

This paper is subject to revision. Statements and opinions advanced in this paper or during presentation are the author's and are his/her responsibility, not the Association's. The paper has been edited by NADCA for uniform styling and format. For permission to publish this paper in full or in part, contact NADCA, 3250 N. Arlington Heights Rd., Ste. 101, Arlington Heights, IL 60004, and the author.

Thermally-Activated Processes in Zinc Die Castings and Their Effects on Properties

By

F. E. Goodwin

International Zinc Association

L. H. Kallien and W. Leis

GTA Foundry Technology, Aalen

ABSTRACT

Thermally activated processes in zinc diecasting include the initial solidification behavior that results in distinct patterns of microstructure; ageing, both natural and artificial, that results in changes in mechanical properties and dimensions; and diffusion under load that results in creep. Heat flux during the casting process is influenced by gate velocity and therefore cavity fill time and also die temperature. This paper reviews results obtained during the last 10 years in the context of a general approach to thermally activated processes in an effort to unify our knowledge of process-structure-property effects. The goal is to give a sounder basis for predicting casting mechanical properties and other behavior over a range of industrially relevant conditions.

INTRODUCTION

For many engineered parts, zinc die castings offer the quickest way between molten metal and the finished component. The advantages of the low melting temperatures of zinc alloys are manifest in the very high die lives that can be achieved, sometimes exceeding 1 billion parts, the very high precisions of dimensions that can be realized, together with repeatability, the use of the hot chamber die casting process and improved die filling behavior seen at typical casting temperatures. Especially with high-fluidity alloys, ultra-thin die castings, down to 0.2 mm (0.0078") wall thickness, offer opportunities for lightweight parts. Lower processing temperatures also favor lower oxidation losses and less reaction with processing equipment that can cause dross. The low solidus temperature of Zn-Al die casting alloys, together with their relatively high specific heat, is also exploited to provide very high surface quality parts, capable of achieving great surface detail. However the low solidification temperature also leads to thermally-induced phenomena such as aging, creep and dimensional stability that can be observed at room temperature. Nevertheless, zinc die cast components are routinely used at temperatures up to 100°C.

Much research has been carried out during the last ten years, co-sponsored by NADCA and IZA. This work has mainly focused on the alloys shown in Table 1: the traditional Zamak alloys, together with the HF alloy and ZA-8. All of these alloys have small permissible levels of Pb, Cd, Sn, Fe, Ni and Si. Much of the research work conducted has been carried out using flat plate specimens, 0.4, 0.8, 1.5 and 3.0 mm (0.016, 0.032, 0.06 and 0.12”). By conducting casting and aging treatments under controlled conditions together with mechanical property testing, the effects of thermally-activated processes on alloys behavior have been determined.

Table 1. Compositions of Zinc Casting Alloys (balance Zn), ASTM B86 and B989

| Composition Mass % | Alloy Name | | | | |
|-----------------------|------------|-----------|-----------|-------------|------------|
| | 2 | 3 | 5 | HF | ZA-8 |
| Al | 3.5-4.3 | 3.5-4.3 | 3.5-4.3 | 4.3-4.7 | 8.0-8.8 |
| Cu | 2.5-3.0 | 0.25 max | 0.75-1.25 | 0.035 max | 0.8-1.3 |
| Mg | 0.02-0.05 | 0.02-0.05 | 0.03-0.08 | 0.005-0.012 | 0.015-0.03 |
| All Others | 0.112 | 0.112 | 0.112 | 0.036 | 0.09 |

MICROSTRUCTURAL DETAILS

The Al-Zn phase diagram as shown in Figure 1, in which an extremely low solubility for Zn in Al and vice versa is seen at room temperature. However, the thermal activation for diffusion of these metals in each other will allow for a reduction of some of the microsegregation in the as-cast microstructure to occur by both natural and artificial aging. Regarding crystal structures, zinc is hexagonal and aluminum is face-centered cubic and therefore transformations of phases with aging will result in dimension changes. Cu is a common additive to these alloys, as shown in Table 1. Cu stabilizes the Al-Zn solid solutions in subject alloys and also forms the CuZn5 hexagonal epsilon phase as a precipitate.

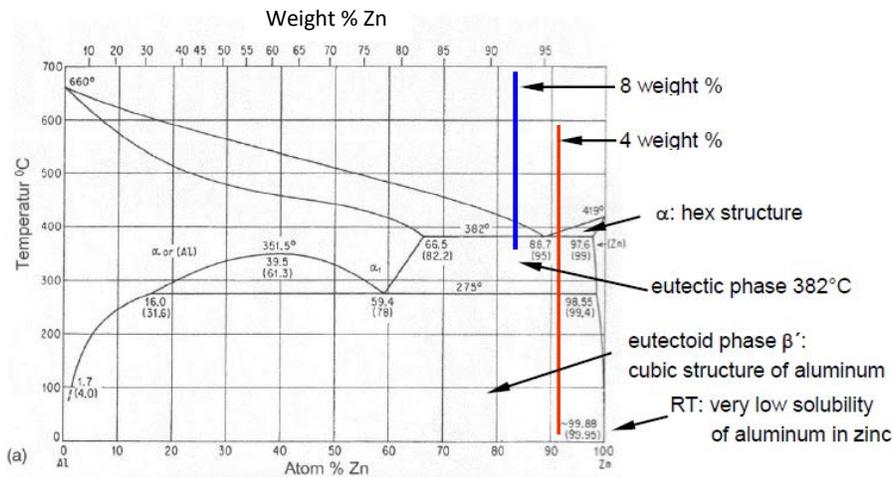


Figure 1. Al-Zn Phase diagram (Reference 1)

The hypoeutectic alloys (2,3,5 and HF) exhibit a Zn primary phase with a dendritic or rosette shape surrounded by an extremely fine eutectic phase, as shown in Figure 2a,b. The HF alloy has a finer primary phase grain size, together with the same fine eutectic, Figure 2c. The hyper-eutectic ZA-8 alloy also has a very fine Al-rich primary phase in a super-fine eutectic, as shown in Figure 2d. The very fine lamellar structures of the eutectic phase have very high concentration gradients between the lamella. This means that a very short time is required for reduction of the segregation of Zn and Al over these short distances. The coarse primary phase grains have a lower concentration gradient within the grains and a greater distance from grain center to grain boundary. This reduces the speed of the diffusion process within the primary phase, compared to the eutectic phase, by several orders of magnitude.

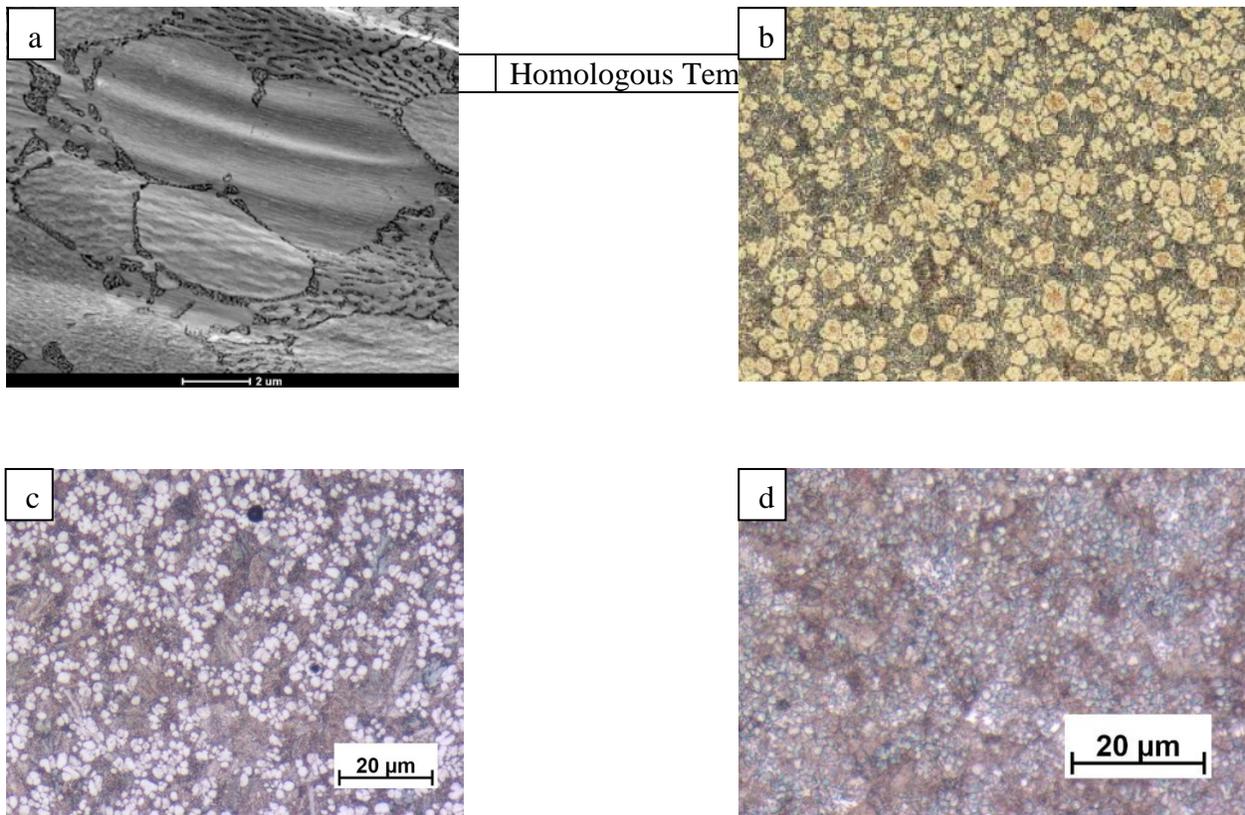


Figure 2. Microstructure of Zn die castings a. High magnification of Alloy 5 b. Low magnification of Alloy 5. c. HF alloy d. ZA-8 (Reference 2)

THERMALLY-INDUCED PROCESSES

The homologous temperature is an expression of the temperature of material as a fraction of its melting point temperature, using the Kelvin scale. Typically, an increase of a homologous temperature over 0.4 leads to a decrease of the atomic bonding forces, together with the shear strength of the material, and an exponential increase in the number of vacancies. Table 2 shows the homologous temperature for several metals at three ambient temperatures: -35, 22 and 85°C. The homologous temperature of Zn can be seen to increase from .36 to .54 as temperatures increased across this range. Mg has similar behavior, while Al has a much lower homologous temperature, which is still very much higher than Fe. The shear modulus of a metal is directly related to the number of vacancies present and this is greatly influenced by temperature. The concentration of vacancies c^a_L is expressed as a function of the shear modulus G and Boltzmann

Table 2. Homologous temperatures for several pure metals at three different service temperatures

| Service T °C | -35 | +22 | +85 |
|--------------|-----|-----|-----|
| Zn | .36 | .45 | .54 |
| Mg | .32 | .41 | .50 |
| Al | .28 | .35 | .42 |
| Fe | .16 | .20 | .24 |

constant $k = 8.62 \times 10^{-5} \text{ eV}/^\circ\text{K}$ by the following formula:

$$(1) \quad c_L^a = e^{-\frac{G}{kT}}$$

There are three different thermally activated processes resulting in observed alloy behavior. First, the process of reduction of microsegregation in the eutectic phase leads to changes in mechanical properties. For Zn alloys, this occurs naturally at room temperature over about one year before aging is typically finished. If parts are artificially aged at 100°C, the aging can be completed after one day. Second, the process of reduction of microsegregation in the eutectic phase leads to dimensional changes. It takes about one year of natural aging at room temperature for dimensional changes to become very slow. By contrast, they can be accelerated by heat treatment of 100°C for about 10 hours to fully stabilize the components. Third, the self-diffusion process under load over the whole microstructure causes creep behavior. The creep rate depends exponentially on temperature and is also influenced by time and stress, using a power function equation.

INFLUENCE OF TIME AND TEMPERATURE ON CHANGES IN MECHANICAL PROPERTIES

Aging is a thermally-activated process that leads to a change of mechanical properties and dimensions of the function of time and temperature, without imposition of a load. Aging is a process predominantly taking place in the eutectic phase of all of the tested zinc alloys. Alloys 2, 3, 5, HF and ZA-8 exhibit a decrease in yield strength, ultimate tensile strength, fatigue strength and an increase in fracture elongation and creep rate after aging. Figure 3 shows the results of one year of natural aging time, in comparison with artificial aging treatments and the effects of these treatments on ultimate tensile strength. The grouping of the artificial aging points is indicative of the thermal activation process. Figure 4 shows the two-year natural aging behavior for a 1.5-millimeter flat coupon of each of the Alloys 2, 3, 5, HF and ZA8. These are all cast with a gate velocity of 40 meters per second, with a die temperature of 160°C. Most of the aging curves in Figure 6 approximate an error function which also indicates a diffusion process. The activation of each of the five alloys is different and therefore the response of each alloy to natural aging and artificial aging conditions are different. Within the microstructures, the greater response of the zinc and aluminum atoms to aging is the reduction of segregation within the fine eutectic phase.

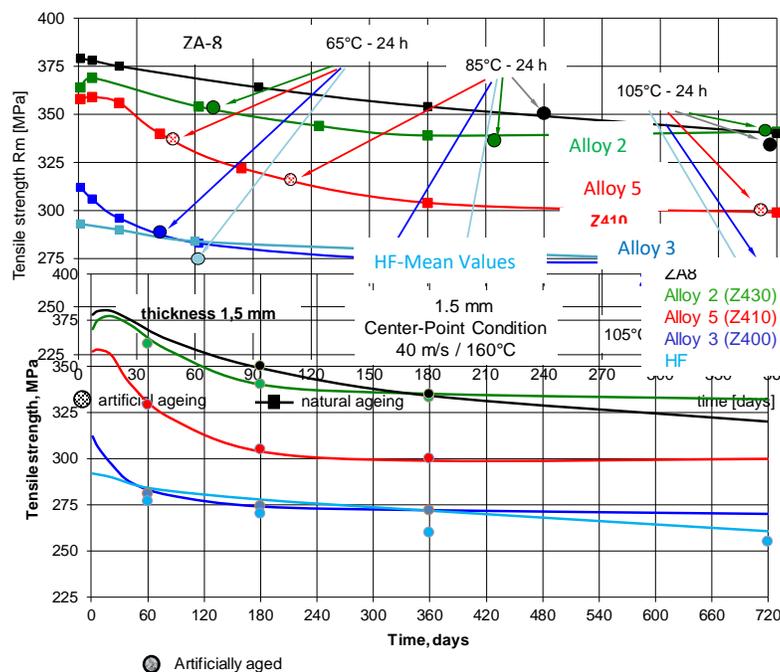


Figure 3. artificial tensile

Effect of natural and ageing treatments on strengths of zinc alloys

Figure 4. Effect of 2 years of artificial ageing on tensile strengths of zinc alloys

Table 3 shows the mechanical properties after 2 years of natural aging for die castings with a wall thickness of 1.5 mm and a die temperature of 160°C (320°F), together with a gate velocity of 40 m/s (130 ft/s). This long period of aging fully stabilizes properties. The fracture elongation is mainly dependent upon porosity here, not depending strongly on aging conditions. The hardness values do depend strongly on aging conditions.

Table 3. Mechanical properties after 2 years natural ageing

| Alloy | Yield strength, MPa (psi) | Tensile strength, MPa (psi) | Fracture elongation | Hardness HB |
|-------|---------------------------|-----------------------------|---------------------|-------------|
| 3 | 200 (29,000) | 260 (37,700) | 10% | 100 |
| 5 | 250 (36,250) | 300 (43,500) | 7% | 115 |
| 2 | 280 (40,600) | 325 (47,130) | 5% | 125 |
| ZA-8 | 240 (34,800) | 325 (47,130) | 4% | 120 |
| HF | 215 (31,180) | 265 (38,430) | 2% | |

Figure 5 shows the general relationship between mechanical properties and process conditions. From the center point of experiments run, which used a die temperature of 160°C and a gate velocity of 40 m/s (130 ft/s), ultimate tensile strength was seen to increase or decrease by 4% as gate velocity increases or decreases, respectively. At a constant gate velocity, ultimate tensile strength was seen to decrease or increase 5% as the die temperature is increased or decreased, respectively.

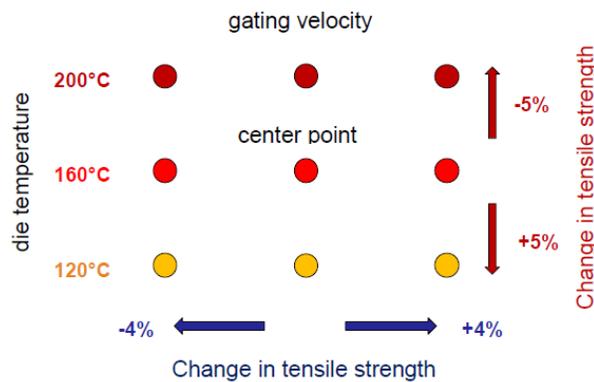


Figure 5. Summary of casting process strength

influence of the main die parameters on tensile strength

A lower die temperature results in a shorter solidification time and therefore a finer microstructure, thus producing a higher yield and tensile strength. A lower die temperature gives better mechanical properties, together with a higher gate velocity. The results of casting variation experiments conducted on the HF alloy is shown in Figure 6. The results here are seen for four die casting section thicknesses: 0.4, 0.8, 1.5 and 3 millimeters, using three different die temperatures: 120, 160 and 200°C (248, 320 and 392°F). The Chvorinov equation³ depends upon the conditions of

heat flow together with die cavity geometry and is used to determine local solidification time. Calculated local solidification times for the HF alloy using a range of casting conditions is shown in Table 4.

Table 4. Calculated solidification times for the HF alloy, using Chvorinov's Rule³, T_F =die temperature

| thickness in mm (in.) | solidification time in ms | | |
|-----------------------|---------------------------|---------------------------|---------------------------|
| | $T_F = 120^\circ\text{C}$ | $T_F = 160^\circ\text{C}$ | $T_F = 200^\circ\text{C}$ |
| 0.8 (0.032) | 16 | 19 | 23 |
| 1.5 (0.06) | 57 | 68 | 83 |
| 3.0 (0.12) | 228 | 270 | 330 |

The relationship between solidification time and tensile strength is shown in Figure 6. This trend is consistent with the Hall-Petch relationship between grain size and ultimate tensile strength.

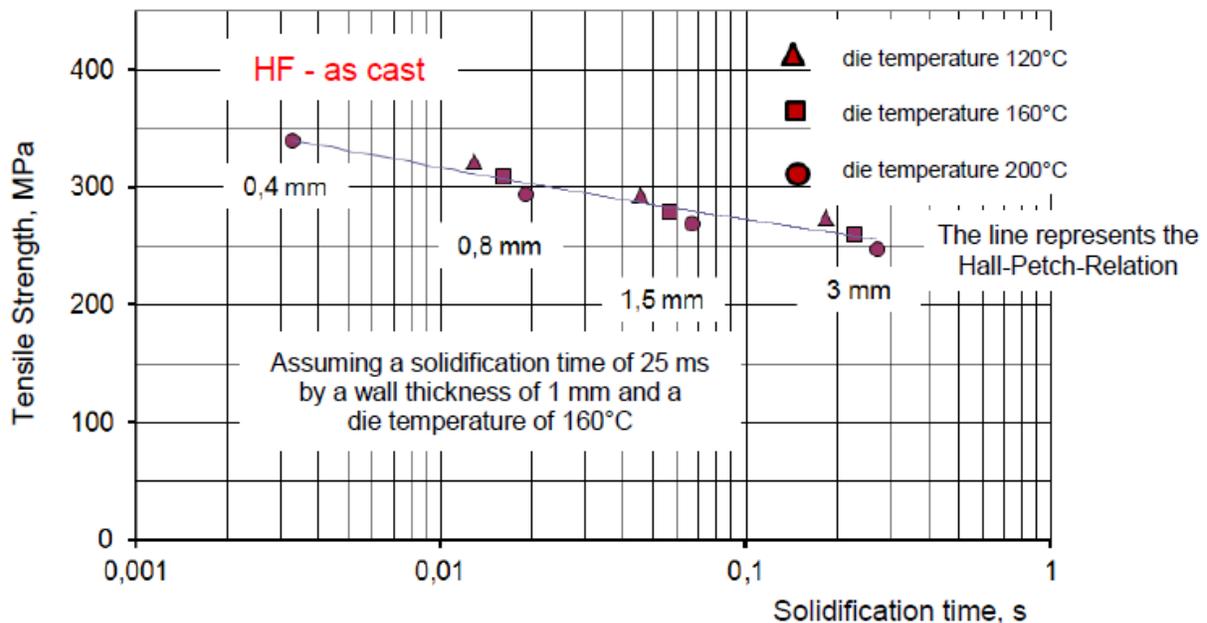


Figure 6. Relationship between local solidification time and tensile strength for as-cast HF alloy. The casting section thicknesses and die temperatures are indicated for each data point

CREEP IN ZINC DIE CASTING ALLOYS

Creep is a time-dependent plastic deformation of a material at a constant load and is often encountered with zinc die casting applications. While it cannot be prevented, it can be accommodated by proper design. In zinc die casting alloys, vacancies are the cause of creep deformation and their number depends on the Arrhenius law. Other creep mechanisms can include the glide and climb of dislocations and the relative displacement of grains by grain boundary sliding and mechanical twinning. Creep deformation in zinc die casting alloys mainly occurs in the eutectic phase rather than in the primary phase. Therefore, the aging of the die casting, which influences the state of the eutectic phase, mainly determines the creep rate. Because creep in zinc alloys depends upon the movement of vacancies (and therefore atoms), creep can be predicted by identifying the activation energy of diffusion in this creep process.

Creep consists of three different stages: primary, secondary and tertiary. The primary creep stage exhibits a very high strain rate which decreases with time and ends after 1-2% of accumulated strain. Strain hardening, depending upon the buildup of dislocations within the alloy, is a dominant factor at this stage. Secondary creep is characterized by a balance of strain hardening and recovery as the dislocations that build up with plastic deformation are

recovered as the result of thermal annihilation. The tertiary creep stage includes a reduction of cross section and a buildup of internal pores, and for most of this time strength tends to increase. In zinc alloys, the tertiary stage is very short because fracture occurs not long after the tertiary stage is entered. Typical for zinc alloys is a distinct primary creep stage, for which an example is shown in Figure 7 for Alloy 3. This used a 1.5 mm as-cast sample with an imposed load of 90 MPa (13,050 psi).

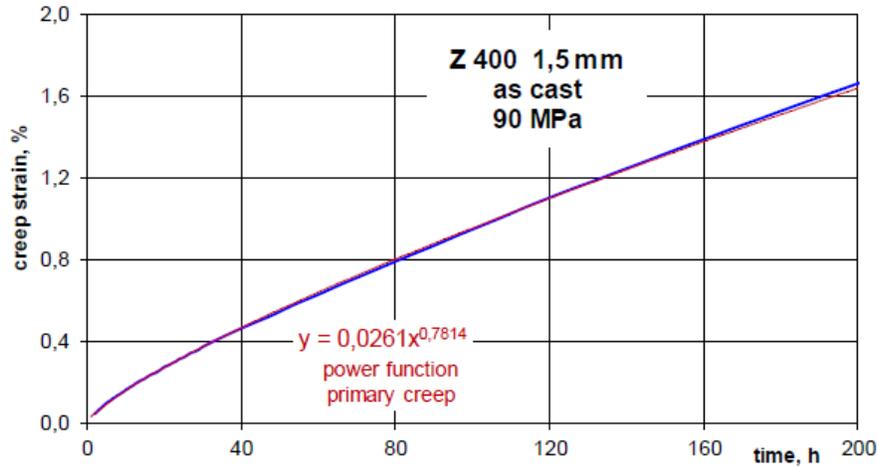


Figure 7. Primary creep of Alloy 3 at room temperature and imposed load of 90 MPa (13,050 psi), experimental data (blue) and power function line (red)

The creep strain “ ϵ ” over this range of primary creep as a function of time “ t ” can be mathematically expressed as a power law function:

$$(2) \quad \epsilon = c \cdot t^a \Rightarrow t = \left(\frac{\epsilon}{c} \right)^{\frac{1}{a}}$$

where a is a constant and C is a stress-dependent coefficient. The derivative of this power law function gives the creep rate:

$$(3) \quad \dot{\epsilon} = \frac{\epsilon}{dt} = a \cdot c \cdot t^{a-1}$$

With this equation, the creep rate for specific creep strains can be calculated. The calculated creep rate values are used to obtain the stress exponent “ n ” in Norton’s equation for secondary creep:

$$(4) \quad \dot{\epsilon}_s = A \cdot \left(\frac{\sigma}{G} \right)^n \cdot e^{-\frac{Q}{R \cdot T}} \quad n = \left(\frac{\log \dot{\epsilon}}{\log \sigma} \right)$$

where A is the Arrhenius factor, σ/G is the normalized stress, G is the shear modulus (GPa), n is the stress exponent, Q is the activation energy of deformation (kJ/mol), R is the gas constant (kJ/mol °K) and T the temperature (°K). The activation energy Q for creep can be determined by conducting creep tests over a range of temperatures. The activation energy for self-diffusion of zinc is found to be $Q=94$ kJ/mol. The arrows in Figure 8 show the relative values of creep rate for Alloy 3 at four different temperatures. It can be seen that the creep rate at 120°C, as 10,000 times that at 25°C..

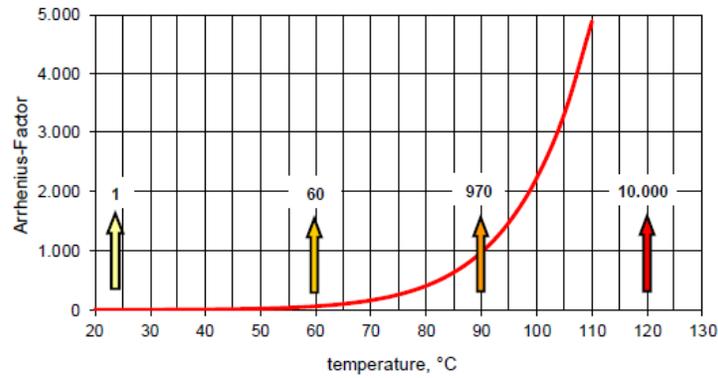


Figure 8. Effect of temperature on Arrhenius factor “A” in equation 4 and the relative magnitudes of secondary creep rate (arrows)

The stress exponent n is strongly dependent upon the actual creep elongation and lies between 4 and 7. The stress exponent can be calculated from the power law function, which is a slope of the creep lines, as shown in Figure 9. This figure shows the secondary (second stage) creep rate for Alloys 2, 3, 5 and ZA-8. The value of the exponent n can be determined from the experimental results. These exponents are shown in Tables 5 and 6 for the Alloys 2, 3, 5, HF and ZA-8.

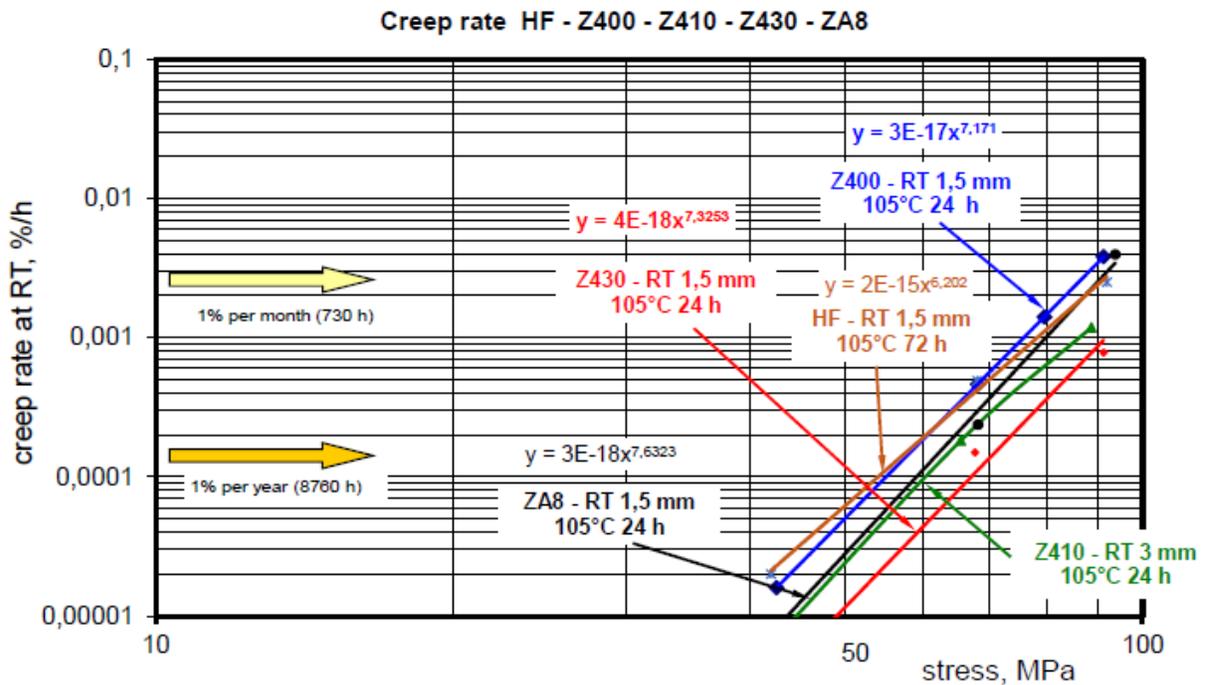


Figure 9. Room temperature secondary creep rates for zinc alloys, aged at 105°C (221°F) for times indicated. Power law equations corresponding to the experimental data are also shown

Table 5. Exponent a of the power law function (Equations 2 and 3) for several alloys and conditions

| Exponent a | Alloy 3 | Alloy 5 | Alloy 2 | ZA8 | HF |
|-------------------------------|---------|---------|---------|------|------|
| RT / 1.5 mm 105°C / 24 h | 0,59 | 0,49 | 0,51 | 0,52 | 0,59 |
| RT / 3.0 mm 105°C / 24 h | | 0,44 | | | |
| RT / 1.5 mm 105°C / 1000 h | | 0,65 | | | |
| 85°C / 1.5 mm 105°C / 24 h | | | | 0,79 | |

Table

6.

Exponent n of

Norton's equation (Equation 4) for several alloys and conditions

| Exponent n | Alloy 3 | Alloy 5 | Alloy 2 | ZA8 | HF |
|-------------------------------|---------|---------|---------|------|------|
| RT / 1.5 mm 105°C / 24 h | 7.10 | 7.07 | 7.32 | 7.63 | 6.20 |
| RT / 3.0 mm 105°C / 24 h | | 7,10 | | | |
| 85°C / 1.5 mm 105°C / 24 h | | 4.18 | | | |

INFLUENCE OF ARTIFICIAL AGING TIME ON CREEP

The effect of aging time was investigated by creep testing Alloy 5 specimens that had either been held at 105°C for up to 1,000 hours or naturally aged for 21 years at Umicore. Figure 10 shows that samples aged for more than 20 hours show higher creep rates than the as-cast samples. Moreover, with higher aging times the distinction between the thinner 1.5-millimeter samples and the thicker 3.0-millimeter samples becomes much more distinct. This is related to the finer eutectic size in the thinner samples in the higher diffusion rates that can occur with aging.

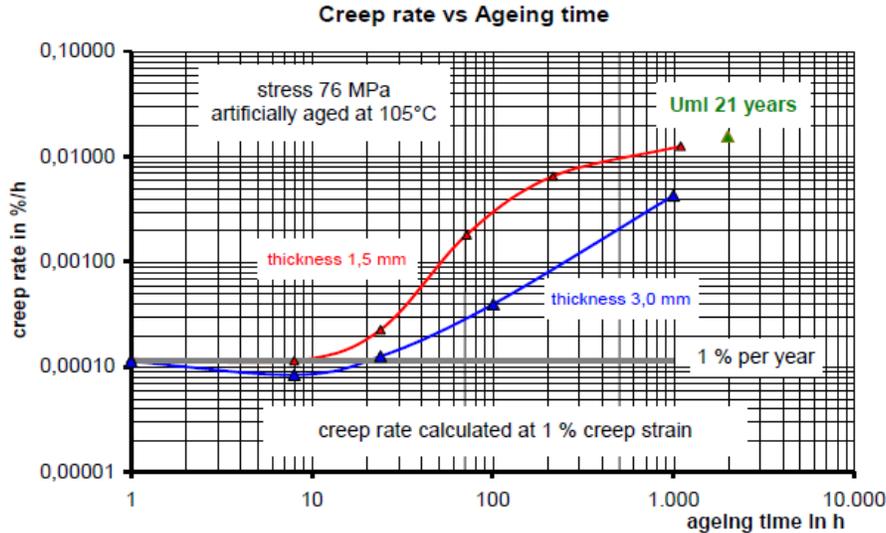


Figure 10. Room temperature creep rate vs. ageing time for Alloy 5 at 2 section thicknesses

A comparison of the creep results of the five alloys discussed here is shown in Figure 11. Comparing the composition values in Table 1, it can be seen that Cu content influences creep rate by a factor of 4, when comparing Alloys 3 and 2. There is less than 30% difference in creep rate between Alloys 5 and 2. ZA8 creep performance lies between Alloys 3 and 5; however, the ZA8 specimens had a natural aging process of an additional six years.

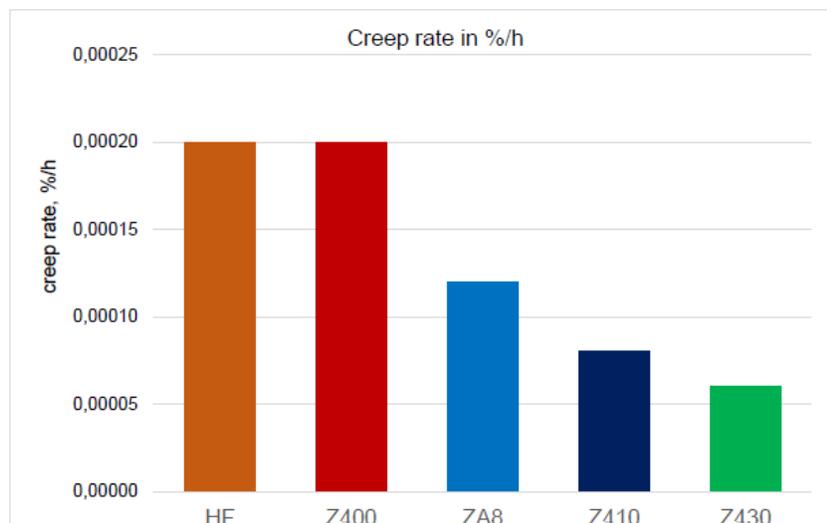


Figure 11. Room temperature creep rate under 60 MPa (8700 psi) stress for zinc die casting alloys with 1.5 mm (0.06") section thickness after 1% creep strain. All samples were aged for 24h at 105°C except ZA-8 that was naturally aged for 6 years

CONCLUSIONS

1. Aging in Zn is time-dependent, thermally-activated process, mainly in the eutectic phase, caused by the very low solubility of the alloying elements, mainly aluminum, in zinc.
2. Aging in all Zn alloys tested is significant at room temperature.
3. After nearly one year of natural aging, aging for Alloys 2, 3 and 5 is complete.
4. The decrease in tensile strength after one year of artificial aging is less than 15%. Fracture elongation is mainly determined by the presence of porosity in the samples but was observed to increase by 50-100% in the aged condition.
5. Artificial aging for 24 hours at 105°C serves well to provide the same aging benefits as one year of natural aging.
6. Regarding creep behavior, all of the zinc alloys show the same general behavior, with a distinct primary creep stage, during which creep rate strongly decreases with time. The primary creep behavior can be mathematically expressed with a power law function.
7. The value of the coefficient c in the primary creep power law equation is dependent upon stress. Temperature, microstructures and alloy type can reflect strain hardening and recovery behavior in these alloys.
8. The exponent a in the power law equation has little dependence on stress but is sensitive to the applied temperature and alloy type. An increase in temperature results in an increase of the exponent value. A low value of the exponent means a higher potential for strain hardening.
9. Secondary creep behavior is well described by Norton's equation. The stress exponent is mainly influenced by the alloy type.
10. In all experiments described here, only power law creep mechanisms were observed. This largely depends upon the diffusion of atoms and vacancies.

REFERENCES

1. Gottstein, G.: *Physikalische Grundlagen der Materialkunde*. 3. Auflage (2007) Springer. ISBN 978-3-540-71104-9.
2. M. Heuser, IFAM Bremen, private communication

3. Chvorinov, N., Giesserei, v. 27, p. 177, 1940