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## **New Mechanical Properties Data for Zinc Casting Alloys**

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### **ABSTRACT**

Recent results from this continuing research program have determined the effects of die casting production variables such as die temperature and section thickness on the mechanical properties of zinc alloys 5 and ZA-8 in as-cast, artificial and natural ageing conditions. New creep data for Alloy 5 and ZA-8 is also be presented.

### **INTRODUCTION**

Hot chamber die casting is a highly productive technology for making high-precision zinc parts with the highest available surface quality. Although traditional 4% Al (Zamak) zinc alloys have a relatively high density of 6.7 g/cm<sup>3</sup> and ZA-8 a density of 6.3 g/cm<sup>3</sup> compared to Al and Mg-based alloys, they are used in automotive, electronics, builders hardware and many other applications because of their attractive combination of mechanical properties, availability in wall thicknesses down to 0.25mm and their ease of surface finishing. Zinc die castings are completely recyclable.

The low solidus temperature of 386°C (727°F) has consequences for both creep and ageing behavior of zinc casting alloys that are related to solid state diffusion. Room temperature ageing results in changes in mechanical properties and dimensions, but these can be stabilized by artificial ageing. Until today very few statistically reliable data have been published on the effects of ageing of zinc alloys on mechanical behavior, not only at room temperature but the range between -35°C and +85°C (-31 and 185 °F) that is of interest for automotive and other applications. Past publications have described this work for Alloy 3; this paper describes the most recent results obtained for zinc alloys 5 and ZA-8.

### **EXPERIMENTAL PROCEDURE**

The procedure of casting and experimental design used in this project was described in the 2011 NADCA paper.<sup>1</sup> The designed experiment for Alloys 5 and ZA-8 involved 27 different casting conditions, including three levels of wall thickness, injection velocity and die temperature, together with three temperatures of tensile testing and selected temperatures and stresses for creep testing that differed for each of these alloys. The experimental design permitted all effects on tensile strength to be examined using statistical analysis. Five replicates were tested for each condition for tensile testing. Wall thicknesses cast in each alloy were 0.8, 1.5 and 3.0 mm. Die temperatures of 120, 160 and 200°C were used. Gate velocities of 25, 40 and 55 m/sec. were used. All specimens were made on a newly-updated, Frech DAW 80 hot chamber die casting machine with 80 tons of locking force. Detailed data logging was included in the process, with measured data being plunger

velocity, hydraulic pressure, internal die pressure and temperature. The calculated filling times and solidification times are shown in Tables 1 and 2. After production, the plates were kept in a deep freeze at  $-20^{\circ}\text{C}$  until ageing and other testing work began.

## RESULTS

### DENSITY, POROSITY AND MICROSTRUCTURE

The compositions of the Alloys 5 and ZA-8 castings used in this work are shown in Table 3. The density and porosity of the tensile bar castings was measured using Archimedes' principle, measuring the casting weight in air and water. Alloy 5 is a hypoeutectic alloy with primary phase of zinc; the primary zinc phase is observed to be surrounded by eutectic in the microstructure of Figure 1. By contrast, ZA-8 is a hypereutectic alloy where aluminum solidifies first, followed by solidification of the surrounding eutectic, Figure 2. Figures 1 and 2 show alloys that were cast using dies at the same temperature and injection velocity. The microstructure of ZA-8 is much finer than that of Alloy 5, which can be expected to influence ageing and creep behavior.

### ARTIFICIAL AGEING AND TENSILE STRENGTH

Both artificial and natural ageing were carried out on the tested alloys. The effects of artificial ageing on the tensile strength of ZA-8 is shown in Figure 3. Similar to work reported in the 2011 and 2012 NADCA papers,<sup>1,2</sup> the tensile strength of ZA-8 decreases with increasing section thickness and also decreases with increasing ageing temperature for a 24-hour ageing period. The 2012 paper included only the ageing conditions of  $85^{\circ}\text{C}$  for 24 hours and  $105^{\circ}\text{C}$  for 24 hours. The new data shown here includes ageing results for  $50^{\circ}$  and  $65^{\circ}$  at 24 hours and  $105^{\circ}$  for 72 hours. For the room temperature tested samples, the trends are seen to be consistent with regard to increased temperature and ageing time. The effect of die casting production parameters on the as-cast tensile strength of ZA-8 are shown in Figure 4. Wall thickness and injection velocity combine to provide the given solidification time shown on the horizontal axis, and these times can be referenced to Tables 1 and 2. The dependence of tensile strength on this solidification time is shown in this graph. It can be seen that there is a dependence of tensile strength on injection velocity, but a weaker dependence on die temperature. Figure 5 shows similar data for Alloy 5. The influence of artificial ageing temperature, for a period of 24 hours on tensile strength of Alloy 5 is shown in this figure. Tensile tests were carried out at  $-35$ ,  $+23$  and  $+85^{\circ}\text{C}$  to provide the curves shown. If the ageing results of Figures 3 and 5 are depicted in a diagram plotting the reciprocal temperature  $1/T$  against the log of time, using both the 72-hour, 24-hour and other results, a curve is produced with a slope of  $-Q/K$ , where  $Q$  is the activation energy of ageing as shown in Figure 6. The activation energy for ageing of ZA-8 is shown to be  $74\text{kJ/mol}$ . It was reported in the 2012 NADCA paper that the corresponding activation energy for Alloy 5 was  $67\text{kJ/mol}$ , the difference being due to the higher aluminum content for ZA-8 in this case.

### NATURAL AGEING AND TENSILE STRENGTH

Figure 7 shows the time required to achieve artificial ageing at a given temperature for Alloys 5 and ZA-8 that will give the same tensile properties as natural ageing at room temperature for one year. Consistent with industrial experience, times on the order of one day are seen with ageing temperatures in excess of  $90^{\circ}\text{C}$ . Table 5 shows the correlation between time and temperature for the ageing behavior of Alloys ZA-8 and Alloy 5 based on the data of Figure 7. This investigation has shown that ageing of ZA-8 can be essentially completed after  $2\frac{1}{2}$  years of natural ageing, or after one day of artificial ageing at  $105^{\circ}\text{C}$  for 24 hours. Tensile strength as a function of test temperature and wall thickness over the full range of natural ageing times for samples tested in this program, up to two years, is shown in Figure 8. The full range of natural ageing times was only tensile tested at room temperature; however, the end points and other intermediate points were also tensile tested at  $-35^{\circ}\text{C}$  and  $+85^{\circ}\text{C}$ . The results are consistent and show the decrease of tensile strength with increased ageing time. Results from an ILZRO program at Centre de Recherches de Metallurgiques that began 25 years ago<sup>3,4</sup> provided additional samples that were later stored by Umicore and are now included in this program. These provided artificial ageing times of 8 years and 25 years. The effects of natural ageing for these longer periods of time are combined with the natural ageing results of this program for each of the three casting section thicknesses that were cast: 0.8, 1.5 and 3.0 mm, as shown in Figures 8, 9 and 10. The decrease in tensile strength for each of the wall thicknesses with natural ageing time is observed. When these data are

plotted in Figure 12, a consistent natural ageing behavior can be seen for tensile strength. This confirms that natural ageing behavior continues beyond the two-year period.

## CREEP TESTING

Creep tests were performed as a function of time and temperature according to DIN 50118. Creep tests at room temperature used stresses between 40 MPa and 100 MPa. At the test temperature +85°C, stresses between 12 MPa and 50 MPa were used. Figure 13 shows creep results for samples that were cast with a die temperature of 160°C using an injection velocity of 40 m/sec. These samples were then artificially aged at 105°C for 24 hours. The 1.5mm section thicknesses were tested at room temperature at stresses of 43.1, 69.2 or 94.5 MPa. The 3.0mm-thick samples were tested at either 90 or 80°C at a stress of 12 MPa. When these same data are plotted on a log-log graph, the curves become basically linear, as shown in Figure 14. Linear behavior is seen at both short and long times. The end of primary creep can be estimated as between 1 and 2% of creep strain. After primary creep there is only tertiary creep in zinc alloys because stress increases during plastic deformation under creep by reduction of the cross section of the specimens. The straight lines on a logarithmic scale at low strains allow creep behavior to be described by a power law function. This function was described in the 2012 NADCA paper.<sup>2</sup> Additional data for 1.5mm-thick samples is shown in Figure 15. These were also artificially aged at 105°C for 24 hours before creep testing. The creep tests shown were carried out at either room temperature or 85°C, with 3 stresses being used at each test temperature. These can also be plotted on a log-log scale to show linear behavior, therefore permitting an activation energy of 94 kJ/mol to be calculated, using the same technique described in the 2012 NADCA Congress paper.

Additional creep data for Alloy 5 were also produced in the most recent work. Creep strain as a function of wall thicknesses is shown for Alloy 5, artificially aged at 105°C for 24 hours before creep testing, Figure 16. A higher wall thickness is seen to reduce the creep rate because of the larger grain sizes observed in the microstructure. The slope of the creep curves can be obtained to determine creep rate. The relationship between creep rate in this primary range as a function of temperature for Alloy 5, also artificially aged at 105°C for 24 hours, is shown in Figure 17.

## DISCUSSION

The results of this and the 2012 NADCA paper<sup>2</sup> show that for Alloy ZA-8 and Alloy 5 all ageing and creep phenomena are thermally activated and follow the Arrhenius law. The activation energy is, however, different for these two alloys. It is approximately 74 kJ/mol for ageing of ZA-8, while for creep it is approximately 94 kJ/mol. For Alloy 5, it is 67 kJ/mol for ageing and 94kJ/mol for creep, as reported previously in Reference 2. The 94 kJ/mol corresponds to the activation energy for self-diffusion of zinc. The maximum solubility of Al in Zn is 0.05 weight percent at room temperature. The driving force for ageing is the reduction of segregation of aluminum in the primary phase that occurs during initial casting. For ZA-8, this segregation occurs in the aluminum-rich primary phase which has a higher solubility for zinc. Therefore, the drop in strength with ageing is higher and the ageing takes much longer than in Alloy 5, despite the finer microstructure shown in Figure 2. Artificially ageing for 105°C in 24 hours can give a practical stabilization of ZA8, equivalent to natural ageing of 2 ½ years; however, extended work showing 25 years of natural ageing shows that additional ageing occurs. The die casting process parameters investigated here, including wall thickness, injection velocity and die temperature, only have a small influence on creep behavior compared to ageing. The greatest process parameter influence is wall thickness, which influences the microstructural fineness and therefore the diffusion lengths that are active during the creep process. It should be noted that the mechanical properties of ZA-8, cast with the three section thicknesses reported here, are high in comparison with aluminum and magnesium die casting alloys, even after ageing of ZA-8.

## CONCLUSIONS

1. Ageing behavior of zinc die casting alloys is activated at room temperature for Alloy 5 and Zamak alloys of similar composition. It is caused by the low solubility of Al in zinc at room temperature, whose microsegregation is reduced as a result of the ageing process. For ZA-8, the solubility of zinc in the aluminum primary phase is much higher, but the diffusion process is still driven by the reduction of segregation within the as-cast structure.

2. Ageing in zinc die castings is diffusion-controlled. The diffusion process starts immediately after ejection from the die. The activation energy for ageing is 67 kJ/mol for Alloy 5 and other Zamak alloys with 4% Al, and 74 kJ/mol for ZA-8.
3. For ZA-8, ageing at 105°C for 24 hours can remove many of the ageing changes to properties that would normally be seen with natural ageing over an extended period of time; however, results from samples that have been aged for much longer periods of time indicate that ageing does continue at a lower rate for many years. By contrast for Alloy 5, ageing at room temperature is completed after one year, or after ageing for 95°C for 24 hours.
4. The creep behavior of zinc die casting alloys is caused by self-diffusion of zinc and is thermally activated according to the Arrhenius Law. The activation energy for creep in the alloys studied is 94 kJ/mol.
5. Creep and die casting alloys is a function of time. The creep rate decreases with time when the stress is constant. Primary creep is active up to 1-2% of creep elongation. After creep strain of 1%, the creep rate increases because of reduction of area in the test specimen. No secondary creep is observed in the curves shown in this work. Creep behavior is best described up to a maximum of 1% creep strain by a power law function.
6. Because of the higher degree of segregation of zinc between the primary and secondary phases in the as-cast structure and the greater potential for homogenization by ageing, the loss of tensile strength of ZA8 with ageing is higher compared with Alloy 5; however, even after this loss of tensile strength, ZA8 is still stronger than counterpart die cast aluminum and magnesium alloys.

## REFERENCES

1. Goodwin, F. E. "Ageing Properties of Zinc Alloys," NADCA 2011 Congress, Columbus, OH, September 19-21, 2011
2. Goodwin, F.E., Kallien, L.H. and Leis, W., "New Mechanical Properties Data for Zinc Casting Alloys" Proceedings NADCA 2012 Congress, October 7-10, 2012, Indianapolis, IN, North American Die Casting Association.
3. Walmag, G., Murphy, S., Skenazi, A., and Goodwin, F.E. "The Influence of Casting Process Parameters on the Properties and Microstructures of Zinc Alloys 3 and 5," Proceedings of the 16th International NADCA Die Casting Congress and Exposition, September 30-October 3, 1991, Detroit, MI
4. Goodwin, F.E., Walmag, G., Murphy, S. and Wegria, J., "The Influence of Process Parameters on the Properties and Microstructures of Zinc Alloys 2 and ZA-8," Proceedings of 14th International Pressure Die Casting Conference, May 4-5, 1993, Birmingham, U.K.
5. Chvorinov, N., Giesserei, v. 27, p. 177, 1940

**Table 1. Cavity fill times for the specimen thicknesses and gate velocities used during the designed experiments**

thickness in mm	Cavity filling time in ms		
	$v_A = 25$ m/s	$v_A = 40$ m/s	$v_A = 55$ m/s
0.8	14	10	7
1.5	18	13	9
3.0	22	16	11

**Table 2. Calculated solidification times, using Chvorinov's Rule (reference 5)**

thickness in mm	solidification time in ms		
	$T_F = 120^\circ\text{C}$	$T_F = 160^\circ\text{C}$	$T_F = 200^\circ\text{C}$
0.8	16	19	23
1.5	57	68	83
3.0	228	270	330

**Table 3. Compositions of the alloys studied in this project**

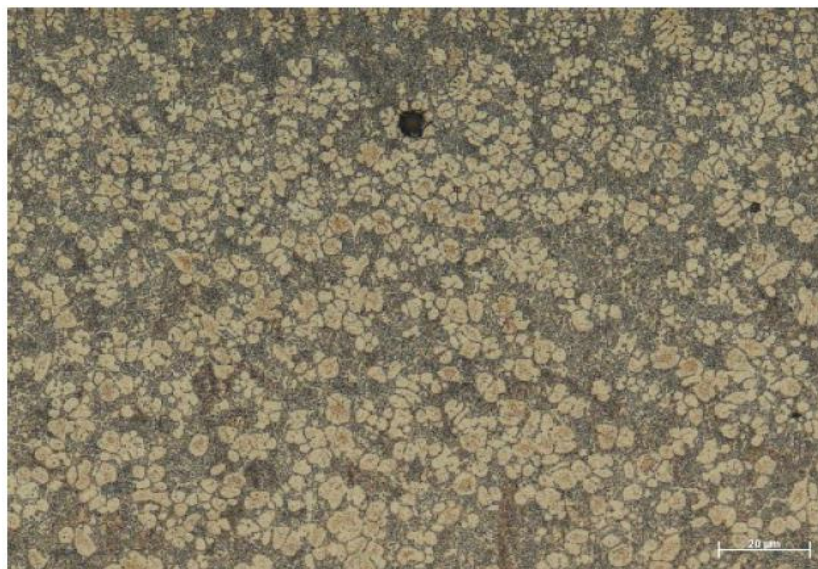
	Al	Cu	Mg	Fe	Pb	Cd	Sn	Ni	Si
Alloy 5	4.0	0.85	0.053	0.0009	0.002	0.0004	0.0001	0.0001	0.0011
ZA-8	8.5	0.92	0.020	0.004	0.002	0.0005	0.0006	0.0002	0.0061

**Table 4. Density and Porosity of Test Bar Castings Used in this Work**

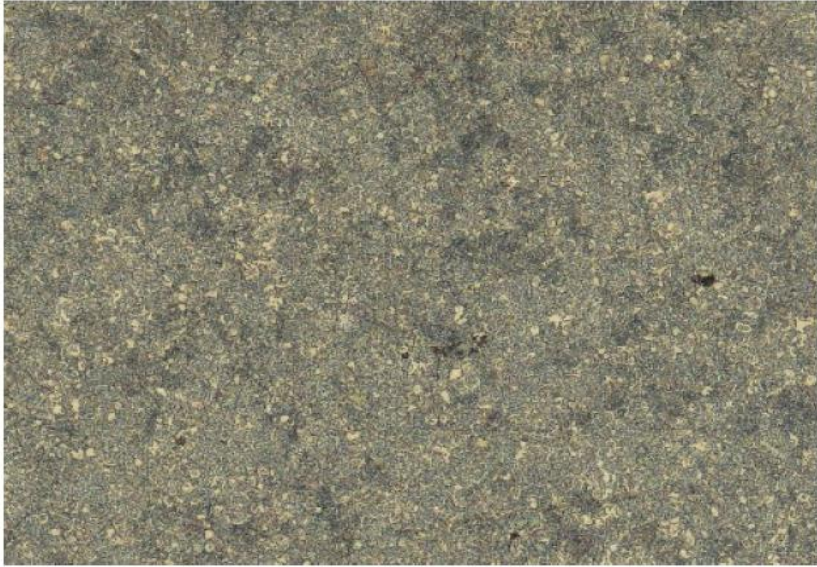
Alloy	Property	wall thickness, mm		
		0.8	1.5	3
ZA-8	Density, g/cm <sup>3</sup>	6.28 ± 0.03	6.27 ± 0.01	6.27 ± 0.01
	Porosity, %	0.35	0.41	0.43
Alloy 5	Density, g/cm <sup>3</sup>	6.54 ± 0.06	6.61 ± 0.02	6.64 ± 0.01
	Porosity, %	1.97	1.02	0.43

**Table 5. Correlation of time and temperature for the ageing behaviour of ZA-8 and Alloy 5**

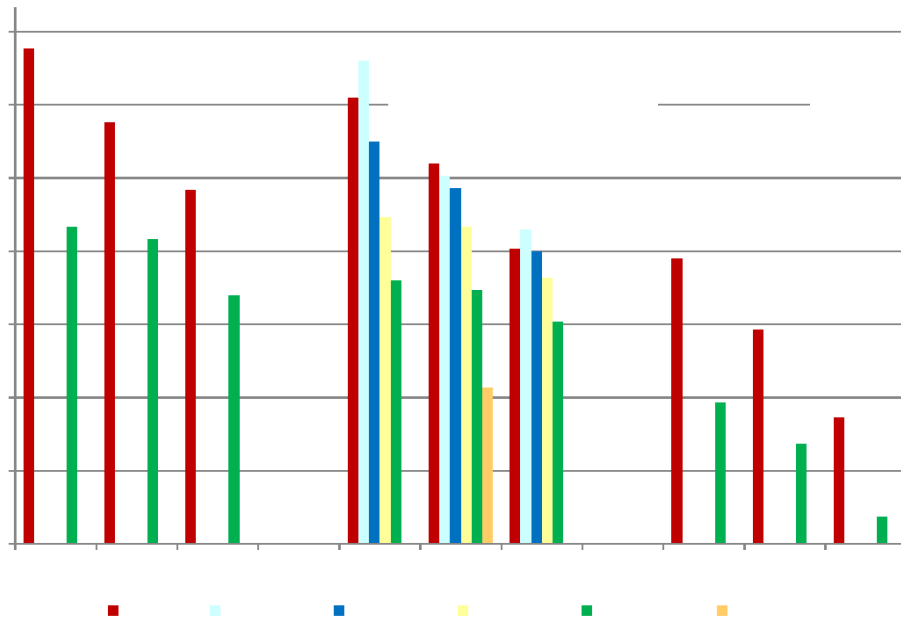
temperature in °C	0	23	50	80	105	120
ageing time ZA-8	30 years	2.5 years	70 days	7 days	1 day	0.5 days
ageing time Alloy 5	10 years	1 year	37 days	4 days	1 day	0.4 days



**Figure 1. Microstructure of Alloy 5, thickness 3 mm, casting conditions 120°C / 55 m/s**



**Figure 2. Microstructure of ZA-8, thickness 3 mm, casting conditions 120°C / 55 m/s**



**Figure 3. Tensile strength as a function of testing temperature, wall thickness and artificial ageing conditions for ZA-8**

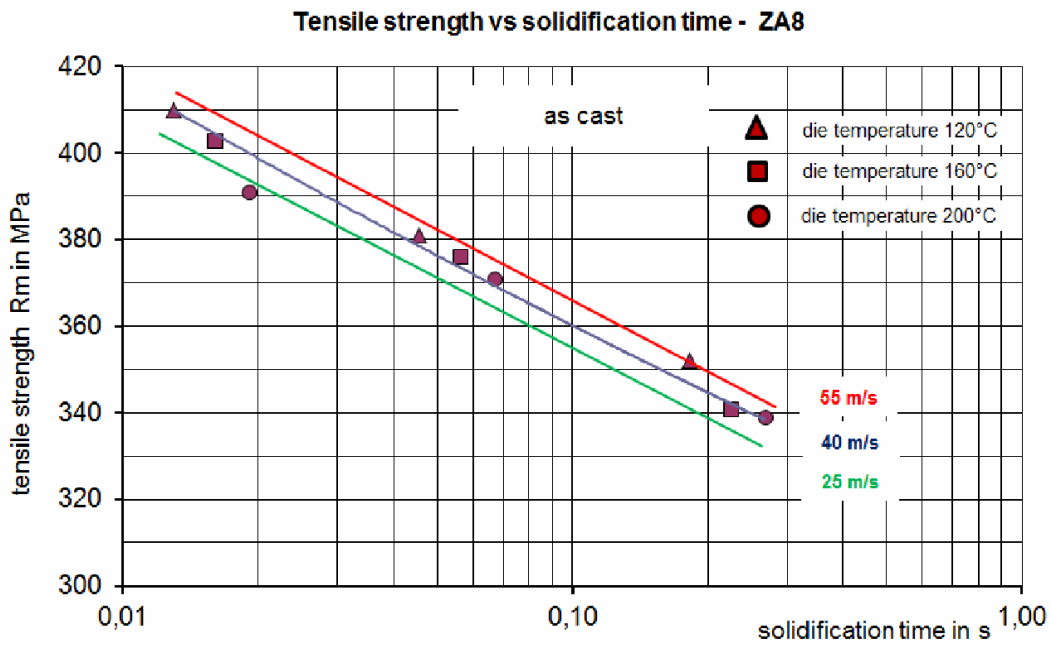


Figure 4. Effect of die casting process parameters on tensile strength of ZA-8

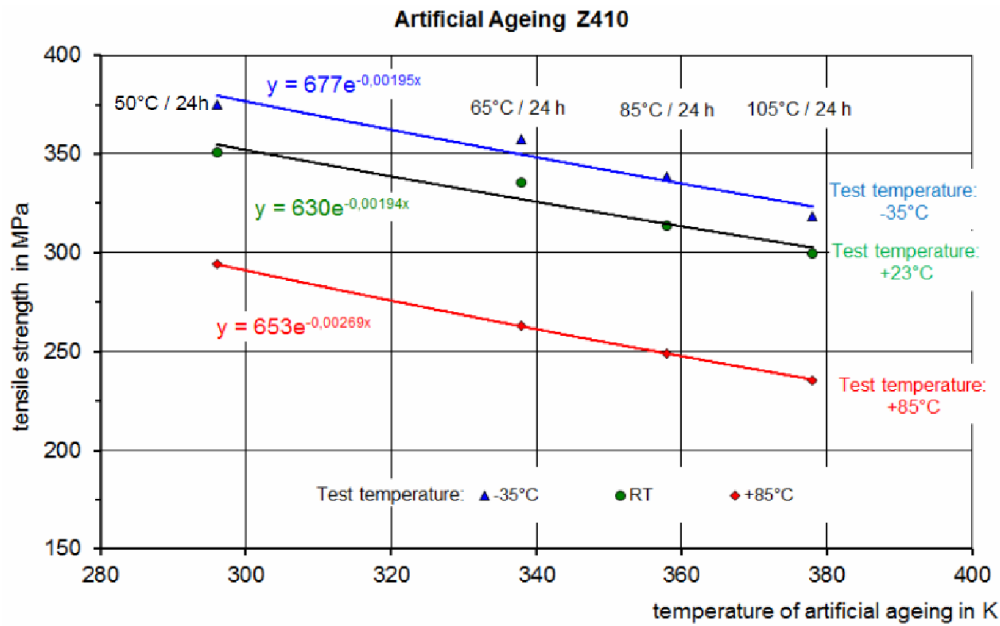


Figure 5. Influence of the artificial ageing temperature and testing temperature on Alloy 5 tensile strength

67.43 kJ/mol for ZA8, 67.43 kJ/mol for Alloy 5

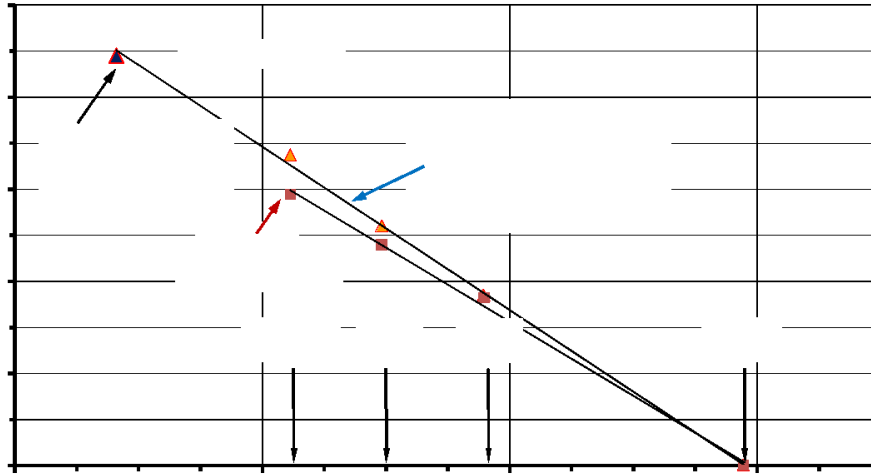


Figure 6. Arrhenius plot of time  $\ln(t/t_0)$  versus influence of temperature  $1/T$  during ageing for calculation of the activation energy

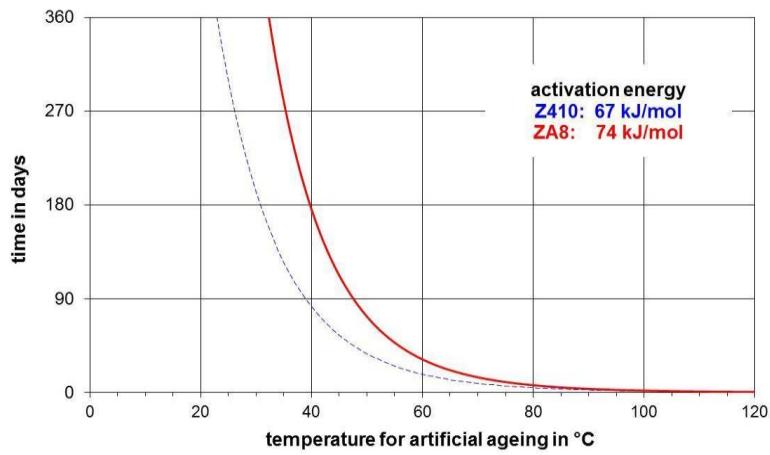
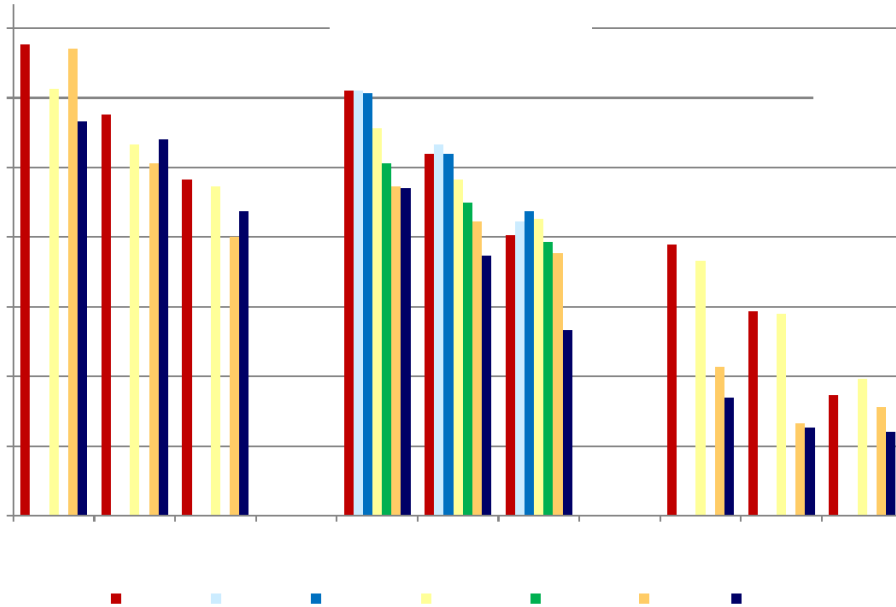
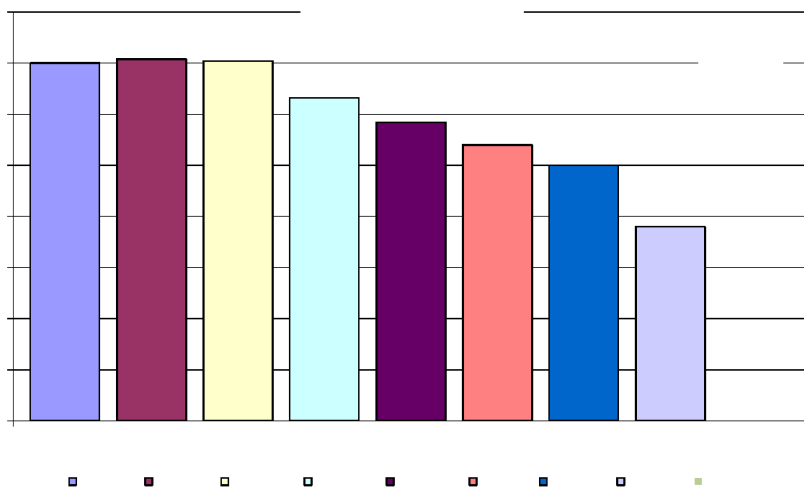


Figure 7. Required time as a function of temperature for artificial ageing to reach a natural ageing of 1 year at RT of ZA-8 (red) and Alloy 5 (blue)

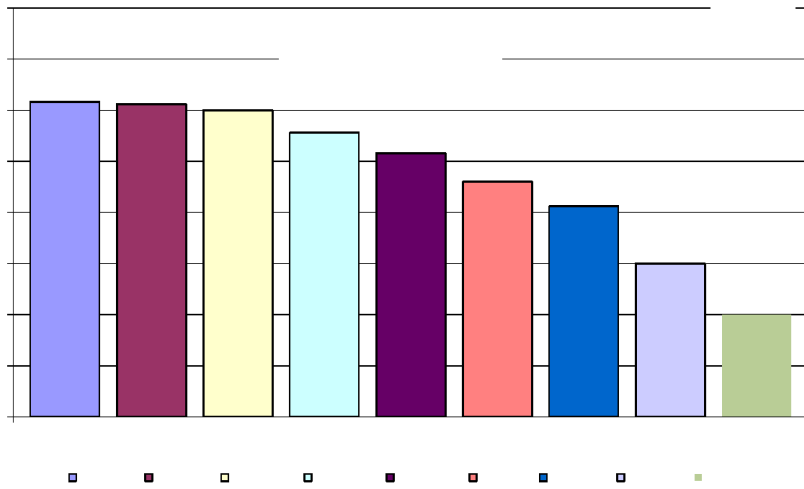




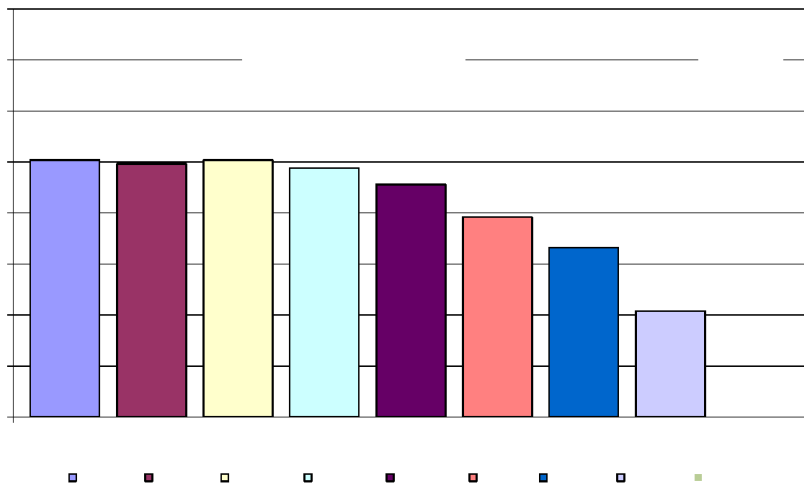
**Figure 8. Tensile strength as a function of testing temperature and wall thickness during natural ageing of ZA-8**



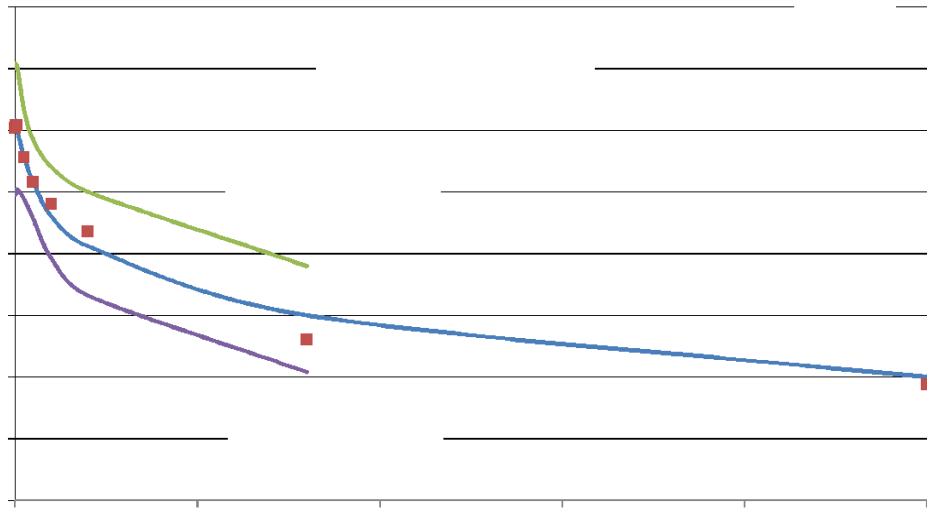
**Figure 9. Long term natural ageing of ZA-8 specimens with a wall thickness of 0.8 mm**



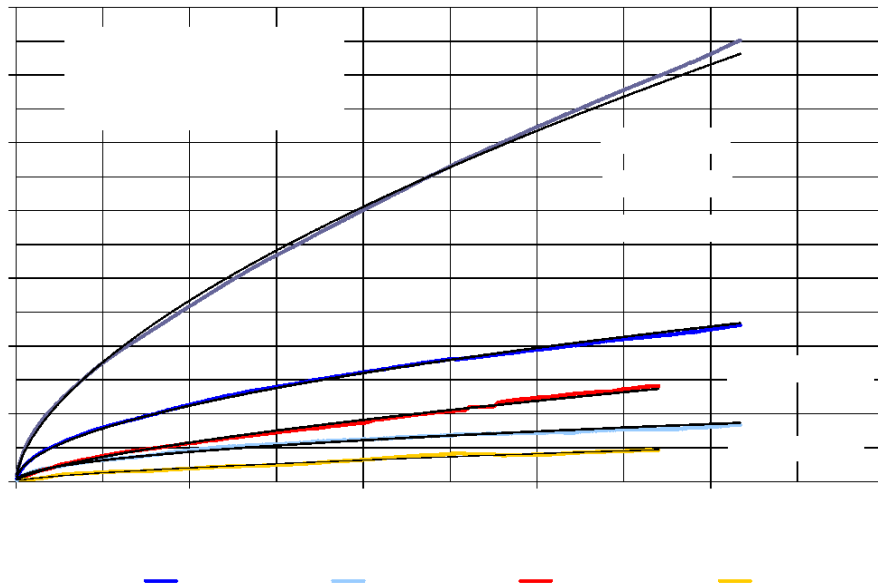
**Figure 10. Long term natural ageing of ZA-8 specimens with a wall thickness of 1.5 mm**



**Figure 11. Long term ageing of ZA-8 specimens with a wall thickness of 3.0 mm**



**Figure 12. Long term ageing of ZA-8 specimens using Umicore specimens, tensile strength**



**Figure 13. Creep behavior for ZA-8 after artificial ageing (105°C / 24 h), specimen thickness 1.5 mm at room temperature and 3.0 mm at 80 (90)°C, linear scale**

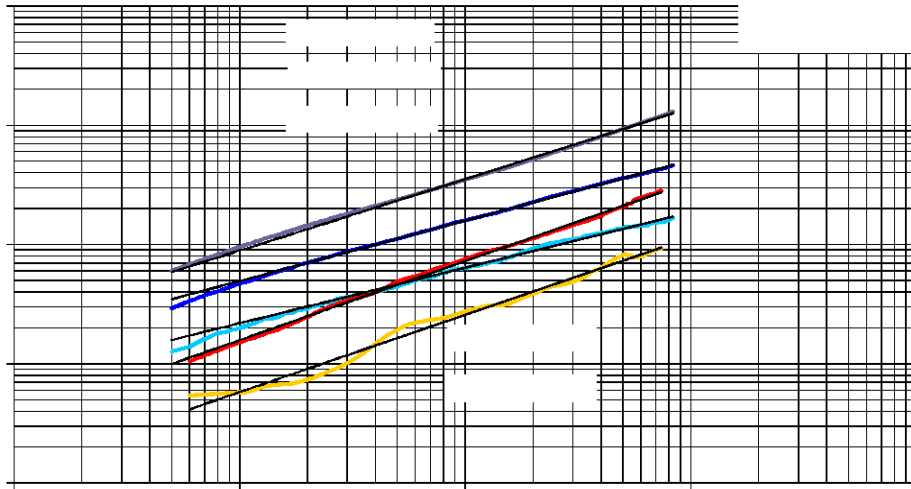


Figure 14. Creep behavior for ZA-8 after artificial ageing (105°C / 24 h), specimen thickness 1.5 mm at room temperature and 3.0 mm at 80 (90)°C, logarithmic scale

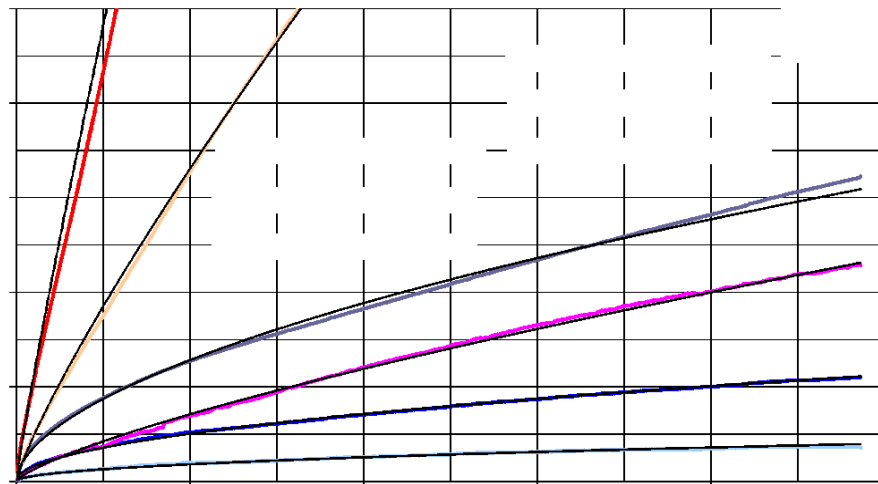
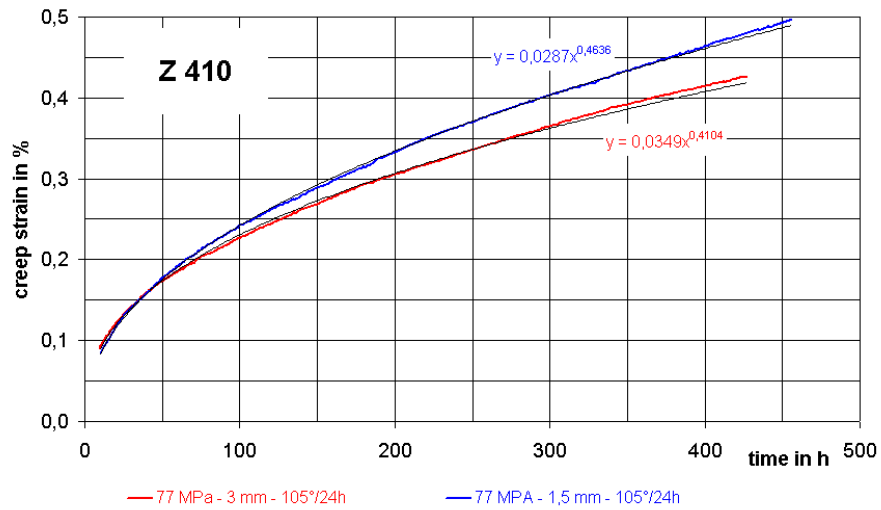
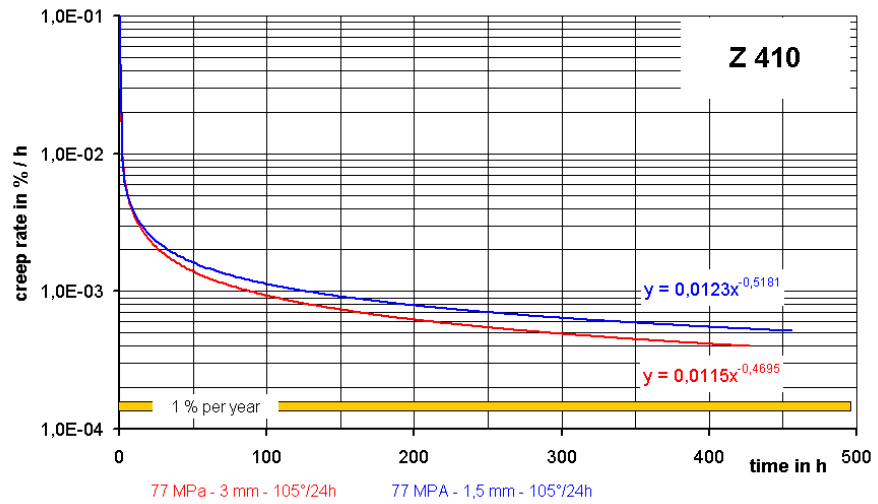


Figure 15. Creep behavior for ZA-8 after artificial ageing (105°C / 24 h) at room and 85°C, specimen thickness 1.5 mm, linear scale with power function values



**Figure 16. Creep strain as a function of wall thickness for Alloy 5, artificially aged at 105°C / 24 h, creep testing at room temperature**



**Figure 17. Creep rate as a function of wall thickness, Alloy 5 artificially aged at 105°C / 24 h, creep testing at room temperature**