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EFFECT OF AGEING ON MECHANICAL PROPERTIES OF Pb AND Sb ADDED AZ91 MAGNESIUM ALLOY

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ABSTRACT

Elemental additions such as Pb and Sb have been carried out in AZ91 magnesium alloy to study their effect on ageing behavior of AZ91. Discontinuous precipitation is greatly suppressed with the addition of Pb and hence the ageing kinetics and peak hardness is reduced. Sb addition also suppress the discontinuous precipitation but in lesser extend. Due to the hard intermetallic Mg_3Sb_2 present in the Sb added alloy, their peak hardness is not affected much and slight improvement in hardness is observed indeed, despite the suppression discontinuous precipitation.
Key words: AZ91 Mg alloy: Alloying addition: Ageing: Discontinuous precipitation: Mechanical properties

1.INTRODUCTION

Magnesium alloys finds increased usage in industrial applications, especially in automotive industry because of its' light weight (30% less than Al, and 75% less than steels), superior specific mechanical properties compared to aluminum alloys or steels [1]. Among these alloys, AZ91 (9Al-1Zn-0.2 Mn) is the most common commercial magnesium alloy, which is endowed with the best combination of good castability, improved mechanical strength and higher ductility [2]. However, the safe use of AZ91 is restricted to 120oC temperature beyond this temperature considerable loss in strength is evidenced. Hence, it is obvious that their application as structural materials is restricted due to the reduction in their mechanical properties at increasing temperatures. Therefore, a need has been felt to improve the mechanical properties of this alloy at high temperatures.

High temperature tensile and creep studies conducted on the AZ91 alloy have revealed coarsening of β-phase $Mg_{17}Al_{12}$ at higher temperature due to their low melting point (437^{o}C) which intern reduces its strength properties [3]. Another major problem encountered with this alloy is that the structural instability during high temperature exposure. Dynamic discontinuous precipitates occur at the grain boundaries from the supersaturated eutectic solid solution lead to the sliding of grain boundaries and weaken the material [4]. In recent years, effort has been made to improve the high temperature properties of AZ91 alloy by minor alloying additions. Studies on the addition of Sb, Ca, Bi, Sr etc. to AZ91 alloy have shown improved the high temperature properties [5-7]. This improvement in mechanical properties is attributed mainly to the introduction of high temperature thermally stable intermetallics in the microstructure due to the addition of alloying elements. However, the effect of these elemental additions on ageing behavior of this alloy is not explored so for. Since dynamic discontinuous precipitates present in this alloy have a definite role on mechanical properties, the present work is focused to study the effect of ageing behavior on the mechanical properties of Pb and Sb added AZ91 alloy.

2. EXPERIMENTAL

2.1 Casting

The AZ91 magnesium alloy used for this experiment was prepared by melting together with the required quantities of commercially available pure Mg, pure Al, pure Zn and Al-10Mn master alloy. Melting was carried out in a steel crucible in a resistance furnace under proper flux cover. Addition of Pb and Sb was carried out when the melt temperature was 700^{o}C. 2% of Lead was added in pure form whereas 0.7% antimony addition was carried out in the form of Al-10Sb master alloy. The melt was refined at 720^{o}C and then held for 20 min. for settling the oxide particles. The refined melt was poured in to a metallic mold, which was coated with die coat and preheated to 250^{o}C. Sulphur powder dusting was carried out to avoid oxidation and burning during pouring.

2.2 Heat Treatment

Samples of size 15 mm dia. and 15 mm height machined out from the castings were solution treated at 410^{o}C for 24 hr in a muffle furnace. To avoid the oxidation of these samples during solution treatment, a mixer of 20% coke and 80% foundry sand bed was kept inside the oven separately to reduce the oxygen present inside the furnace. Our earlier studies have shown that this simple method effectively reduced the oxidation of the specimens. These samples were then quenched in cold water. These quenched samples were subsequently aged at 200^{o}C up to 50 hr to perceive the ageing kinetics of the AZ91 base alloy.

2.3 Thermal Analysis

In order to study the corollary of Pb and Sb addition on the solidification behavior and phase formation during solidification of AZ91 alloy, thermal analysis studies were carried out using DTA thermal analyser. The melt having 720^{o}C temperature was poured in to a pre heated metallic cup. A thermocouple located in the center of the cup, facilitated the measurement of the temperature during solidification.

2.4 Microstructural Characterization

Microstructural samples were superficially ground using 400 grit paper then polished with 0.25μm diamond paste subsequently etched by an etchant (solution of 5 ml acetic acid, 10 ml H_2O, 6 g picric acid and 100 ml ethanol). Optical microscopic studies were carried out using Leica DMRX Microscope with Q-Win image Analysis software. X-ray diffraction studies were carried out on the alloy containing Pb and Sb using Phillips PW 1710 Powder Diffractometer with Cu -$K_{\propto}$ radiation. The composition of Sb bearing intermetallic phases and the distribution of the alloying elements were examined in a JEOL, JSE 35C Scanning Electron Microscope (SEM) attached with an Energy Dispersive Spectroscope (EDS). The chemical composition analysis of these alloys carried out using an Inductively Coupled Plasma Spectrometre (ICP Plasmascan, model LABTAM 8410) is presented in Table 1.

2.5 Mechanical Properties

Tensile specimens in accordance with ASTM E8 Standard were machined out from the castings and some of the samples were heat treated as said above. The room tensile tests were performed on as cast and heat treated AZ91 alloy samples with out with out addition using Instron Universal Testing Machine with a cross head speed of 2 mm/min.

3.RESULTS

3.1 Microstructure

3.1.1 As cast microstructure

Figure 1 shows the typical microstructure of permanent mould cast AZ91 alloy. It consists of α-Mg solid solution containing Al, Zn, and $Mg_{17}Al_{12}$ massive eutectic phase. Both partial and completely divorced kinds of eutectic are noticed. Laminar kind of precipitates is also observed in the vicinity of massive second phase. From SEM observation (Figure 1 b), it can be clearly seen that the AZ91 alloy consists of two kinds of $Mg_{17}Al_{12}$ particles having same composition. One is massive $Mg_{17}Al_{12}$ particles with irregular shape and the other one is small needle like laminar particles surrounding the massive particles. The results of microanalysis by EDS reveal that both the particles have same chemical composition.

Figure 2 shows the microstructures of AZ91 containing Pb and Sb. With addition of 2% Pb to the AZ91 alloy no new phase was observed in the microstructure (fig 2a). However, small addition of Pb significantly reduces the discontinuous precipitates at grain boundaries (see Fig. 2a). The microstructure of 0.5%Sb added AZ91 alloy is shown in Figure 2b. A block strip kind of phase is noticed along with the massive $Mg_{17}Al_{12}$ phase at the grain boundaries. Using both the SEM-EDS and XRD analysis this phase is identified as Mg_3Sb_2. It is also noticed that almost all the Mg_3Sb_2 phase appeared along with the $Mg_{17}Al_{12}$ phase at the grain boundary.

The XRD analysis performed on all the samples to identify the phases present in the existing alloys is presented in Figure 3. From these results it can also be observed that the base alloy contained two phases: α Mg matrix and β-$Mg_{17}Al_{12}$ phase. Small addition of Pb does not cause the formation any new phases in the as cast microstructure, so its XRD pattern is similar to that of AZ91 except the presence of Pb peaks as shown in the fig 3a. It is also evident from the careful EDS analysis which shows many tiny Pb particles presented throughout the grain. However, in Sb added alloy the peak corresponds to Mg_3Sb_2 is observed besides the peaks of α-Mg and $Mg_{17}Al_{12}$ phase.

3.1.2 Heat treated microstructure

The microstructure of the solution treated (410^{o}C for 24 hr) samples ensures that all the $Mg_{17}Al_{12}$ redissolved in to matrix and aluminum is homogeneously distributed throughout the microstructure. Some Mn bearing phases are seen with all solution treated microstructures and in addition to that Sb containing phases are also seen with Sb added alloy. The other specialized feature is that the grain boundary of the base alloy (AZ91) was clearly seen with solutionized condition (Figure 4) whereas the grain boundary is not seen in Pb and Sb added structure.

The microstructural changes are noticed in the samples aged at 200^{o}C. Figure 5 presents the microstructures of AZ91 and Pb and Sb added alloy samples aged at 200^{o}C for 120 min. The significant microstructural difference observed in these samples is the amount of discontinuous precipitates at the grain boundary. The presence of black phase at the grain boundary indicates the initiation of discontinuous precipitates in AZ91 alloy (see Fig.5a). The microstructures of Pb and Sb added AZ91 alloy (Fig. 5 b&c respectively) are seen with less amount of discontinuous precipitates compared to the AZ91 alloy. Among these three microstructures, the presence of discontinuous precipitates is very less seen in the Pb added alloy, which indicates the addition of Pb effectively suppresses the nucleation of discontinuous precipitates. As the ageing time is increased, the number of nucleation sites is found to increase besides growing the already formed discontinuous phases to the adjusted grains. However, the growth rate is found to be slow with Sb and Pb added samples. After 320 min., the discontinuous precipitates are ceased and the aluminum precipitates out as continuous phase throughout the grain.

3.2 Ageing Behavior

The aging behavior of AZ91 alloy without and with different level of pb and Sb additions is shown in the Figure 6. In general the ageing curves can be divided in to four distinct regions as follows [8]:

1. A incubation period where the hardness is not increases with time
2. A rapid increase in hardness with respect to time
3. Slow down in the rate of hardening nearer to the peak hardness
4. Leveling off at the peak hardness

The hardness values measured for the alloys at different temper conditions are given in Table 2. It can be noticed from the table that in general the addition of Pb does not affect much the as cast and the solutionized hardness where as a marginal decrease in the peak hardness is noticed with Pb added AZ91 alloy. It is also observed that the ageing kinetic is slow with the presence of Pb. This is due to the suppression of discontinuous precipitation. The time required to reach the peak hardness increases compared to the base alloy. Eventhough marginal increase in hardness is noticed in both the cast and solutionized conditions of the Sb added alloy as compared to AZ91 alloy due to the presence of hard and stable Sb bearing precipitates, no significant improvement in the peak hardness is obtained. However, at any given time, during the ageing process either same or higher hardness values are obtained in the Sb added alloy compared to the base alloy in spite of the suppression of discontinuous precipitation.

3.3 Thermal Analysis

Figure 7 shows the cooling curves under a cooling rate of app 0.5 $^{o}C/s$. From the discontinuities (plateau region) in the cooling curve, the liquidus (TL) and solidus (TS) temperatures can be readily determined [9] subsequently the total solidification time can also be calculated. Solidification time is defined as the time to cool the alloy from the start of solidification to its completion, that is, from the liquidus to the solidus temperatures. These data are also given in the table 3. Addition of Pb shifts the liquidus temperature of AZ91 by 5^{o}C upwards but it depresses the solidus (eutectic) temperature by 8^{o}C. Decrease in both the liquidus and solidus temperature is observed with Sb addition. Because of these shifts in temperatures the total solidification time are also changed. Incase of Pb added alloy it is increased to 394.19 sec. and for Sb added alloy solidification time increased to 449.48 sec as compared to the base alloy solidification time of 386.06 sec.

3.4 Mechanical Properties

Tensile properties of the as cast and aged alloy samples tested at ambient temperature is shown in Figure 8. Small addition of Sb to AZ91 alloy is found to increases ultimate tensile strength but not much improvement is noticed in ductility compared to the base alloy. However no such improvement in tensile properties is noticed in the Pb added alloy. In the peak aged condition, the strength properties of all alloy are higher than the as cast one. Higher strength and ductility values obtained in the Sb added alloy compared to the other alloys studied is due to the presence of hard and thermally stable Mg_3Sb_2 phase.

4.DISCUSSION

4.1 Microstructure

Both the microstructural and XRD analyses on the as cast AZ91 confirm that the alloy contains only two phases (α-Mg and β –$Mg_{17}Al_{12}$) which very well coincides with the earlier studies [10, 11]. The divorced kind of eutectic observed with AZ91 alloy is due to the presence of zinc which influenced the solidification behavior of Mg-Al alloys. Due to the high segregation tendency of zinc during cooling, degree of constitutional under cooling ahead of the solid-liquid interface at the early stages of primary dendrite growth considerably increases. This reduces the interdendritic spacing, which favors the divorced eutectic [10]. The non equilibrium cooling during solidification in the cast iron mold used in the present investigation also contributes to the divorced eutectic formation. Continuous cooling after the eutectic temperature has lead to the formation of laminar precipitates around the massive β phase from the super saturated eutectic α-solid solution [11].

As expected addition of Pb has not lead to formation of any component with Al or Mg because of its very good solubility (45% at 195^{o}C) in Mg [12] and in the present study all the Pb added might have gone in to the solid solution. But the solid solubility of Sb in Mg at room temperature is almost negligible and in this study, the added Sb has combined with Mg to form Mg_3Sb_2 intermetallics. These solidification features are reflected in the cooling curves obtained using thermal analysiser. Normally the- Mg solid nucleation starts at a liquidus temperature and it is grow as a dendrite till the solidius temperature reaches where eutectic takes place {near equilibrium α- Mg + $Mg_{17}Al_{l2}$). These temperatures depend upon the cooling rate. From the table4 it is clear that addition of Pb to the AZ91 does not influence the solidification pattern much. However the observed depression in the eutectic temperature (6^{o}C) indicates that the β phase gets refined slightly. Same kind of eutectic temperature shift was observed with Sb added alloy also. In addition, solidification curve for Sb added AZ91 alloy shows additional temperature plateaus. The discontinuity at around 550^{o}C represents the formation of Mg_3Sb_2 intermetallic (ref fig 2 b). Another discontinuity at around 520^{o}C might be indicating some oxides formation due to the burning at the top, which is an exothermic reaction during which lot of heat is evolved. Due to this, the solidification time is found to increases with Sb addition.

4.2 Ageing kinetics

The aging curves for all the alloys tested show similar trend. Moreover, the peak hardness values do not vary much with the presence of alloying additions. The most significant finding in the aged microstructure of the alloy containing Pb and Sb is the absence of the large regions of discontinuous precipitates, which dominates the initial stages of ageing in AZ91 alloy. Even though some thickening of grain boundaries is observed in Pb added alloy aged for 60 min compared to the AZ91 alloy, there is no subsequent growth of discontinuous precipitates because the nucleation process of discontinuous precipitation is a function of the ageing temperature, Al content in the solid solution and the grain size [13]. Moreover the process for both the nucleation and growth of discontinuous precipitation in Mg-Al alloys is highly diffusion controlled. Presence of Pb and Sb throughout the grain might have effectively inhibited the diffusion process required for discontinuous precipitation. This could be achieved by increasing either the number of low angle grain boundaries or the number of boundaries with a high concentration of coincidence lattice sites. A detailed SEM and TEM studies are currently in progress.

Due to the suppression of discontinuous precipitation, it is expected that more aluminum is available for continuous precipitation in the later stage of ageing process. However the maximum hardness values obtained clearly indicate that the number/amount of precipitates is not changed much due to the presence of alloying elements. Same kind of observation has been made with cadmium and sliver additions [8] and gold addition [14]. However significance of these additions lies on the fact that it reduces the dynamic discontinuous precipitation during high temperature exposure which is responsible for the grain boundary sliding in Mg alloy as reported in the literature [3, 4]. Hence improvement in creep properties is obvious.

4.3 Mechanical properties

Considerable improvement in the mechanical properties of Sb added alloy compared to the base alloy is noticed. This improvement in strength is attributed to the presence of hard Mg_3Sb_2 intermetallic at the grain boundary. However the Pb added alloy does not show any improvement in the strength. Even though some improvement due to the solid solution strengthening is expected with the Pb alloy, suppression in the discontinuous precipitation reduces its strength properties. This is also clearly seen with aged samples. This confirms the studies of Bettles et al [15] who noticed improvement in strength with the discontinuous precipitation. However this is not true in case of Sb added alloy where the strength properties are improved considerably by the presence of hard Sb bearing intermetallic. For all the alloys tested, improved strength properties are obtained for peak aged condition as compared to the as cast condition. This is due to the fact that during solution treatment all the aluminum present in the alloy is dissolved and evenly distributed throughout the matrix making more aluminum available for precipitation during ageing. This is in consistent with the result of Celotto [2] that the volume of fine continuous precipitates is more in the peak aged condition than the as cast condition.

5.CONCLUSION

Following conclusions are derived from this study:

- Addition of 0.5% Sb lead to the formation of a hard Mg_3Sb_2 intermetallic in the as cast microstructure of AZ91 alloy whereas 2% Pb addition forms a solid solution with Mg.
- Addition of both the Pb and Sb elements in AZ91 alloy suppresses the formation/growth of discontinuous precipitates in the as cast as well as in the aged conditions. Among them, Pb is more effective in suppression.
- Addition of Pb and Sb does not change the precipitation behavior of AZ91much however addition of Pb marginally reduces the peak hardness besides slowing down the ageing process whereas Sb addition has lead the peak hardness to increase marginally.
- Sb added alloy has lead to considerable improvement in mechanical properties over the base alloy in all temper conditions due to the presence of hard Mg_3Sb_2 phase.
- Due to the suppression in discontinuous precipitates the mechanical properties of Pb added alloy is marginally reduced in both as cast and peak aged condition.

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TABLES

Table 1. Chemical composition of the alloys

Alloy	Al	Zn	Mn	Sb	Pb
AZ91	8.5	0.7	0.2		
AZ91+Pb	9.2	0.9	0.2		1.7
AZ91+Sb	8.3	0.9	0.4	0.7	

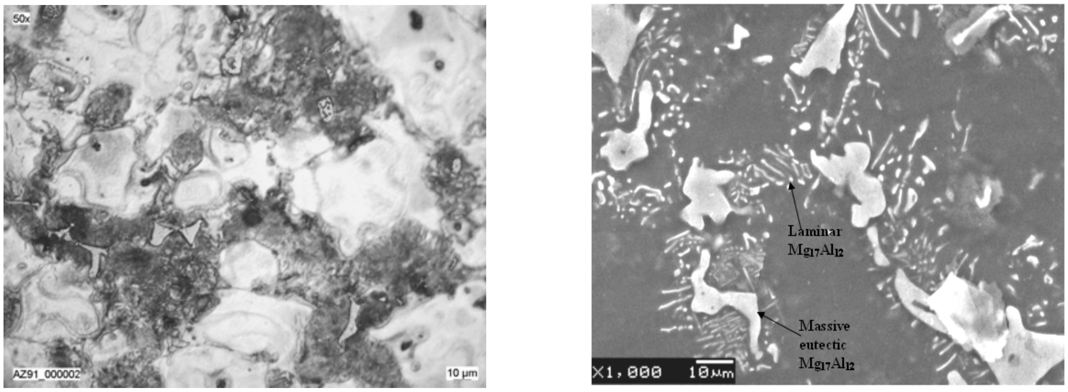
Table 2. Hardness value and ageing time for AZ91 alloy with and without alloying addition

Alloy	As cast Hardness, BHN	Solution Treated Hardness, BHN	Peak Hardness, BHN	Total Time to Peak Hardness, min
AZ91	63.9	58.8	83	1140
AZ91+ 2% Pb	62.85	58.2	79	1440
AZ91+ 0.7% Sb	65.8	62.4	86	1320

Table 3. Transformation temperature for AZ91 alloy with and without alloying additions

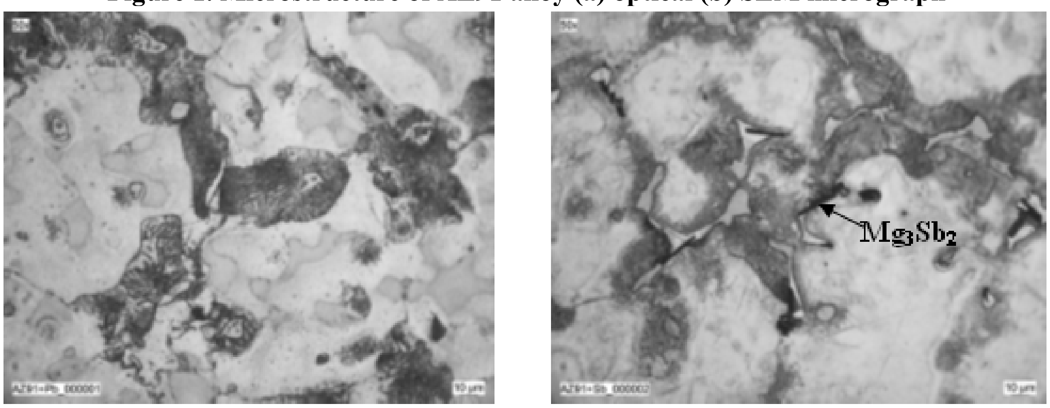
Alloy	Liquidus Temperature, ^{o}C	Solidus Temperature, ^{o}C	Solidification Time, Sec
AZ91	611.14	424.73	386.06
AZ91+2%Pb	613.86	418.38	394.79
AZ91+0.7%Sb	610.23	422.92	449.48

FIGURES



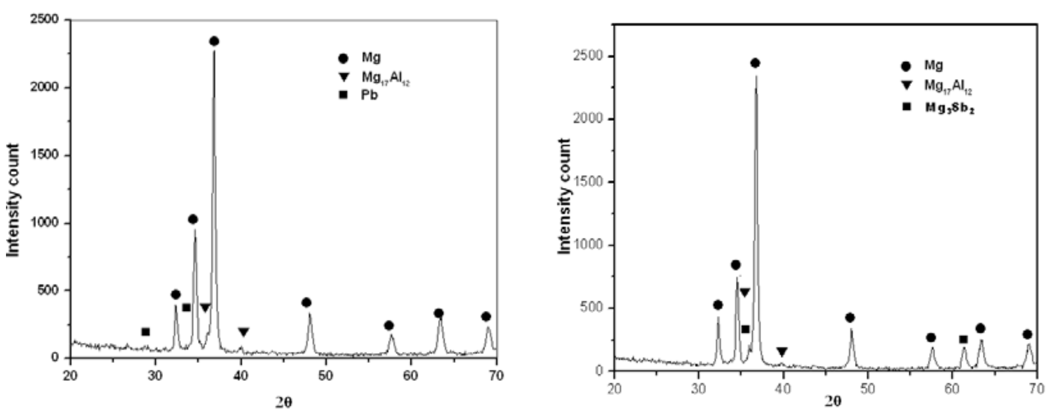
(a) **(b)**

Figure 1. Microstructure of AZ91 alloy (a) optical (b) SEM micrograph



(a) **(b)**

Figure 2. Optical microstructure of (a) AZ91+2Pb (b) AZ91+0.7Sb



(a) **(b)**

Figure 3. XRD pattern (a) Pb added AZ91 (b) Sb added AZ91

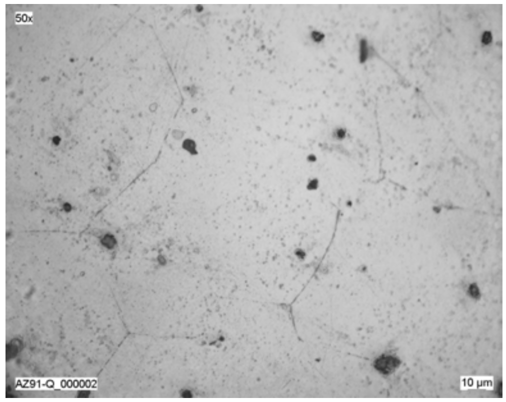
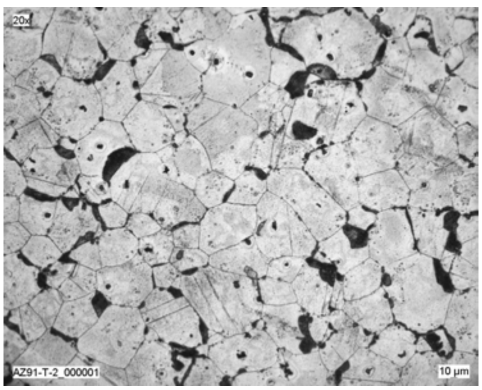
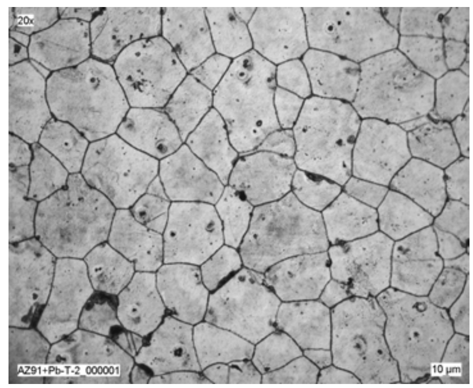


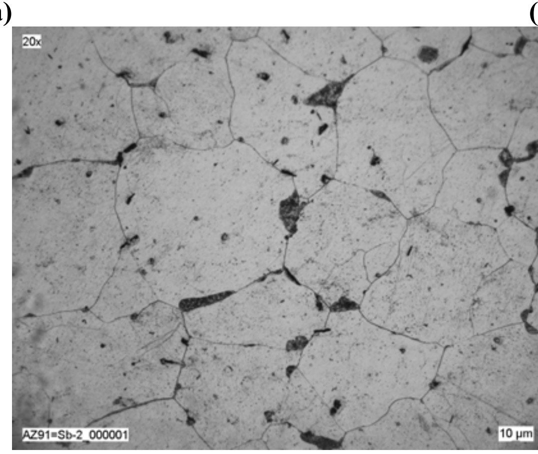
Figure 4. Microstructure of AZ91 alloy at solution treated condition



(a)



(b)



(c)

Figure 5. Microstructure of 120 min aged samples (a) AZ91 (b) AZ91+2Pb (c) AZ91+0.7Sb

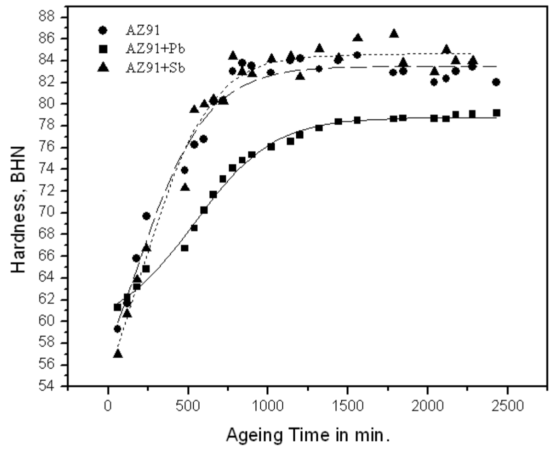


Figure 6. Age hardening behavior of AZ91 with and without Pb and Sb addition at 200^{o}C

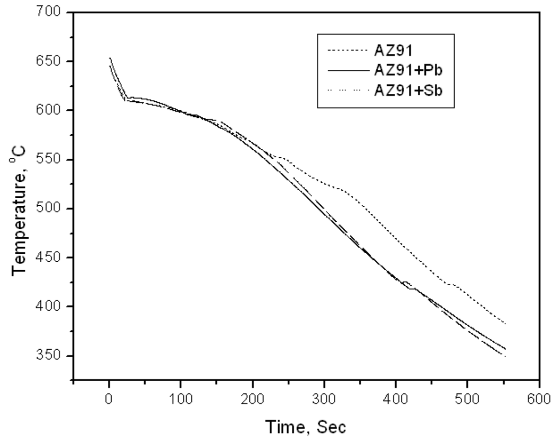


Figure 7. Cooling curves for AZ91 alloy with and without additions

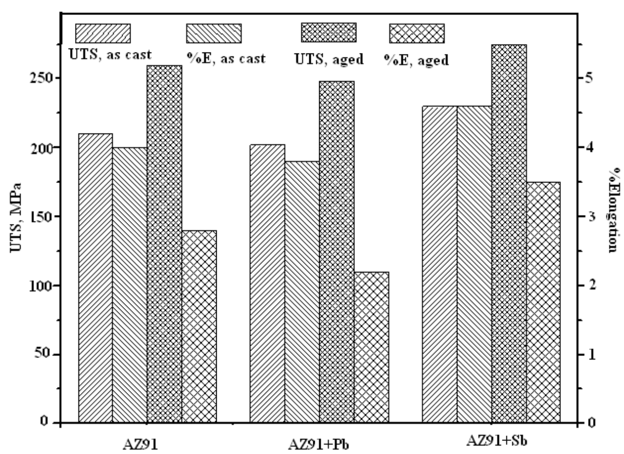


Figure 8. Mechanical properties as cast and aged AZ91 alloy with different alloying addition