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THE EFFECT OF COOLING RATE FROM THE HOMOGENISATION TEMPERATURE
ON THE MICROSTRUCTURE OF HIGH STRENGTH 7000 SERIES ALLOYS.

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Abstract

High strength 7000 series alloys are in a complex phase field and a variety of low melting
point eutectics are formed during casting. The presence of these phases requires that great
care is taken during commercial homogenization procedures, to ensure that the soluble phases
dissolve and redistribute through the matrix to as great an extent as possible. The
temperatures must be low to avoid localised melting at temperatures between 475°C and
495°C. However, little attention has been paid to the effect of cooling rate from
homogenization on the reformation of low melting point eutectics with there implications on
further processing. This study examines alloy chemistries within the 7010/7050 type which
are "fully" homogenized and cooled at different rates. The microstructures generated are
studied with a combination of optical microscopy and differential scanning calorimetry. The
structures formed are correlated with simple models based on diffusion theory. The
implications with regard to subsequent processing are drawn.

Introduction

Extensive work has been conducted on the precipitation reactions of 7000 series alloys [1-3].
Using this information it is possible to optimise process conditions for the alloys, such as
homogenisation schedule, rolling temperature and solution treatment temperature. However,
due to the occurrence of chemistry segregation profiles during commercial casting of "big"
ingots (> 400mm thick) the alloys become significantly more difficult to satisfactorily
homogenise and hence further down-process. This effect is most dramatically experienced
when low melting point eutectics liquate during processing leading to a significant
deterioration in final properties; however low melting point eutectic phases may also
reprecipitate during slow cooling from the homogenisation temperature thus negating the
solutionising work of the homogenisation treatment. Experience has shown that the
homogenisation sequence employed can leave a small fraction of the S (Al_2CuMg) phase in
the matrix, even after a cold water quench (approximate melting temperature 495°C which
is well in excess of processing temperatures employed). In the commercial process, however,
it is unsatisfactory to quench ingots direct from the homogenisation temperature due to

concerns over ingot cracking. Hence air cooling is employed giving a significantly slower cooling rate. This paper highlights the influence of cooling rate from the homogenisation temperature on the re-formation of low melting precipitate phases in AA7XXX type alloys. Extensive differential scanning calorimetry investigations (D.S.C.) have been conducted on the ingot regions high in zinc, magnesium and copper at which the low melting eutectic precipitates are most likely to exist. The D.S.C. information used indicates the energy associated with precipitate reactions and the temperatures at which the reactions initiate. From this information it is possible to indicate the relationship between the energy required for precipitate phase formation and the volume fraction of the precipitate phase formed (as seen by optical examination). Previous work[4] suggests that the proportion of S phase and the energy released due to the melting of the S phase during D.S.C. analysis of a Al-8.2Zn-2.2Mg-2.6Cu-0.12Zr alloy are directly related. It has been found that the mechanism of S phase formation is very similar to that involved in the formation of the low melting eutectic phase formed at temperatures below that of S phase in the D.S.C. traces of AA7010 [5]. It is proposed that this analysis will be adequate to estimate both the proportion of S and the proportion of the low melting eutectic phase present in homogenised material after cooling from the homogenisation temperature.

Experimental

Specimens approximately 20x20x10mm in size were taken from a 440mm thick AA7010 commercial ingot at the richest chemistry position;
          (nominal chemistry AA7010; Al-6.2Zn-2.3Mg-1.75Cu-0.14Zr ≤ 0.12Si ≤ 0.15Ti)
All the samples were homogenised at a maximum temperature of 475°C in computer controlled furnaces accurate to $\pm$ 1°C. The samples were then cooled linearly at the controlled cooling times described in table 1. After cooling from the homogenisation temperature the specimens were prepared for optical examination to highlight the relationship between cooling time and the proportion of intermetallic phases which develop during cooling.

To investigate the precipitation sequences of the samples a slice was taken ≈ 2mm thick from each sample, and ≈ 50mg D.S.C. specimens prepared from these slices. The analysis was conducted with the aid of a T.A. Instruments 910 D.S.C., the reference being Aluminium (99.995% purity). The D.S.C. cell was purged continuously during testing with Argon gas at a flow rate of 300ml/min and a heating rate of 20°C/min was used for all material investigated.

Results

Typical micrographs of as quenched material and material cooled at 30°C/hour from the homogenisation temperature are presented in figures 1a and b respectively. There is a significant difference between the two structures with the material after the slow cool exhibiting a large proportion of cell boundary precipitation which does not appear in the quenched material. It is anticipated that the extended time at elevated temperature which the slower cooled material experiences enables significant elemental diffusion to occur and hence increased precipitation is seen.

Typical D.S.C. traces produced from the quenched material and the slow cooled material are presented in figures 2 a and b respectively. In the upper temperature region of the trace 450 → 550°C there exists a difference between the precipitation phases present as a function of the cooling rate. One endothermic energy trough exists in the cold water quenched material which begins at ≈ 490°C and reaches its maximum energy at ≈ 499°C. As the cooling rate is reduced to 30°C/hour two endothermic peaks exist in the temperature range under investigation, one corresponding to that found at ≈ 498°C in the quenched material, but having a smaller magnitude, and a larger endothermic energy trough highlighting an alternative dissolution reaction beginning at ≈ 479°C and peaking at ≈ 484°C. If the energy associated with the endothermic reactions occurring between 450-500°C are considered, see table 1, it becomes apparent that the amount of energy associated with the precipitate dissolution reactions steadily increases with increased cooling time. This suggests that an increased tendency for precipitate formation will occur with a reduction in the cooling rate.

The energy from the experimental endothermic dissolution peaks associated with low melting eutectic phases are presented in Table 1 along with the time to cool the material down to room temperature. This table indicates that as the time to cool the material is reduced and hence cooling rate increased then a reduction in the estimated proportion of low melting eutectic occurs (calculated using equation 3).

If this is taken further and the estimated volume fraction of precipitate calculated from the D.S.C. information is plotted against (cooling time)$^{1/3}$, see figure 3, then it becomes apparent that the volume fraction of precipitate present is proportional to the time to cool the material.

<u>Discussion</u>

The microstructural developments seen are consistent with the cooling time controlling the diffusion time available for precipitation from remaining elemental segregation during cooling from the homogenisation temperature, i.e. diffusion time is proportional to cooling time. The tendency for precipitates to form in the interior of grains during cooling at relatively slow cooling rates is a consequence of fluctuations in solute concentration throughout the material providing small clusters of atoms which act as nuclei for the precipitates to form over the extended time period at elevated temperature which the material is exposed to under slow cooling.

Much information has been reported by Mondolfo[1] concerning 7xxx series alloys and the precipitation reactions which occur and it is suggested here that the precipitates which form will be dependent on the rate of cooling from the homogenisation temperature as has been seen in the optical microscopy investigation. From the information presented by Mondolfo[1] it is suggested that during solidification the predominant low melting eutectic reactions will generate S phase (Al_2CuMg) at ≈518°C (in Al-Cu-Mg alloys) and $Al + Al_2CuMg + Al_2Mg_3Zn_3 + MgZn_2$ at ≈ 475°C, however the presence of the intermetallic phases Mg_2Si and Al_7Cu_2Fe should also be expected prior to homogenisation, as they originate in the cast structure. From the D.S.C. information presented in this report it becomes apparent that the cooling rate from the homogenisation temperature controls the degree to which precipitation occurs within this material. The slower cooling rate (longer cooling time) suggests that the

prominant melting sequence occurs at $\approx 475°C$ with a large energy trough present for the 30°C/hour cooling rate indicating the melting of $Al + Al_2CuMg + Al_2Mg_3Zn_3 + MgZn_2$ existing in combination with a higher temperature trough at $\approx 495°C$. However, there is a transition from the double reactions seen at $\approx 475°C$ and $\approx 495°C$ in the material after slow cooling to a single dominant energy trough at $495°C$ in the C.W.Q. material, see table 2. As has been reported above the endothermic energy trough at $\approx 475°C$ is associated with the eutectic reactions $Al + Al_2CuMg + Al_2Mg_3Zn_3 + MgZn_2$ and the energy trough at $\approx 495°C$ with the melting of Al_2CuMg (S phase), slightly lower than $518°C$ because the zinc lowers this temperature.

It becomes possible to estimate the proportion of eutectic phase which has been formed during the cooling step by making use of equation (1) [4] and the energy associated with dissolution of the precipitate phase during D.S.C. analysis. The D.S.C. analysis has shown that the dissolution energy associated with the low melting point precipitates reduces with increase in cooling rate from the homogenisation temperature. This has also been seen during optical examination by a reduction in the proportion of precipitates forming. It therefore seems reasonable to assume that the proportion of precipitate which forms is directly related to the size of the dissolution peak during D.S.C. investigation. This has been quantified [4] by the following equation;

$$E\ (Energy(cal/g)) = -0.1587 + 0.1581 \times V_f \qquad (1)$$

where   E is the D.S.C. energy required for precipitate dissolution,
                        V_f is the volume fraction of precipitate.

This converts to;
$$E(Energy(J/g)) = 3.52V_f - 2.478 \qquad (2)$$

This equation has been slightly modified to take into account the level of intermetallics which are not dissolved during homogenisation (i.e. cold water quenched sample) giving;

$$E_{tot}(Energy(J/g)) = 3.52(V_t + V_i) - 2.478 \qquad (3)$$

where, E_{tot} is the total energy associated with melting reactions in the temperature range 450 - 550°C,
               V_t is the volume fraction of dissolvable low melting eutectic,
               V_i is the amount of intermetallic remaining after cold water quench.

V_i has been calculated as an average from all the quenched material investigated and represents 0.96% of retained S phase after homogenisation (from an average energy value of 0.90 J/g). From this can be calculated the remaining volume fraction of removable intermetallics and this is presented as the normalised volume fraction V_t in table 1.

It has been identified that the proportion of low melting point eutectic formed during the cooling of AA 7010 from the homogenisation temperature is directly proportional to the cooling time, the cold water quenched material generating no low melting eutectic phase. However, from the results there was a significant difference between the proportion of low melting eutectic phase remaining after cooling at 50°C/hour and after cold water quenching.

Hence, figure 3 suggests that a minimum period of time (incubation time) exists before which little if any low melting eutectic is developed during cooling, i.e. $(1.54)^3$ which equals 3.65 hours. This indicates that a cold water quench from the homogenisation temperature is unnecessary to minimise the volume fraction of low melting eutectic. Hence a more moderate cooling time will be sufficient and hence from this cooling time it can be calculated that the average cooling rate necessary will be $\approx 130\,^{\circ}$C/hour, which is much less rapid than that experienced during a cold water quench. This plot also highlights that the proportion of low melting eutectic retained during cooling is controlled by diffusion since it follows a $t^{1/3}$ relationship as expected.

Conclusions

(1)   Low melting precipitates (T_M approximately $475\,^{\circ}$C) develop during slow cooling of alloy AA7010 from the homogenisation temperature.

(2)   It has been observed that the estimated proportion of precipitate which forms during cooling from the homogenisation temperature is directly proportional to the (cooling time)$^{1/3}$ indicating a diffusion controlled process.

(3)   The proportion of low melting eutectic developed during cooling from the homogenisation temperature can be minimised by use of a bulk·cooling rate exceeding a critical cooling rate of $\approx 130\,^{\circ}$C/hour.

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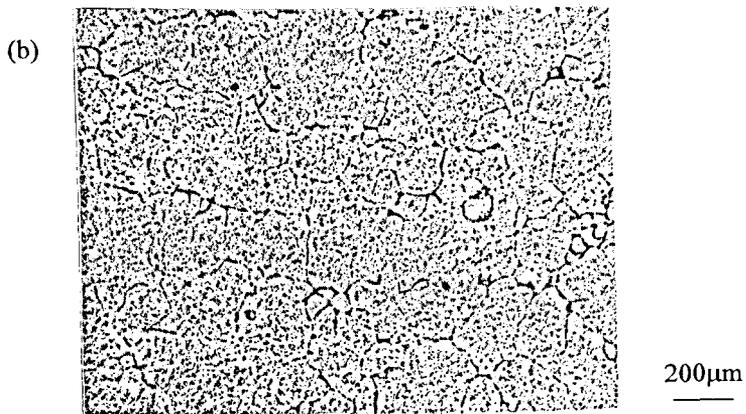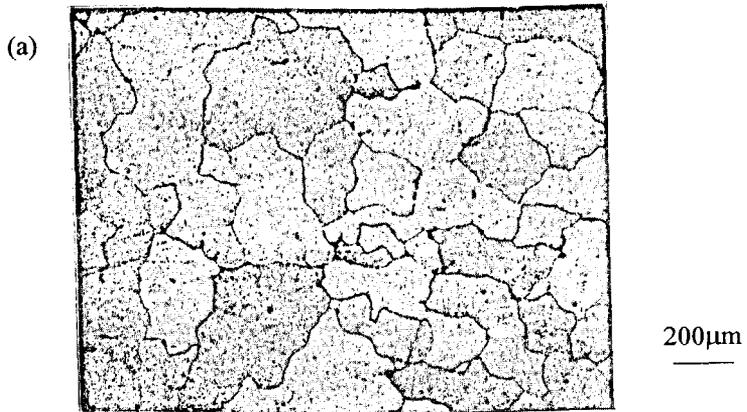
(a)

200µm

(b)

200µm

Figure 1. Typical micrographs from material (a) water quenched
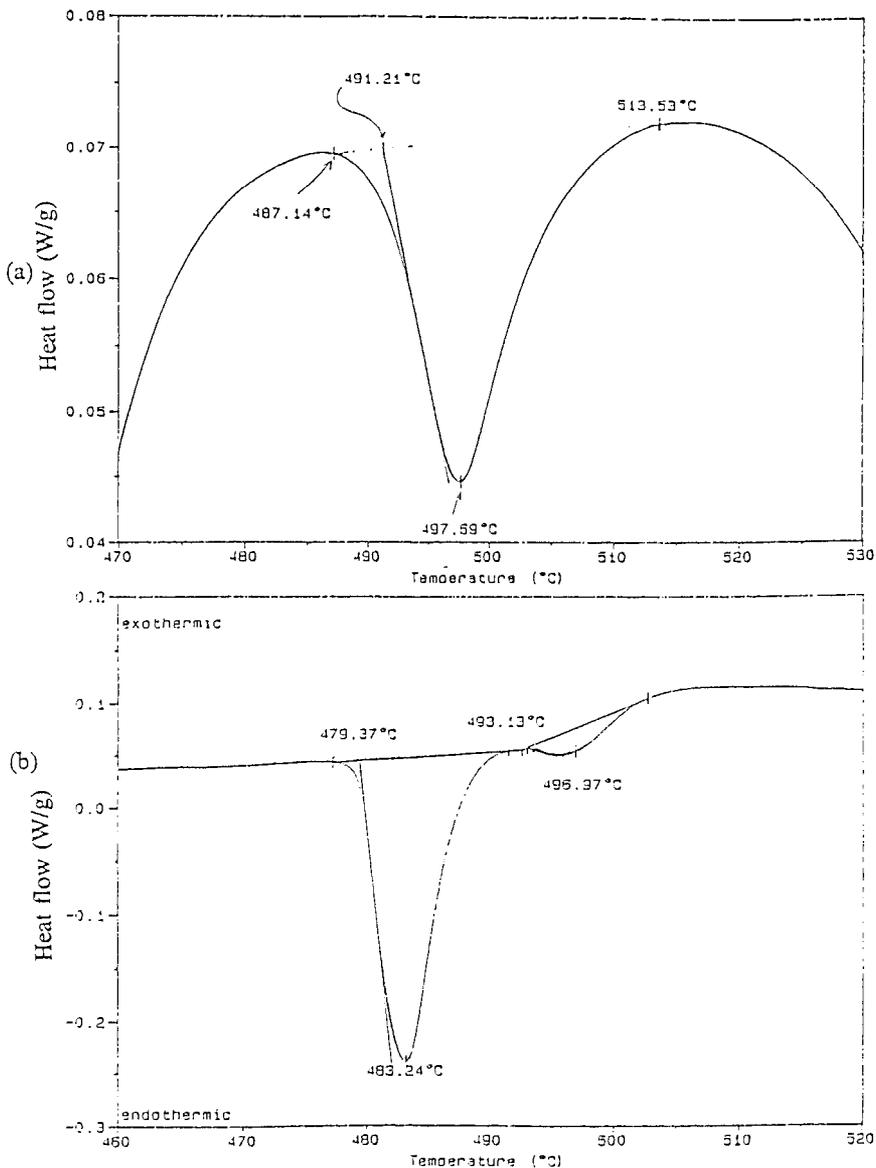and (b) slow cooled (30°C/hour) from the homogenisation temperature.

Figure 2. Typical D.S.C. traces produced from material (a) water quenched and (b) slow cooled (30°C/hour) from the homogenisation temperature.

Table 1 The volume fraction of low melting eutectic formed during cooling from the homogenisation temperature and the cooling time to room temperature.

Dissolution energy associated with precipitates (J/g)	Volume fraction V_t of precipitate formed (%)	Cooling time (hours)	(Cooling time)$^{1/3}$ (hours)$^{1/3}$
18.4	4.97	90	4.48
12.5	3.30	45	3.56
9.5	2.44	30	3.11
5.9	1.42	15	2.47
4.7	1.09	9	2.08
0	0	≈ 0 (C.W.Q.)	≈ 0

Table 2 The average dissolution energies calculated from the eutectic reactions in the temperature range 450 - 500°C as a function of cooling rate involved.

Cooling rate (°C/hour)	Total dissolution energy (J/g)	Energy of 475°C trough (J/g)	Energy of 495°C trough (J/g)
5	18.4	18.4	0.0
10	12.5	12.5	0.0
15	9.5	9.4	0.1
30	5.9	5.6	0.3
≈ 5000 (C.W.Q.)	0.9	0.0	0.9

Figure 3; Influence of cooling time on the estimated volume fraction of low melting eutectic present·

■ Estimated volume fraction Vt   ——— line fit, Vt = 1.66t^(1/3) - 2.55

Estimated volume fraction of low melting eutectic Vt (%)

(Cooling time from homogenisation temperature)^0.3333 (hour)^0.3333