Creep behaviour of Deep Cryogenic Treated AZ91 Magnesium alloy

E. Gariboldi, Q. Ge, N. Lecis – Politecnico di Milano – Italy
S. Spigarelli, M. El Mehtedi – Università Politecnica delle Marche – Italy

ABSTRACT

The Deep Cryogenic Treatment (DCT) is known to have beneficial effects on mechanical behavior/properties of some alloys. It was also reported to be beneficial for the creep strength of Mg alloys. The present study is aimed at checking the effect of DCT on the high temperature behaviour of the Mg alloy AZ91 by means of comparative creep tests at 100 and 200°C carried out on high pressure die-cast specimens. In addition, the role played by initial microstructure was investigated by comparative creep tests on annealed and solution treated specimens. The mechanical tests were joined to optical and scanning electron microscopy observations on the creep specimens prior and after their high temperature exposure and to Differential Scanning Calorimetry analyses to investigate the thermal stability and the microstructural evolution of the alloy. The investigations results demonstrated that the effect of initial microstructure is by far more important for the creep properties of the Az91 alloy than the cryogenic treatment. DSC analyses revealed to be a useful tool to get information on the microstructural stability in view of the development of microstructure-based creep models.

RIASSUNTO

È noto che il trattamento criogenico (Deep Cryogenic Treatment, DCT) ha effetti benefici sul comportamento meccanico di alcune leghe. Esso è stato proposto anche per migliorare la resistenza a creep di leghe di magnesio. L'articolo riporta i risultati di uno studio sperimentale inteso a verificare questa possibilità per la lega di Mg AZ91. L'indagine ha anche considerato l'effetto della diversa condizione microstrutturale iniziale della lega confrontando il comportamento a creep a 100 e 200°C di provini pressocolati con quello di provini successivamente soggetti a trattamento termico. La stabilità microstrutturale della lega AZ91 è stata indagata sia mediante osservazioni microstrutturali, sia mediante prove di calorimetria differenziale a scansione (DSC). I risultati dello studio hanno dimostrato che il ruolo svolto dal trattamento criogenico è ben inferiore rispetto a quello della condizione microstrutturale iniziale, ricollegabile ad esempio al processo di ottenimento dei componenti. Le analisi DSC, poco onerose in termici di tempo e di materiale, hanno consentito di fare valutazioni sulla stabilità microstrutturale della lega nelle varie condizioni. I risultati di queste analisi possono fornire utili informazioni per lo sviluppo di modelli di comportamento a creep che includano le caratteristiche microstrutturali iniziali delle leghe.

KEYWORDS

Magnesium AZ91, creep, deep cryogenic treatment, DSC, thermal stability.

INTRODUCTION

Heat treatments carried out at low temperatures consist in the cooling and holding a material below room temperature. Industrially, on a lab-scale, the sub-zero heat treatment can be performed using dry ice as cooling agent for treatment temperatures down to about -80°C. Alternatively, spraying or immersing the component into a liquefied gas is possible. In case of liquefied nitrogen the holding temperatures can be as low as -192°C. Treatments carried out below -80°C are typically classifieds as cryogenic treatments, while those close to the liquefied nitrogen temperature are referred as deep cryogenic treatment (DCT) [1].

Sub-zero treatments are well known to have beneficial effects on the mechanical behaviour of alloys such as tool steels, for which [1-2] they typically increase the final amount of martensite, but can also reduce excessive thermal stresses by means of controlled cooling and heating rates [2]. Beneficial effects have been observed also in other alloys undergoing martensitic transformations [3].

Recent investigations on the effects of DCT were also carried out on austenitic stainless steels (see [4] as an example) while, in the author's knowledge, no recent work dealing with effects DCT was published in literature for Al or Mg alloys apart from a work on a die-cast Mg alloy [5].

Asl and co-workers [5] suggested that DCT can improve the mechanical properties, and in particular the creep strength, of one of the most applied Mg alloys, i.e. AZ91, containing 9%Al, 1%Zn as alloying element. This alloy, as other based on the Mg-Al system, is of interest in the aerospace and automotive application due to their low density. Unfortunately, the good property combines with a relatively low ductility related to the HCP crystal structure of magnesium. Additionally the melting temperatures of most Mg-Al alloys do not exceed 600°C, resulting in poor creep strength and, from a practical point of view, in maximum service temperatures not exceeding 100°C. In this context the results proposed by Asl and co-workers, i.e. that holding an AZ91 alloy at -198°C for 20 h leads to a substantial decrease of the minimum creep rate at 200°C with respect to the untreated alloy, could be of industrial interest and worth to be deeply investigated.

In AZ91 alloy, which microstructure is typically made of primary α grains surrounded by (α+β) divorced eutectic, the origin of this strengthening effect was attributed to changes in the morphology of the β particles, where β is the name given to the intermetallic phase $Mg_{17}Al_{12}$ resulting in a reduction of the propagation rate of the existing defects. The explanation does not sound fully convincing, and thus additional investigations should be addressed to verify and explain the role of DCT on the microstructure and creep behaviour of die-cast alloys.

The present study is aimed at checking the effect of DCC treatment on the high temperature behaviour of the same Mg AZ91 alloy by means of comparative creep tests carried out on DCT or simply high pressure die-cast specimens. In addition the role played by initial microstructure will be investigated by comparative creep tests on annealed and solution treated specimens. The thermal stability of the different conditions will also be investigated.

MATERIALS AND EXPERIMENTAL

AZ91 alloy cylindrical tensile testing bars characterized by gauge diameter and length of 5 and 35 mm, respectively, were produced by high-pressure die-casting. Part of the bars was then heat treated to obtain two microstructural conditions in addition to the as-cast one. A set of specimens was solution treated by holding it at 400°C for 4h (ST400 condition). Another set of specimens was annealed at 300°C for 4h (AT300 condition).

Bars of each microstructural condition were then deep cryogenic treated by means of an industrial plant. The cooling from Room Temperature down to the liquid nitrogen temperature was performed at a controlled rate of 0.7°C/min, the holding period at about -192 °C lasted 24 h and then the specimens were heated back to RT at a controlled heating rate of 0.5 °C/min. The thermal cycle, here presented in Figure 1, is not far from that obtained by means of lab-scale equipment by Asl and co-workers [5].

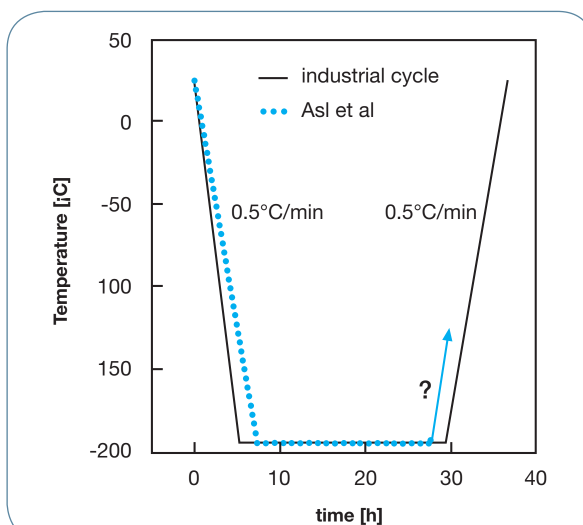

Fig. 1: Controlled thermal cycles followed by the AZ91 creep specimens during the deep cryogenic treatment in the present and Asl [5] studies (solid and dotted lines, respectively).

Creep specimens were then obtained from bars by machining their gripping ends both to fit the loading train of creep machines and to locate the extensometer gripping system. Short-term creep tests were performed on lever-arm machines at 100 and 200°C for times up to 500h.

Some material was sampled from the gripping ends of the specimens crept for longer times to perform microstructural (LOM and SEM) observations and Differential Scanning Calorimetry (DSC) analyses, comparing the results with those on the corresponding initial microstructural condition.

DSC tests were performed with a Setaram Labsys TG-DTA system, equipped with a detector configured for DSC analyses in a temperature range from RT up to 800°C and fluxed with nitrogen. These tests samples (about 60 mg each) were heated at 20 and 40°C/min from RT to 500°C, then cooled back to room temperature at 20°C/min.

RESULTS

The creep bars of AZ91 alloy in the as cast condition (AC) were characterized by a fine microstructure (Figure 2a and 4 in LOM and SEM micrographs at low and high magnification, respectively). The rapid cooling of this Mg-Al alloy with Al content lower than that of maximum solubility in Mg (12.6 mass%) led first to the separation of pro-eutectic α-Mg, progressively richer in Al, with coring effects. The completion of solidification occurred at the eutectic temperature (437°C), at which divorced eutectic including β-Mg17Al12 and α-Mg phases formed. The latter phase formed at eutectic temperature is a supersaturated solid solution of Al in Mg (Al~12%), and will be referred as indicated as α^* to distinguish it from proeutectic α-Mg, significantly poorer in Al in its core. Further cooling to room temperature caused some fine secondary β-particles precipitation from Al-rich regions. The resulting distribution of β-phase in the as cast condition is thus highly inhomogeneous, since large particles and several fine precipitates can be observed in the region of divorced eutectic and a few fine particles can be found in cored primary α-Mg grains.

The microstructure of the material in AT300 condition was more complex (Figure 2b and 4). β-particles in the divorced eutectic slightly increased their size with respect to the AC microstructure. Additionally, some relatively coarse secondary β-particles were noticed. Further, reasonably the average amount of Al in α solid solution, tending to equilibrium at 300°C, was higher than in the as die-cast material.

After solution treatment at 400°C (ST400) the microstructure was substantially homogeneous (Figure 2c), and consisted only of α-Mg phases. Thus, in this microstructural condition, α phase has the same chemical composition of the alloy, intermediate between that of the supersaturated α^* within divorced eutectic in the same condition and that of the core of primary α-Mg grains in AC condition.

LOM micrographs (Figure 2d and 2e) suggest that deep cryogenic treatment did not alter the above microstructures. The only difference revealed

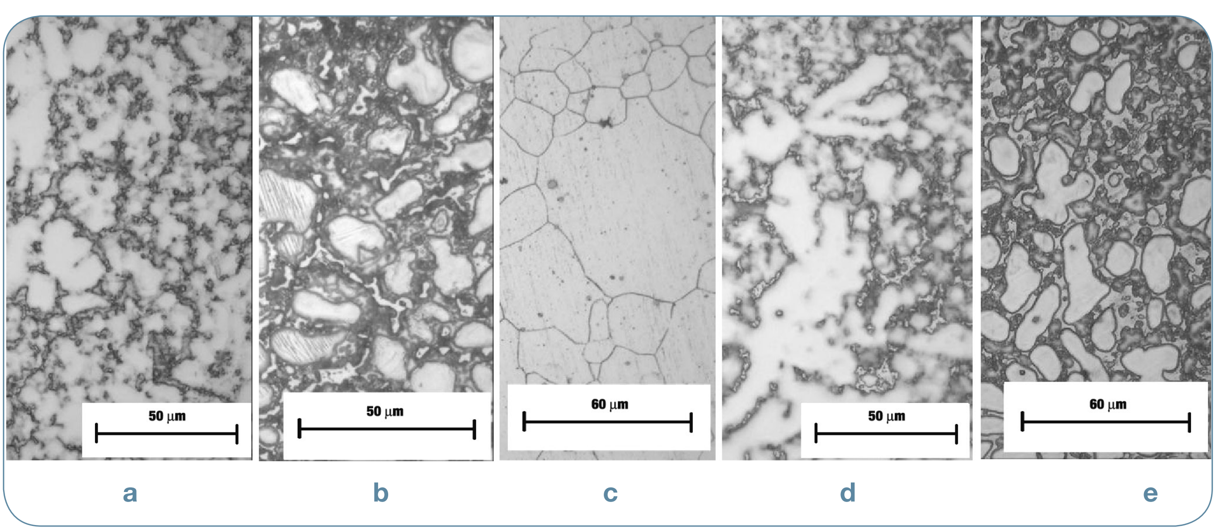

Fig. 2: Light optical micrographs of the AZ91 alloy in different microstructural conditions. a) as die- cast (AC), b) annealed at 300°C for 4h (AT300), c) solution treated at 400°C for 4h (ST400), and in conditions a and b followed by deep cryogenic treatment (AC+DCT and AT300+DCT, shown in figures d and e, respectively).

by SEM observations was the presence of very fine precipitates (reasonably of β phase) in the supersaturated α* phase in the AC+DCT sample (Figure 4).

The main creep properties of the investigated alloy tested in different microstructural conditions are presented in Figures 3a and 3b in terms of the classical stress vs. time to rupture and strain rate vs. stress double logarithmic plots, respectively. It is clear that the creep properties of the AC condition tested with and without DCT are substantially the same, either at 200°C, temperature at which literature data were available for comparison purposes, and at 100°C. Creep ductility, expressed in terms of reduction of area, is of 18-20%, slightly lower for the tests carried out at 200°C. Results corresponding to other initial conditions confirmed the close creep properties of the material prior and after DCT.

The creep strength of the solution treated specimens was slightly higher than that of as cast specimens for short-test duration, slightly lower for test durations exceeding 50 h. The stress-dependence index (Norton's index) derived as the slope of the curves in the stress-strain rate plot is about 3.5 for specimens solution treated at 400°C, while for the AC specimens tested at the same temperature and stress range it is of about 5 (5,4 and 4,8 for specimen with and without DCT). At 100°C the Norton's index of AC and AC+DCT condition increased to about 10.

In the short-time range (at the highest investigated stress levels) specimens heat treated at 300 °C behaved similarly to the AC ones, but they progressively lost creep strength both with respect to AC and ST400 specimens. The slope of the curves in the stress-strain rate plot decreased with applied stress. Under this microstructural condition the final reduction of area of the material was about 23%.

The microstructural stability of the material was investigated in the reference condition (AC) and in that annealed at 300°C; in the latter case the microstructure should be quite similar to that resulting from that of cast parts a slower solidification and cooling rate. The exposure time of these specimens, tested at the minimum stress level for each microstructural condition, were in some cases rather different, ranging from 70 to more than 450 h. SEM micrographs of the specimen prior and after creep testing are presented in Figure 4.

After exposure at 200°C the formerly α* regions of the AC and AC+DCT specimens presented a very high density of fine precipitates of β-phase. The precipitation (but a concurrent coarsening of previous extremely fine particles cannot be excluded) extended also in regions of primary α grains initially containing relatively high Al content and located close to the eutectic. The formation of an high amount of β-phase locally reduced the Al-content in solid solution to that in equilibrium at 200°C. Nevertheless, the exposure time at this temperature was far from being sufficient to homogenize the Al content within primary α grains and Al remained at very low levels at their core.

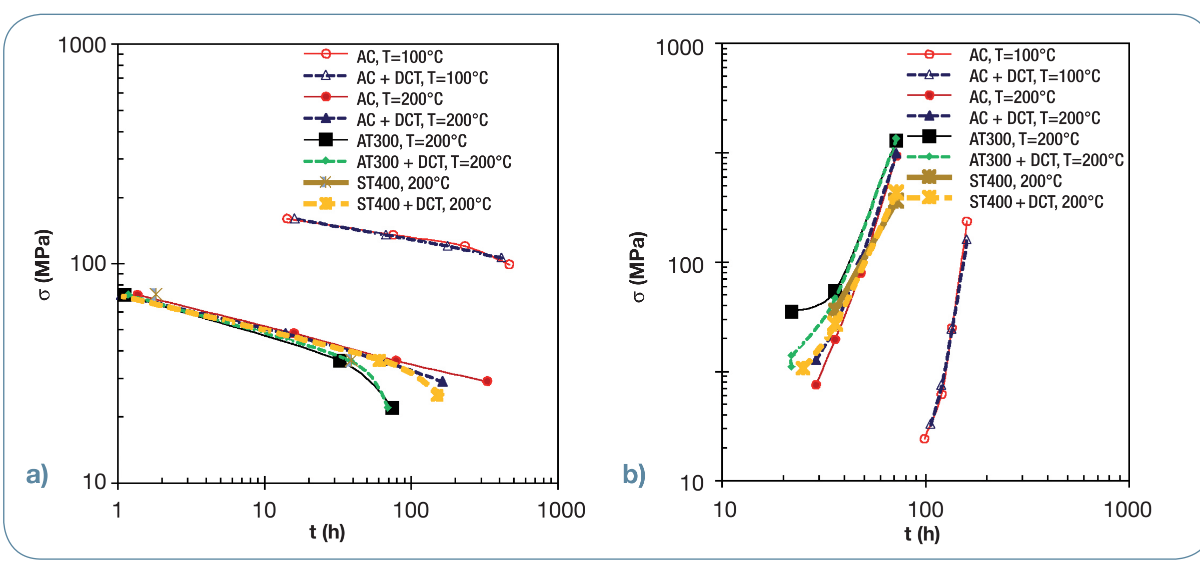

Fig. 3: Results of creep tests in terms of stress vs. time to rupture (a) and minimum strain rate vs. stress (b).

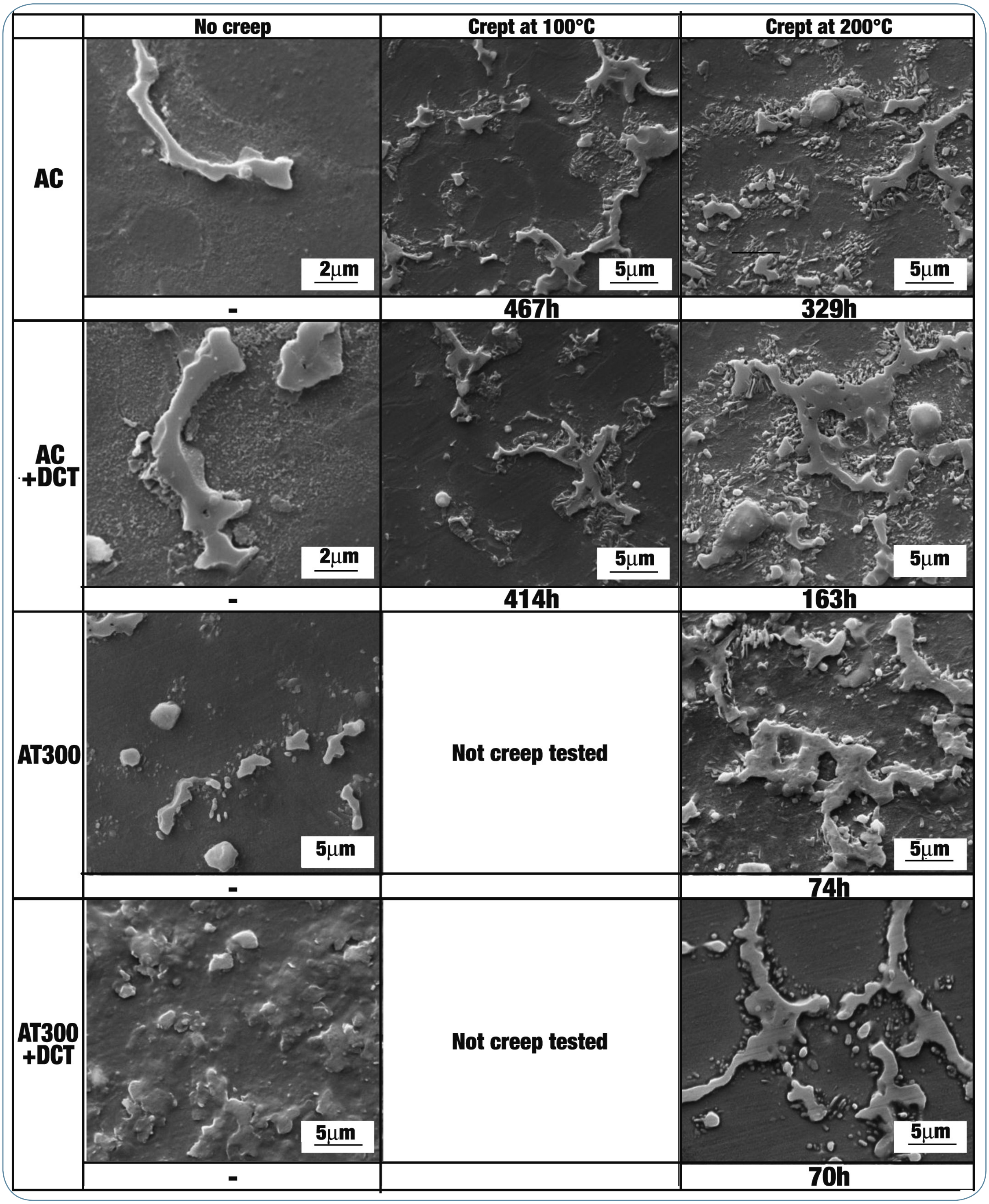

Fig. 4: Microstructures of the AZ91 alloy in different initial microstructural conditions prior and after exposure at high temperature during creep tests.

When the same AC and AC+DCT materials were exposed at 100°C, for even longer times, very fine β- precipitates formed only within the formerly α^* regions in divorced eutectic, where supersaturation of Al is very high. Reasonably the Al distribution within primary α grains remained close to the initial one.

The exposure at 200°C of the material previously annealed caused a further evolution of the microstructure. Due to the only partial homogenization occurred at 300°C and to the higher solubility of Al in α at 300°C with respect to that at the creep one, some fine β-particles formed in Al-rich α phase. Their amount seemed to be lower in material further subjected to a DCT treatment before creep tests.

The heat flow heating curves of DSC runs carried out at 20 and 40 °C/min are presented in Figures 5a and 5b, respectively. Some endothermic events, corresponding to downward deviations of the curves, can be observed: a broad peak at temperatures between 340 and about 470°C (B) to which a sharp peak at about 440°C (C) overlaps. Finally, an endothermic deviation at about 480°C can be interpreted as part of a fourth, large peak (D). A broad exothermic peak (A) is also suggested at temperatures around 300°C. Different microstructural conditions affected the temperature and/or enthalpies associated to the peaks and, in some cases, even their presence. The onset/ending temperatures of events A and B cannot be easily identified as a consequence of the wide compositional ranges of the α phase that made the associated transformation concurrently occur in different regions of the same DSC sample. Further, most peaks are more evident when thermal scans were performed at higher heating rate and the inhomogeneous material has less time to evolve toward structures of equilibrium at each temperature.

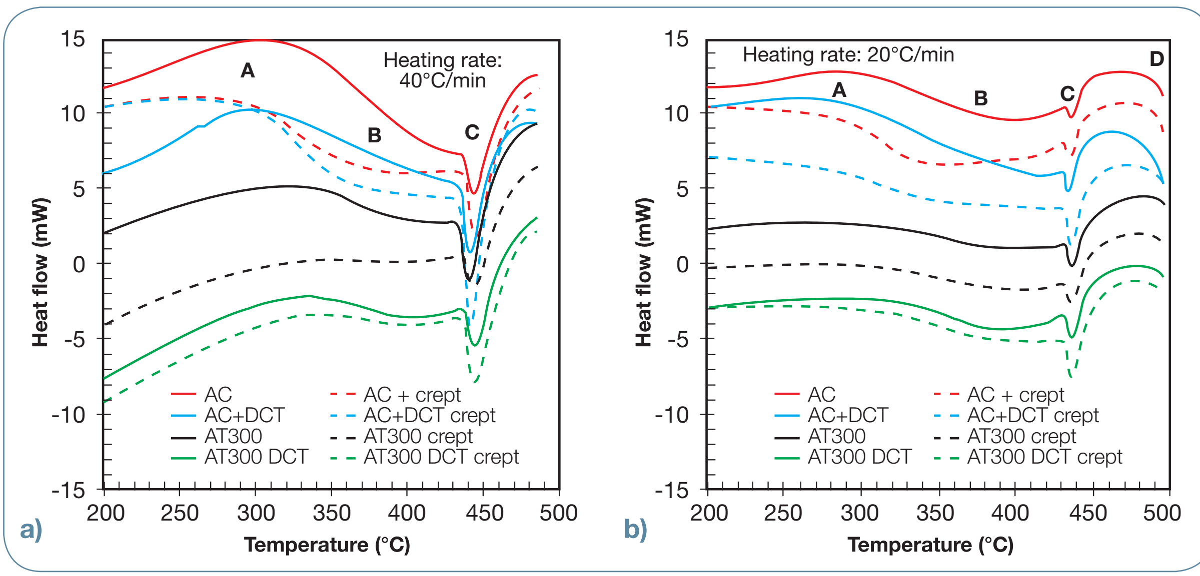

Fig. 5: Heat flow curves of DSC runs performed at heating rates of 40 °C/min (a) and 20 °C/min (b) on samples in different microstructural conditions prior and after creep tests at 200°C. In both figures the heat flow curves were vertically shifted for comparison purposes.

Clear similarities can be observed between heat flow curves corresponding to the same heat treatment but with and without a further DCT. Also the effect of high temperature exposure during creep tests is roughly the same for specimen with or without DCT, with the only exception of a slight shift toward higher temperatures of peak B observed in the AC+ DCT condition (crept for far shorter time).

In the AC and AC+DCT conditions, all four peaks appear in the corresponding DSC curves , while after the prolonged exposure at 200°C during creep tests the broad peak A is substantially absent, while the second seems is shifted towards lower temperatures.

Focusing the attention on the curves corresponding to the annealed samples (AT300, AT300+DCT), peak A is less evident than in as cast samples and shifter to higher temperatures, peak B is less pronounced too, while peaks C is substantially unaltered, and the onset of peak D is slightly shifted towards higher temperatures.

DISCUSSION

The microstructures of AZ91 alloy investigated ranged from that of rapidly cooled as cast (AC) parts, where non-equilibrium divorced eutectic surrounded primary α grains with severe coring effects, to those of completely homogeneous α grains after solution treatment at 400°C. The effects of deep cryogenic treatment on all these microstructures were slightly visible in SEM analyses only in the AC condition, where they corresponded to the presence of extremely fine precipitates in the α* phase.

DSC analyses, joined with microstructural observations can help understanding the presence of microstructural changes induced by DCT, as well as those occurred during heat treatments or exposure at high temperature.

The heat flow curves in the AC condition can be easily commented on the basis of the study carried out by Bassani et al. [6] on the microstructural stability of high pressure die-cast specimens of AM60 alloy. The alloy, namely containing 6% Mg and less than 0.5%Mn as alloying elements, falls in the same region of the Mg-Al phase diagrams of AZ91 alloy. Thus, they have similar equilibrium and non-equilibrium structures, even with differences in the amount, composition and transformation temperatures.

- Peak A (exothermic) could be related to the formation of fine β-precipitates, more abundant in the α regions rich of Al.
- Peak B can be associated to the dissolution of the β-Mg17Al12 phase at grain boundaries and to the redistribution of Al in the α-Mg matrix. The dissolution of β phase and the concurrent smoothing of coring effects characteristics of the AC structure is more efficient in DSC runs carried out at low heating rate. Peaks A and B can partly overlap, being both precipitation and dissolution temperature ranges related to local composition, this latter widely inhomogeneous in the investigated alloy, particularly in the AC and AC+DCT conditions.
- The sharp peak C is a typical melting peak. At this temperature, very close to the eutectic temperature, the divorced eutectic melts. Peak C is less pronounced at low heating rate, since the volume of eutectic regions has been severely reduced by phenomena occurring at lower temperature. Even slower heating rates would have probably led to the absence of this peak.
- Finally, peak D is another melting peak. Its onset temperature, lower than that for the nominal alloy composition (about 515°C) is related to the inhomogeneous Al distribution still left after overcoming peak C temperatures. As a matter of fact, high-Al regions having about 12%Al can start melting at temperatures of as low as 450 °C.

Taking into account the phenomena corresponding to the above thermal events, the less marked peak A and the anticipated onset of peak B in AC+DCT curve with respect to AC curve could reasonably correspond to a less marked formation of β precipitates in a material where very fine particles of this phase formed during DCT.

In the annealed specimens where, although coring effects were not completely cancelled, locally in regions of high Al content α phase reached its equilibrium composition at 300°C by the formation of β phase in fine particles or adding to the existing eutectic particles. Peaks A and B corresponding to AT300 and AT300+DCT were thus not particularly evident and shifted toward at high temperatures due to a limited formation and then dissolution of fine β particles. DCT following annealing did not substantially change the heat flow curve response of the annealed material, suggesting similar microstructural features.

The heat flow curves of the materials crept at 200°C reveal the evolution of material occurred during creep test. Peak A disappeared in DSC curves of AC crept and AC+DCT crept conditions, reasonably as a result of the previous occurrence of the precipitation of fine β particles. The partial Al homogenization induced by the high-temperature exposure at 200°C (particularly long in specimen AC) smoothed and anticipated the visible onset of peak B, corresponding to a reduced amount of dissolved β particles.

The main effect of temperature exposure on AT300 and AT300+DCT conditions, as revealed by

comparisons of the corresponding crept/uncrept heat flow curves, is simply the completion of fine β precipitation needed to locally reach the equilibrium at 200°C. This is the reason for the absence of the corresponding peak A in the curves of the annealed and later crept material. The coarsening of secondary β precipitates in crept condition is the cause of the moderate shift of peak B to higher temperatures in annealed and crept conditions. On the other hand, the time spent at 200°C was not sufficient to homogenize the composition on the grain-size scale and peak C confirms the presence of an amount eutectic structure similar to that of the AC structure. All in all, the thermal stability of the alloy heat treated at 300°C is relatively good.

Moving now to the creep properties of the AZ91 alloy in the investigated microstructural conditions it can be stated that deep cryogenic treatment does not significantly influence the rupture times and minimum strain rate at a given temperature and under a defined applied stress of the as cast AZ91 alloy. Rather, a weak tendency to have lower times to rupture and higher minimum strain rates and rate after DCT can be, with some difficulty, envisaged from a close analysis of Figures 3a and 3b, respectively.

In order to clarify the effect of microstructure on the creep properties by comparing experimental to literature data available over a more extended range of strain rates, these latter were temperature-normalized considering an Arrhenius-type dependence of the strain rate, taking into account as activation energy Q that of self-diffusion of Mg, 135kJ/mol [7]. It was thus obtained the graph presented in Figure 6. Here experimental data in the AC and AC+DCT conditions obtained by creep tests performed at 100 and 200°C roughly lay on the same curve. In the very high stress region, the data obtained by the present study are close to with the curve of minimum creep rate data presented by Somekawa et al. [8] for AZ91 tested after annealing at 300°C. In the intermediate stress range the normalized strain rate data are not far from the curve obtained by Sklenicka et al. [9] for the same alloy in the T6 condition. On the other hand, a deviation from the latter curve is observed for applied stresses lower than 70 MPa. In this low stress regime, the response of the alloy is particularly sensitive to the initial state, while DCT does not play any important role. This behaviour is fully consistent with the observation given by Spigarelli in [10] where it was suggested that the content of alloying elements in solid solution and the size and distribution of the precipitates are the key factors to understand the variation in the mechanical response of the alloy.

The peculiar microstructure of die-cast Mg alloys strongly affects their creep behavior. A detailed discussion on this point is given in [9] and the reader can refer to this paper, where a microstructure-based constitutive model for this class of alloys was also proposed. The application of the model to the present case is beyond the aims of the present paper. Nevertheless, the information on the microstructural changes occurred during creep tests derived by thermal stability studies of the AZ91 alloy can help to better understand and model the creep behavior of this class of material alloys, as they did for heat treatable Al alloys [11-12].

The effect of heat treatments on the creep properties of the AZ91 alloy is far more important than that of the following DCT treatment. This behavior substantially conflicts with the previously mentioned data available in the literature for the same alloy [4], here rearranged in terms of the normalized strain rate and shown in Figure 6. Data in the AC condition substantially agree both with the present experimental and the other literature curves. On the other hand, after deep cryogenic treatment literature data revealed a far lower creep strain rate. This exceptional performance of DCT treated AZ91 specimens seems dubious, even considering possible microstructural differences with respect to the presently investigated AC and AC+DCT conditions related to the fact that the AZ91 alloy tested by Asl and co-workers was produced and DCT using lab-scale equipment. The role played by DCT was in fact here proved to be minimal with respect to that induced by initial microstructural changes.

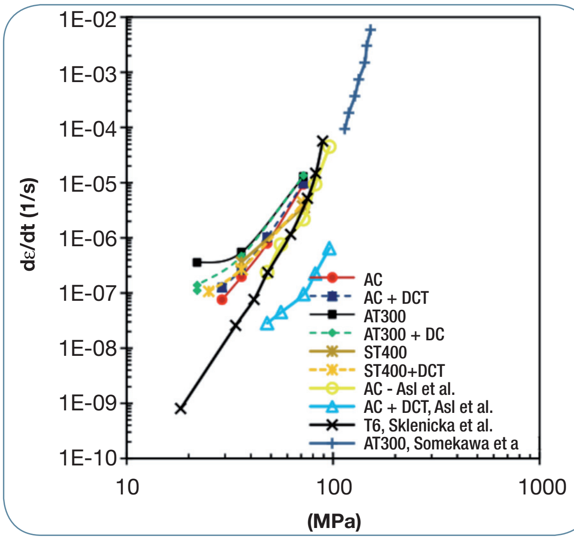

Fig. 6: Comparison between the present and literature creep data of AZ91 alloy temperature- normalized minimum creep strain rate vs. stress plot.

CONCLUSIONS

The effect of DCT on the creep response and microstructural stability of an AZ91 magnesium alloy produced by die-casting was investigated at 100 and 200°C. Deep Cryogenic Treatment played a negligible role on the creep behaviour of the Mg alloy not only in the as cast condition, but also when the alloy microstructure was modified by heat treating prior to DCT. By contrast, the different creep response of the as cast, annealed and fully solution treated material underlined, once again, the importance of the initial microstructural condition on the high temperature behaviour of the die-cast Mg alloys. Differential Scanning Calorimetry runs and microstructural analyses confirmed the similarities of structures obtained with and without DCT. These analyses also revealed that the thermal stability of the alloy heat treated at 300°C is relatively good with respect to that of the material in the AC condition. Thus, DSC analyses on crept material could be a suitable source of information for the development of microstructure-based creep models for die-cast structures taking into account microstructural evolution.

REFERENCES

[1] D. DAS, A.K. DUTRA and K.K. RAY, Mater. Sci. ENG. A, 527 (2010) p. 2158-2163.

[2] V. FIROUZDOR, E. NEJATI, F. KHONNAMIZADEH, J. Mater. Proc. Technol. 206 (2008) p. 467-472.

[3] G.Z. MA, D. CHEN, Y. JIANG, W. LI, Intermetallics, 18 (2010) p. 1254-1257.

[4] P. BALDISSERA, Materials and design, 31 (2010) 4723-4730.

[5] K.M. ASL, A. TARI, F. KHOMAMIZADEH, Mater. Sci. Eng. A523 (2009) p. 27-31.

[6] P. BASSANI, E. GARIBOLDI, A. TUISSI, J. Thermal Anal. Calorim. 80 (2005) p. 739-747.

[7] S. S. VAGARALI, T.G. LANGDON, Acta Metall. 29 (1982) p. 1969-1982.

[8] H. SOMEKAWA, K. HIRAI, H. WATANABE, Y. TAKIGAWA, K. HIGASHI, Mater. Sci. Eng. A407 (2005) 53-61.

[9] V. SKLENICKA, T.G. LANGDON, J. Mater. Sci. 39 (2004) p. 1647-1652.

[10] S.SPIGARELLI, Mater. Sci. Eng., A 492 (2008) p. 153–160.

[11] G. ANGELLA, P. BASSANI, E. GARIBOLDI, D. RIPAMONTI, Aluminium Alloys, Proc. Conf., Ed. J. Hirsch, B. Skrotzki, G. Gottstein, Vol.1 (2008) p. 1062-1067.

[12] E. GARIBOLDI, F. CASARO, Mater. Sci. Eng. A462 (2007) p. 384-388.