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Thermoelectric Power Characterization of 7xxx Aluminium Alloys During Ageing

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The ageing behaviour of two 7xxx aluminium alloys was studied using the thermoelectric power (TEP) measurement technique. In the natural ageing process, the TEP, like the electrical conductivity, decreases with increasing ageing time, which is caused by GP zone formation. In the artificial ageing process, the electrical conductivity presents a monotonous increase. However, the TEP indicates a four-stage ageing behaviour. The TEP increases sharply during early heating-up stage, and then decreases consecutively with increasing isothermal ageing time. This reflects different characteristics for different stages of ageing. The turning point of the transformation from η' to η in the TEP measurement corresponds well with the ageing time for the peak hardness. In addition, TEP detects the difference in precipitation kinetics between the two 7xxx alloys during ageing.

Keywords: *Thermoelectric power; 7xxx aluminium alloys; precipitation; ageing.*

1. Introduction

Thermoelectric power (TEP) is the magnitude of an induced thermoelectric voltage in response to a temperature difference across a material. The TEP of alloys is strongly influenced by the solute content, lattice strain, microstructural changes, material processing and time-dependent phase transformation [1]. TEP measurements have been employed to follow the precipitation kinetics in some aluminium alloys during the artificial ageing [2-5]. Such a technique has the advantages that it is relatively simple, it is easy to implement and the measured parameter is highly sensitive to microstructural changes.

The usual precipitation sequence of 7xxx series Al alloys can be generalized as [6,7]:

Solid solution → GP → η' → η

The current work was conducted in order to evaluate the influence of the ageing state of two 7xxx alloys on TEP values. The conductivity and hardness HV measurements and DSC measurements were preformed to identify the formation of precipitates. A correlation was found between the TEP and the hardness measurement as a function of the ageing time.

2. Experimental

The alloy compositions used in this research are given in Table 1. The AA7021 alloy is free from Cu while AA7081 contents Cu and higher Zn and Mg. The atomic ratio of Zn/Mg (=1.4) is the same in the two alloys.

Table 1 The composition of alloys given in wt%

Alloy	Zn	Mg	Cu	Si	Fe	Mn	Zr	Ti
AA7021	5.0-6.0	1.2-1.8	<0.25	<0.25	<0.40	<0.10	0.08-0.12	<0.10
AA7081	6.9-7.5	1.8-2.2	1.2-1.8	<0.12	<0.15	<0.25	0.06-0.15	<0.06

The two alloys were processed to sheets of 1 mm thick. The ageing response of the alloys was investigated after solutionizing treatment at 475°C for 30 minutes, followed by a water quench. The ageing consists of the following steps:

- Natural ageing for two weeks at room temperature (20°C)
- Heating up to 140°C (heating rate of 30°C/hour)
- Ageing at 140°C

TEP values were measured by means of the Techlab TEP measuring unit [8]. The measurement device is composed of two junctions (cylindrical blocks made from pure aluminium as reference). The specimen to be measured can be assembled between the two junctions as a connection. The two junctions are brought at a temperature T and T+ΔT respectively. Due to this temperature difference both metals (specimen and reference) will react differently. This will cause a difference in the voltage between the two junctions (ΔV). The TEP value (ΔS) is defined as the ratio ΔV/ΔT. ΔS can be expressed as the difference of the thermoelectric power of the two metals, i.e. $\Delta S=S_{sample}-S_{reference}$. Specimen size for the TEP measurement is 90 x 6 x 1 mm. The low temperature block was set at T = 15°C and the difference between the low and high temperature blocks is ΔT = 10°C. The resulting TEP signals were measured with a high precision voltmeter with a resolution of below 0.5 nV.

The conductivity of the alloys was measured by the eddy current technique. These measurements were conducted at room temperature with a Sigmatest D 2.068 on specimens having a thickness of 2 mm. Microhardness tests were done with a Vickers diamond indenter with a pyramidal shape and a load 50 gram was used with duration 30 s. Six measurements were taken randomly for each sample and the average value and the standard deviation were calculated. The differential scanning calorimeter measurements were performed in a DSC-50 Perkin Elmer apparatus with a heating rate of 20 °C/min to 550 °C in argon atmosphere.

3. Experimental results

The overall evolution of the TEP against ageing time (natural ageing and artificial ageing at 140°C) for AA7021 is shown in Fig. 1. For comparison, the conductivity change was also plotted. Clearly, TEP provides more information than the conductivity does.

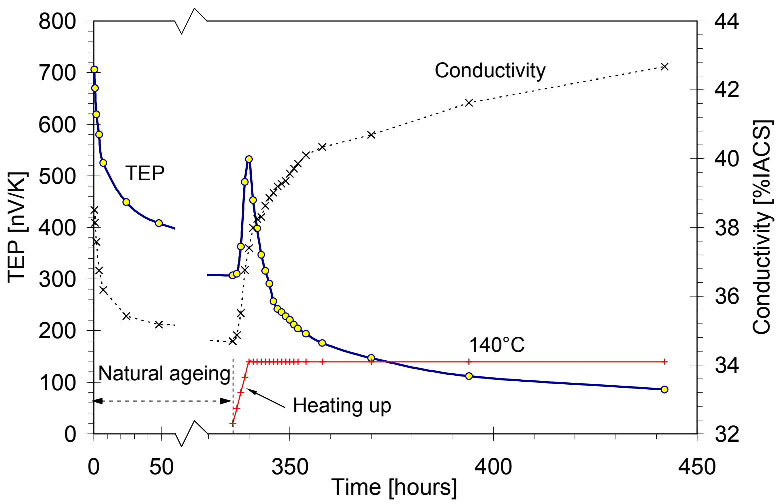

Fig. 1 The evaluation of the TEP and the conductivity of AA7021 alloy during ageing, after solution-treated at 475°C and water quenched.

3.1 Natural ageing

The evolution of the TEP, conductivity and hardness during natural ageing of the two alloys is shown in Fig. 2. During natural ageing, both the TEP value and conductivity decrease as the ageing time increases. A fast decrease can be found in TEP and electrical conductivity at short times, followed by a much slower decrease at longer times. This trend is in agreement with various reports in the literature [9]. Two distinct stages can be observed on the TEP and/or conductivity versus log(t) plots. TEP and conductivity decrease linearly with the logarithm of time in each stage. The transition point is found to be the same for both measurements, which is 24 hours for AA7021, 12 hours for AA7081, respectively.

The TEP in the as-quenched AA7081 is higher than that in the AA7021. However, the TEP value decreases faster in the AA7081 than that in the AA7021 in the early stage (within 12 hours after water quench). This indicates that the presence of Cu in the Al-Zn-Mg alloy accelerates the formation of GP zones.

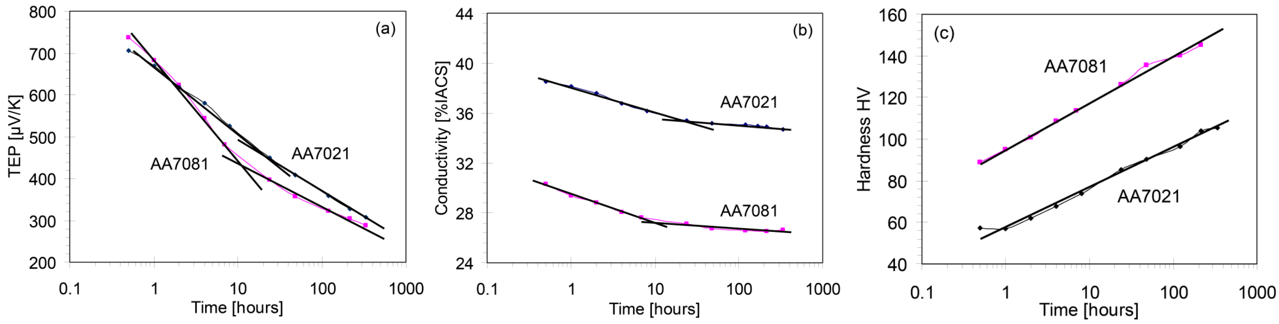

Fig. 2 The evolution of TEP, conductivity and hardness during natural ageing.

All alloying elements decrease the conductivity of the aluminium when they are dissolved in the solid solution. Therefore, it can be expected that the conductivity of the AA7081 alloy is lower than that of the AA7021 because of the higher alloying contents in AA7081. There is no obvious difference in the decreasing rate of the conductivity in the two alloys.

Hardness measurements performed on the samples with the same ageing history showed an increase, which also suggests the formation and growth of clusters have taken place during natural ageing. The hardness increases faster in the AA7081 than in the AA7021.

3.2 Artificial ageing at 140°C

The artificial ageing includes the heating-up stage and the isothermal ageing at 140°C. Fig. 3 shows the evolution of TEP, conductivity and hardness of the two alloys during artificial ageing. In Fig. 3, the left hand part of the figures is plotted as a function of the temperature during the heating-up stage at a rate of 30°C/h, while the right hand part is plotted as a function of the time when isothermal ageing at 140°C.

In the artificial ageing at 140°C, TEP measurements for two alloys have similar behaviour vs. time and show four consecutive stages, as shown in Fig. 3a.

Stage 1: the TEP increases from the natural aged value to a maximum achieved at the temperature of 140°C for the AA7021, 110°C for the AA7081 during heating-up stage.

Stage 2: the TEP decreases continuously for up to 2 hours after isothermal ageing at 140°C.

Stage 3: the TEP decreases slightly faster in a transitory stage between 2 hour and 10 hour during isothermal ageing.

Stage 4: the TEP decreases with a reduced rate after about 10 hours of ageing.

The increase in the TEP in AA7081 during heating-up is much smaller compared with that in AA7021. The level of the entire TEP curve of the AA7081 during artificial ageing is lower than that of the AA7021 over the time span measured. The largest difference appears at the beginning of the isothermal ageing and this difference becomes smaller as the ageing time increases.

As shown in Fig. 3b, the conductivity demonstrates a monotonous increase during the artificial ageing in both the heating-up stage and the isothermal stage. The conductivity shows a faster increase during the heating-up stage and then, a transitory stage, a slow increase in conductivity can be found between 0 and 2 hours after that of the isothermal ageing at 140°C. Thereafter, the conductivity shows a faster increase again.

The evaluation of the hardness during artificial shows a 4-stage ageing behaviour, in correspondence with the TEP evaluation, as shown in Fig. 3c. Associated with the increase of TEP during the heating-up stage of the artificial ageing, the hardness curves show a small decrease. For longer ageing times, the hardness curves show different stages linked to different microstructural states.

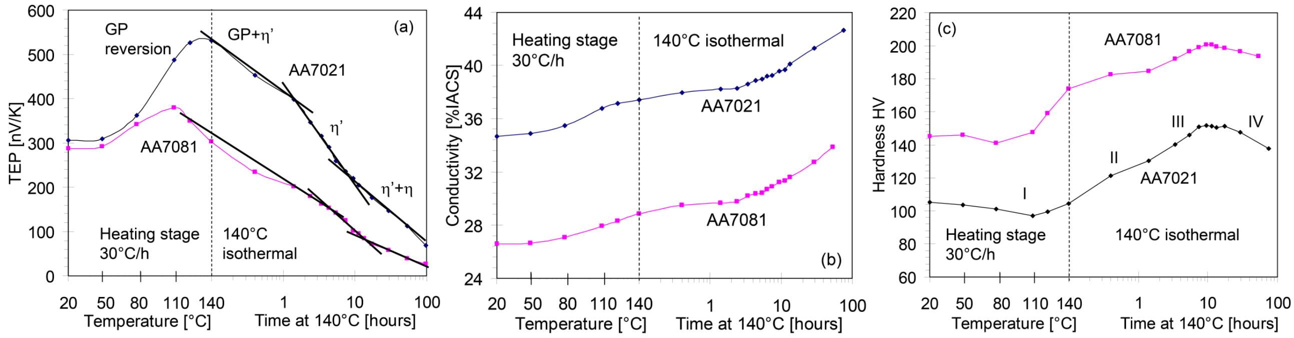

Fig. 3 The evolution of TEP, conductivity and hardness during artificial ageing at 140°C.

3.3 DSC analysis

To understand the microstructural change during the heating stage, DSC runs were conducted on the samples with the following treatments: (1) water quenched + 2 week natural aged, (2) water quenched + 2 week natural aged + heated up to 110°C or 140°C at 30°C/h + water quenched. Fig. 4 shows DSC thermograms recorded for both alloys. According to the literature [6,7], the individual events in the *natural* aged samples can be identified as follows:

(1) The endothermic peak A corresponds to the partial dissolution of GP zones. This peak appears at the same temperature in the two alloys. This peak indicates that the GP zones have been formed during natural ageing.

(2) The exothermic peak C in AA7021 alloy appears in the temperature range from 200 to 270 °C. In the AA7081 alloy, this exothermic peak extends over a wider temperature range and can be split into 4 peaks: B, C, D and E. Peak B, C and E can be interpreted as the precipitation of η', the transformation of η' into η, and the transformation of η into T phase at higher temperatures [7], while peak D is not clear.

(3) The endothermic peak F corresponds to the dissolution of the various phases. The peak temperature is at 340°C in the 7021 alloy and at 440°C in the 7081 alloy.

Significant microstructural changes happen during the heating-up stage of artificial ageing. In the sample heated-up to 140°C at 30°C/h, the peak A in the DSC curve fully disappears in the AA7021, which indicates that the revision of the GP zones formed during natural ageing has occurred during the heating-up stage. While in the AA7081, the peak A in the sample heated up to 110°C shifts to a higher temperature and the area becomes smaller compared with that in the natural aged sample. Peak B shifts to a lower temperature. For an endothermic reaction, the peak temperature is an indication of the relative stability of the pre-existing precipitates. The area of the peak A becomes smaller, indicating that some GP zones have dissolved during heating-up to 110°C. The shift of the peak A to a higher temperature reflects the fact that some GP zones have become more stable during heating-up. The endothermic peak A is not present on the DSC trace of the samples heated up to 140°C. However, another endothermic peak B' appears at a temperature range of 169-200°C, which was identified as the dissolution of η' phase [6]. This fact indicates that the formation of the η' phase has taken place during heating up from 110°C to 140°C in the AA7081 alloy.

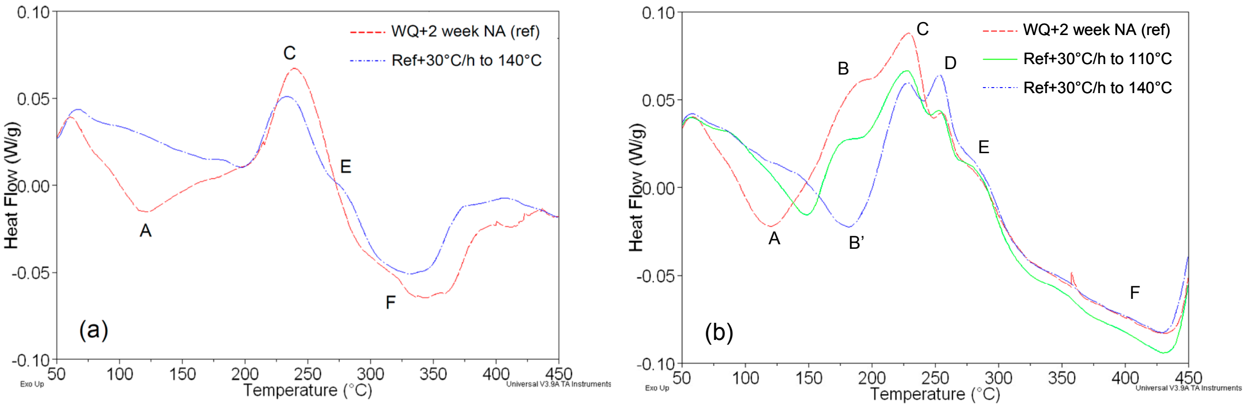

Fig. 4 DSC thermograms conducted after water quench and 2 weeks natural ageing, and after water quench and 2 weeks natural ageing, then heating up to 110°C or 140°C at heating rate of 30°C/h, (a) AA7021, (b)AA7081.

4. Discussion

The most salient finding in this experiment is that TEP can provide more information about the evolution of the precipitation process and the characterization of its kinetics during artificial ageing than the conductivity and hardness measurements do in 7xxx alloys. The TEP results need to be discussed further.

During the ageing of a solution treated sample, the conductivity can change due to the annihilation of quenched-in vacancies, cluster-formation and depletion of solutes from the matrix as well as the formation of precipitates. Among these processes, only cluster formation and semi-coherent η' can lead to a decrease in conductivity [1]; vacancy annihilation and solute depletion both lead to an increase in conductivity. Incoherent precipitates η have little influence on conductivity.

The evolution of the TEP during the precipitation is mainly governed by two effects. The first effect arises because the solute content in solution gradually decreases, as precipitation proceeds, leading to a TEP change. The main alloying elements such as Zn, Mg and Cu in solute solution in 7xxx alloys have a positive influence on the TEP value of Al [1-4]. Therefore, the depletion of Zn, Mg, and Cu in the solid solution during the ageing process will lead to a monotonous decrease in the TEP of an alloy.

The second effect is attributed to an intrinsic influence of the coherent or semi-coherent precipitates which form during ageing. It was shown that this effect is expected to depend on the type, size, morphology and volume fraction of the precipitates [3,4] and that the sign and amplitude of the effect are reasonably well rationalized in terms of Bragg scattering by coherent precipitates [4]. It is generally understood that the coarse incoherent precipitates have no effect on the TEP.

Table 2. The effect of the microstructures on the TEP, conductivity and hardness

	Vacancy annihilation	GP zone formation	GP zone reversion	Solute depletion	η' semi-coherent	η in-coherent
TEP	--	decrease	increase	decrease	decrease	--
Conductivity	increase	decrease	increase	increase	decrease	--
Hardness	increase	increase	decrease	--	increase	decrease

The effect of the microstructural change during ageing on the TEP, conductivity and hardness in 7xxx was summarized in Table 2. From these effects, the 4-stage ageing behaviour detected by TEP measurement (in Fig. 3) in the two 7xxx alloys can be understood as follows.

Stage 1, GP reversion: the increase in TEP during heating-up can be linked to the dissolution of small non-stable GP zones formed during quenching or during natural ageing at room temperature.

Less increase in TEP of AA7081 indicates less reversion of GP zones. This fact manifests that the addition of Cu results in an increase in the stability of GP zones formed at room temperature, and in a decrease in the nucleation temperature for the η' phase. The DSC analysis and the drop in the hardness during the heating stage confirm the dissolution of the some GP zones.

Stage 2, GP+η': stable GP zones grow up to critical size and transform to η'. The coherent GP zones or semi-coherent η' precipitates as well as the depletion of the alloying elements leads to a decrease in the TEP.

Stage 3, η': a fast drop in the TEP results from the growing semi-coherent η' precipitates and the depletion of the alloying elements.

Stage 4, η'+η: a slow decrease in the TEP is only related to the depletion of alloying elements from aluminium matrix. The tuning point of η' to η transformation corresponds to the ageing time for the peak hardness.

TEP increase in the stage 1 in the AA7081 is much smaller than that in the AA7021 and the GP reversion stage ends in a lower temperature. This fact demonstrates that the Cu in the Al-Zn-Mg alloy promotes the development of η' from GP zones. The TEP drops slower during stage 2 and stage 3 in the AA7081, which indicates that Cu addition stabilizes the GP zones and η' during the artificial ageing. Thus, the TEP yields also the difference in precipitation kinetics between the two 7xxx alloys.

5. Conclusions

1. TEP measurements are very sensitive to microstructural changes in 7xxx alloys, in which the main elements such as Zn, Mg and Cu have a positive thermopower in an aluminium matrix.
2. TEP provides more information about the evolution of the precipitation process and the characterization of its kinetics during ageing than conductivity measurement does in 7xxx alloys.
3. TEP indicates that the reversion of GP zones takes place during heating-up stage of the artificial ageing. As this process will affect the kinetics and size of the strengthening η' phase, more attention should be paid to the investigation of the heating rate on the ageing behaviour.
4. TEP demonstrates that the addition of the Cu in the Al-Zn-Mg alloy stimulates the formation of GP zone in the natural ageing. Cu promotes the development of η' from GP zones and stabilizes the GP zones and η' during the artificial ageing.

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