

THE 4TH INTERNATIONAL CONFERENCE ON ALUMINUM ALLOYS

ZIRKON IN ALLOY AA 7108 USED FOR BUMPERS

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Introduction

In the production of bumpers, Raufoss A/S uses alloys belonging to the lower or intermediate strength regime of the 7000-series. AA 7108 is a group of alloys with 5-6 wt% Zn and 0.8-1.8 wt% Mg. The alloys typically realize yield strengths in the range 320-420 MPa (extrusions in T6-condition) and provide satisfactory formability.

Both formability and T6-strength are reduced if the profile recrystallizes after extrusion or solution heat treatment. Zr can be successfully added to 7000-series alloys to make them more resistant to recrystallization, and this paper deals with such topics as the alloying of Zr, the optimum amount of Zr and the homogenization process in which the precipitation takes place.

The optimum Zr-addition

Control of the phase diagram

The proper amount of Zr is controlled by the solubility of Zr in aluminium. Al-Zr forms a peritectic system, and the solid solubility is higher than the liquid solubility at the peritectic temperature, Figure 1. According to Figure 1 the Zr-concentration should not exceed 0.11 wt% in order to prevent primary Al_3Zr -particles to form in the liquid. If the solidification process follows the Scheil equation, which is reasonable as no solid state diffusion of Zr is likely, the aluminium grain will exhibit a centre with 0.28 wt% and a grain boundary with no Zr.

In order to check whether the phase diagram in Figure 1 describes the liquid solubility of Zr in Al correctly for the 7108-alloy, samples (slightly conical cylinders with radius approximately 10 mm

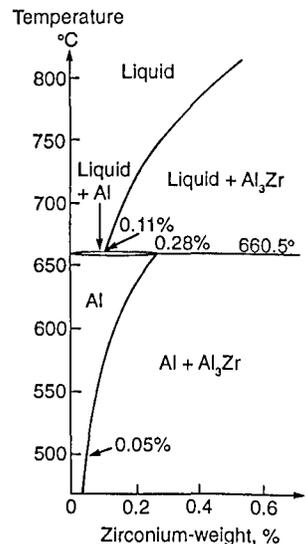


Figure 1. The Al-Zr binary phase diagram, after Phillips [1]

and height 70 mm) with 0.21 wt% Zr were melted at 660 °C and kept for 1 hr, 4 hrs and 16 hrs followed by centrifuging in order to collect the particles in the melt at the bottom of the sample, Figure 2.

The amount of centrifuged particles was then determined by image analysis and the Al_3Zr type of particles was confirmed by microprobe analysis. From the calculated amount of Zr in the particles the points in the phase diagram in Figure 3 could be plotted.

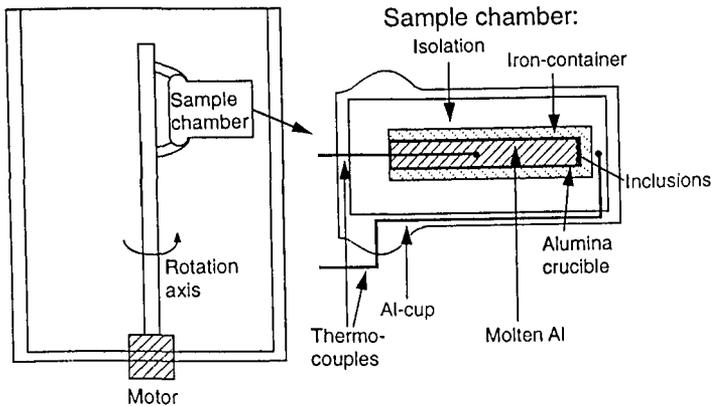


Figure 2. The centrifuge used to separate particles in the liquid sample.

It is observed that the three points at 660 °C corresponding to the three holding times differ in Zr-concentration, but not in a systematic way with increasing holding time. Three melts at 700 °C, 740 °C and 800 °C were also centrifuged. As expected, no particles were found in the 800 °C-sample, while it is interesting to note that a small amount of particles was found in the 740 °C-sample. This indicates that the solubility of Zr is lower (but only slightly lower) than 0.21 wt% at 740 °C.

The conclusion is that the binary phase diagram presented by Phillips applies well. The measured points in Figure 3, indicating an increased solubility at 660 °C, should be interpreted with care, as there is a possibility that not all the particles are centrifuged effectively. Consequently, the sample with the highest amount of particles, i.e. the lowest calculated solubility, is the most reliable.

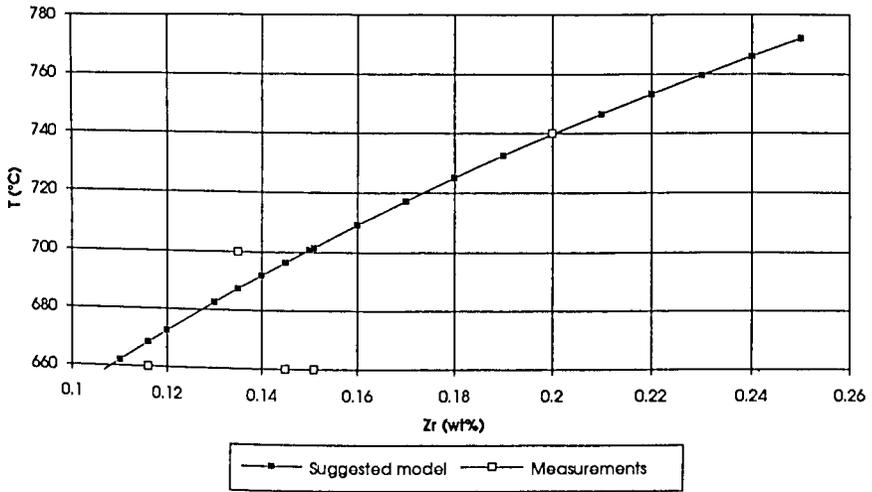


Figure 3. Measured liquid solubility of Zr in liquid 7108-alloy. The three measured points at 660 °C correspond to a holding time of 1 hr (highest solubility), 4 hrs (lowest solubility) and 16 hrs (intermediate solubility).

Determination of Zr in solid solution

The amount of Zr in solid solution has been measured directly with the microprobe on as DC-cast samples with 0.11, 0.16 and 0.21 wt% Zr. 40 arbitrary points in each sample were determined. As Zr segregates strongly, it was still a possibility that the 40 points would not give an average of Zr in solid solution. To ensure that points near grain centers or grain boundaries were not over-represented, also Zn and Mg was measured. These elements segregates eutectically, i.e opposite of Zr.

Table I. Results from microprobe measurements of Zr in solid solution in DC-cast samples.

Alloy	Average of 27-29 points from centre to dendrite boundary			Average of 40 arbitrary points		
	Zr	Zn	Mg	Zr	Zn	Mg
4/93 (5.2 Zn, 0.81 Mg, 0.11 Zr)	0.090	3.78	0.97	0.071	4.66	0.85
8/93 (5.4 Zn, 0.80 Mg, 0.21 Zr)	0.159	5.14	1.11	0.173	5.43	0.92
2054 (5.3 Zn, 1.23 Mg, 0.16 Zr)	0.128	5.46	0.86	0.135	5.34	1.39

The results are presented in Table I. It has been shown experimentally, by dissolving the sample in butanol and collecting the intermetallic particles on a filter (see [2] for a description of the dissolution technique), that the amount of Zn and Mg bound up in particles is very small, i.e. the average matrix concentration should be almost the same as the alloy concentration. It is observed from Table I that the average Zn and Mg-concentrations are close to that of the alloy, and consequently the average Zr-concentration would also be representative for the total amount of Zr in solid solution.

The results clearly show that it is possible to dissolve more than 0.11 wt% Zr in DC-cast materials. Another proof for this was obtained by measuring the amount of primary Al_3Zr in the 0.21 wt% alloy, finding that this amount corresponds to maximum 0.04 wt% Zr.

Alloying of Zr

Primary Al_3Zr is always found in the as cast material, more the more Zr that is added. It is also evident that the liquid concentration of Zr is not following the liquidus slope in the phase diagram in the casting process, as an average of 0.17 wt% Zr in solid solution has been measured. It is obvious that the cooling of the melt in the gate between furnace and casting table and in the casting process itself, is too high to allow for precipitation of Al_3Zr up to the amount prescribed by the equilibrium phase diagram. In the cast material we observed large regular plates of Al_3Zr , constituting the main fraction of the Al_3Zr primary particles, but also agglomerates of significantly smaller particles. As a hypothesis it was suggested that the large particles originate from the furnace, while the smaller precipitated in the gate or during casting.

The furnace temperature has been 730 °C in the conducted casting experiments, i.e. slightly below the solubility limit for the 0.21 wt% Zr-sample. It is therefore not surprising to find large Al_3Zr -particles in this alloy. However, similar particles are to some extent found in samples with Zr below the solubility level at the furnace temperature. These particles can, providing our hypothesis is correct, only be formed as a result of incomplete dissolution of the alloyed Zr-granulates, or eventually as a result of local cold spots in the furnace.

Zr has so far been added to the melt as large (typically 10 gr.) lumps of 99% Zr. When adding Zr this way, the dissolution is very slow if no stirring is applied, Figure 4. It is also evident from the figure that stirring is not crucial if Zr is added as an Al90Zr10 master alloy or if the Zr-granulates are crushed (typically 0.02 gr.). As a conclusion it seems rather probable that the added Zr-lumps sink rapidly to the bottom of the furnace when the stirring is incomplete, and thereby fail to dissolve. There are totally 10 intermediate phases between Zr and Al, [3], and the final reaction, being the dissolution of Al_3Zr , will not always be completed during the time between alloying and casting. These arguments and the results presented in Figure 4 confirm that the large Al_3Zr -particles may well originate from undissolved Zr-granulates.

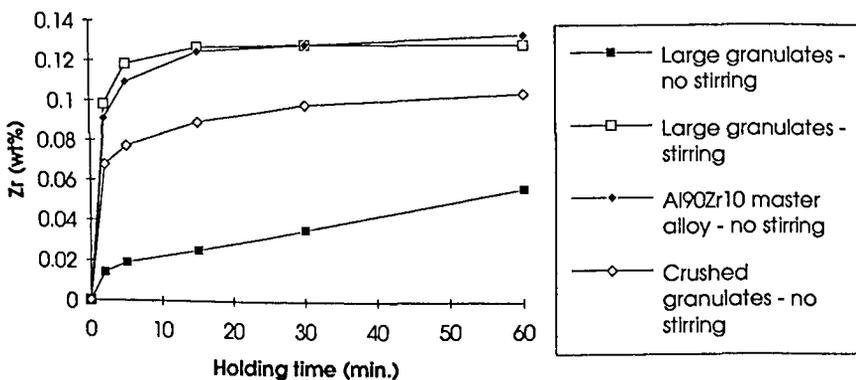


Figure 4. Alloying 0.12 wt% Zr to the melt at 740 °C. Some loss is probable when the crushed granulates was added.

Homogenization

During homogenization, or rather during the heating up to the homogenization temperature, small Al_3Zr dispersoids precipitate from the supersaturated matrix. The larger fraction of particles, f , and the smaller particles, r , the larger the Zener-drag (f/r), and the higher the recrystallization resistance, [4]. The upper homogenization temperature is determined by events such as dispersoid coarsening and dissolution, while the lower temperature could be determined by that necessary to get nucleation of precipitates within a reasonably short time. In practise, the lower temperature will be determined by that necessary to dissolve Mg_2Si and Zn_2Mg -particles formed during solidification, and to vanish out concentration gradients. These topics will not be adressed in the present paper, but from published phase diagrams it can be concluded that it is the Mg_2Si -dissolution that requires the highest temperature and the Si-content should consequently be kept as low as possible.

Experimental procedure

The Al_3Zr -dispersoids will be rather inhomogenously distributed as a result of the non-uniform distribution of Zr in the matrix, making a direct measurement of the Zener-parameter f/r very difficult. A possible way of characterising a homogenized condition with respect to its recrystallization resistance is simply to deform the material and check the recrystallization resistance by series of heat treatments.

Tables II, III and IV show the different homogenization conditions that were investigated. After homogenization the material was cold-rolled 80%. A flash-annealing prior to the cold-rolling was done in order to minimize any differencies in strain-hardening due to cold aging. The samples were then heat treated in an air-circulated furnace at temperatures from

Table II. A summary of investigated one-step homogenization conditions. All samples are cold-rolled 80% before recrystallization annealing. Standard deviation of 10 hardness measurement values are shown in paranthesis.

Homogenization treatment				Recryst. annealing		Results	
Sample no.	Heating rate (°C/hr)	Temp. (°C)	Time at Temp. (hrs)	Temp. (°C)	Time (min.)	Hardness (HV)	Recryst. degree
1	60	300	0.5	450	32	37.5 (1.5)	Fully
	"	"	"	500	4	32.5 (0.7)	Fully
2	60	400	24	475	32	48.3 (1.0)	Little
	"	"	"	500	32	45.9 (1.4)	Partly
	"	"	"	525	32	42.2 (1.6)	Mostly
3	>5000	400	24	525	32	42.8 (1.7)	Mostly
4	60	425	24	525	32	50.2 (0.9)	Little
5	60	425	168	525	32	51.7 (1.2)	Very little
6	60	450	1	500	32	46.4 (1.5)	Partly
	"	"	"	525	32	42.7 (1.2)	Mostly
7	60	450	4	500	32	50.3 (0.9)	Very little
	"	"	"	525	32	46.2 (1.0)	Little/partly
8	60	450	24	500	4	51.3 (1.3)	No
	"	"	"	500	32	47.8 (1.2)	No/very little
	"	"	"	500	128	40.7 (1.4)	Very little
	"	"	"	525	32	46.2 (1.3)	Little
9	>5000	450	24	525	32	39.4 (1.6)	Mostly
10	60	475	4	525	32	46.0 (3.3)	Little/partly
11	60	475	24	525	32	51.5 (1.2)	Very little
12	60	500	1	500	32	52.9 (1.4)	Little
	"	"	"	525	32	42.4 (1.1)	Little/partly
13	60	500	4	500	32	51.5 (1.7)	Little
	"	"	"	525	32	46.9 (1.2)	Little/partly
14	60	500	24	500	32	48.6 (1.0)	Partly
	"	"	"	525	32	44.3 (1.4)	Partly/mostly
15	180	500	4	525	32	45.5 (1.6)	Little
17	>5000	500	1	525	32	38.6 (1.0)	Fully
18	>5000	500	4	525	32	37.0 (0.7)	Fully
19	>5000	500	24	525	32	41.0 (1.5)	Mostly
20	60	525	1	525	32	45.3 (2.0)	Partly
21	60	525	4	525	32	45.6 (2.9)	Partly
22	60	550	1	475	32	47.9 (0.6)	Partly
	"	"	"	500	32	47.7 (1.3)	Partly
	"	"	"	525	32	45.3 (1.1)	Mostly/partly
23	60	550	4	475	32	45.1 (0.8)	Partly/mostly
	"	"	"	500	32	43.8 (1.4)	Mostly
	"	"	"	525	32	42.8 (0.9)	Mostly
24	60	550	24	475	32	38.6 (0.7)	Fully
	"	"	"	500	32	40.2 (1.0)	Fully
	"	"	"	525	32	39.1 (1.0)	Fully

Table III. A summary of investigated two-step homogenization treatments with slow heating (60 °C/hr) to the lowest temperature, and fast heating (>5000 °C/hr) to the final temperature.

Homogenization treatment					Recryst. annealing		Results	
Sample no.	Temp.1 (°C)	Time at Temp.1 (hrs)	Temp.2 (°C)	Time at Temp.2 (hrs)	Temp. (°C)	Time (min.)	Hardness (HV)	Recryst. degree
25	350	8	500	4	500	32	50.1 (0.7)	Very little
26	400	8	500	4	500	32	52.5 (0.8)	Little
	"	"	"	"	525	32	49.3 (1.3)	Little
27	450	8	500	4	500	32	53.5 (0.9)	Very little
	"	"	"	"	525	32	46.0 (1.7)	Little/partly

Table IV. A summary of investigated homogenization treatments with fast heating (>5000 °C/hr) to the lowest temperature, immediately followed by a slow heating (60 °C/hr) to the final temperature.

Homogenization treatment					Recryst. annealing		Results	
Sample no.	Temp.1 (°C)	Time at Temp.1 (hrs)	Temp.2 (°C)	Time at Temp.2 (hrs)	Temp. (°C)	Time (min.)	Hardness (HV)	Recryst. degree
28	350	0	475	24	525	32	42.9 (1.5)	Mostly
29	350	0	500	4	525	32	39.9 (0.9)	Mostly/fully
30	400	0	475	24	525	32	38.5 (0.8)	Fully
31	400	0	500	4	525	32	39.4 (0.9)	Fully

400-525 °C for times in the range 4-128 minutes, depending on the state of homogenization. The samples were quenched and put directly in liquid nitrogen. The hardness could then be determined with a minimum of cold aging contribution. Micrographs of the final structure were, however, used as the main indicator for the recrystallization resistance.

Results

The results are summarized in tables II, III and IV. It is worth noticing that the information gained from hardness values and grain structure is in very good agreement.

To avoid any significant recrystallization after a 32 min. heat treatment at 525 °C on samples homogenized with a heating rate of 60 °C/hr, the end temperature should be at least 425 °C. At this temperature a 24 hr treatment is rather effective, and a 168 hr treatment even more. At 450 °C and even at 475 °C the result is better after 24 hrs than after a shorter time. At 500 °C,

however, the 24 hr treatment is too long and better results are achieved after 4 hrs. At 525 °C the recrystallization resistance decreases slightly, while at 550 °C the structure is nearly completely recrystallized after only 1 hr. If the heating rate is increased from 60 to 180 °C/hr. the result seems to be very little influenced.

A two-step process provides, as expected, good results, but not better than what is possible to achieve with a one-step process with low heating rate, Table III.

If a high heating rate (>5000 °C/hr) is used, the results will always be worse regarding recrystallization resistance. It is a significant difference between heating the material with 60 °C/hr from room temperature and from 350 °C, compare sample no.11 and 28, and no.15 and 29. Starting at 400 °C the difference is even more pronounced. It is evident that clustering of Zr and probably some nucleation mechanism taking place below 350 °C is very decisive for the final Al₃Zr dispersoid distribution. It is possible that Zn₂Mg-particles precipitated in the early stage of the homogenization process is responsible for the Al₃Zr nucleation. Such a mechanism is observed to be effective for the precipitation of Al₁₈Cr₂Mg₃ in AlZnMgCu-alloys with Cr as the dispersoid forming element, [5].

Conclusions

- The binary Al-Zr phase diagram suggested by Phillips describes the liquid solubility of Zr in alloy 7108 rather well.
- The time in the gating system and in the liquid pool is too short to give precipitation of Al₃Zr in the amount corresponding to equilibrium conditions. Consequently it is possible to get more than 0.11 wt% Zr into solid solution after DC-casting.
- If the furnace temperature is above 740 °C it is recommended to use 0.20 wt% Zr in the alloy. To ensure a complete dissolution of Zr, alloying with a Al90Zr10 master alloy is highly beneficial compared to large Zr-granulates.
- A slow heating rate is necessary to ensure a fine distribution of Al₃Zr after homogenization. It has been demonstrated that the slow heating must take place below 350 °C. Slow heating (60 °C/hr) and long time (>24 hrs) at 425-475 °C gives a very recrystallization resistant structure, but also 4 hr at 500 °C gives an acceptable structure. At 525 and especially at 550 °C the recrystallization resistance decreases.

References

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