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Extended summary

Microstructural stability and creep of magnesium alloys

Curriculum: Ingegneria meccanica e gestionale

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Abstract. The present work aims at quantifying the role of microstructural instability on the high temperature mechanical response of the AZ31 magnesium alloy. The effect of static grain growth has been investigated, by analyzing the data obtained after heat treating at 100, 200 and 300 °C different samples of a rolled AZ31. Grain growth was thus observed under static condition only at 300 °C, since minor grain growth occurred during annealing at lower temperature.

The study then addressed the traditional constitutive models of creep to take into account the effects of chemical composition and of the grain size. Although creep is usually correctly described by a diffusion-controlled dislocation creep equation, other mechanisms may be important. Grain boundary sliding (GBS) and diffusional flow may in fact dominate deformation especially in fine grained materials. Each of these mechanisms is considered to operate independently of the others and has a particular dependence of creep rate with stress, temperature and grain size.

Analyses demonstrated that the behavior of hcp Mg–Al alloys follows, in general terms, the same well known scheme typical of fcc Al–Mg alloys, also in respect to the existence of two regimes, the first characterized by an n = 3 stress exponent, and the second described by the modified form of the Garofalo equation. A low stress regime dominated by grain boundary sliding was also observed in fine-grained alloys. A similar approach was used to analyze creep and plasticity of Mg-Zn alloys. For these reasons, the creep model equations have been rewritten to take into account the role of grain boundary sliding. Thus modified models was used to describe the creep response of different Mg alloys. By comparing the data obtained by several researchers with the model curves calculated by corrected equations, the agreement was excellent for the single-phase AZ31 alloy as well as for more complex materials.

Keywords. Creep, grain-size effects, magnesium alloy, microstructure, plasticity.

1 Problem statement and objectives

The high temperature response of Mg–Al alloys, and in particular of the AZ31 (Mg–3Al–1Zn) has aroused significant interest in recent years among the researchers operating in this field; a recent study has thus attempted to rationalize the difference in behavior observed when comparing data obtained by different testing techniques, namely constant load/constant stress creep and constant strain rate testing in torsion, compression or tension.

A major problem, frequently encountered when investigating the creep response of the Mg–Al alloys, is that at relatively low temperature (100–150 °C) the experimental data lie in the regime of power-law breakdown, resulting in anomalously high values of the stress exponent (n>7); in this regime of applied stress, the usual power law should be then replaced by the Garofalo equation.

The objectives of the present research is, on one hand, to quantify the effect of grain growth and DRX on the high temperature mechanical response and study the static stability for the AZ31 alloy. On the other hand, an extensive bibliographic recompilation on creep data for the AZ31 alloy allow us to introduce a set of creep laws, which in addition to the microstructure evolution equations are suitable for describing the entire range of the strain rate-stress-temperature map for creep in AZ31 alloy giving a unitary model for it.

2 Research planning and activities

The activities of the research began making a collection of literature data obtained by several researchers. Following, was started the experimental activities for the characterization of the alloy AZ31. The effect of grain size on the high temperature mechanical response has been investigated. The basis of the analysis was a phenomenological description, which took into account the existence of two well defined regimes, the first characterized by a n = 3 stress exponent, and the second described by a modified form of the Garofalo equation, indicating the transition from a viscous-glide to climb as rate controlling mechanisms. The description was modified by introducing a further parameter, the grain size. The study then addressed the traditional constitutive models of creep to take into account the effects of chemical composition and of the grain size. Thus modified models was used to describe the creep response of different Mg alloys, comparing the data obtained by several researchers with the model curves calculated by corrected equations.

3 Analysis and discussion of main results

3.1 Microstructural characterization of the alloy AZ31

A microstructural stability analysis of AZ31 alloy was performed. The present work aims at quantifying the role of microstructural instability on the high temperature mechanical response of the AZ31 magnesium alloy. The effect of static grain growth has been investigated, by analysing the data obtained after heat treating at 100, 200 and 300 °C different samples of a rolled AZ31. Grain growth was thus observed under static condition only at 300 °C, since minor grain growth occurred during annealing at lower temperature.

A comparison of the experimental data obtained from the present microstructural analysis with a theoretical equation well known and used in various experimental

$$d^m = d_i^m + Kt = d_i^m + K_0 t \exp(Q_g / RT) \qquad (I)$$

where m = 6 is an exponent of growth, d is the initial grain size, K is a parameter dependent on temperature, Qg = 92 kJ/mol is the activation energy for the growth mechanism, and K_0 = K_0 = 1.50x10^{13} micron^6/h is a constant recalculated in the present study.

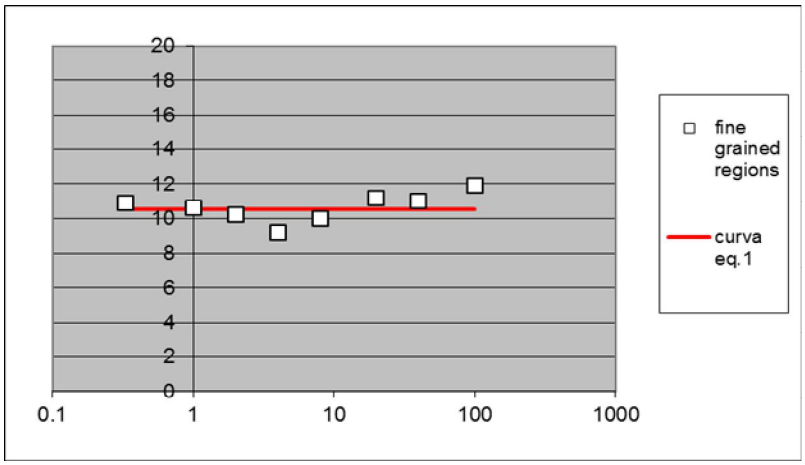


Figure 1. Comparison experimental data of grain size to 100 °C with eq.I.

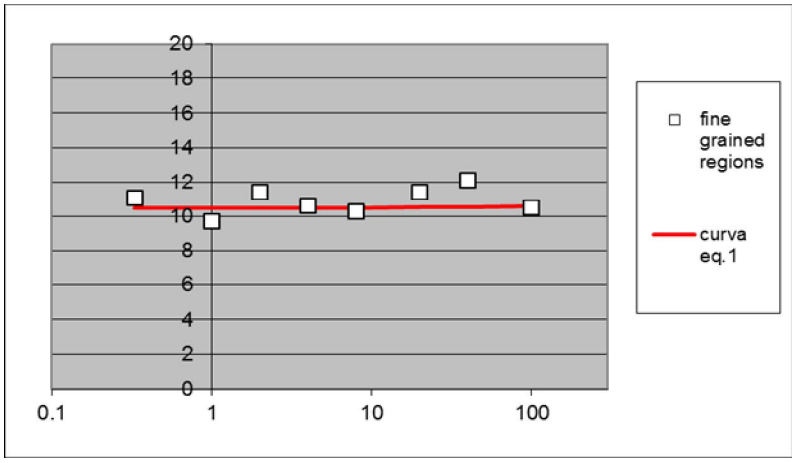


Figure 2. Comparison experimental data of grain size to 200 °C with eq.I

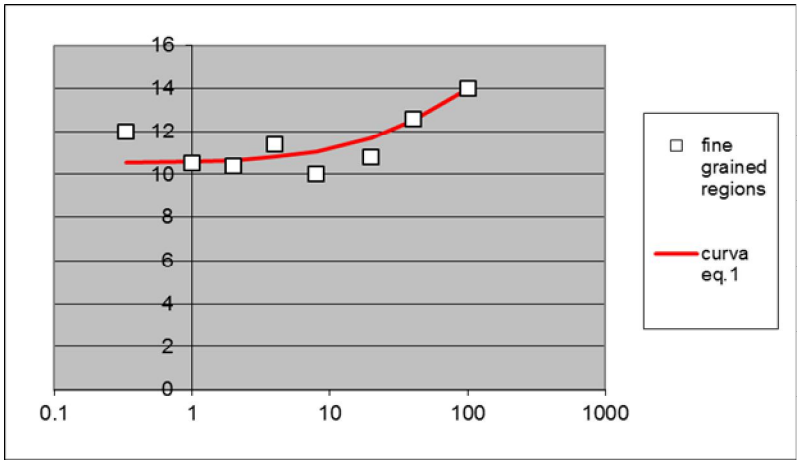


Figure 3. Comparison experimental data of grain size to 300 °C with eq.I

3.2 The constitutive model

The creep model here presented is based on two traditional constitutive equations, i.e. the Garofalo relationship

$$\dot{\varepsilon_d} = A\,\{sinh[\alpha\,(\sigma/G)]\}\exp(-Q/RT) \quad (1)$$

and the Norton equation

$$\dot{\varepsilon_d} = A'(\sigma/G)^n\,\exp(-Q/RT) \quad (2)$$

where $\dot{\varepsilon}_d$ is the minimum creep rate (or the testing strain rate in case of constant strain rate tests) associated with dislocation motion, σ is the applied stress, *T* is the absolute temperature, *n* is the stress exponent, α, *A* and *A'* are material parameters, *Q* is the creep activation energy, *G* is the shear modulus and *R* is the gas constant. While Eqn.2 is valid in the low strain rate / high temperature regimes typical of creep, Eqn.1 is more general, and can be used also above the power-law breakdown which usual characterized the experiments carried out in the intermediate temperature regime (100-150°C in the case of Magnesium alloys). Equation (1) reduces to Equation (2) when the applied stress is low.

The model takes into account the class A behaviour [1] observed in Mg alloys [2], i.e. the existence of two different creep regimes: i. a low strain-rate regime, with $n = 3$ stress exponent, typical of alloys where deformation is controlled by viscous glide of dislocations in an atmosphere of solute atoms; ii. a high strain rate regime, where creep is climb controlled, and $n = 5$. In addition, the role of grain boundary sliding is also quantified. Each regime will be described separately in the following.

In the high-strain rate regime, creep is controlled by climb, $n = 5$, *Q* is equivalent to the activation energy for lattice self diffusion in Mg (Q_l); in many cases, the creep experiments were carried out at relatively low temperature (100-150°C), and, as a result, most of the data lie above the power-law breakdown. Thus, the model is based on the use of Equation (1) [3], properly modified to take into account the effects of chemical composition and of the grain size [4]. Major alloying elements considered in the present study are Al and Zn in Mg-Al and Mg-Zn alloys respectively. These alloying elements play two major roles, namely: i. a solid solution strengthening effect; ii. a particle strengthening effect in those cases where

precipitation of secondary phase particles occurs. The particle-strengthening effect has been neglected in this study, which considers data obtained above 200°C, where particle coarsening or even dissolution occur.

The most obvious effect of the elements in solid solution is to reduce the strain rate, for a given stress, even in the climb-controlled creep regime. In this respect the behaviour of the Mg-Al alloys is formally similar to that of the materials belonging to the Al-Mg system [1]. The stress exponent in climb-controlled creep remains constant, but the strain rate vs applied stress curve shifts toward lower values of the strain rate as the content of elements in solid solution increases. This behaviour can be modelled by supposing that either *A* or α change with the content of element in solid solution. Preliminary studies on Al-alloys [5,6] seem to suggest that α is particularly sensitive to variations in chemical composition. The analysis of the data obtained by Sato and co-workers for Mg-Al [7] (Figure 4a) and of a collection of literature results for Mg-Zn (see [8] for a detailed description) thus gave

$\alpha = 69.6 / c_{Al}^{0.37}$ (3)
and
$\alpha = 85 / c_{Zn}^{0.3}$ (4)

where c_{Al} and c_{Zn} were the concentration of Al and Zn in solid solution (Figure 4b).

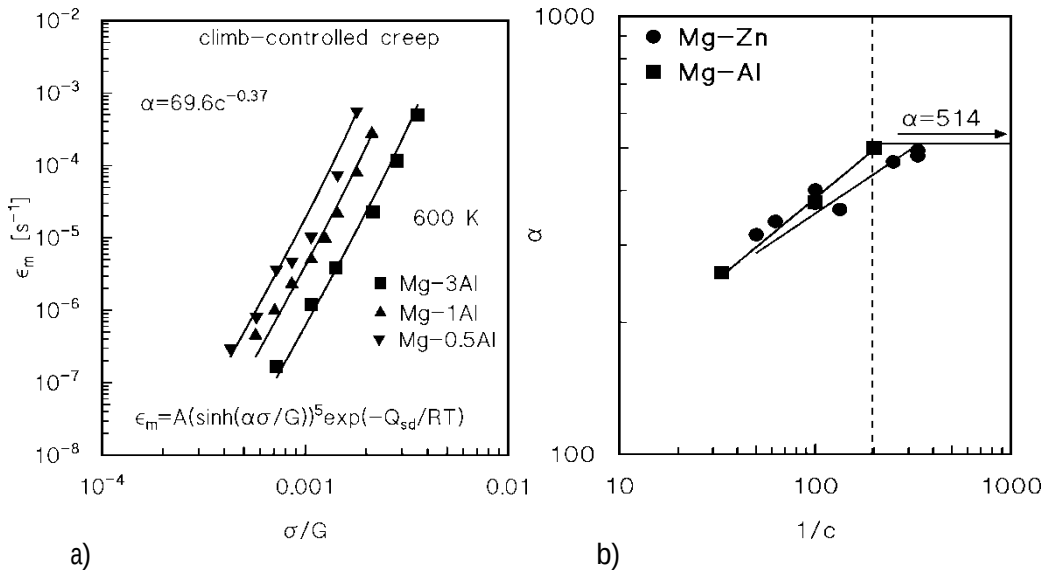


Figure 4. a) Strain rate vs stress for Mg-Al coarse-grained dilute alloys tested at high temperature [7] (the grain size was 170 μm); b) variation of α with the concentration of the major alloying element (Al or Zn) in solid solution [8].

The grain size effect on the dislocation-creep properties of the AZ31 magnesium alloy has been investigated by comparing data obtained by testing materials of similar chemical composition but different initial microstructure [9-12]. The results of this analysis confirmed the presence of a weak but not negligible effect of the grain size in the climb-controlled regime. The Equation (1) was thus modified as follows:

$\dot{\varepsilon_d} = A(b/d)^p \{sinh[\alpha\ (\sigma/G)]\}^5 \exp(-Q/RT)$ (5)

where *d* is the grain size and *b* is the Burgers vector, with *p* = 0.6 [4]. The model Eqn.5 was successfully used to describe the high temperature response of a Mg-4Al-1Ca alloy [13,14].

The existence of a low stress regime where the creep data can de described by a power law with *n* = 3 (see ref. [2] for a review of the literature data), suggested that, in Mg-Al alloys, deformation could be controlled by viscous glide of dislocations in atmospheres of Al-solute atoms, a behaviour which is intrinsically similar to that of Al-Mg dilute alloys [1,7]. Combination of the traditional models with the findings of several studies on AZ31 [2] led to an equation in the form:

$$\dot{\varepsilon_d} = A^*(c_{Al})^{-1} (b/d)^{p^*} (\sigma/G)^3 \exp(-Q^*/RT) \quad (6)$$

which takes into account both the effects of the content of Al in solid solution and of the grain size. In this regime *p*=0.4 and *Q**=101 kJ/mol [2]. This value of the activation energy *Q**, which was calculated by interpolating data from both strain rate changes (SRC) experiments and continuous tests, is substantially lower than the theoretical value, i.e. the activation energy for diffusion of Al in Mg (143 kJ/mol).

Strain rate changes experiments [11,12], which present the advantage of obtaining different data from a single experiment with a limited grain growth, led some authors [12] to suggest that at sufficiently high temperature, grain boundary sliding (GBS) substantially contributes to the deformation of the sample. The resulting creep model equations should be thus rewritten in the form

$$\dot{\varepsilon} = \dot{\varepsilon}_{GBS} + \dot{\varepsilon}_{disl} = A_{GBS}(b/d)^{p'}(\sigma/G)^2 \exp\left(-\frac{Q_{GBS}}{RT}\right) + \dot{\varepsilon_d} \quad (7)$$

where *p'* is 2 or 3, Q_{GBS} is equivalent to Q_l or to the activation energy or grain boundary diffusion (Q_{GB}), which, in Mg, is close to 92 kJ/mol [15], while the $\dot{\varepsilon}_d$ term assumes the form of Equations (5) or (6). It can be here observed that the anomalously low *Q** value computed by interpolating constant stress, constant strain rate and SRC experiments, can be the result of the concurring operation of viscous glide (characterized by a value of the activation energy similar to that of self diffusion) and GBS.

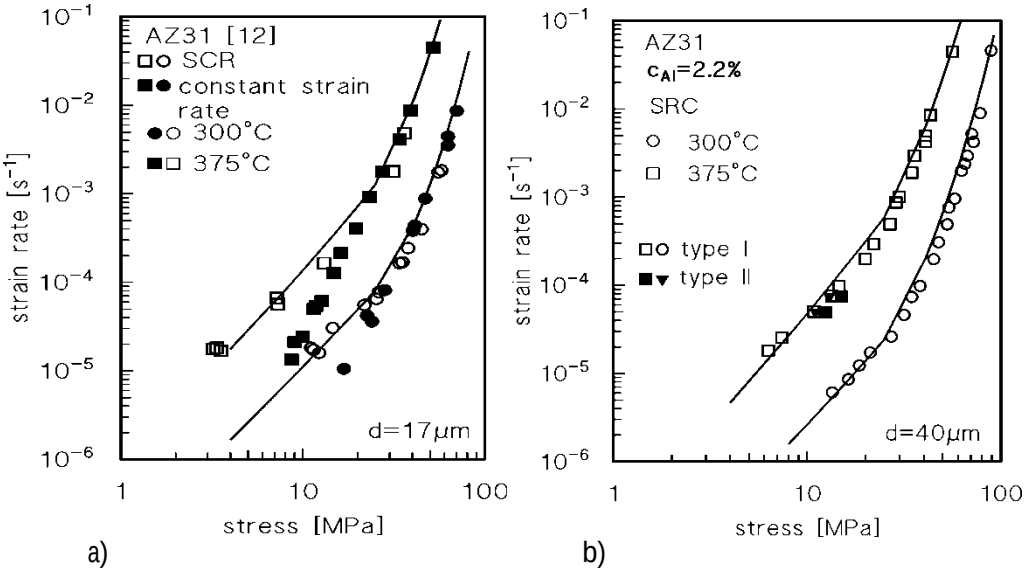
3.3 Description of creep data for Mg-Al and Mg-Zn alloys

This section analyses the accuracy of the model in describing the creep response of different Mg alloys. In all these cases the same *A*, *A* and* A_{GBS} values were used.

3.3.2 The AZ31 alloy

The AZ31 alloy contains a low amount of Al, and can be considered a single-phase material, since only limited precipitation of $Mg_{17}Al_{12}$ in form of coarse particles occurs during cooling from rolling or extrusion temperature (typical initial conditions for creep testing). Figure 5 plots the data obtained by del Valle et al [12] by SRC and continuous experiments, and the model curves calculated by Equation (7) with c_{Al}=2.2% (at.). The values of the activation energies Q_l, Q* and Q_{GBS} were the theoretical 135, 143 and 92 kJ/mol respectively. The agreement between the SCR data and the model curves is excellent, even though the only free parameters were the A, A* and A_{GBS} constants. The deviation between the curves and the constant strain rate experiments, as clearly suggested by del Valle et al., can be at-

tributed to the marked grain coarsening which occurs during the low-strain rate experiments, an effect that will be later discussed.

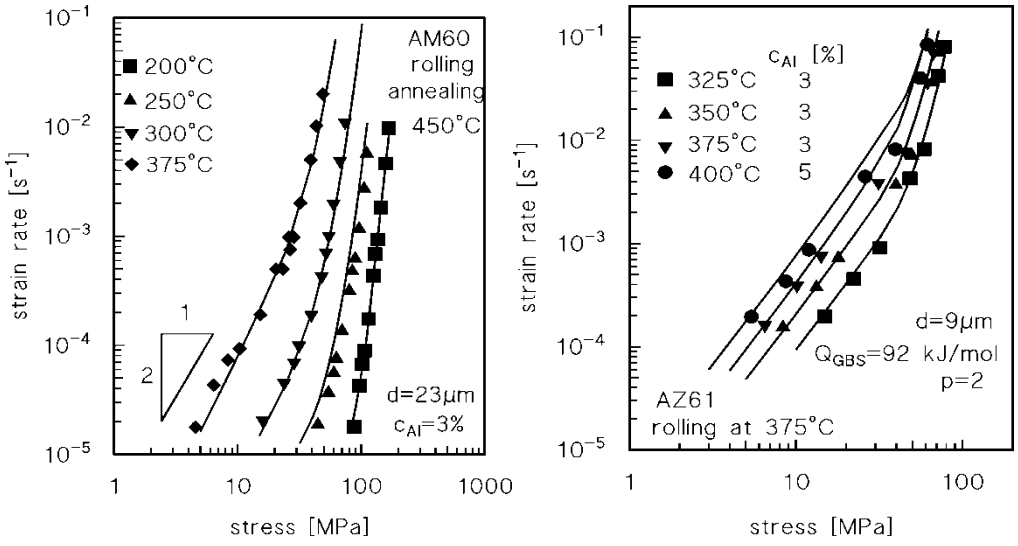


a) b)

Figure 5. Strain rate as a function of applied stress for SCR and constant strain rate tests [12]. Concentration of Al in solid solution in at.%.

3.3.3 The AM60 and AZ61 alloys

Recent investigations analysed the high temperature response of the AM60 [15] and AZ61 [16] alloys with fine grain sizes, tested by the SRC technique. A common feature of these investigations is the existence of a low-stress regime at temperatures above 300°C, characterised by a stress exponent close to 2 (Figure 7), an indication of the possible role of GBS as rate-controlling mechanism. The limited intergranular precipitation of $Mg_{17}Al_{12}$, in these cases, is thought to have a beneficial effect in retarding or even suppressing grain growth, thus maintaining the fine grain size which is a prerequisite for the occurrence of GBS [16]. The analysis of the data obtained by del Valle and Ruano [15] suggests that GBS assumes a significant role, and can be described with $p' \cong 2$ and $Q_{GBS} = Q_{GB}$. Figure 6 shows the model curves obtained by assuming that $c_{Al} = 3\%$, i.e. that a minor but non negligible fraction of Al is combined with Mg, to form the intermetallic precipitates which retard grain growth. The values of the different parameters were those calculated to obtain the plots in Figure 5. The correlation between model curves and experimental data is in both cases very good.



a) b)

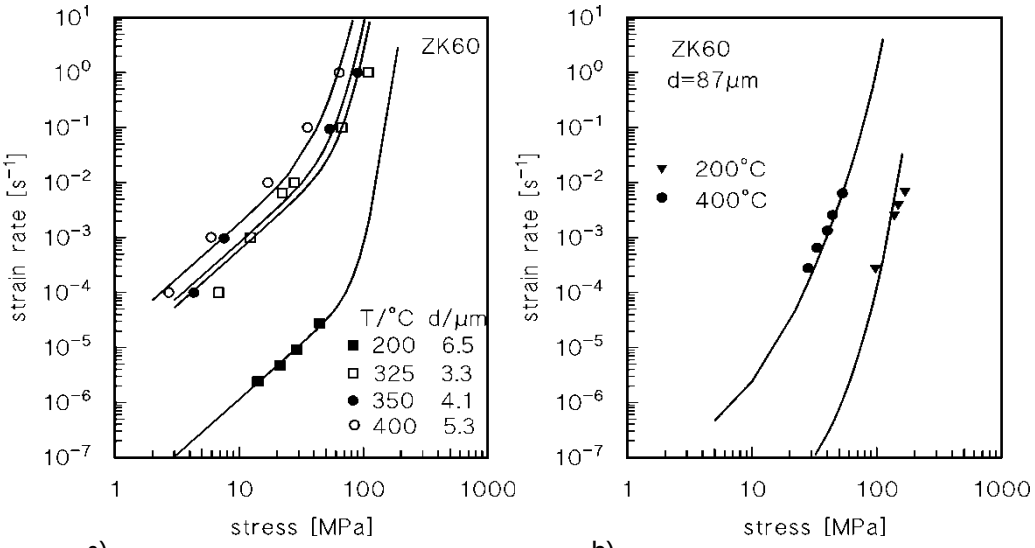
Figure 6. Strain rate vs stress for an AM60 (d =23 μm) [15] (a) and an AZ61 (d = 9 μm) [16]. All these data were obtained by the strain rate change technique (SRC).

3.3.4 The ZK60 alloy

Only few data on the high temperature response of Mg-Zn alloys are available, and in most cases they apply to the ZK60 [17-19]. In these alloys the existence of a regime of viscous-glide controlled deformation has been not unambiguously ascertained, being the amount of Zn in solid solution ($c_{Zn} \cong 0.023$) relatively low. At temperatures above 200°C, Zn is completely in solid solution. Zr acts as a grain refiner, and for this reason the ZK60 exhibits a fine grain size [20]. Again, Equation (7) with the same values of the parameters was used. The simple substitution of the relevant grain size results in an excellent description of the experimental data. Figure 5 shows an additional dataset obtained by Watanabe et al [21] by testing a ZK60 with ultra-fine grain sizes. All the data in the Figure were obtained by using continuous tests under constant strain rate or constant load. The analysis of Figure 5 confirms that the use of a p' exponent of 2 is more than adequate to quantify the grain size dependence of the strain rate at 200°C.

3.4 Effect of grain growth

The model Equation (7), in combination with Equations (5) and (6), gives an excellent description of the SRC data obtained by different authors on different materials. Yet, two major features still need to be clarified: i. the relevance of the n = 3 regime; viscous glide in many cases, in particular for fine-grained metals, is obscured by the concurring effect of GBS, which results in higher strain rates; ii. the quantification of the effect of grain growth during continuous tests.



a) b)

Figure 7. Strain rate vs stress for ZK60 with different grain sizes: a) data from [17]; b) data from [18].

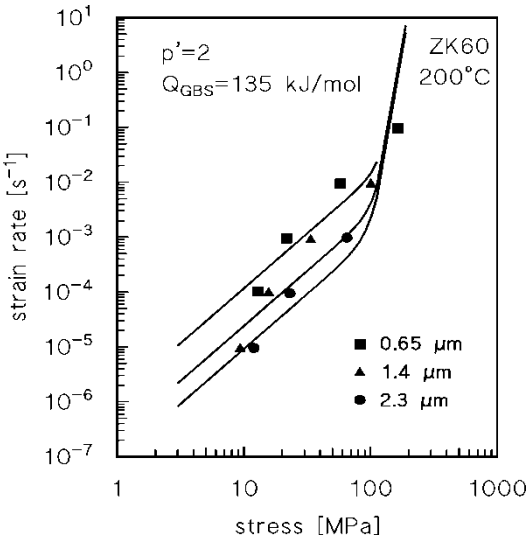
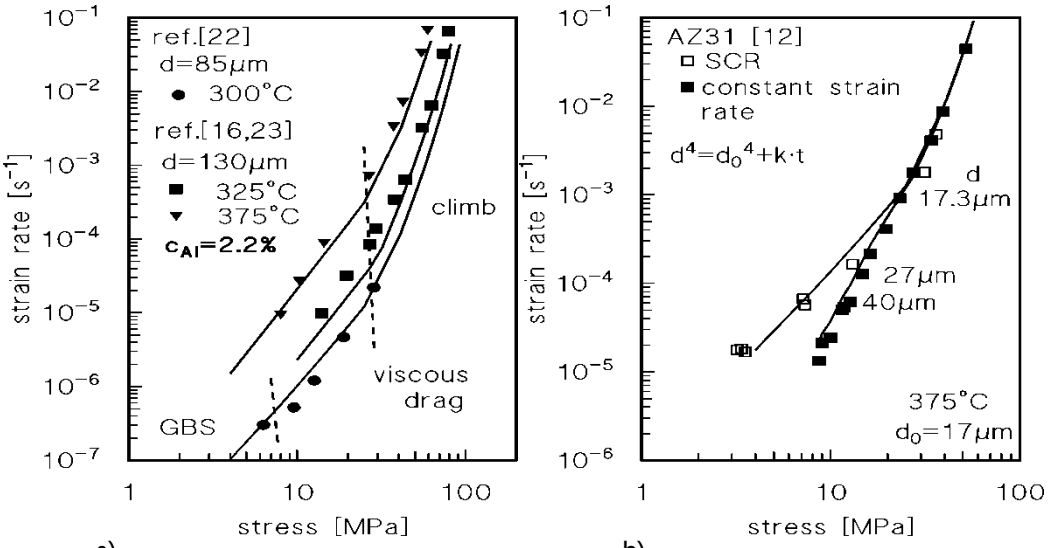


Figure 8. Strain rate vs stress for ZK60 with different grain sizes at 200°C [21].

The first issue is analysed in Figure 9a, which plots the data obtained by Kitazono et al [22], by Kim at al [16], and by Mukai et al [23] by testing AZ31 alloys with coarse grain size (d=85-130μm). The initial grain size was high enough to substantially reduce the potential effect of grain growth. The model Eqn.(7) describes very well the experimental data; the figure also reports the transitions stresses from viscous glide to dislocation climb, and from GBS to viscous glide, i.e. the applied stress corresponding to $\dot{\varepsilon}_{GBS} = \dot{\varepsilon}_d$. It can be easily observed that viscous glide is rate controlling in a relatively large range of applied stresses. This observation in turns demonstrates that high temperature deformation is controlled by viscous glide of dislocations in all those cases in which a relatively coarse-grained alloy is tested in the low-stress regime.



a) b)

Figure 9. a) Strain rate vs stress for the creep experiments on coarse grained AZ31 [16,22,23], and model curve; b) grain-growth corrected curve describing the AZ31 data obtained by continuous tests by del Valle et al. [12]. The Figure also reports the value of the grain size in correspondence of the peak flow stress in some of the experimental conditions.

The second issue, i.e. the effect of grain growth during continuous tests, is addressed in Figure 9b. Del Valle et al. measured the grain growth during a test at 375°C, under a strain rate of 5×10^{-5} s^{-1} [12]. These data permit to estimate the growth law, i.e. the dependence of the grain size on testing time *t*, which assumed the form:

$$d^4 = d_0^4 + Kt \qquad (8)$$

where d_0 was the initial grain size (17μm), and *K* a temperature-dependent constant. This relationship allows the estimation of the grain size in correspondence of the peak flow stress for the continuous curves carried out at this temperature. Substitution of the calculated *d* values into Eqn.(7) gives the model curve illustrated in the Figure. Again, the correlation is excellent; this simple analysis unambiguously confirms that the combination of constitutive equations (5), (6) and (7) is able to describe, in a wide range of temperature and applied stresses, the high temperature behaviour of magnesium alloys, once the grain size instability is properly taken into account. The use of Eqn.(7) also allows to quantification of the grain growth occurring during a standard SCR test at 375°C. A SRC experiment, in the form used by del Valle and co-workers and described in [12,15], typically consists in an initial deformation under a high strain rate (10^{-3} s^{-1}), followed by a jump down to 10^{-5} s^{-1}. Subsequently, the strain rate is increased in successive jumps; at the end of the test, the grain size calculated by Eqn.(7) increases from 17 to 18.4 μm, i.e. grain growth is almost negligible.

The above discussion demonstrates that a rationalization of the different experimental behaviour observed by testing Mg alloy is possible, once the different microstructural parameters (grain size and concentration of elements in solid solution) are considered and quantified. Moreover, a deformation mechanisms map can be drawn by combining the

constitutive equations for the various mechanisms (Figure 10). The Figure is only a representative example, which was obtained for Mg-Al alloys at 300°C.

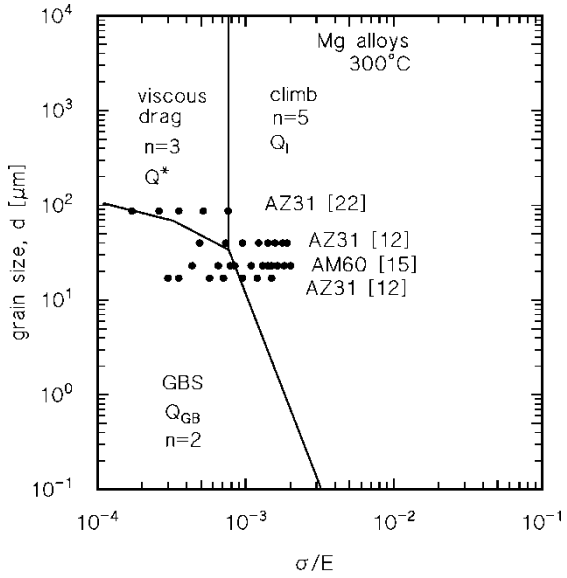


Figure 10. Deformation mechanisms map for Mg-Al alloys at 300°C by Eqns. (5)-(7).

4 Conclusions. The study of microstructural stability of the alloy AZ31 Mg, thermally treated under static conditions (in absence of applied stress), has shown that the structure remains almost unaltered for samples treated at 100 °C and 200 °C. The specimens have a structure which is relatively homogeneous, equiaxed and do not present a significant growth of grain, probably also due to recovery processes and static recrystallization which lead to the nucleation of new grains.
At 300 °C and over 4 hours of treatment, are observed the first transformations of the grains with a competitive growth and their coalescence to assumed a coarse size.
The profiles of Vickers microhardness tests confirm the results of metallographic tests, indicating a behavior of the alloy substantially stable at the temperatures of 100 and 200 °C and a slight variation of the hardness to 300 °C.
Once studied the static stability of the alloy, it has gone to make an appropriate integration of the traditional constitutive equations (Norton and Garofalo) to take account of the effects of chemical composition and grain size on the properties in the creep regime in which it is governed by the dislocations, which has led to a modified version of the equation of Garofalo. This form was further supplemented with the contribution of the sliding grain boundary, as it was found that the global mechanism of plastic deformation may be the result of different mechanisms concomitant.
Once selected the theoretical values for the activation energy for self-diffusion, by diffusion of Al in Mg and by diffusion at grain boundary and using the same values for the constants A, A* and AGBS, it has gone to apply the definitive constitutive model analyzing its accuracy in describing the creep response of different Mg alloys. The correlation between the curves of the model and the experimental data obtained from the literature was excellent.
The research concludes providing a system of constitutive equations that are able to describe the response to creep of Mg alloys. Further investigation could be taken to give add-

ed value and better accuracy of these models on various topics that may govern the deformation as the role of textures.

References

[1] Yavari P, Langdon TG (1982) *An examination of the breakdown in creep by viscous glide in solid solution alloys at high stresses*, Acta Metall. 30:2181-2196.

[2] Spigarelli S, El Mehtedi M (2010) *Creep as an extension of cold working: A unified approach to high temperature deformation of AZ31 Magnesium alloy*. Mater. Sci. Eng. A527: 5708-5714.

[3] Spigarelli S (2008) *Constitutive equations in creep of Mg-Al alloys*, Mater. Sci. Eng. A492:153-160.

[4] Spigarelli S et al (2011) *Effect of grain size on high temperature deformation of AZ31 alloy*, Mater. Sci. Eng. A528:6819-6826.

[5] Bardi F et al (2003) *An analysis of hot deformation of an Al-Cu-Mg alloy produced by powder metallurgy*, Mater. Sci. Eng. A339:43-52.

[6] S. Spigarelli et al. (2003) *A study of the hot formability of an Al-Cu-Mg-Zr alloy*, J. Mater. Sci. 38:81-88.

[7] Sato H, Oikawa H (1991) *Transition of creep characteristics of HCP Mg-Al solid solutions at 600-650K*. In Brandon DG et al (Eds) Strength of Metals and Alloys, Freund, London, 463-470.

[8] Spigarelli S, El Mehtedi M (2009) *Constitutive equations in creep of wrought Mg-Zn alloys*, Mater. Sci. Eng. A527:126-131.

[9] Kitazono K et al (2001) *Internal stress superplasticity in polycrystalline AZ31 magnesium alloy*, Scripta Mater. 44:2695-2702.

[10] Somekawa H et al (2005) *Dislocation creep behavior in Mg–Al–Zn alloys*. Mater. Sci. Eng. A407: 53-61.

[11] Kim H-K, Kim W-J (2007) *Creep behavior of AZ31 magnesium alloy in low temperature range between 423 K and 473 K*, J. Mater. Sci. 42:6171-6176.

[12] Del Valle JA et al (2005) *Deformation Mechanisms Responsible for the High Ductility in a Mg AZ31 Alloy Analyzed by Electron Backscattered Diffraction*. Metall. Mater. Trans. 36A: 1427-1438.

[13] Milicka K (2008) *Creep threshold of a Mg-4Al-1Ca alloy*, Kov. Mater. 46:323-329.

[14] Spigarelli S, El Mehtedi M (2009) *Microstructure-related equations for the constitutive analysis of creep in magnesium alloys*, Scripta Mater. 61:729-733.

[15] Del Valle JA, Ruano OA (2007) *Separate contribution of texture and grain size on the creep mechanisms in a fine-grained magnesium alloy*, Acta Mater. 55:455-466.

[16] Kim WJ et al (2001) *Superplasticity in thin magnesium alloy sheets and deformation mechanisms maps for magnesium alloys at elevated temperatures*, Acta Mater. 49: 3337-3343.

[17] Watanabe H, Mukai T (1999) *Superplasticity in a ZK60 magnesium alloy at low temperature*, Scripta Mater. 40:477-484.

[18] Galiyev A et al (2001) *Correlation of plastic deformation and dynamic recrystallization in magnesium alloy ZK60*, Acta Mater. 49: 1199-1207.

[19] Spigarelli S et al (2010) *Enhanced plasticity and creep in an extruded Mg–Zn–Zr alloy*, Scripta Mater. 63: 617–620.

[20] Lee YC et al (2000) *The role of solute in grain refinement of Magnesium*, Metall. Mater. Trans. 33A:2895-2906.

[21] Watanabe H et al (2001) *Realization of high-strain rate superplasticity at low temperatures in a Mg-Zn-Zr alloy*. Mater. Sci. Eng. A307:119-128.

[22] Kitazono K et al (2001) *Internal stress superplasticity in polycrystalline AZ31 magnesium alloy*, Scripta Mater. 44: 2695-2702.

[23] Mukai T. et al (2000) *Experimental Study of The Mechanical Properties at Elevated Temperatures in Commercial Mg-Al-Zn Alloys for Superplastic Forming*, Key Engineering Materials. 171–174: 337-342.