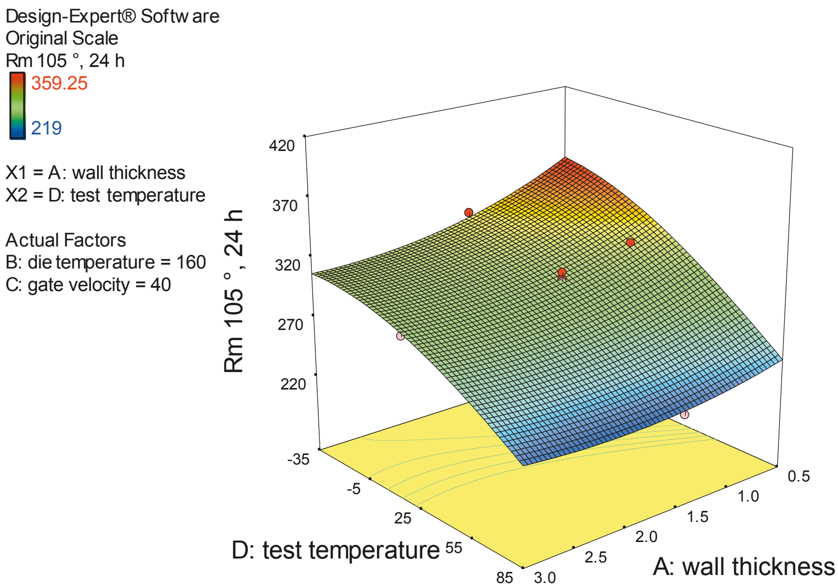

Figure 21: **Tensile strength as a function of wall thickness and testing temperature, artificially aged at 105 °C for 24 hours**

Figure 22: **Creep testing equipment with 12 temperature controlled test stations**

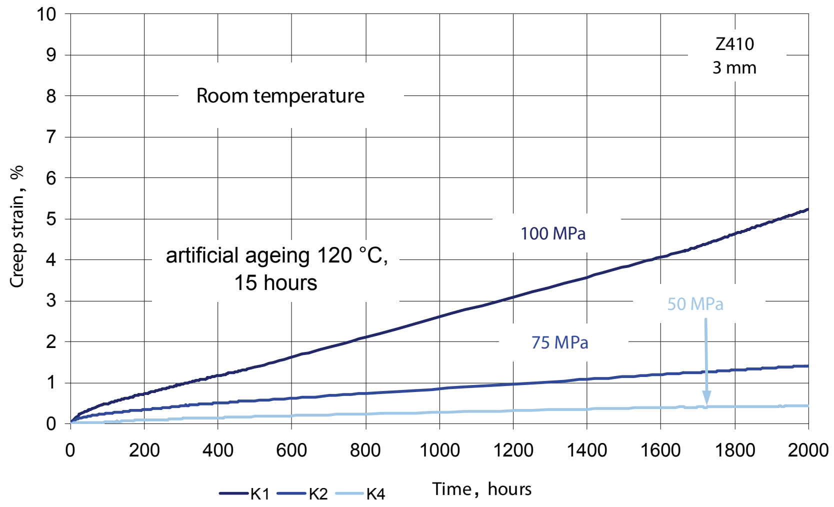

Figure 23: Creep elongation as a function of time and stress of Z410 at room temperature

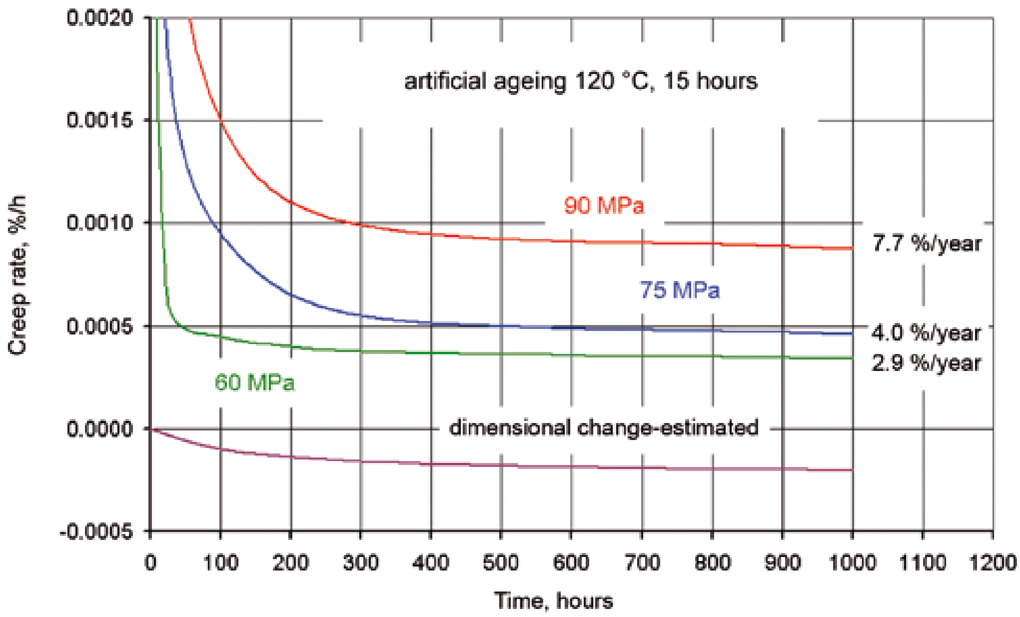

Figure 24: Primary and secondary creep rate of Z410

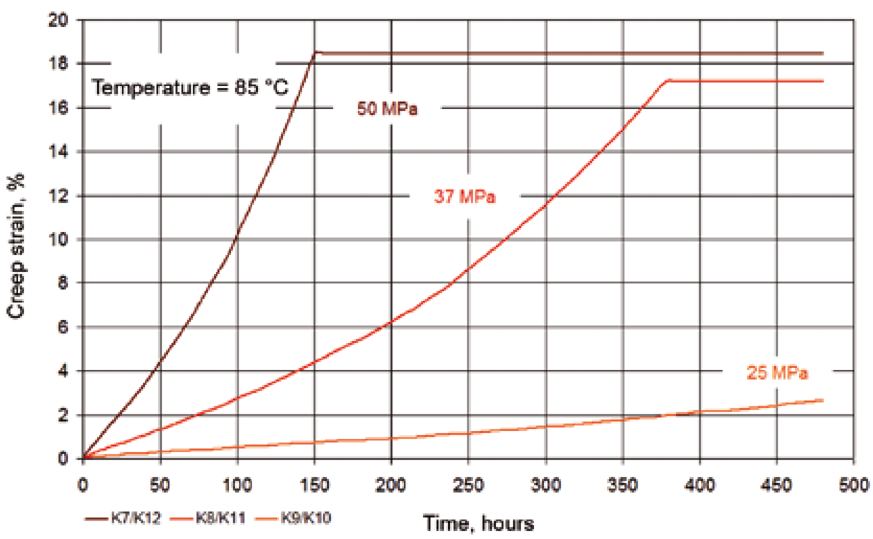

Figure 25: Creep elongation as a function of time and stress of Z410 at +85 °C

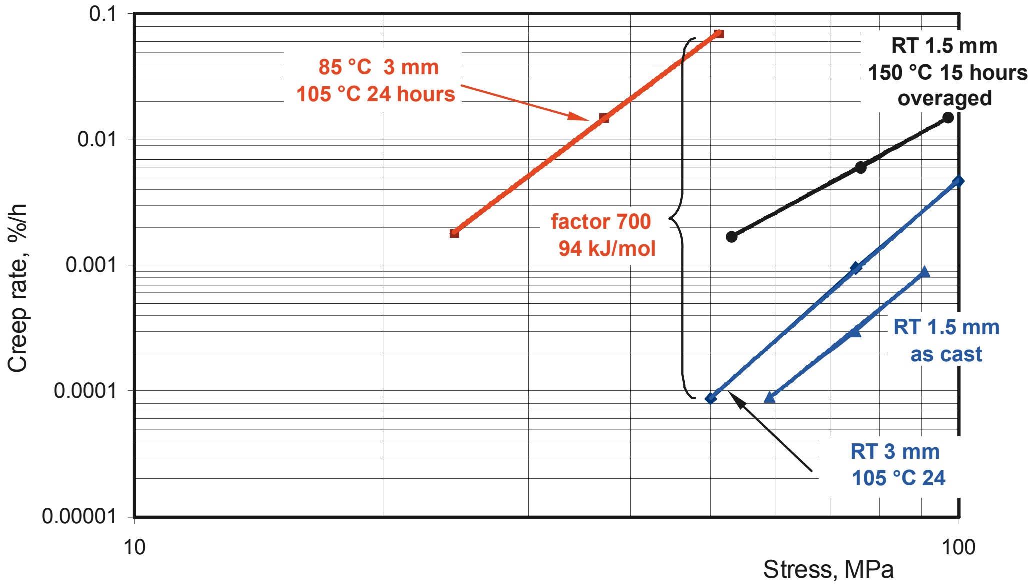

Figure 26: Stress exponent and activation energy for secondary creep of Z410 measured at 1 % creep elongation

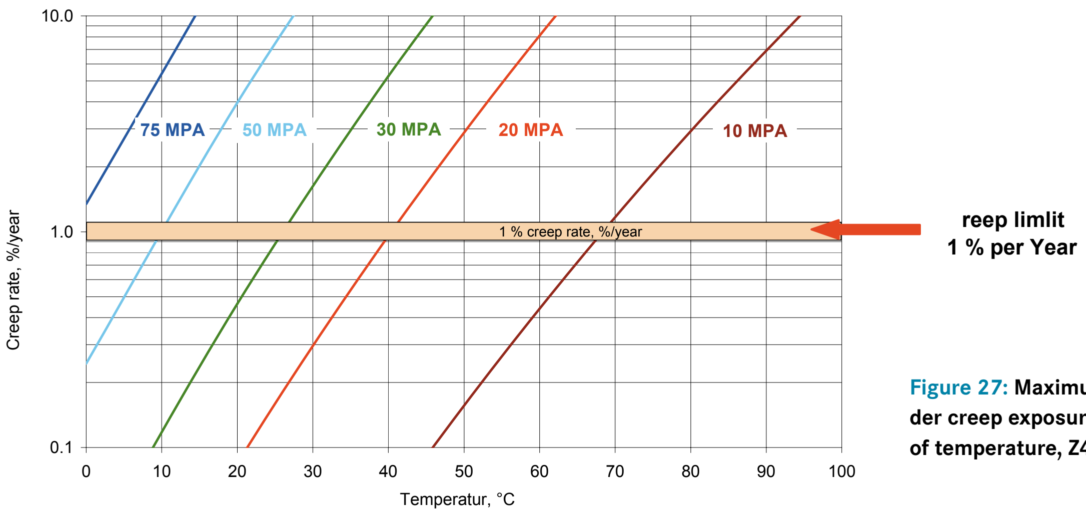

Figure 27: Maximum of stress under creep exposure as a function of temperature, Z410

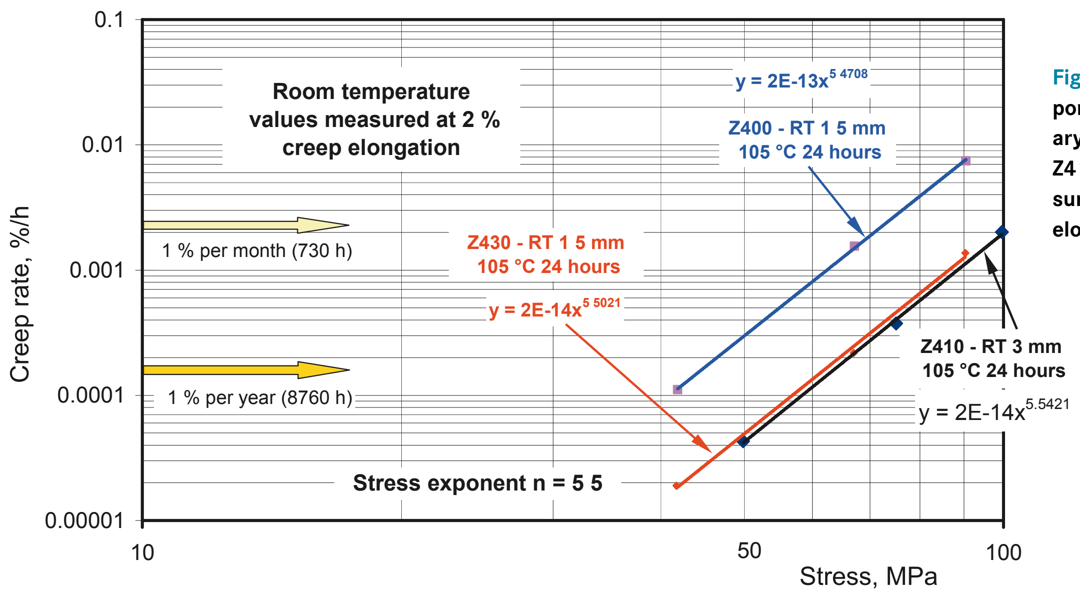

Figure 28: Stress exponent for secondary creep of Z400, Z410 and Z430 measured at 1 % creep elongation

Figure 29: Mikroton 654 resonant testing machine for fatigue tests (20 kN)

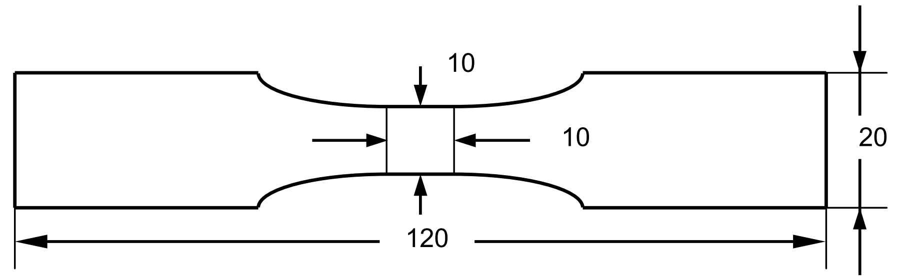

Figure 30: Shape of the utilized specimens for fatigue tests

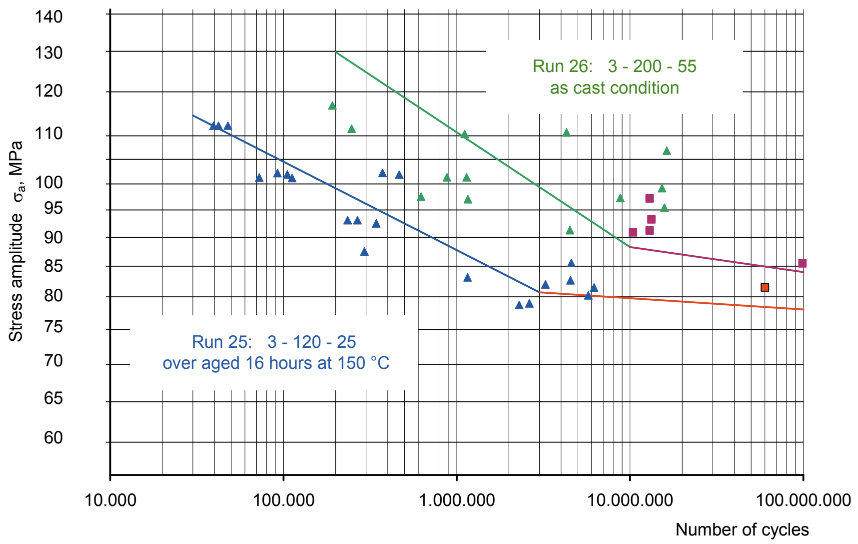

Figure 31: S/N-curves (extended fatigue test) at R = -1 (compression and tension) of specimens in as cast condition and after artificial ageing (over ageing)

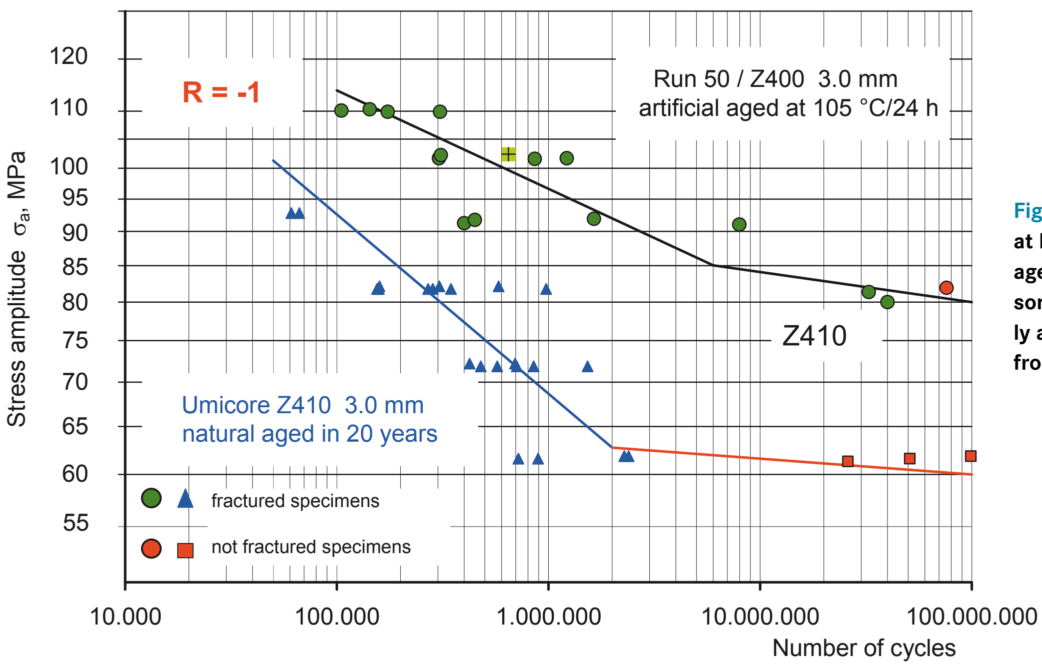

Figure 32: S/N-curves at R = -1 of artificially aged Z400 in comparison of 20 year naturally aged Z410 specimens from Umicore

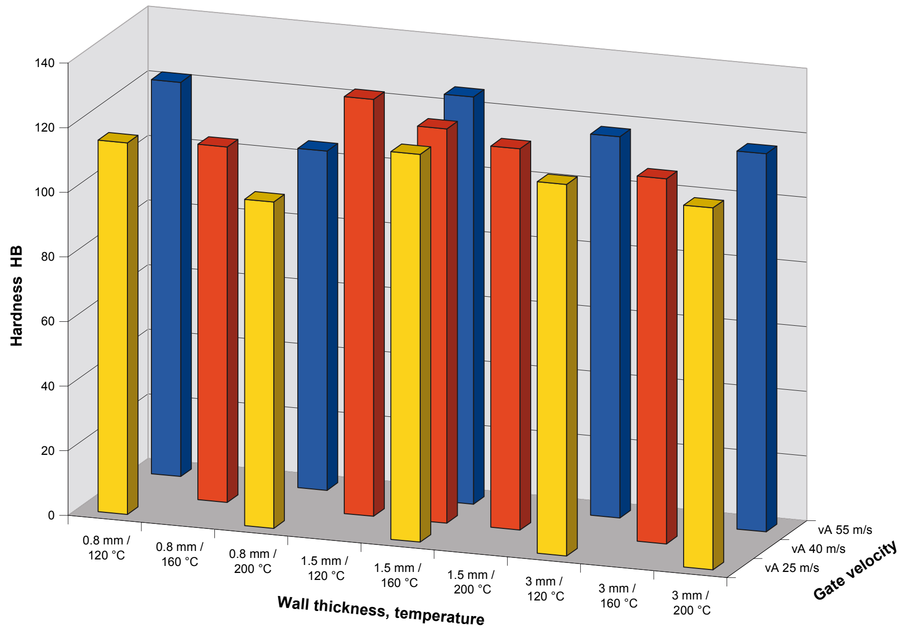

Figure 33: Hardness as a function of processing parameters of Z410 as cast condition, thickness and die temperature show strong influence on hardness. Gate velocity has no influence on the hardness.

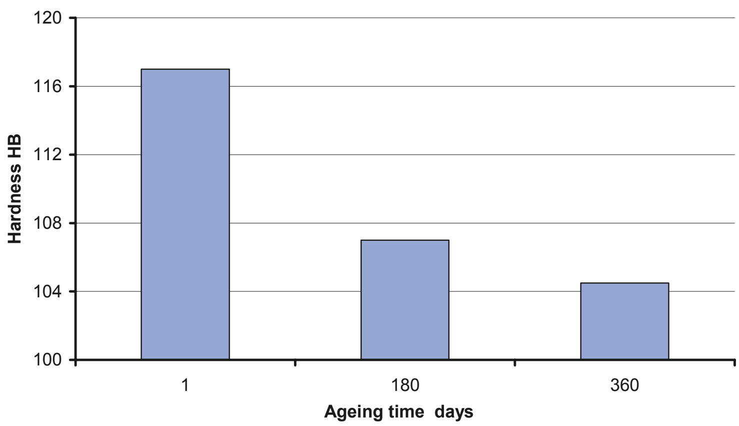

Figure 34: Hardness of Z410 as a function of natural ageing time

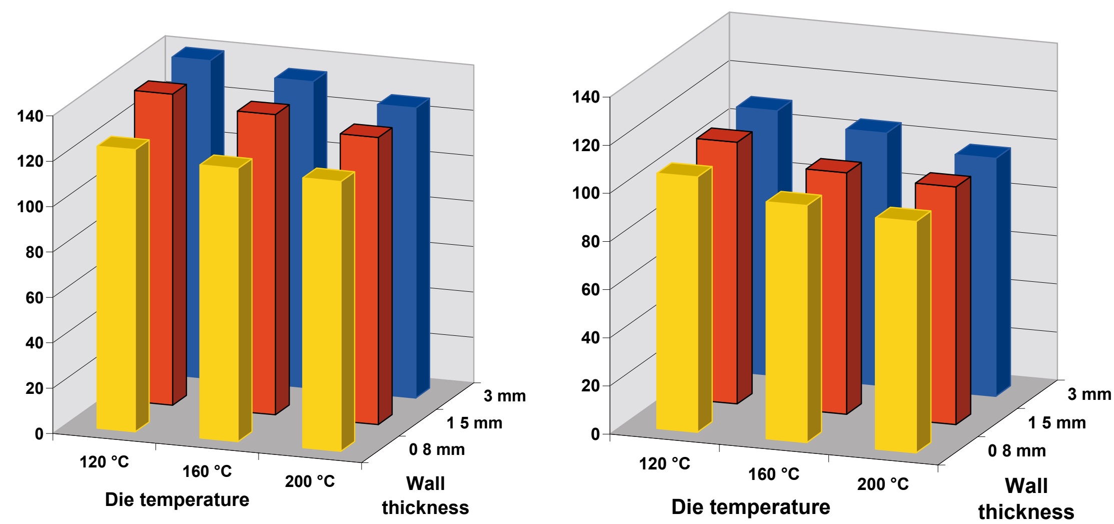

Figure 35: Hardness of Z400 (a) and Z430 (b), as cast condition

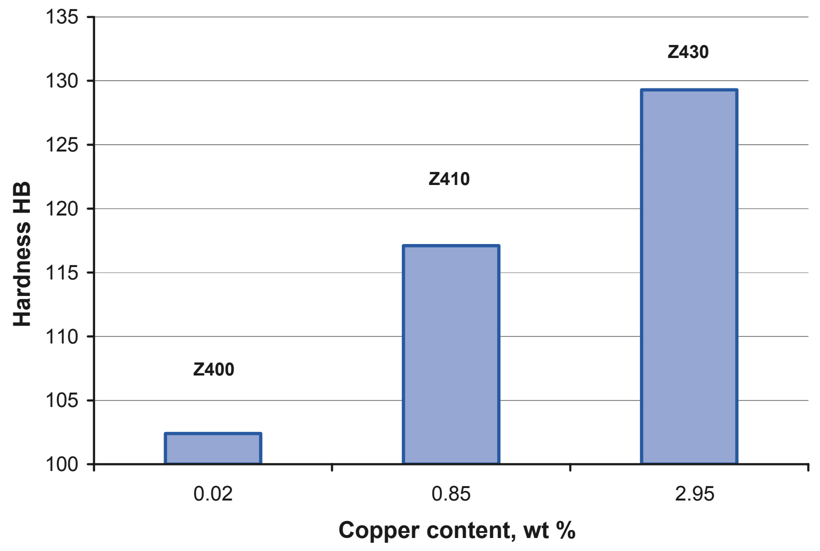

Figure 36: Hardness (average values) as a function of copper content

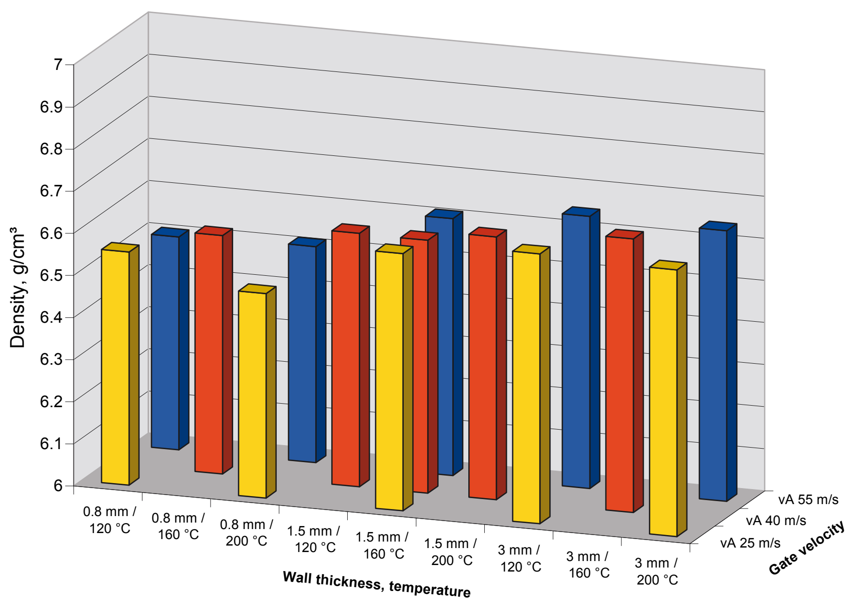

Figure 37: Density of the parts as a function of processing parameters

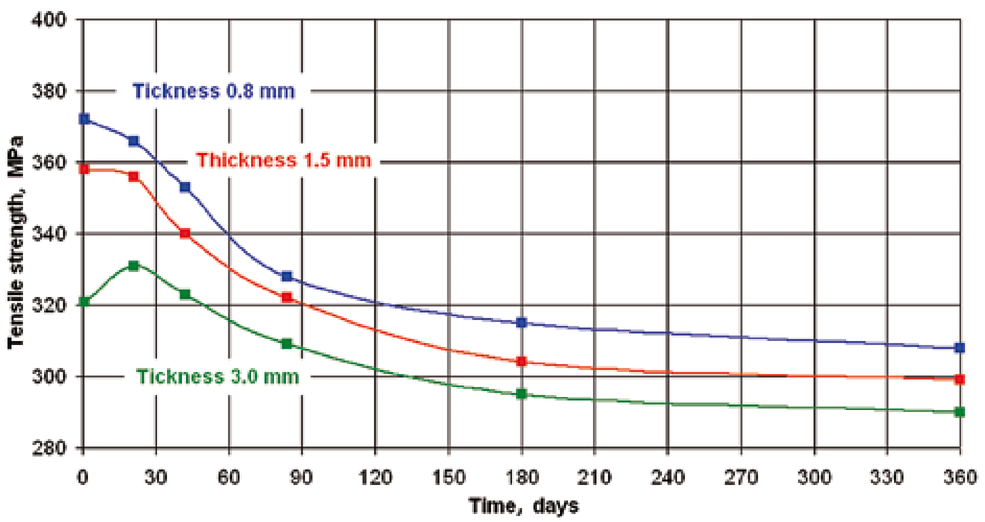

Figure 38: Decrease of tensile strength at RT for Z410 as a function of time and wall thickness through the ageing process

Table 8: Creep parameters for secondary creep (coefficient of creep rate A, stress exponent n, activation energy Q for self diffusion of zinc)

Alloy / thickness	A, %/h	n	Q, kJ/mol
Z410 / 3.0 mm	4.7 · 105	4.15	94.1
Z400 / 1.5 mm	2.1 · 106	4.6	94.1
Z430 / 1.5 mm	3.9 · 105	4.15	94.1

Table 9: Average values of density and porosity of Z410

	Wall thickness, mm		
	0.8	1.5	3.0
Density, g/cm³	6.54 ± 0.06	6.61 ± 0.02	6.64 ± 0.01
Porosity, %	1.97 ± 0.94	1.02 ± 0.26	0.48 ± 0.13

Table 10: Correlation of time and temperature for the ageing behavior of Z410

Temperature in °C	-20	0	23	50	80	105	120
Time	100 years	10 years	1 year	37 days	4 days	1 day	0.4 days

Table 11: Chemical composition of the used alloys

	Chemical elements, wt %								
Alloy	Al	Cu	Mg	Fe	Pb	Cd	Sn	Ni	Si
Z400	4.0	0.000	0.041	0.013	0.0024	0.0004	0.0001	0.0003	0.0008
Z410	4.0	0.85	0.053	0.0009	0.002	0.0004	0.0001	0.0001	0.0011
Z430	3.8	2.95	0.040	0.001	0.002	0.0005	0.0002	0.0003	0.0005

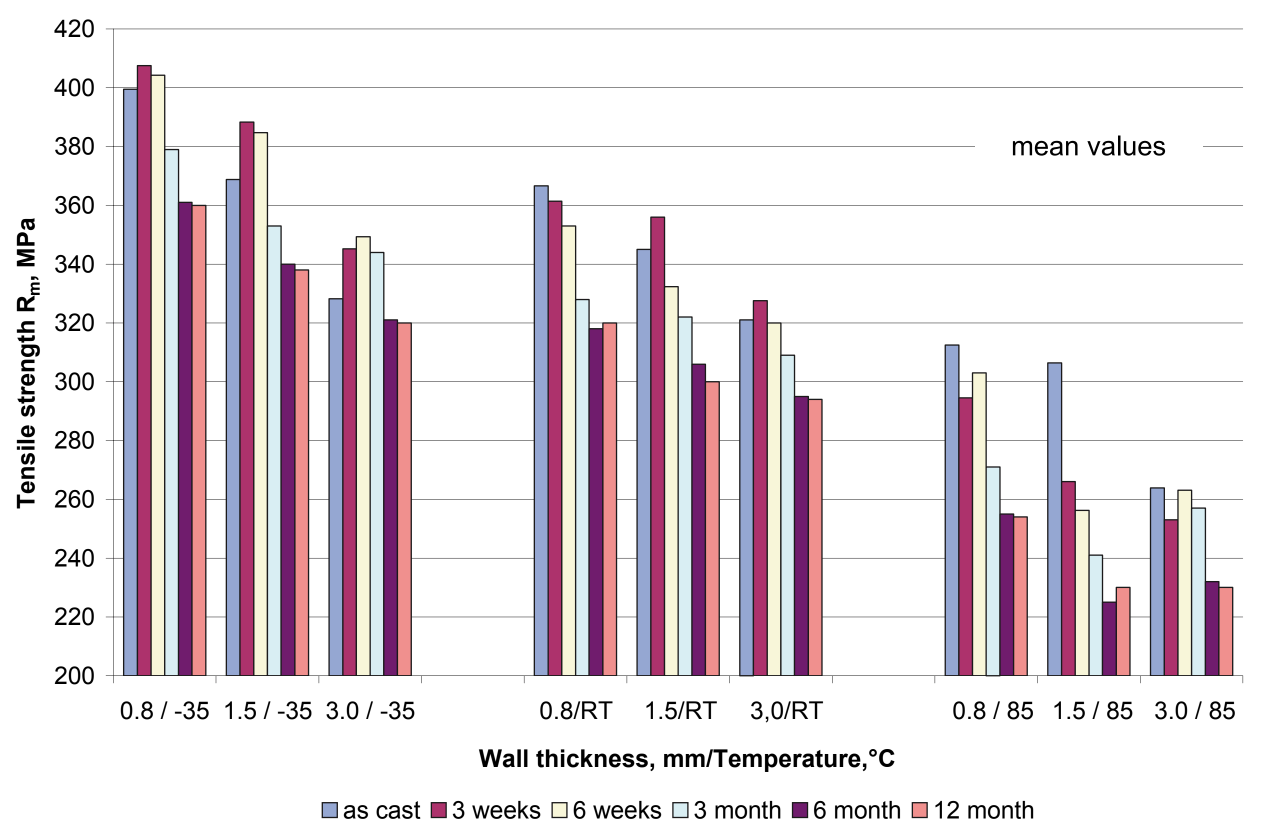

Figure 39: Tensile strength as a function of testing temperature and wall thickness through the natural ageing process of Z410

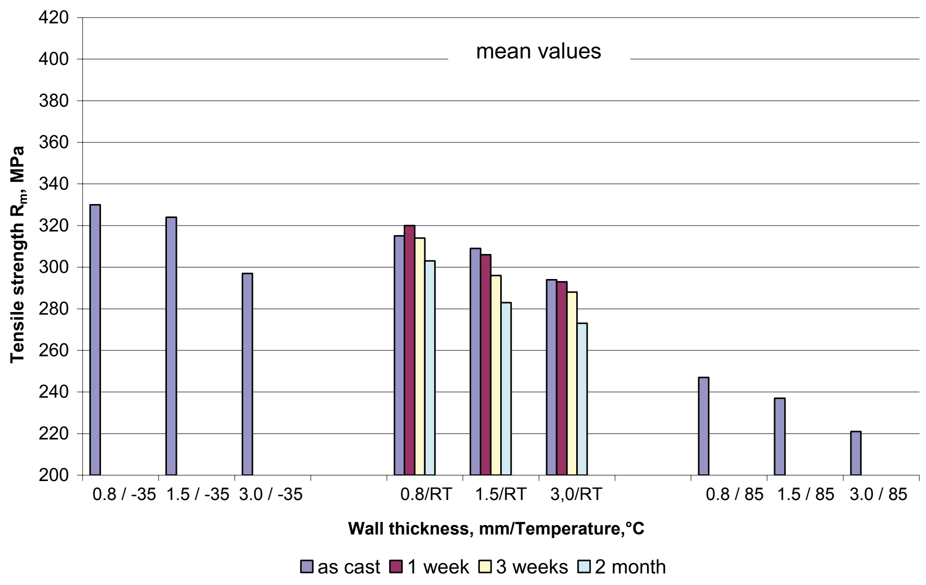

Figure 40: Tensile strength as a function of testing temperature and wall thickness through the natural ageing process of Z400

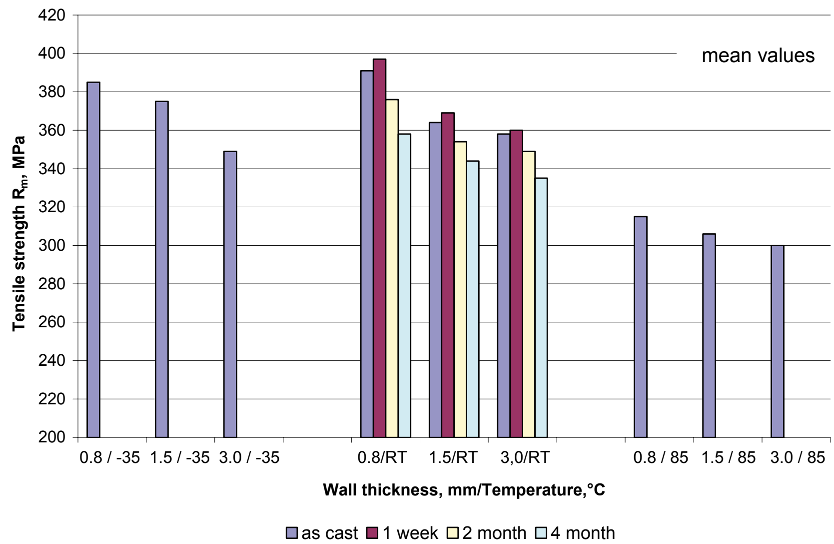

Figure 41: Tensile strength as a function of testing temperature and wall thickness through the natural ageing process of Z430

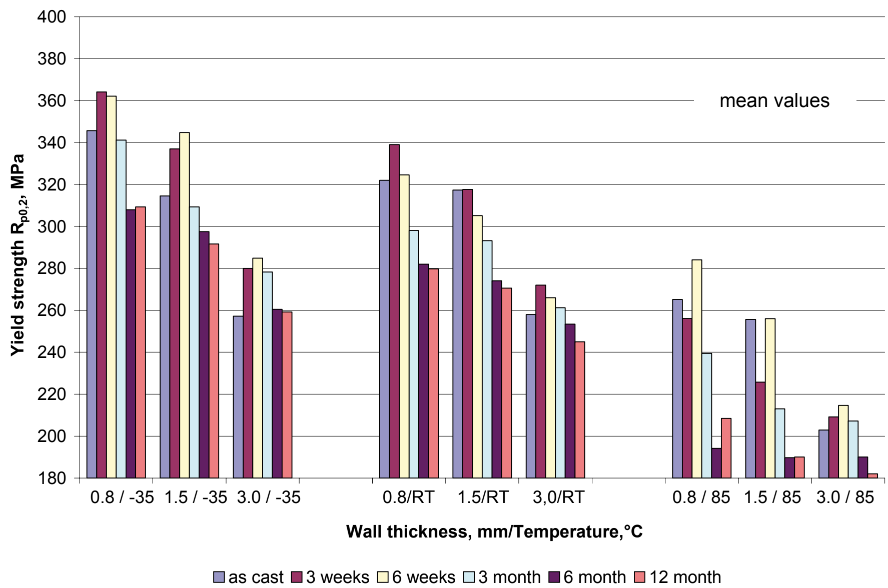

Figure 42: Yield strength as a function of testing temperature and wall thickness through the natural ageing process of Z410

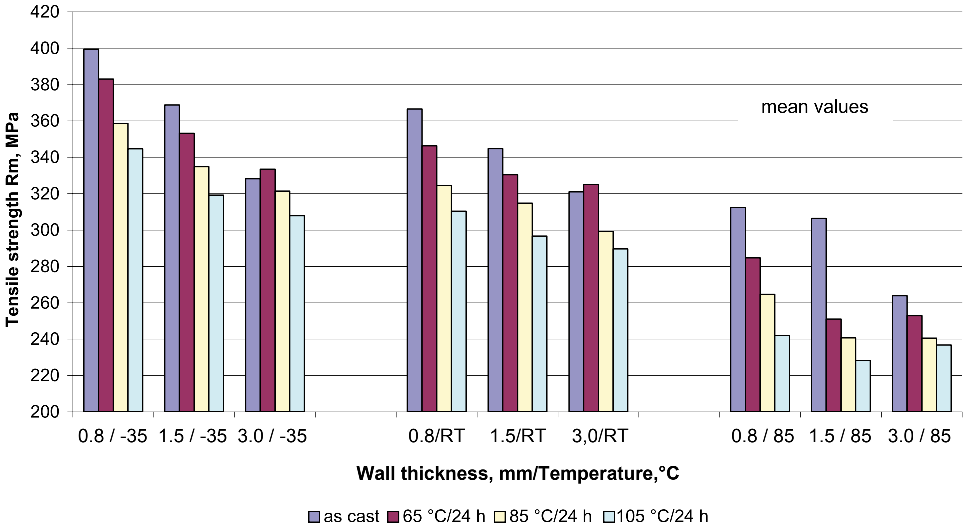

Figure 43: Tensile strength as a function of testing temperature and wall thickness through the artificial ageing processes of Z410

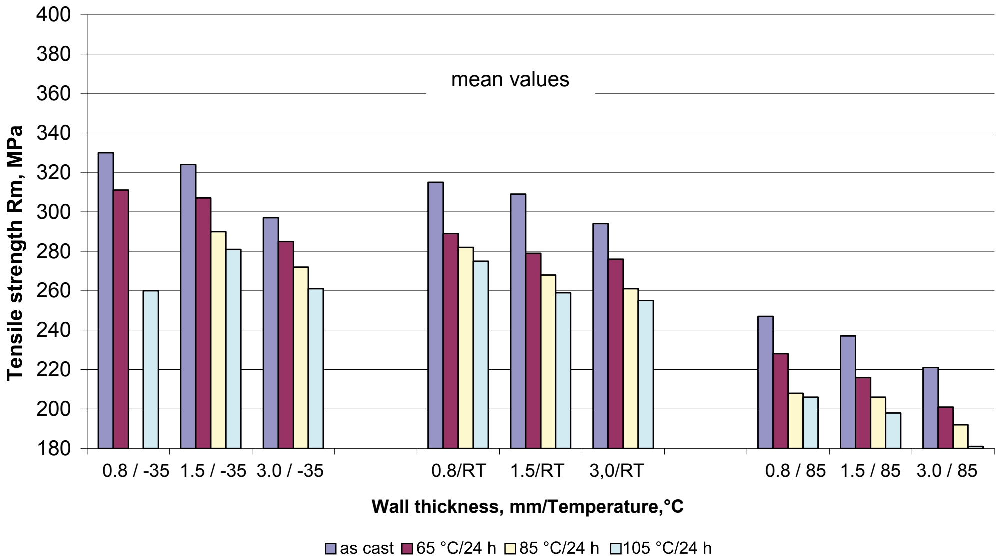

Figure 44: Tensile strength as a function of testing temperature and wall thickness through the artificial ageing processes of Z400

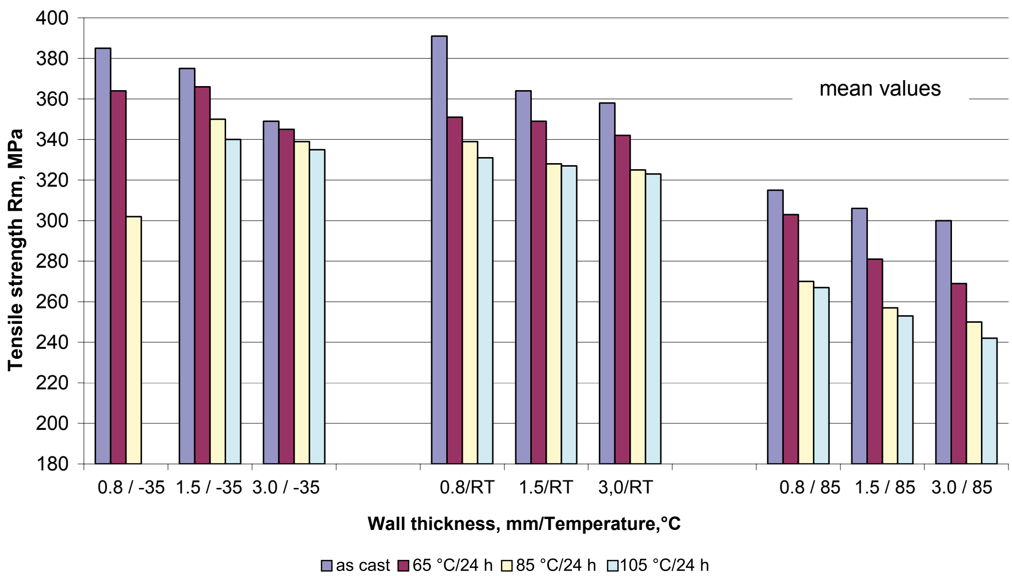

Figure 45: Tensile strength as a function of testing temperature and wall thickness through the artificial ageing processes of Z430

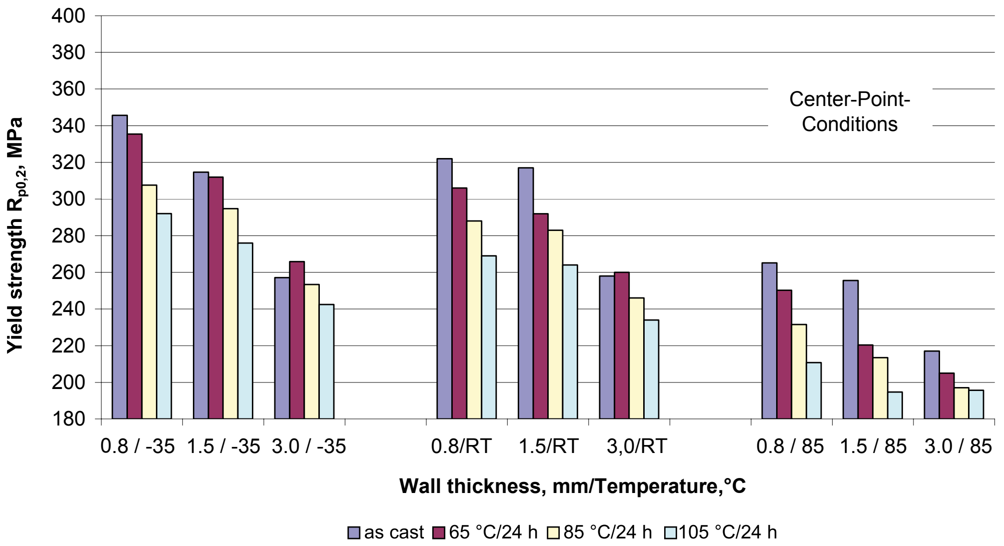

Figure 46: Yield strength as a function of testing temperature and wall thickness through the artificial ageing processes of Z410

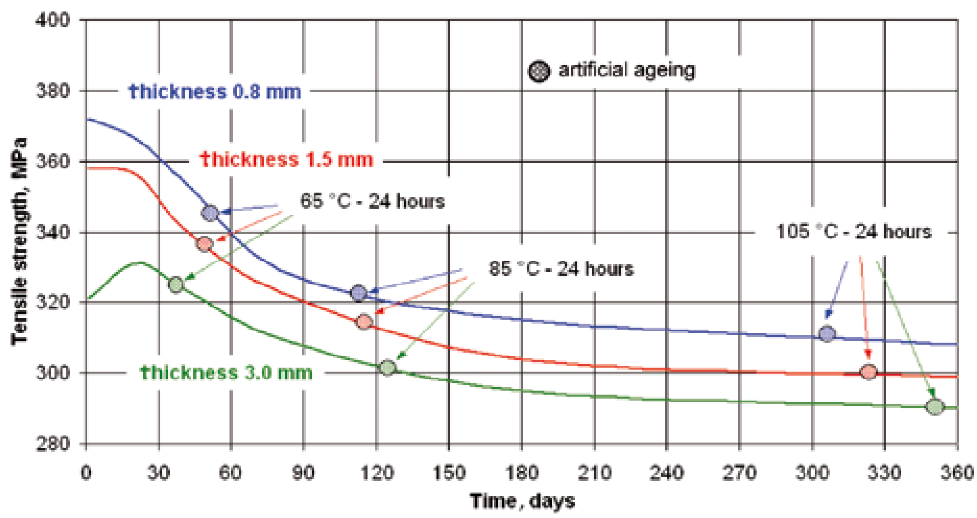

Figure 47: Ageing behaviour (decreas of tensile strength) in comparison of natural and artificial ageing of Z410 as a function of wall thickness

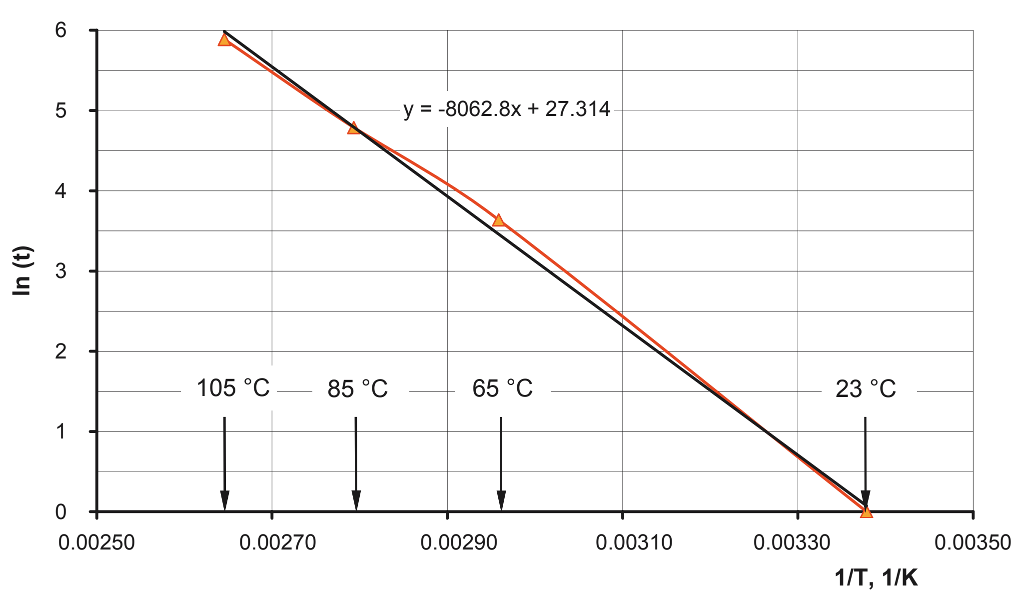

Figure 48: Arrhenius plot of time ln(t) versus influence of temperature 1/T during ageing for calculation of the activation energy

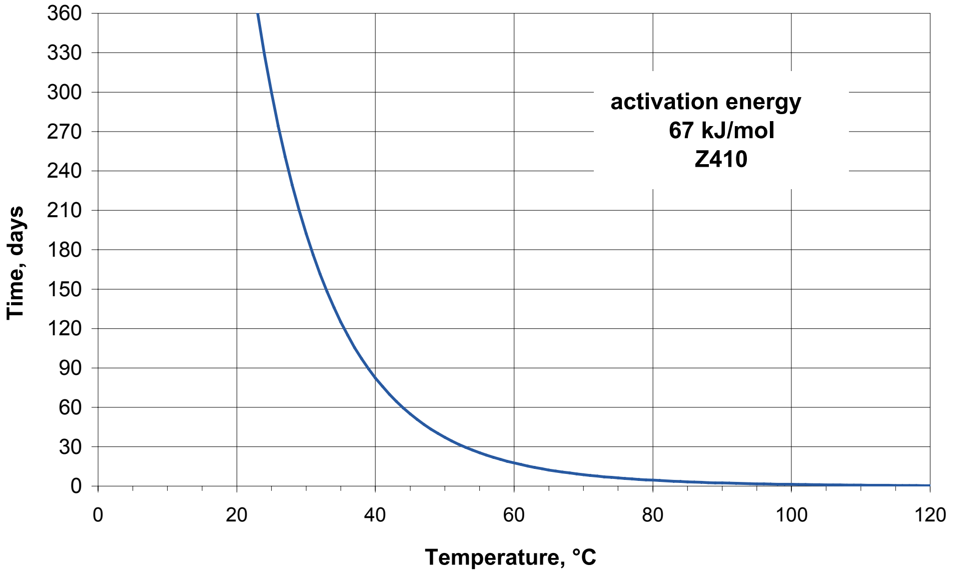

Figure 49: Required time as a function of temperature for artificial ageing to build up a natural ageing of 1 year at RT of Z410

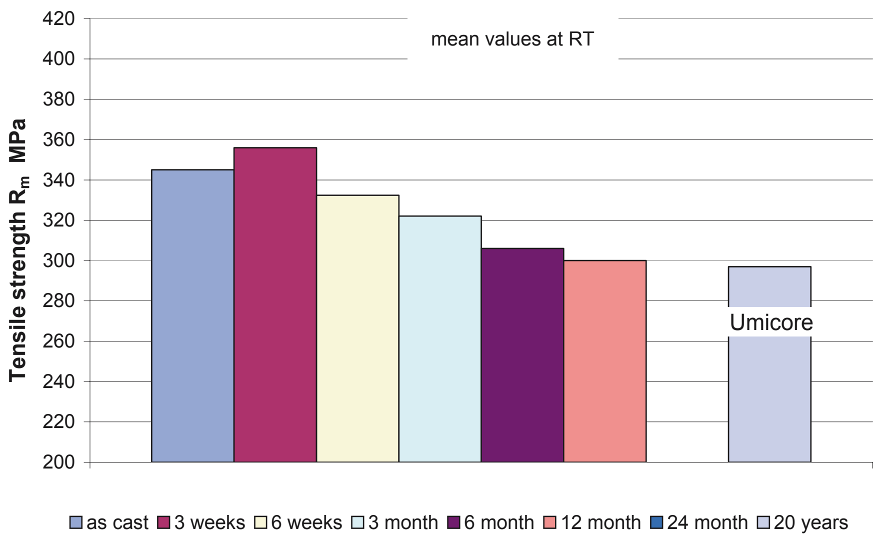

Figure 50: Additional value of tensile strength (average value of 25 specimens with 1.5 mm wall thickness, unknown process parameters) after 20 years natural ageing (Umicore)

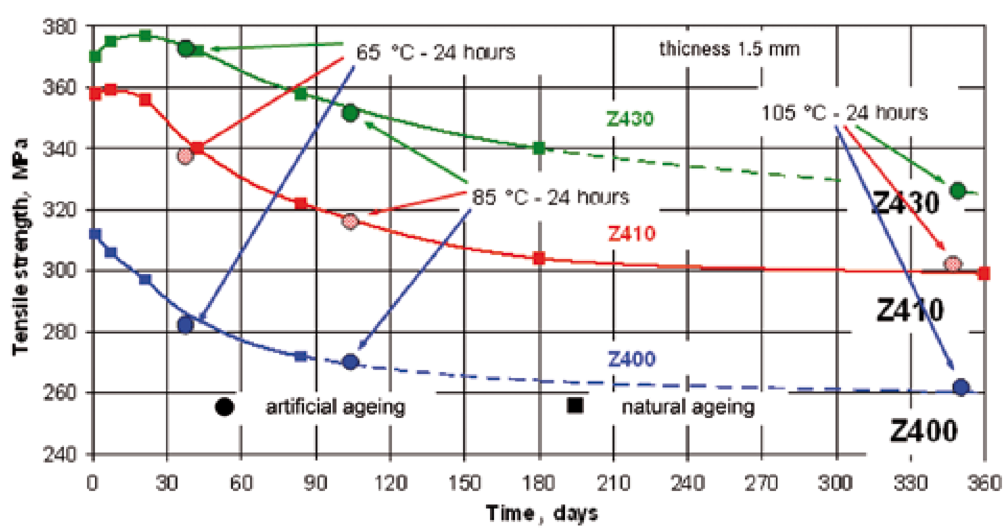

Figure 51: Ageing behavior (decrease of tensile strength) in comparison of natural and artificial ageing of Z400, Z410 and Z430 as a function of time, broken lines represents expected values

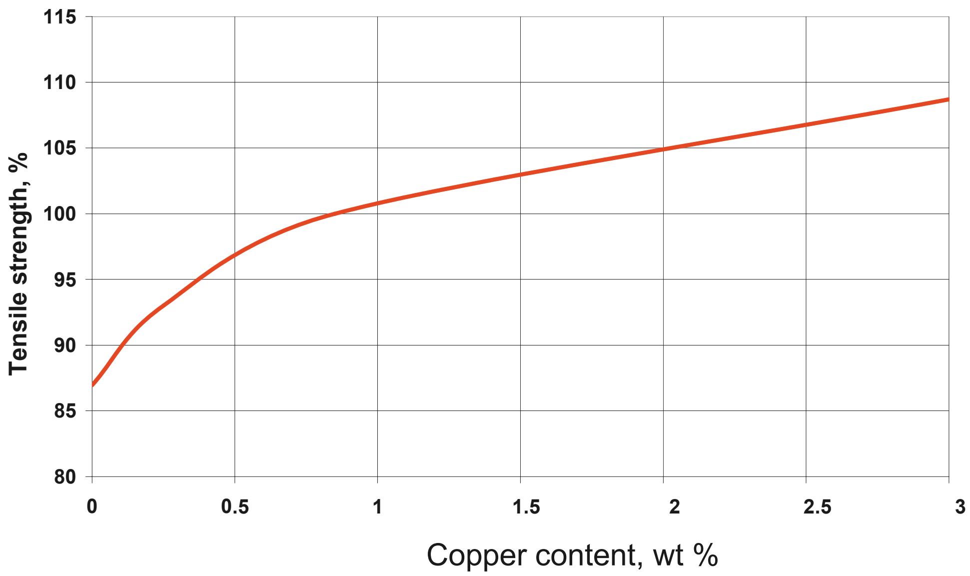

Figure 52: Influence of copper on tensile strength (referring to Z410 as 100 %) at RT after artificial ageing 24 hours/105 °C

110 HB. One can detect that the gate velocity has no influence on the hardness (Figures 33 and 34).

A cold die leads to high hardness data, probes under 0.8 mm show deflection and cannot tested properly. The comparison of the hardness data for Z400 and Z430 as cast is depicted in Figure 35. Out of DOE one can calculate the influence of the copper content on the hardness (Figure 36).

3.4.6 Density and porosity

Density and porosity have been tested according to Archimedes through weight in air and in water. Figure 37 shows the influence of die temperature wall thickness and gate velocity on the density. The wall thickness shows a strong influence. The porosity varies 0.5 % and 2 % (Table 9).

3.4.7 Natural Ageing

Natural ageing:
Tensile strength and yield strength decrease with ageing, the elongation increases. Data have been achieved for Z410 for up to 1 year so far, for Z400 until 2 months and Z430 until 4 months.

For Z410 the drop in tensile strength is shown in Figure 38. This behavior is similar for all alloys. The drop in strength should follow according the 2. Fick-Law. However there are differences based upon the following facts:

- The error function is described using a diffusion coefficient which is independent from the concentration, this is not the case.
- Not only aluminum but also copper diffuses.

Figure 39 shows the ageing behavior of Z410, Figure 40 of Z400 and Figure 41 of Z430 as a function of testing temperature, wall thickness, die temperature and gate velocity. Figure 42 shows the same influences on the yield strength for Z410.

Artificial ageing:
Artificial ageing was performed for all alloys:

- 65 °C for 24 hours;
- 85 °C for 24 hours;
- 105 °C for 24 hours.

The tensile strength after artificial ageing for Z410 is shown in Figure 43, for Z400 in Figure 44 and for Z430 in Figure 45 as a function of testing temperature and wall thickness at center-point-conditions and Figure 46 depicts the change of the yield strength after artificial ageing for Z410.

Figure 47 shows that for Z410 artificial ageing at 65 °C for 24 hours equals a natural ageing of 45 days. Ageing at 85 °C for 24 hours equals approx. 120 days and 105 °C for 24 hours equals natural ageing of 1 year.

If depicted in a diagram temperature 1/T against the log of time one achieves the activation energy as -Q/k (Figure 48). With this slope in Figure 48 one achieves the activation energy for ageing for Z410:

$$Q = 8062 \cdot 8{,}31\ \text{J/mol} = 67\ \text{kJ/mol} \qquad (4)$$

Figure 49 shows the time which is necessary at a certain temperature for artificial ageing for Z410 to achieve natural ageing of 1 year contents numeric data for this. As a result the storage at -20 °C of the probes prevents natural ageing for 2 years (Table 10).

Umicore supplied probes out of Z410 which have been aged for 20 years Figure 50. These probes fit very nicely into the test data and show that after 1 year natural ageing is more or less finished.

3.5 Comparison between ZP0400, ZP0410 and ZP0430

Table 11 depicts the chemical composition of the 3 alloys. As discussed in 2 („State of the knowledge") and shown in Figure 5 copper increases the strength and increases the solubility of aluminum.

Figure 51 shows the direct comparison for all 3 alloys and a wall thickness of 1.5 mm for center-point-conditions (die temperature 160 °C, gate velocity 40 m/s) for tensile strength at room temperature.

Figure 51 shows that all alloys age. Copper increases the strength and decelerates the ageing behavior.

Related to the as cast strength after artificial ageing of at 105 °C for 24 hours Z400 shows 83 %, Z410 84 % and Z430 still 88 % of the original strength.

The copper free alloy ages according to Figure 51 much faster which is in correlation to literature data [6] (**Figure 52**).

4 Summary

Compared to other die casting alloys zinc-alloys gain the highest mechanical values. The low melting temperature allows high production rates using hot chamber technology and die lives exceed 1.000.000 shots. Zinc alloys can be cast in extremely small wall thicknesses down to 0.5 mm or less. However, the low liquidus temperature leads to ageing phenomena depending on time, changes in measures and creep under load.

The results show that all phenomena are thermally activated and follow an Arrhenius law. The activation energy however is different: for ZP0410 and ageing it is approx. 67 kJ/mol and for creep it is approx. 94 kJ/mol.

The maximal solubility of aluminum in zinc is 0.05 wt % at room temperature. Ageing is based upon the segregation of aluminum into cubic face centered phase at room temperature which leads also to the measure changes as the centered cubic face structure has a smaller lattice constant. Copper is basically responsible for the higher mechanical properties but copper also segregates at lower temperatures.

Ageing is based upon diffusion. Micro structural investigations using TEM show that ageing is based upon segregation. Aluminum segregates completely. Copper increases the solubility of Aluminum and increases the strength. The measurement shows a reduction of tensile strength after one year of up to 16 % at the Z410 alloy. The strongest effect among the tested parameters is the wall thickness which strongly influences the cooling rate and the structure of the material. The influence of the gate velocity and the die temperature is much lower and only changes the mechanical properties by 3-4 %. Using an artificial ageing of 105 °C and 24 hours all processes influencing the mechanical properties are terminated and the material properties are stable over time.

The creep behavior is a self diffusion process which can be described using diffusion kinetics. The production parameters only have small influence on the creep behavior. Overageing of the material at 150 °C and 15 hours increases the creep rate by the factor of 4-5. All data have been gained using DOE and statistical analysis.

Artificial ageing is always necessary when using zinc alloys to finish the diffusion processes. The artificial ageing at 105 °C for 24 hours should be used. Temperatures over 120 °C must be avoided as other phase transformations will take place.

Conclusions:

- The ageing behavior of zinc die casting alloys is activated at room temperature and caused by the low solubility of aluminum in zinc at room temperature.
- Ageing is diffusion controlled. The diffusion process starts immediately after ejection out of the die.
- For Z410 ageing at room temperature is finished after 1 year, for Z400 half a year (expected) and for Z430 after 2 years (expected).
- The drop in tensile strength and yield strength after completed ageing is ~15 %.
- Natural ageing can be simulated by an artificial ageing at 105 °C for 24 hours.
- The mechanical properties of zinc die casting alloys after ageing are high compared to aluminum- and magne sium alloys.
- The creep behavior of zinc die casting alloys is caused by self diffusion of zinc and is thermally activated according to Arrhenius law.
- Creep in zinc die casting alloys is a function of time, the creep rate decreases with time when stress is constant.

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Keywords