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Interaction of Creep and Ageing Behaviors in Zinc Die Castings

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ABSTRACT

Zinc casting alloy research, based on funding from the USA Department of Energy and the NADCA Technology Administration Group has recently focused on the new HF (high fluidity) alloy and also the further development of creep properties data for Alloy 5. Room temperature ageing and creep results have been extended for the HF alloy. The effect on Alloy 5 casting section thickness on creep properties is under current investigation; available data and analysis are described. The new results will be put in the perspective of other zinc alloy data and include a scientific basis of explanation of the observed results.

INTRODUCTION

Recent research on zinc alloys have focused on both creep resistant compositions for high temperature applications and high fluidity compositions for ultra-thin die-casting technology.

The Zamak family of alloys was developed in the 1930s by the New Jersey Zinc Co. The most common Zamak alloy is Alloy 3; Alloys 5, and 7 are also popular in North America while Alloys 2 and 5 are also popular in Europe. These alloys have an attractive combination of engineering properties such as low cost, high strength and stiffness, and ease of use in hot-chamber die casting machines for large scale production. However, their application at higher temperatures is limited by their creep properties [1]. Past research has found improvements in the creep properties of the zinc based alloys through both increasing the composition of the primary alloying element Al (the ZA alloys), and through smaller additions of other alloying elements including Li, Cr, Ti, and Ca [2] and also Al, Ba, Co, Cu, Mg, Ni (3). The ACuZinc alloys patented by General Motors in 1991 [3] identified Al and Cu as being the most desirable two alloying elements for improving creep resistance. This was further refined by development of a near-ternary eutectic alloy developed by the Council for Scientific and Industrial Research (CSIR) and the International Zinc Association (IZA) [4,5] each showing improved creep resistance, this latter alloy has been commercialized by Eastern Alloys as EZAC®.

Alloy 7 is specified as a lower Mg content version of Alloy 3 which exhibits increased fluidity allowing it to either be cast at lower temperatures or to fill thinner die cavities [5]. Some Mg is beneficial in improving intergranular corrosion resistance. In addition to low Mg levels, increasing the Al content has also been shown to improve fluidity [6]. The eutectic composition (5 wt%) has the highest fluidity however this composition is of little practical use due to its very low impact strength [7]. A modified version of Alloy 7 with higher Al and the same low Mg content called the HF alloy has been developed which shows noticeable improvement in fluidity [8]. An alloy near the Zn-Al-Cu ternary eutectic, called Superloy or GDSL, also exhibits improved fluidity [9]. The compositions and casting fluidities for these alloys are shown in Figure 1.

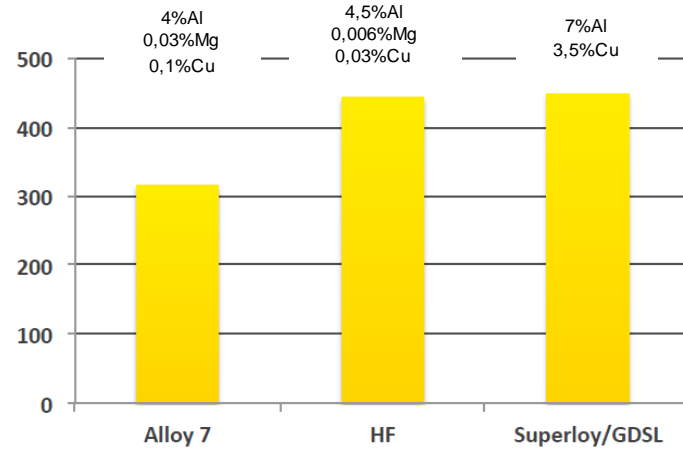


Figure 1: Ragone fluidity distances of Alloy 7, HF and Superloy, cast at 435°C

The research reported in this paper used alloy compositions shown in Table 1. As discussed above, the HF alloy gives high casting fluidity with a low Mg content, however in this work the Mg was kept at normal Zamak levels.

Table 1- Chemical composition of the used alloys

Alloy	Al	Cu	Mg	Fe	Pb	Cd	Sn	Ni	Si
3	4,0	0,000	0,041	0,013	0,0024	0,0004	0,0001	0,0003	0,0008
5	4,0	0,85	0,053	0,0009	0,002	0,0004	0,0001	0,0001	0,0011
2	3,8	2,95	0,040	0,001	0,002	0,0005	0,0002	0,0003	0,0005
ZA-8	8,5	0,92	0,020	0,004	0,002	0,0005	0,0006	0,0002	0,0061
HF	4,4	0,004	0,041	0,0019	0,0014	0,0004	0,0002	0,0003	0,0005

The Zamak and HF alloys are all hypoeutectic and are expected to possess microstructures consisting of Zn primary phase surrounded by a Zn-Al eutectic. A representative microstructure for Alloy 5 is shown in Figure 2.

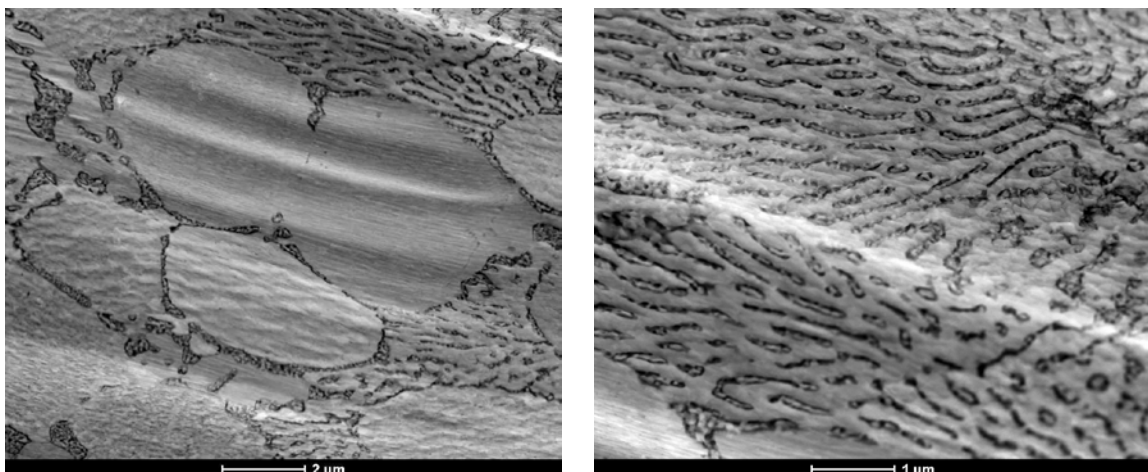


Figure 2- Primary (left) and eutectic phase (right) in Alloy 5 dark: Al-rich, bright: Zn-rich [8]

A recent series of HF alloy casting trials made by Frech has produced castings with thicknesses less than 0.5 mm, typically near 0.2 mm. In comparison with Figure 2, these castings exhibited grain sizes on the order of 1-3 μm and lamellar spacing on the order of 100-200 nm in the eutectic regions. This fine die-cast structure shows improved strength ($\sigma_y = 270 \text{ MPa}$) and elongation to failure of 13%.

CREEP OF ZINC DIE CASTING ALLOYS

Creep is the time dependent plastic deformation of a material at constant load. Plastic deformation is a kinetic process which occurs by a number of competing mechanisms. There are a number of atomic scale processes competing over varying ranges of stress, temperature and time, each of which can dominate mechanics of plastic deformation. These include the glide and climb of dislocations, the diffusion flow of atoms and vacancies, relative displacement of grains through boundary sliding and mechanical twinning [11]. A typical creep curve of Zn-alloys is shown in Figure 3.

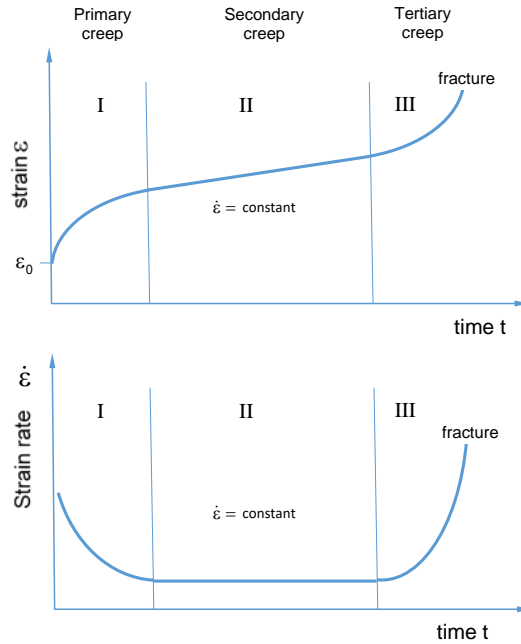


Figure 3- Typical creep curve of Zn-alloys

The primary creep stage exhibits a very high strain rate which decreases with time and has its end after 1 or 2 % of accumulated strain. Strain hardening is a dominant factor in this behavior.

In the secondary creep or minimum creep stage, strain hardening and recovery are balanced, resulting in a constant creep rate. During this stage, substructures like density and orientation of dislocation and size and orientation of subgrains influences the creep process.

The tertiary creep stage is very short because the constant load begins to become an ever increasing stress due to a reduction in cross section and a buildup of internal pores.

CREEP EQUATIONS

Plastic deformation through creep mechanisms can be expressed by the temperature dependent version of Norton's Law

$$\dot{\epsilon}_s = A \cdot \left(\frac{\sigma}{G} \right)^n \cdot e^{-\frac{Q}{R \cdot T}} \quad (1)$$

where A is a constant, σ/G is the normalised 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 is dependent upon the rate controlling deformation mechanism which is dominant for the given stress, temperature and microstructure.

CREEP EQUATIONS FOR PRIMARY CREEP

All the measured samples of the five alloys listed in Table 1 exhibits the same behavior which can be mathematically described with a power function of the type

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

c and a are constant depending from stress, temperature and alloy.

The derivative of this function is the creep rate for a given time.

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

With this formula the creep rate can be calculated for a given time or for given strain.

For example, for Alloy 3 with 67 MPa:

$$\varepsilon = 0.0173 \cdot t^{0.5703} \Rightarrow t = \left(\frac{\varepsilon}{0.0173} \right)^{\frac{1}{0.5703-1}} \quad 470 \text{ h at 67 MPa and 1% strain}$$

$$\dot{\varepsilon} = 0.173 \cdot 0.5703 \cdot t^{0.5703-1} = 0.01 \cdot t^{-0.4297} \Rightarrow \dot{\varepsilon} = 0.0015 \text{ \% /h}$$

Together with Norton's equation the stress exponent n can be calculated:

$$n = \left(\frac{\log \dot{\varepsilon}}{\log \sigma} \right) \text{ from the slopes of the lines shown in Figure 4} \quad (4)$$

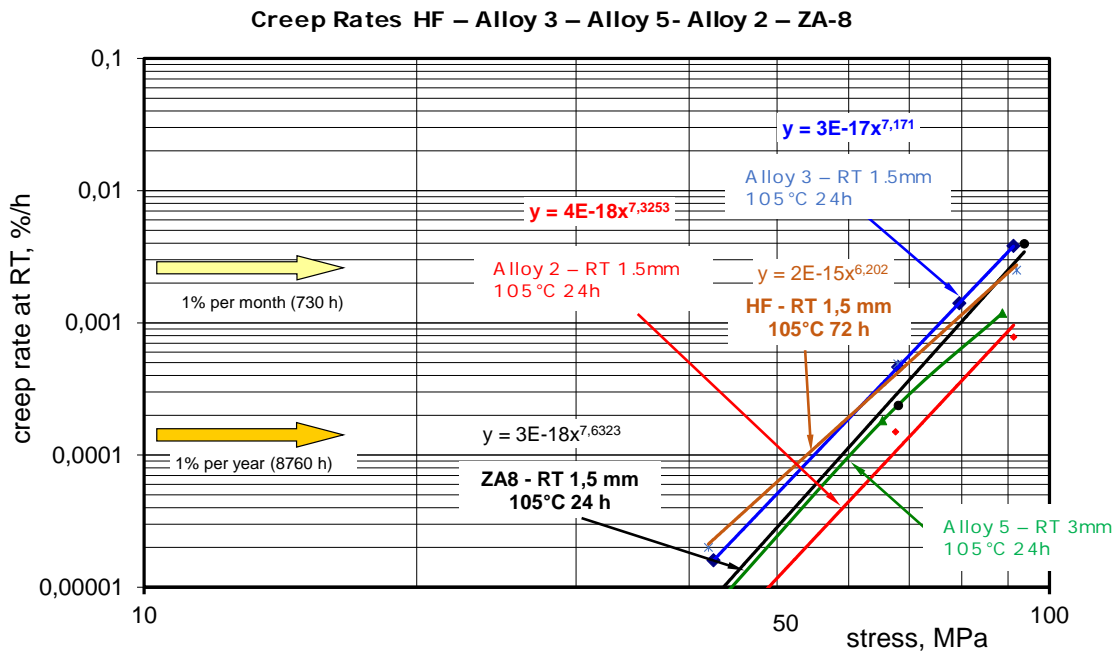


Figure 4- Creep rates from all measured alloys calculated utilizing equation 3

CREEP RESULTS

For the creep tests at room temperature stresses between 40 MPa and 100 MPa were applied; with a test temperature of +85°C stresses between 12 MPa and 50 MPa.

The five alloys in this project typically exhibited relatively long primary creep stage. The end of primary creep can be estimated between 1 and 2 % of creep strain. During the secondary creep stage, a nearly constant creep rate was observed, with a slight increase in creep rate as sample cross section decreased slightly, up to an accumulated elongation of 20%.

A tertiary creep stage was not observed because the maximum elongation that could be accommodated in the creep testing apparatus is 20%.

Figures 5, 7, 8 and 9 shows an example of creep testing results, for Alloy 3, 5, 2 and ZA-8 with 1.5 mm thickness at room temperature. All specimens were aged for 24h at 105°C. The power function equation for each stress as a trend line is included in these figures.

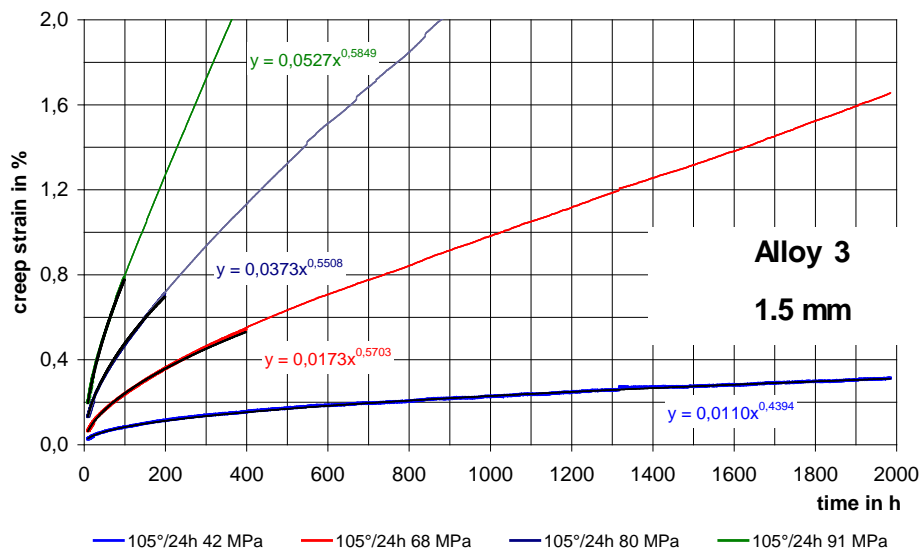


Figure 5- Room temperature creep behavior for Alloy 3 after artificial ageing (105°C / 24 h)

Redrawing Figure 5 as a log-log graph, shown in Figure 6, the Alloy 3 creep results are observed to be flat lines, meaning that the power function is valid.

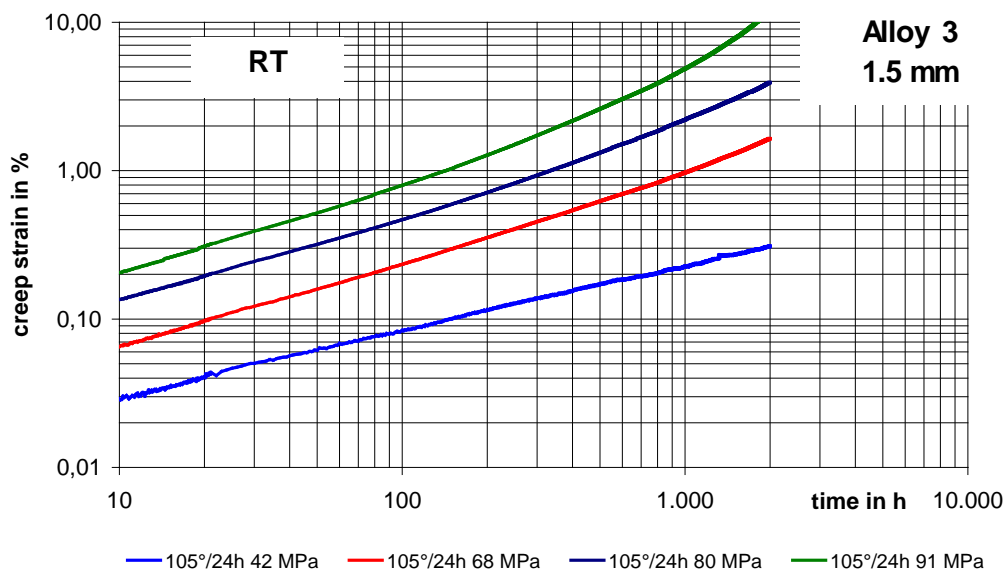


Figure 6- Creep behaviour for Alloy 3 after artificial ageing (105°C / 24 h), log-log scale

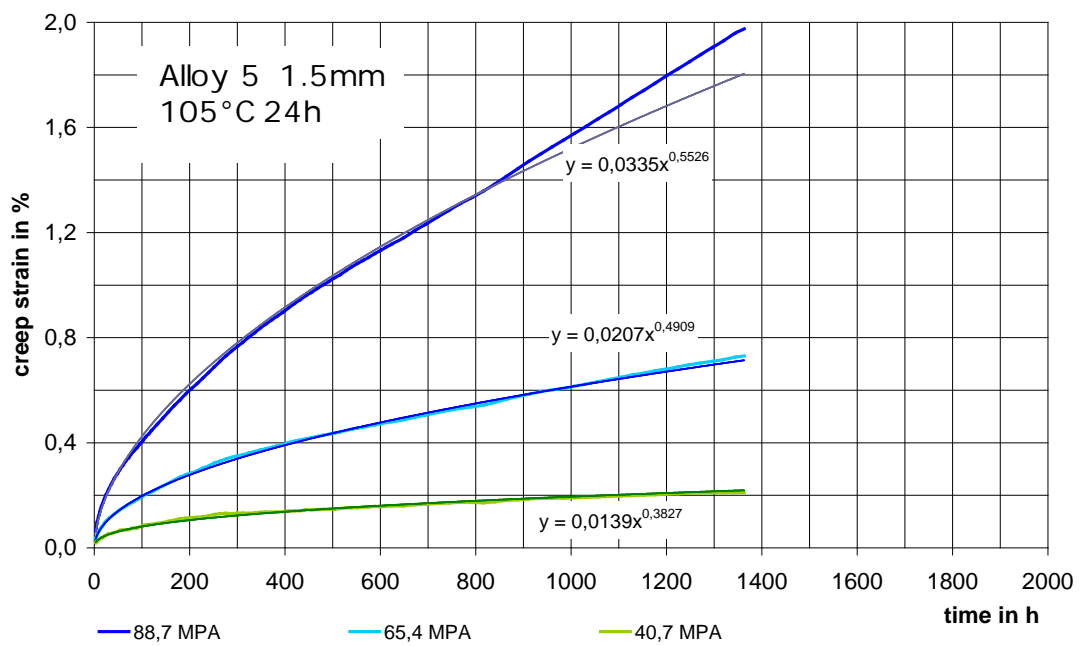


Figure 7- Room temperature creep behavior for Alloy 5 after artificial ageing (105°C / 24 h)

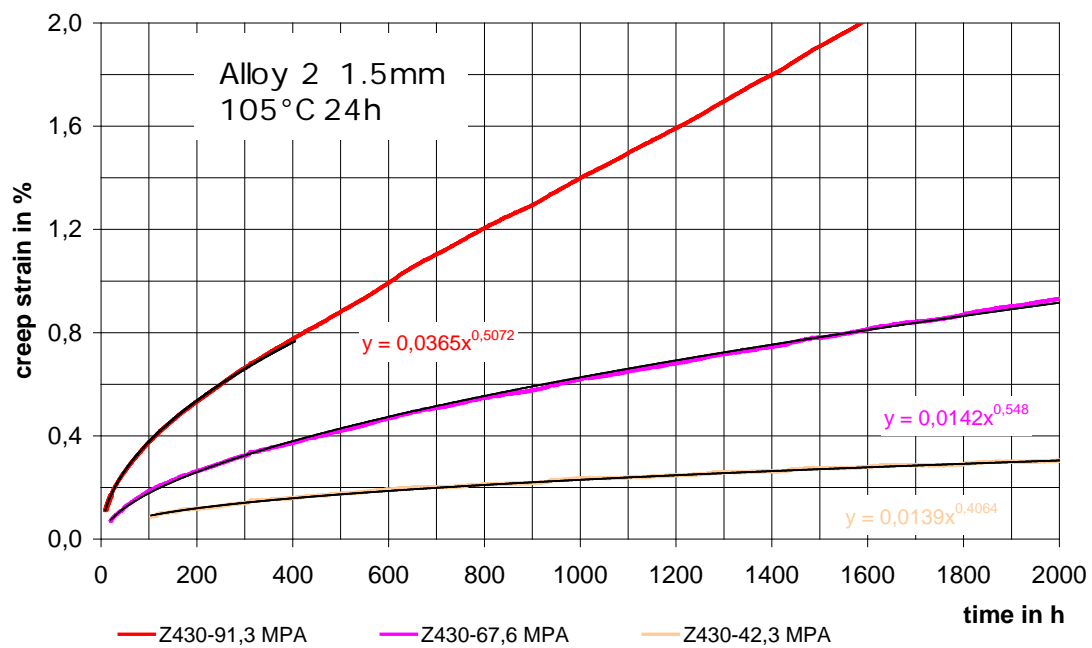


Figure 8- Room temperature creep behavior for Alloy 2 after artificial ageing (105°C / 24 h)

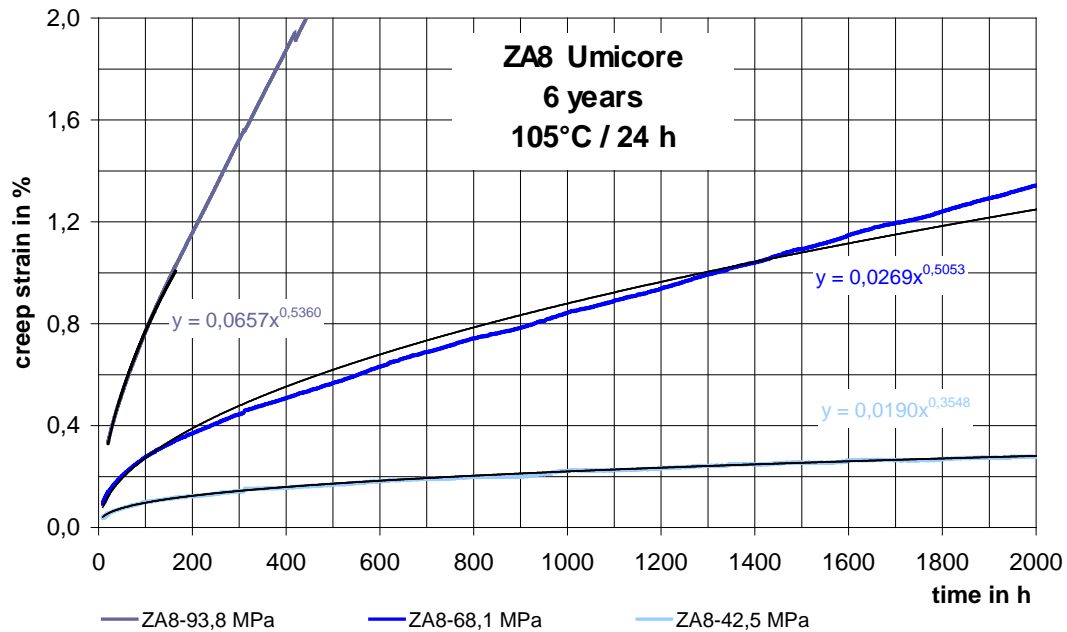


Figure 9- Room temperature creep behavior for ZA8 naturally aged over 6 years after artificial ageing (105°C / 24h)

Room temperature creep results for the 1.5 mm thick HF alloy specimens, both as-cast and aged, are shown in Figure 9. At the two highest stresses, the aged condition has a higher creep rate than the as-cast, while at the lowest stress the two conditions have the same creep behavior.

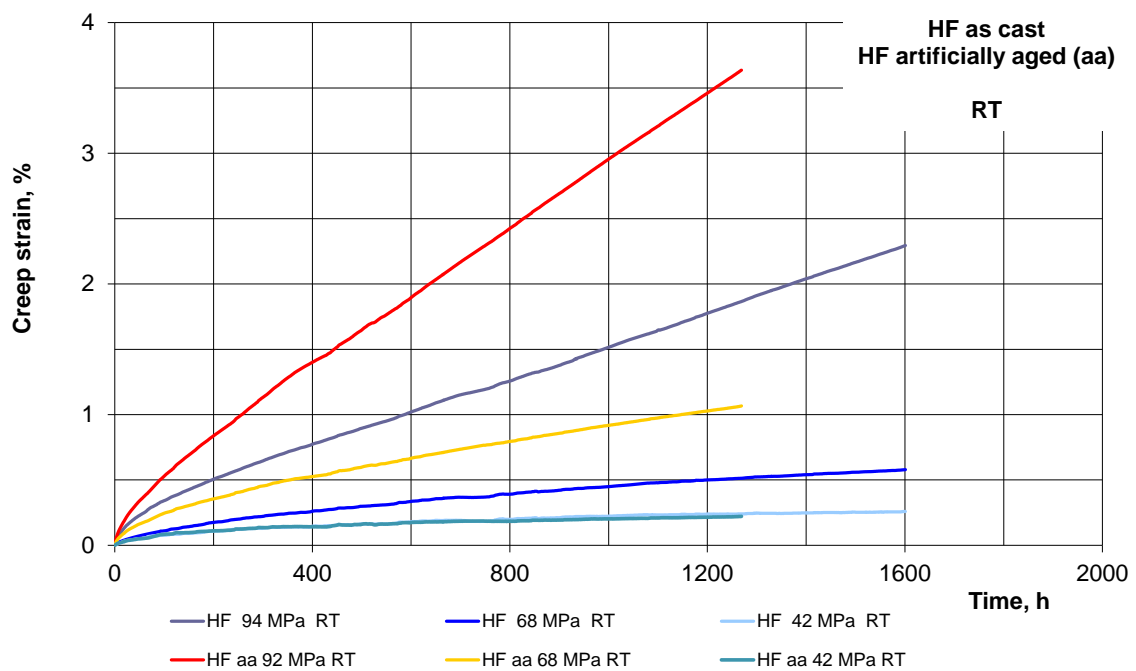


Figure 10- Room temperature creep behavior for HF alloy as cast and artificially aged 3 days at 105°C

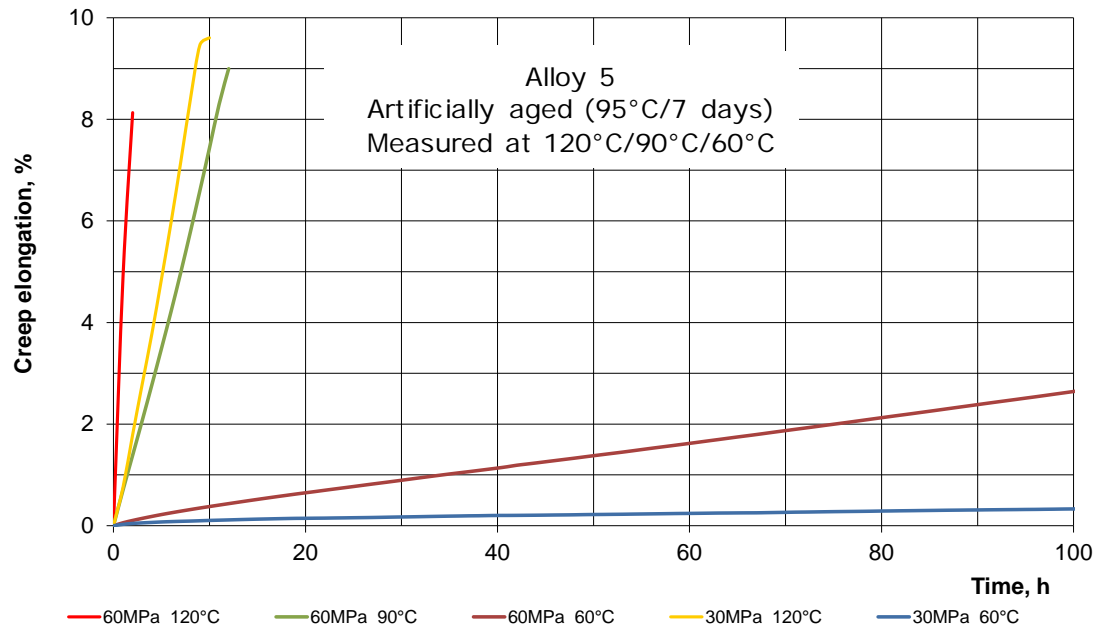


Figure 11- Creep behavior Alloy 5 at elevated temperatures as cast and artificially aged 7 days at 95°C

INFLUENCE OF TESTING TEMPERATURE

The creep behaviour of aged Alloy 5 at 3 temperatures is shown in Figure 11. Creep is a thermal activated process which can be expressed by the Arrhenius law (equation 1). The activation energy for the creep behaviour is the activation energy for self-diffusion of zinc with a value of about 94 kJ / mol. The activation energy leads to an increase of the creep rate between 25°C to 85°C by a factor of 700, as shown in Figure 13.

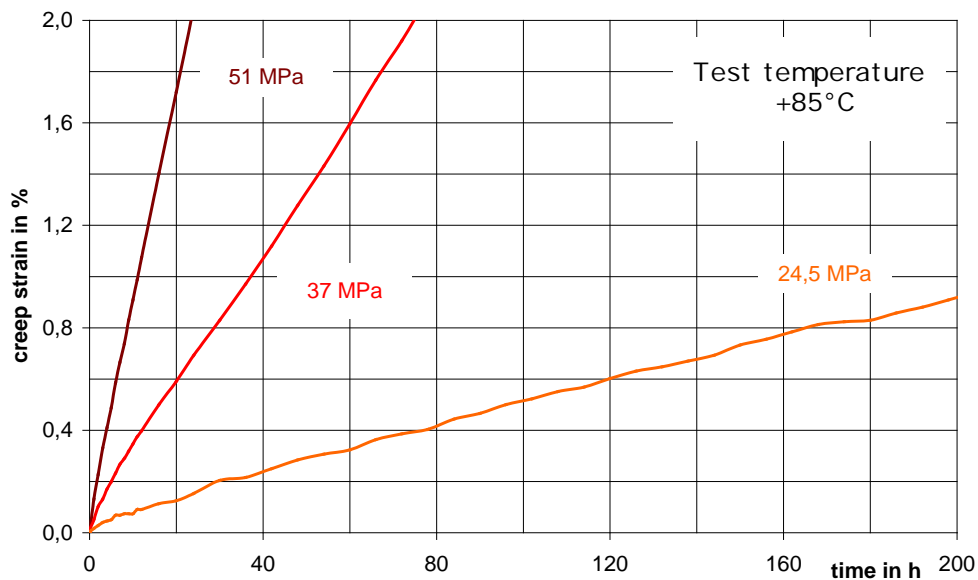


Figure 12- Creep elongation as a function of time and stress of Alloy 5 at +85°C

In all measured cases the Arrhenius law and therefore equation (1) is well confirmed when $Q = 94 \text{ kJ/mol}$ is used.

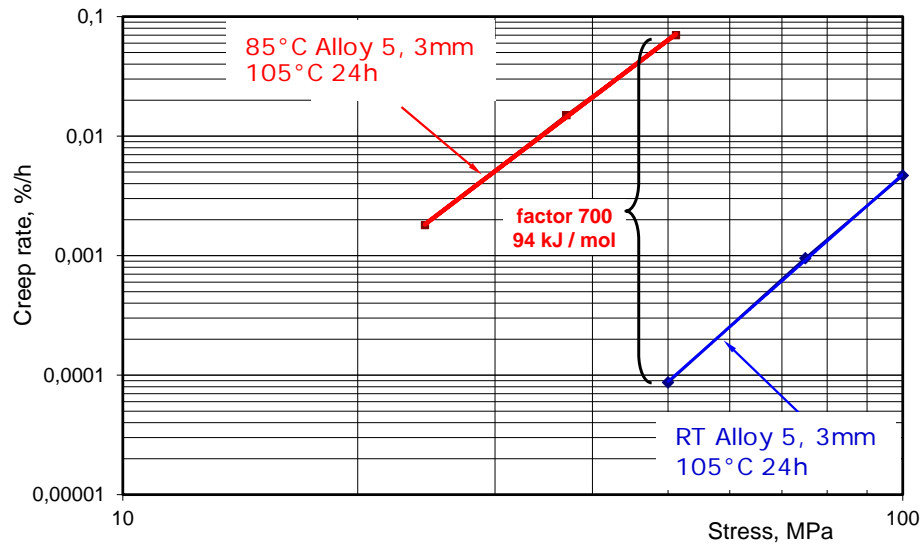


Figure 13- Creep rate of Alloy 5 for two testing temperatures

DETERMINATION OF STRESS EXPONENT

The creep behaviour of aged Alloy 5 at three stresses at 85°C is shown in Figure 12. The stress exponent shown in Equation 4 is strongly dependent on the actual creep elongation and lies between 4 and 7, Figure 14. The stress exponent can be calculated from the power law function which is the slope of the creep curves shown in Figure 13.

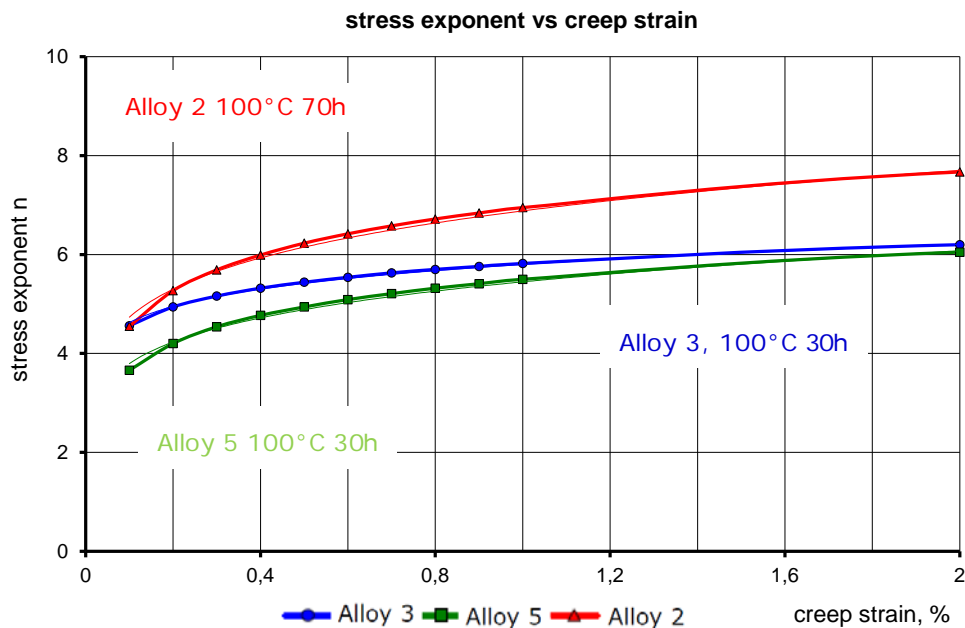


Figure 14- Stress exponent n for Alloys 2, 3 and 5, as a function of creep strain

INFLUENCE OF ARTIFICIAL AGEING TIME

The effect of ageing time was investigated by creep testing of specimens that had been aged at 105°C up to 1000 hours. The results for Alloy 5, with thicknesses of 1.5 and 3.0 mm, are shown in Figure 15. Consistent with Figure 9, samples aged for more than 20h show higher creep rates than the as-cast samples.

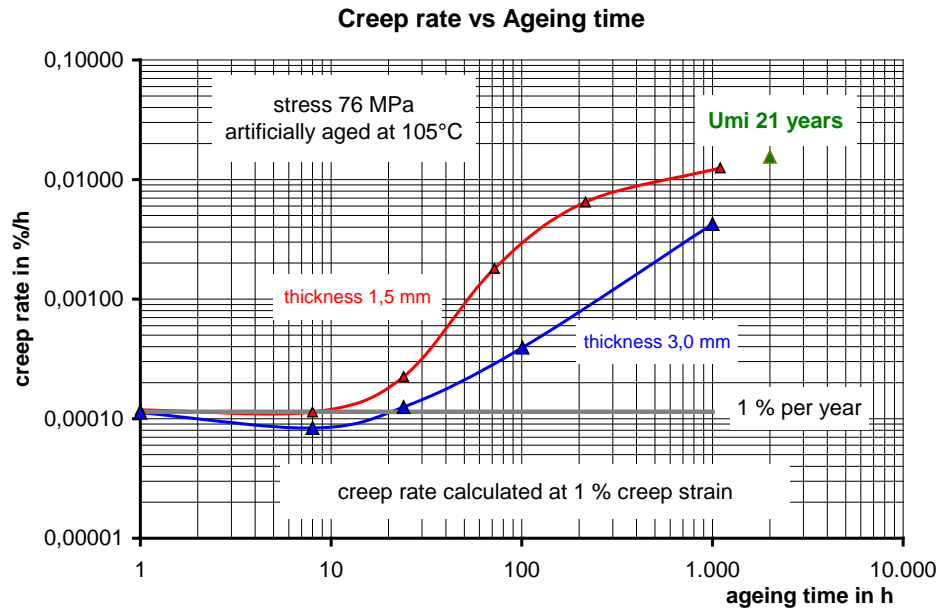


Figure 15- Room temperature creep rate versus ageing time as a function of wall thickness, Alloy 5

For Alloy 5, natural ageing results in a stabilization of short-term tensile properties (tensile strength and yield stress) after one year, and this is equivalent to much shorter ageing times, on the order of a day or two, at higher ageing temperatures [12]. In contrast, creep strength is seen in Figure 15 to decrease continuously over 20 years or longer. The increase of creep rate is nearly 50 times higher after a heat treatment at 1000 hours compared with either 24 hours at 105°C or after a natural ageing for 20 years. In the as-cast structure, the primary zinc phase is larger and more enriched with Al than in the aged samples, and the eutectic is less rich in Al, meaning that the eutectic in the as-cast samples is lower in both volume fraction, and the fraction of the eutectic occupied by zinc-rich lamellae (bright phase in Figure 2) is also lower. The higher fraction of Al atoms in the as-cast primary phase slows the creep-induced diffusion of Zn because of the higher lattice non-uniformity in a more Al-rich Zn crystal lattice. Al has an atom size of 118 pm compared to the 142 pm of Zn. Alloys 2 and 5, with their higher Cu content, are also influenced by the behavior of Cu during ageing. The atom size of Cu, 145 pm, is slightly larger than Zn and will also contribute to slowing of diffusion with the Zn crystal. Later in the ageing process, the Cu-rich epsilon phase is formed, containing about Zn-15%Cu-1.5%Al [13], further depleting the Zn primary phase of alloying elements and reducing Zn grain size, both of which contribute to higher creep rates.

INFLUENCE OF WALL THICKNESS

A greater wall thickness will also reduce the creep rate because of the larger grain size and a lower volume fraction of grain boundaries that are known to increase creep rate under these conditions. Figure 16 shows the creep behavior of Alloy 5 with 1.5 and 3 mm wall thicknesses, together with the exponential approximation and plotted relationship.

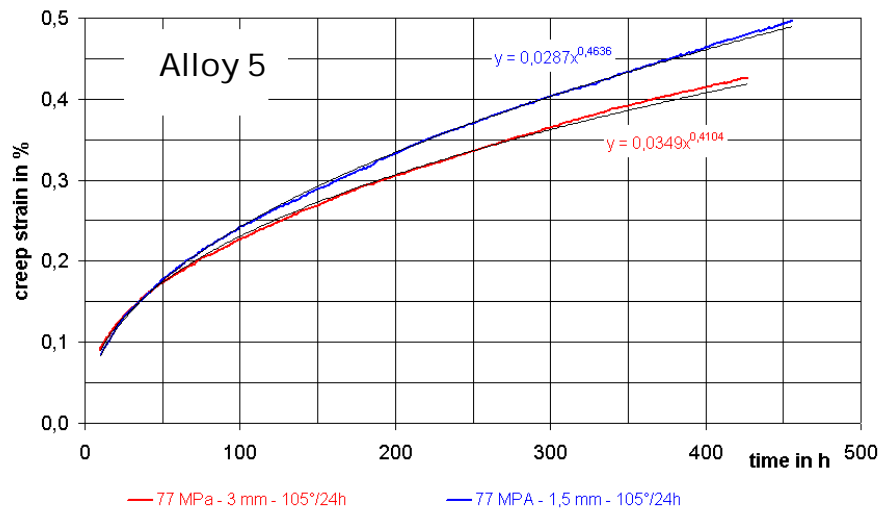


Figure 16- Creep strain as a function of wall thickness, Alloy 5 artificially aged at 105°C / 24 h

AVERAGE CREEP RATE OF THE FIVE MEASURED ALLOYS

Figure 17 shows the creep data of the five alloys in comparison. The Cu content influences the creep rate by a factor of four between Alloy 3 and Alloy 2. Between Alloy 5 and Alloy 2 there is less than a 30% difference. The alloy ZA-8 lies between Alloy 3 and Alloy 5 but the ZA-8 specimens had an additional natural ageing process of 6 years.

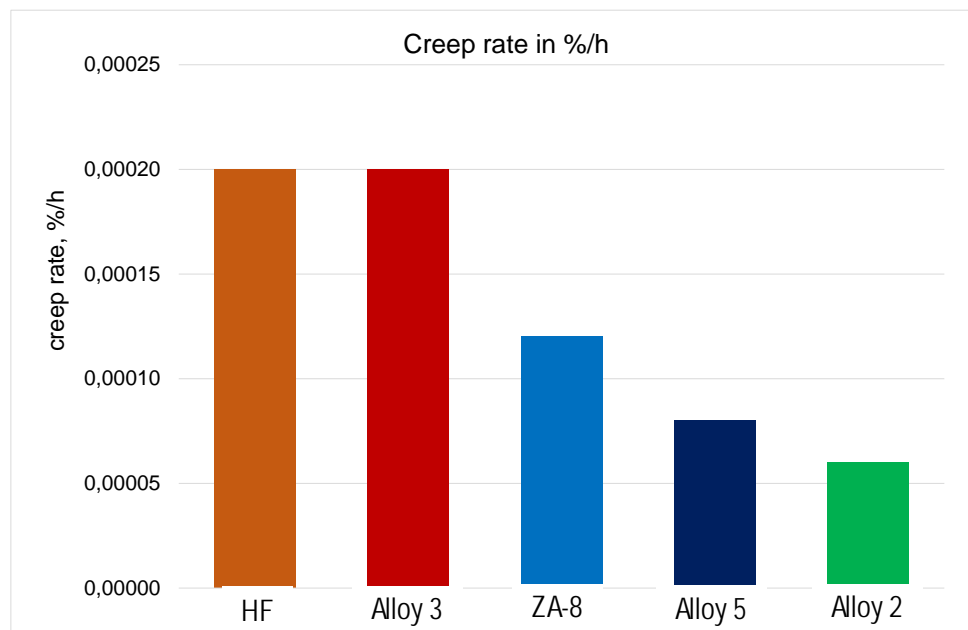


Figure 17- Creep rate with 60 MPa stress at room temperature and 1.5 mm wall thickness after 1 % creep strain (artificially aged 24h/105°C, ZA8 with 6 years natural ageing)

DISCUSSION AND CONCLUSIONS

All the tested zinc die-casting alloys exhibits the same behavior during creep deformation with a distinct primary creep stage during which creep rate strongly decreased increasing elongation because of strain hardening. The primary creep can mathematically expressed with a power law function, Equation 2. The value of the coefficient “c” is dependent upon stress, temperature, microstructure (wall thickness, die temperature) and alloy type through the potential of strain hardening and recovery of the several alloys. The exponent “a” in the power law function has little dependence upon stress but is sensitive to the applied temperature and alloy type. With an increase of the

temperature an increase in the exponent value can be observed. The exponent of the several alloys can roughly written according Table 2. A low value of the exponent means a higher potential for strain hardening.

Table 2-Exponent of the power law function at several alloys and conditions for primary creep

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	

The secondary creep region can always written with Norton´s equation in all used conditions. The stress exponent is mainly influenced by the alloy type, Table 3.

Table 3-Exponent n of Norton´s equation at several alloys and conditions

Exponent n	Alloy 3	Alloy 5	Alloy 2	ZA8	HF
RT / 1.5 mm 105°C / 24 h	5.9	5.7	7.0	7.6	6.2
RT / 3.0 mm 105°C / 24 h		0,44			
85°C / 1.5 mm 105°C / 24 h				0,79	

In all experiments described here, no creep mechanisms other than power law creep, such as Coble (grain boundary diffusion), Nabarro-Herring (bulk diffusion) and Harper-Dorn (dislocation-controlled) (regime $n=1$) were observed. The results all fit into the box near the center of Figure 18.

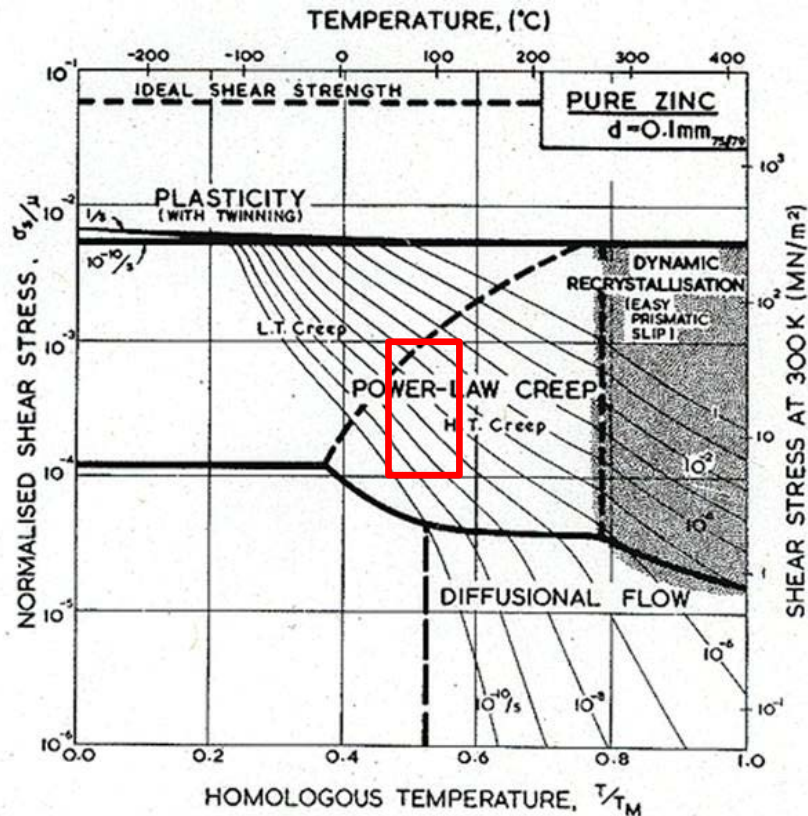


Figure 18- 2D creep deformation mechanism map for coarse pure Zinc, red frame means the region researched in the project [11]

For maximum creep resistance a high Cu content Zn alloy with a coarse microstructure (high wall thickness, and produced using a high die temperature) is necessary. Creep resistance is reduced by artificial ageing for more than one day at 100°C or a higher temperature than 100°C.

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