On the aging of a hyper-eutectic Zn-Al alloy

A. Pola, M. Gelfi, G. M. La Vecchia, L. Montesano

Zinc alloys are widely used in different fields, like handles and locking, fashion and design as well as automotive or electronics, thanks to their good mechanical and technological properties combined with low cost and easy formability. A limit to a wider use of these alloys is the aging phenomenon that causes a drop in their mechanical properties in time. In order to improve their use in competition with more expensive copper and aluminum alloys, in the last years the research has been addressed to develop new Zn-alloys compositions. One of these new alloys, containing 15 wt% of Al and 1 wt% of Cu, appears to be suitable for both foundry and plastic deformation forming processes, as resulted from preliminary laboratory and industrial trials. Being a newly developed alloy, many properties have still to be investigated, to better understand the effective potentiality for proper industrial applications. In this paper the ageing behavior of die-cast Zn-15Al-1Cu hyper-eutectic alloy was studied by means of tensile tests and microstructural analyses. It was demonstrated that the alloy suffers from a drop in mechanical properties, in particular at the very beginning of soaking at high temperature. A first analysis of the microstructure by optical and scanning electron microscope was not able to fully point out the causes of the aging phenomenon.

Keywords: Zinc alloys - Aging - Die-casting - Mechanical properties

INTRODUCTION

Zinc aluminum alloys are used for the production of several functional items like hinge and small gears, and also design parts as handles, taps and fittings. These materials, in fact, guarantee a good compromise between performances and production costs. They also offer good corrosion and wear resistance. Additionally, zinc alloys can be coated with all the traditional deposition techniques improving their aspect according to the specific application [1].

Nowadays zinc aluminum alloys are also good candidates for the all the application fields where moderate mechanical resistance is required, for example as a substitutive material for bronze and brass components in home furnishing and fashion parts.

Zn-alloys can be also used for the production of bearing and bushings as they exhibit for such application high hardness, wear resistance similar to that of bronze and many properties comparable to those of cast steel [2-3]. Moreover these materials have a good machinability [3] that makes easy the manufacture of finished components with the correct tolerances.

The presence of aluminum, in proper percentage, promotes the fluidity of the alloy, increases the mechanical properties and enhances the corrosion resistance in mild aggressive environments. Copper, in percentage between 1 and 3 wt%, improves hardness, tensile strength, wear resistance and creep behavior of the material [4].

A. Pola, M. Gelfi, G. M. La Vecchia, L. Montesano
Università degli Studi di Brescia - DIMI

The main restrictions in using zinc alloys in structural applications are the high density (more than twice of aluminum and similar to that of steel) and the considerable drop of mechanical properties with temperature [5-6]. For this last reason the threshold temperature for the use of zinc alloys is commonly fixed at 80°C.

A further problem affecting zinc alloys is the formation of instable phases during solidification and cooling, able to evolve in time, also at temperature below 100°C [3]. Solid state transformations through much stable configurations can occur, causing a decrease of mechanical properties in time [5]. This drop of zinc alloys properties is normally known as aging.

Studies on conventional Zn-Al alloys aging showed that the phenomenon is enhanced by temperature. In particular, mechanical tests performed maintaining sample at 105°C for different times, showed that the maximum drop of properties occurs in the first 24h while for longer soaking times, the decrease is slower and the mechanical properties tend to set at constant values [6]. Based on these findings some components are artificially aged (24h at 105°C in the case of automotive parts [5]) before their use, in order to stabilize the properties and avoid further drop during the component life.

Fig. 1 shows the Zn-Al binary alloys phase diagram, where the main families of nowadays used Zn-alloys are highlighted. The most common alloys are the so called Zamak (Zamak2, 3 and 5), characterized by an aluminum content of 4% and a copper percentage in-between 0 and 3wt%. The low melting temperature of Zamak, close to 390°C, allows the use of hot chamber high pressure die-casting (HPDC). The hexagonal close packed lattice of these alloys makes them scarcely deformable and not suitable for hot stamping [7].

Other commercial alloys with higher aluminum and copper content are those belonging to the ZA family (ZA8, ZA12, ZA22, and the most widely used ZA27), which are characterized by higher mechanical properties than Zamak family [4]. The melting temperature of these alloys is higher than Zamak ones (over 410°C) and, for this reason, they should be cast only in cold chamber HPDC or in gravity or sand casting, with higher cycle time and costs.

Recently, a new zinc alloy with an aluminum content of 15wt% has been developed. This alloy is characterized by good mechanical properties and high corrosion resistance; it is also suitable for foundry (hot chamber HPDC) as well as hot stamping processes [6]. However, many properties are still not known or under investigation. The aim of this paper is to study the effect of artificial aging, carried out at different temperature and for different holding times, on the tensile properties of this new alloy.

MATERIALS AND METHODS

Tensile test samples in Zn-15Al-1Cu alloy were produced by hot chamber HPDC with a 500 ton machine. The alloy was injected into the die at a temperature of 490 ± 10°C, while mold temperature was set at 250°C. The obtained samples have a round section with a diameter of 9 mm.

Tensile tests were carried out at room temperature according to UNI EN ISO 6892 standard with a INSTRON 8501 machine, set in displacement control mode, with a cross head speed of 0.5 mm/min. Displacement was monitored by an extensometer.

Three samples per condition were tested.

Moreover, on one sample for each aging condition, the elastic modulus was determined with five load-unload cycles in the elastic field, setting a test speed of 0.1 mm/min.

The evolution of the mechanical properties during aging was studied at three different temperatures: 80, 105 and 130°C, and for different holding times up to 240h, as reported in Tab. I.

In the time between the alloy production and the aging treatment, all the samples were maintained at a temperature of -14°C in a freezer, in order to avoid any natural aging.

The “as-cast” samples were tested just after production to evaluate the mechanical properties in not aged conditions (0 hours of aging time, as referred in Tab. I).

Three groups of samples were considered, as a function of the heat treatment temperature. The temperature of 105°C (group A) was selected according to literature findings; in fact, Leis et al. evidenced that, for conventional zinc alloys, the Ultimate Tensile Stress (UTS) of specimens aged at this temperature is similar to that of samples naturally aged for one year [4]. Additionally, as already mentioned, many car producers suggest a pre-treatment of zinc components at 105° for 24 hours before their use, in order to stabilize the mechanical properties [5].

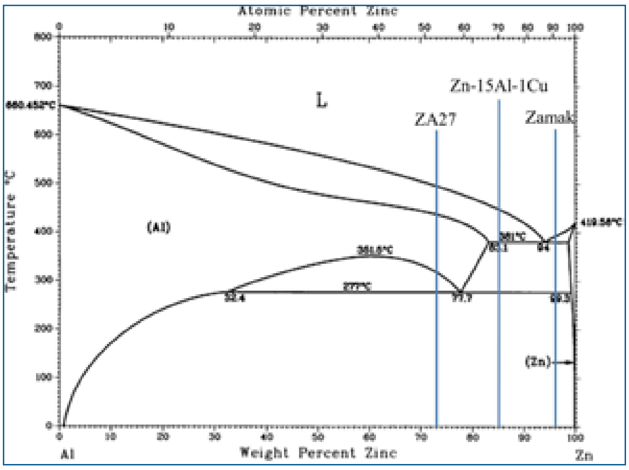


Fig. 1 - Zn-Al phase diagram [8].

The other two temperatures investigated in the present research were chosen 25°C above and below the reference temperature of 105°C. The temperature of 130°C (group B) was set to study the drop of properties at higher temperature, that probably happens with a faster kinetics. On the other hand, the temperature of 80°C (group C) is commonly accepted as the upper limit for the use of zinc alloys [9].

	Time [h]		Time [h]		Time [h]
GROUP A: T = 105°C	0	GROUP B: T = 130°C	0	GROUP C: T = 80°C	0
	1		2		1
	2		8		2
	4		24		4
	8		168		8
	15		240		24
	24				168
	72				240
	168				
	240				

Table. I - scheme of the tensile tests.

It is worth noting that the maximum aging time of 240 hours was chosen to be ten times higher tan to reach almost stable mechanical properties for the traditional zinc alloys [6].

In addition to the mechanical characterization, a microstructural analysis was performed on all samples polished and etched with Nital 2% by means of a Reichert-Jung MeF3 optical microscope, equipped with the Leica QWin image analyzer software. The chemical composition of Zn-Al phases was assessed by means of the Oxford Energy Dispersive Spectroscopy (EDS) microprobe, coupled to the LEO EVO 40 Scanning Electron Microscope (SEM).

	YS [MPa]			UTS [MPa]		
GROUP	A	B	C	A	B	C
t [h]	T=105°C	T=130°C	T=80°C	T=105°C	T=130°C	T=80°C
0	271±6.4			313±7.4		
1	261 ± 1,4		251 ± 4,2	300 ± 7,2		300 ± 0,9
2	248 ± 1,0	242 ± 1,5	255 ± 1,4	310 ± 6,6	306 ± 6,7	312 ± 4,6
4	248 ± 1,0		246 ± 0,7	310 ± 6,6		304 ± 0,4
8	245 ± 3,5	239 ± 3,6	246 ± 0,8	304 ± 0,4	299 ± 3,1	295 ± 6,0
15	246 ± 6,4			296 ± 3,3		
24	236 ± 0,1	225 ± 0,7	290 ± 4,5	295 ± 5,5	281 ± 1,3	290 ± 2,8
72	238 ± 4,6	210 ± 3,5		290 ± 3,8	271 ± 2,4	
168	228 ± 4,7	196 ± 2,1	249 ±5,1	281 ± 2,5	252 ± 3,6	298 ± 4,8
240	224 ±3,6	192 ± 1,2	246 ± 1,4	279 ± 3,5	248 ± 0,4	301 ± 6,3

Table. II - tensile tests results.

RESULTS

TENSILE TESTS

Table II shows the values of the UTS and Yield Strength (YS) of Zn-Al alloy samples artificially aged at different times and temperatures.

Fig. 2 shows the behavior of UTS as a function of the aging time. Similarly to what reported in literature for other zinc alloys [3], the new composition suffers from a strong drop of the mechanical properties in the first 24 hours of aging. Results from samples aged for longer time, however, reveal a further, even though slower, reduction of the UTS. The behavior of the YS is similar to that of the UTS.

For the same aging times, group B samples, i.e. those treated at higher temperature, show lower UTS than group A samples and the reduction of the mechanical properties occurs faster. Comparing the drop of the UTS, group A samples has a drop of 6% in the first 24 hours and 11% after 240 hours. For the group B samples the reduction is 10% in 24 hours and 21% after 240 hours. Finally, in the case of samples C, aged at 80°C, the maximum drop of the UTS after 240 hours is only 4%.

As shown in Fig. 2, the aging at 105°C for 240 hours gives similar UTS and YS values to those obtained at 130°C for 24 hours. From this experimental result, it follows that the same mechanical properties can be achieved lowering the aging time and increasing conveniently the heat treatment temperature. Such aging conditions can be reasonably accepted only if the cast part is not affected by high levels of porosity or other defects that can be modified or worsened by a long stay at high temperature. It should be also taken into account that a soaking at high temperature usually causes a a coarsening and globularizarion of the precipitates.

Finally, a last aging test was performed at 105°C for 720 hours (30 days), aimed at evaluating if a steady state condition of mechanical properties can be finally reached. The UTS and YS measured after this heat treatment were 245 MPa and 193 MPa respectively, which are values close to those obtained after the aging at 130°C for 240 hours, confirming the achievement of almost stable conditions.

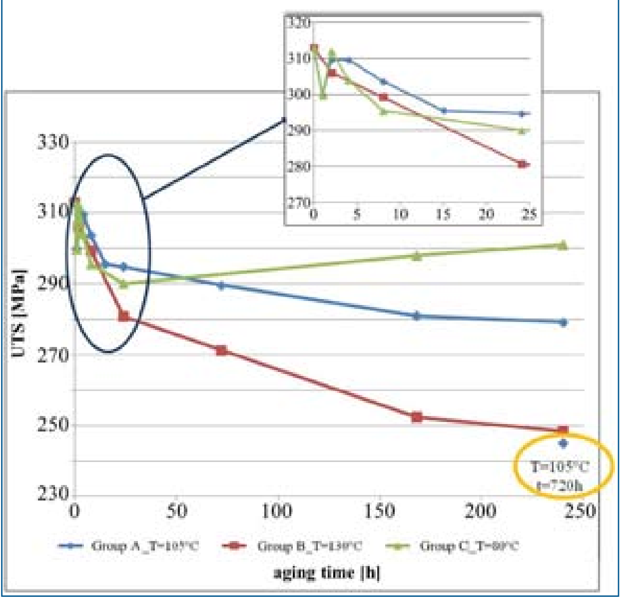


Fig. 2 - Ultimate tensile strength of Zn-Al samples versus aging time.

A conclusion that can be derived from this result is that a heat treatment at 105°C for 24 hours is not enough to reach a complete settlement of mechanical properties for a Zn-15-Al-1Cu alloy. To foresee the behavior of a component designed with this alloy for long service applications, the aging treatment should be performed at higher temperatures.

Additionally, tests carried out on samples aged at 80°C proved that the drop of mechanical properties is strongly slowed down by the reduction of the treatment temperature, confirming that 80°C can be assumed as the threshold temperature also for this alloy

MICROSTRUCTURE

In order to better understand the aging phenomenon, a metallographic characterization of as-cast and aged samples was performed by means of optical microscope. Ac-

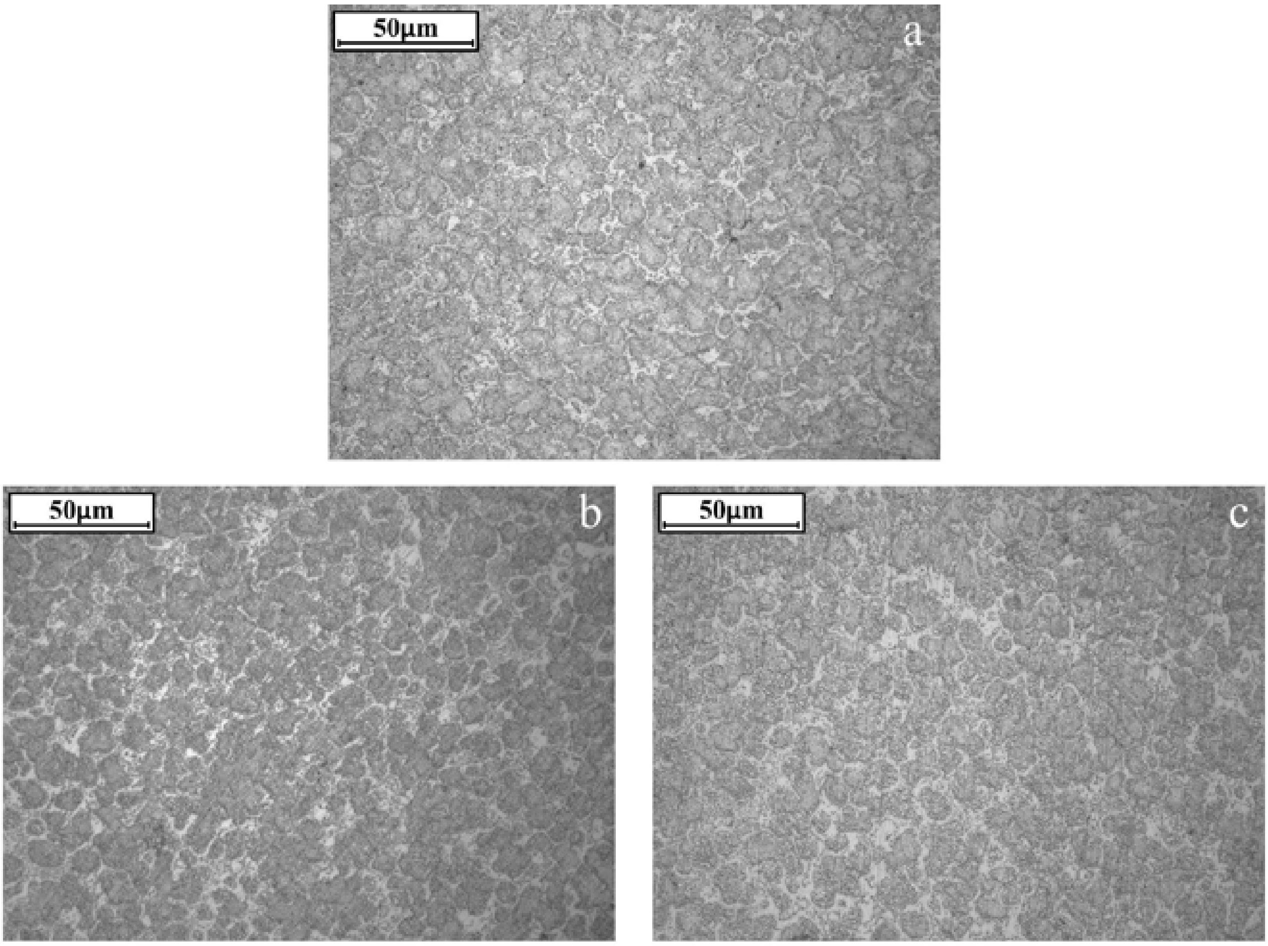


Fig. 3 - Microstructure of Zn-15Al-1Cu alloy die-cast samples a) "as-cast", b) after 240 h of aging at 105°C and c) after 240 h of aging at 130°C.

cording to the phase diagram (Fig. 1), the microstructure of the Zn-15Al-1Cu alloy should be composed at room temperature by Al-rich primary phase and Zn-rich eutectic, both transformed by the eutectoid decomposition.

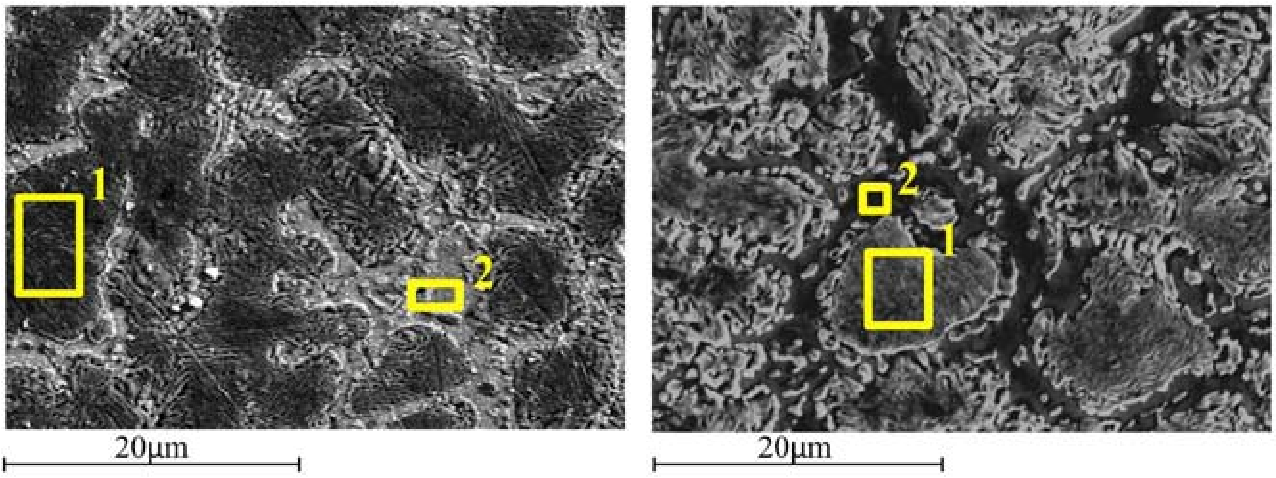
Figure 3 shows the microstructures of samples in different conditions: as-cast (a), aged for 240 hours at 105°C (b) and at 130°C (c). The Al-rich primary grains (dark areas) are surrounded by the eutectic phase (light gray areas). No particular differences can be noted between samples, in terms of size, shape or amount of the different phases. No recrystallization phenomena are detectable.

All samples are almost free from porosity, regardless of the aging conditions, which means that the reduction of the mechanical properties cannot be ascribed to an increase of defects, as can easily occur in die-cast components after long stays at high temperature.

Preliminary SEM analyses were carried out on the samples in the as cast condition (Fig. 4a) and heat treated for 240 h at 130°C (Fig. 4b). Both samples show the eutectoid decomposition of Al-rich primary grains with the consequent formation of a thin lamellar microstructure, surrounded by the Zn-rich eutectic. The Al content of primary dendrites is close to the theoretical value of 32.3% expected from Zn-Al phase diagram. This suggests that notwithstanding the rapid cooling imposed by the production process (HPDC), the microstructure is not far away from the equilibrium state.

Comparing figure 4a and figure 4b some small differences can be appreciated in the microstructure. In particular, the aged sample shows more globular and coarser precipitates at the interface between the phases and the eutectoid lamellae seems to be better defined, maybe as a consequence of a more distinct separation between Al and Zn elements.

Such rearrangement of the microstructure could justify the drop of mechanical properties measured by tensile tests on aged samples. Increasing the temperature, in fact, the atomic mobility is enhanced and solid state diffusion and solute redistribution are promoted. The achievement of a pseudo-equilibrium state at the end of the aging treatment should allow the formation of a structure free from supersaturated solutions, having a lower local lattice deformation. This condition causes a reduction of barriers to the dislocation movement and a modification of the free mean path and, consequently, a lower mechanical resistance. Unfortunately, such modifications are not detectable by optical or electron microscope and also the spatial resolution of EDS microanalysis is inadequate to measure a solute redistribution on so small distances. Transmission



Spectrum	Al	Cu	Zn
1	32.03	0.39	67.58
2	2.11	0.82	97.07

Spectrum	Al	Cu	Zn
1	36.48	0.17	63.34
2	8.98	0.55	90.47

Fig. 4 - SEM analysis performed on the as cast sample (a) and sample treated for 240 h at 130°C (b).

Electron Microscope (TEM) measurements and X-ray diffraction (XRD) experiments are desirable to overcome such limitations and explain the results of tensile tests in terms of the alloy microstructural changes.

CONCLUSIONS

In this paper the aging behavior of the hypereutectic Zn-15Al-1Cu alloy was investigated.

Being a newly developed alloy, no data are up to now available in literature about natural or artificial aging. Tensile tests were performed on samples aged at three temperatures (105, 130 and 80°C) for different soaking times (up to 240 hours and in one case up to 720 hours) to measure the decrease of mechanical properties.

This characterization gave useful information about the potential use of this alloy at relatively high temperatures and allowed to assess the mechanical properties close to steady state conditions.

The results show that in the first 24 hours a fast decrease of mechanical properties occurs at all the investigated temperatures. After this period the reduction of mechanical strength slows. As expected, the aging phenomenon is accelerated by increasing the aging temperature: the reduction of the UTS after 240 hours was 4% at 80°C, 11% at 105°C and 21% at 130°C.

Microstructural analyses carried out by optical microscope and SEM-EDS revealed only small differences between the aged and the as-cast samples. In particular, the aged samples showed a slight coarsening of precipitates at the phases boundary and the eutectoid lamellae appeared better defined, suggesting the redistribution of solute elements. Such microstructural modifications could justify the reduction of mechanical properties measured by tensile tests. To examine more deeply this hypothesis further investigations with other techniques like TEM and XRD are under development.

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