

## Ageing Behaviour of Spray Cast Al-Zn-Mg-Cu Alloys

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### Abstract

Three 7xxx series aluminium SS70, N707 and 7075 alloys containing copper, zinc and magnesium were spray deposited using rapid solidification. Ageing of the 7075 alloy resulted in a peak hardnesses of 147, 186 and 191 MPa after 2, 24 and 48 h at temperatures of 175°C, 130°C and 120°C respectively. The other two alloys, SS70 and N707, were aged at 120°C, and both reached peak hardness after 24 h; SS70 had a peak hardness of 229 MPa and N707 of 228 MPa. A double ageing treatment at 105°C for 5 h then at 175°C for 1 h significantly increased the peak hardness to 185.6 MPa compared to a single stage of ageing at the higher temperatures in the 7075 alloy. TEM analysis of aged specimens revealed two types of precipitate that contributed to age hardening:  $\eta'$  and  $\eta$  (MgZn<sub>2</sub>).

**Key Words:** 7xxx series aluminium alloys, spray casting, age hardening, ageing precipitates, TEM.

## Sprey Dökülmüş Al-Zn-Mg-Cu Alaşımlarının Yaşlanma Davranışı

### Özet

Bakır, çinko ve magnezyum içeren 7xxx serisi alüminyum alaşımları SS70, N707 ve 7075 hızlı katılaştırma yöntemi olan sprej dökümle üretildiler. 7075 alaşımının 175°C, 130°C ve 120°C de yaşlandırılması sonucunda sırasıyla 2, 24 ve 48 saat sonra maksimum sertlik değerlerine ulaşıldı. Bu değerler sırasıyla 147, 186 ve 191 MPa'dır. Diğer iki alaşım SS70 ve N707'in 120°C de yaşlandırılmasında maksimum sertliğe 24 saat sonra ulaşıldı. SS70'in ulaştığı maksimum sertlik 229 MPa ve N707'in ulaştığı değer 228 MPa'dır. 7075 alaşımı 105°C de 5 saat yaşlandırmadan sonra 175°C de 1 saat yaşlandırma şeklinde uygulanan çifte yaşlandırma sonucunda 185,6 MPa sertlik değerine ulaştı. Bu değer 7075 alaşımına 175°C de uygulanan yaşlandırmayla elde edilen sertlikten daha yüksektir. Yaşlandırılmış alaşımlardan hazırlanan TEM numunelerinin incelenmesi sonucunda sertleşmeyi  $\eta'$  ve  $\eta$  çökeltilerinin sağladığı ortaya çıkarıldı.

**Anahtar Sözcükler:** 7xxx serisi alüminyum alaşımları, sprej döküm, yaşlandırma sertleşmesi, yaşlandırma çökeltileri, TEM.

### Introduction

Spray casting is a process developed from work carried out by Singer at the University of Swansea, U.K., during the early 1970s (Singer, 1970, 1972). A schematic diagram of the process is shown in Figure 1. Molten metal passes through a refractory nozzle in the bottom of the crucible. Atomisation of

the molten metal stream by the atomising gas, typically either nitrogen or argon, occurs at the point of exit from the nozzle. The resulting spray of molten metal droplets then impinges on a collector substrate to produce a dense deposit/preform (Apelian et al., 1988).

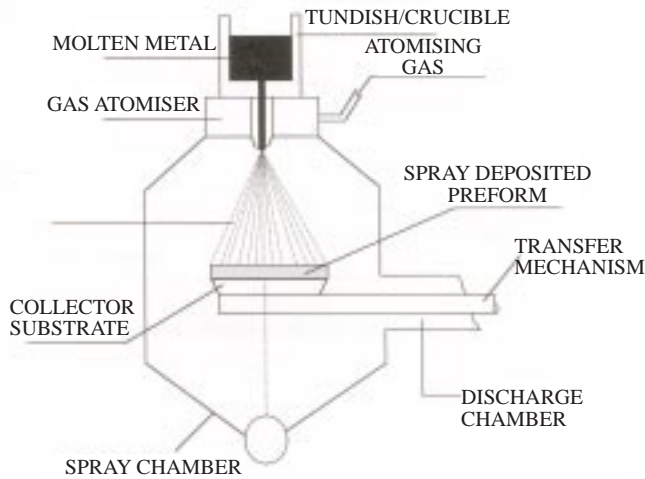


Figure 1. Schematic of the Osprey Process.

Compared to conventional casting, spray casting involves much more rapid solidification, which gives the added benefits of extending the maximum solute content of the alloying elements, reduced macrosegregation and refinement of the alloy grain size (Lavrenia and Grant, 1988).

The alloys investigated in the present study were produced by Alcan Cospray Ltd. in Banbury, U.K., using the spray deposition process. The chemical compositions of the alloys are given Table 1. The main difference between SS70, N707 and 7075 is in the zinc levels. Compared to 7075 alloy, SS70 and N707 have higher zinc content for increased strength. The main strengthening mechanism in these alloys is precipitation hardening by structural precipitates formed during ageing (intermediate  $\eta'$  and equilibrium  $\eta$  ( $\text{MgZn}_2$ )).

Table 1. Chemical composition of SS70, N707 and 7075 alloys (wt.%).

Alloy	Zn	Mg	Cu	Zr	Cr	Fe	Si	Mn	Al
SS70	11.50	2.64	1.16	0.26	<.01	0.05	0.02	-	bal.
N707	10.90	2.16	1.01	0.22	<.01	0.03	0.01	-	bal.
7075	5.6	2.5	1.6	-	0.2	0.4	0.5	0.3	bal.

A practical limit of about 8wt.% is imposed for conventional cast materials because of inherent foundry problems such as solute macrosegregation and cracking (Sanctis, 1991). The spray deposition technique enables the level of zinc in the alloys to be increased. This increases the volume fraction hardening precipitates, thus leading to an improvement in strength. Zirconium and chromium have also been added to form small intermetallics, which control recrystallisation and grain growth (Chen and Knott, 1981). 0.2% zirconium was added to SS70 and N707 instead of chromium, which was used in 7075. SS70 and N707 have lower iron and silicon contents compared to the conventional 7075 alloy.

### Experimental Method

The alloys received from Alcan International Ltd. had been spray cast and then extruded. A 240 mm diameter cylindrical preform was extruded down to a 25 mm diameter rod. N707 was also spray cast as a cylindrical preform, which was 235 mm in diameter and 790 mm in height, extruded down to a

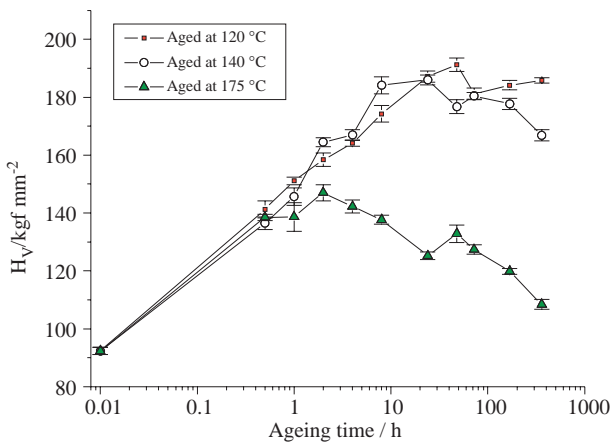
63x25 mm rectangular section. The 7075 alloy was similarly processed, i.e., spray cast to a 240 mm diameter cylindrical preform and extruded to a 65x30 mm rectangular section. Solution heat treatment was carried out in a muffle furnace at 470°C ( $\pm 5^\circ\text{C}$ ) for 0.5 h. After quenching in water, ageing was carried out in a silicone oil bath. The ageing treatments included one step and two step ageing. One step ageing was carried out at 120, 140 and 175°C for selected times. The first step of double ageing was carried out at 105°C and the second step at 175°C for selected times. Age hardening curves were determined using an average hardness value from five Vickers indents, using a 5 kg load.

TEM specimens were prepared by cutting thin slices from the aged samples using a Struers Accutom precision cutting wheel, and then mechanically punching 3 mm discs from these slices. The discs were then thinned in a Struers Tenupol-3 twin jet polisher using 25%  $\text{HNO}_3$  in methanol at  $-20^\circ\text{C}$  with an applied voltage of 9V. The specimens were examined using a Philips CM20 transmission electron microscope at an accelerating voltage of 200 keV.

## Results and Discussion

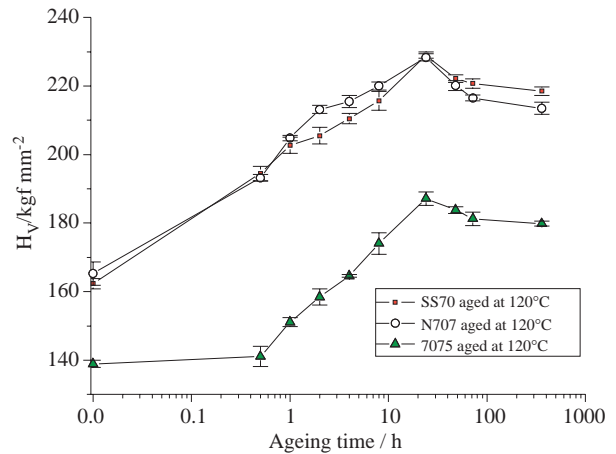
### Ageing and hardness measurements

**One-stage ageing treatment** Initial ageing was carried out on 7075. Samples of 7075 were solution heat treated at 470°C for 0.5 h and then quenched in water. These samples were then aged for various times at 120°C, 140°C and 175°C. The resulting ageing curves are shown in Figure 2. The peak hardness values obtained were 191, 186 and 147 MPa at ageing temperatures of 120°C, 140°C and 175°C respectively. The times to achieve these peak hardness values were 48 h, 24 h and 2 h. These results indicated that the rate of ageing increases markedly with increasing temperature while the peak hardnesses decreases. Ageing curves at 140°C and 175°C show secondary hardening with peaks at 72 h and 48 h respectively (Figure 2).



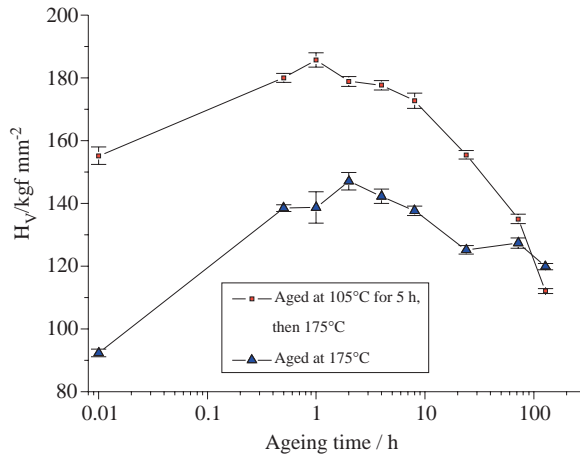
**Figure 2.** Age hardening curve for 7075 at 120°C, 140°C and 175°C.

The hardness values of all three alloys after ageing at 120°C are shown in Figure 3. The peak hardness values achieved at an ageing temperature of 120°C were 229 MPa, 228 MPa and 191 MPa for SS70, N707 and 7075 respectively. The corresponding times to reach these peak hardnesses were 24 h, 24 h and 48 h. As shown in Figure 3, when the Zn content is reduced from 11.5 wt.% in SS70 to 5.6 wt.% in 7075, the peak hardness decreases significantly. Lowering the Zn content from 11.5 wt.% in SS70 to 11 wt.% in N707 causes only a small reduction in peak hardness. As the Zn content in the alloys decreases, the peak hardness values decrease because lowering the Zn content decreases the volume fraction of  $\eta'$  precipitates.



**Figure 3.** Age hardening curves for SS70, N707 and 7075 at 120°C.

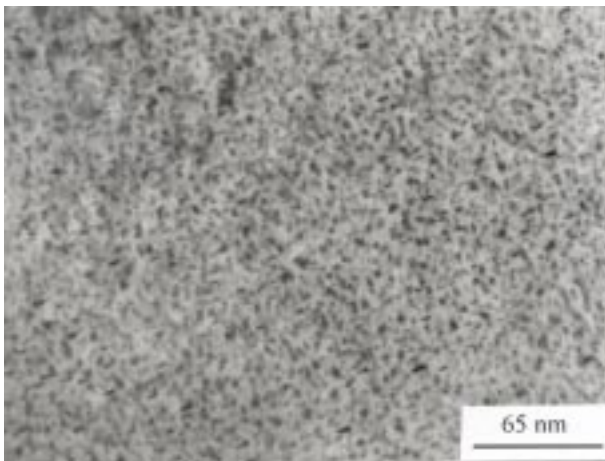
**Two-Stage ageing treatment** Experiments have shown that ageing for a sufficient time at temperatures above about 150°C significantly increased the resistance to stress-corrosion cracking but significantly reduced strength (Staley, 1989; Polmear, 1995). Therefore, a two-stage ageing treatment was developed to provide improved resistance to stress-corrosion cracking (SCC). Double ageing, which is ageing at low temperature followed by high temperature ageing, minimised the strength loss during ageing above 150°C. To carry out the two-stage ageing treatment, samples of 7075 were solution heat treated at 470°C for 0.5 h and water quenched. Samples were pre-aged at 105°C for 5 h and then aged at 175°C. The difference between one-stage and two-stage ageing heat treatments can be seen in Figure 4. A peak hardness of 185.6 MPa was achieved after 1 h at 175°C in the two-stage ageing treatment. Samples aged directly (without pre-ageing) at 175°C after solution heat treatment (one-stage ageing treatment) reached a peak hardness of only 147 MPa after 2 h. Thus, the two-stage ageing heat treatment developed a significantly higher strength than the single ageing treatment due to a finer dispersion of precipitates. The high nucleation rate, which occurs during the low temperature pre-ageing treatment, is responsible for the precipitate refinement. This fine precipitate dispersion is then retained at the high ageing temperature. These fine precipitates then transform to the final precipitates during final ageing. The higher hardness of the sample given the double ageing treatment is due to the higher precipitate density giving rise to a smaller interprecipitate spacing and thus a higher stress is required for dislocation bowing.



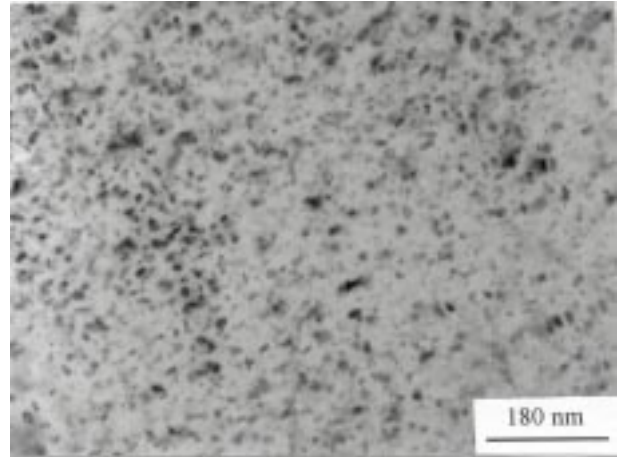
**Figure 4.** Age hardening curve for 7075 aged at 105°C for 5 h and then aged at 175°C (double ageing) and at 175°C with no pre-ageing (single ageing).

### Transmission electron microscopy

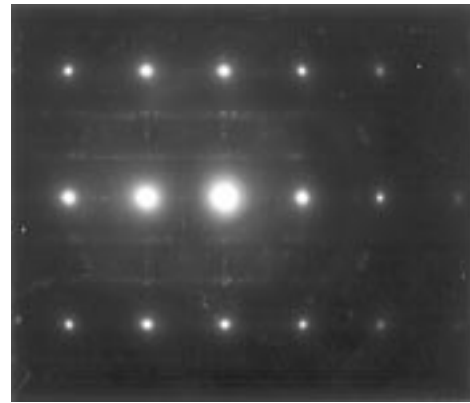
The microstructure of N707 alloy solution heat treated at 470°C for 0.5 h, water quenched and then aged to the T6 (120°C for 24 h) and T7 (105°C for 5 h followed by ageing at 175°C for 8 h) tempers were studied using transmission electron microscopy. Figures 5 and 6 show a set of electron photomicrographs taken from N707 alloy in the T6 and T7 aged conditions. Figures 7 to 9 show fine precipitates of the  $\eta$  and metastable  $\eta'$  type, which were identified by



**Figure 5.** Bright field TEM micrographs of N707 in the T6 temper.



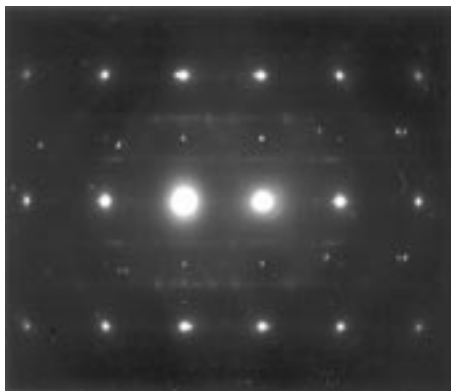
**Figure 6.** Bright field TEM micrographs of N707 in the T7 temper.



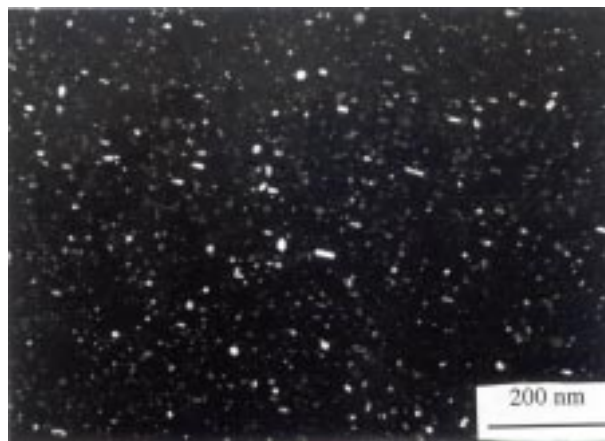
**Figure 7.** Electron diffraction pattern from a sample of N707 for the [112] zone axis in the T7 temper.



**Figure 8.** Electron diffraction pattern from a sample of N707 for the [111] zone axis in the T7 temper.



**Figure 9.** Electron diffraction pattern from a sample of N707 for the [112] zone axis in the T6 temper.



**Figure 10.** Dark field TEM micrograph of N707 in the T7 temper.

their diffraction patterns. These diffraction patterns are consistent with the results published by Park and Ardell (1983) and by Gjønnes and Simensen (1970). The indexed diffraction patterns of the  $\eta$  and  $\eta'$  type precipitates can be found in these articles. Figure 10 shows a dark field image from an N707 sample in the T7 condition. The majority of precipitates appear to be plate shaped in both temper conditions. However, the smaller precipitates appear to be spherical, particularly in the T6 microstructure. The precipitates are distributed very homogeneously and their volume fraction is very high. In the T6 microstructure, the size of the precipitates generally is small, while those in the T7 microstructure are relatively large. In the T6 condition, the precipitate size was in the range 2-7 nm. The precipitate size in the T7 temper was in the range from approximately 10 to 30 nm.

## Conclusions

The rate of ageing increased markedly with increasing temperature while the peak hardnesses decreased.

Solution treated and aged SS70, N707 and 7075 alloys showed peak hardness values of 229, 228 and 191 MPa after 24, 24, and 48 h at 120°C respectively. The 7075 alloy, which has the lowest Zn content, had the lowest peak hardness value. As the Zn content in the alloys decreased, the peak hardness values decreased because lowering the Zn content decreased the volume fraction of  $\eta'$  precipitates.

A double aged 7075 alloy (5 h at 105°C + 1 h at 175°C) showed higher peak hardness than single aged 7075 alloy (2 h at 175°C). The increased peak hardness in the double ageing treatment was attributed to a finer distribution of precipitates, because the higher precipitate density gave a smaller interprecipitate spacing and thus a higher stress was required for dislocation bowing.

In both T6 and T7 temper conditions, the precipitates  $\eta'$  and  $\eta$  were observed. The majority of precipitates appeared to be plate shaped in both temper conditions. Compared to T6 temper, in the T7 temper the precipitates were in general considerably larger.

## References

- Apelian, D., Lawley, A., Mathur, P., Luo, X.J., "Fundamentals of Droplet Consolidation During Spray Deposition", Modern Developments in Pow. Met., Proc. of 1988 Int. Pow. Met. Conf., Orlando, Florida, 19, 397-424, 1988.
- Chen, C.Q. and Knott, J.F., "Effects of Dispersoid Particles on Toughness of High-Strength Aluminium Alloys", Met. Sci., 15, 357-364, 1981.
- Gjønnes, J. and Simensen, Chr. J., "An Electron Microscope Investigation of the Microstructure in an Aluminium-Zinc-Magnesium Alloy", Acta Metall., 18, 881-890, 1970.
- Lavernia, E.J. and Grant, N.J., "Spray Deposition of Metals: A Review", Mat. Sci. Eng., 95, 381-394, 1988.
- Park, J.K. and Ardell, A.J., "Microstructure of the Commercial 7075 Al Alloy in the T651 and T7 Tempers", Metall. Trans. A, 14A, 1957-1965, 1983.

Polmear, I.J., Light Alloys, St Edmundsbury Press, London, 1995.

Sanctis, M.De, "Structure and Properties of Rapidly Solidified Ultrahigh Strength Al-Zn-Mg-Cu alloys Produced by Spray Deposition", Mat. Sci. Eng., A141, 103-121, 1991.

Singer, A.R.E., "The Principles of Spray Rolling of Metals", Met. & Mat., 4, 246-250, 257, 1970.

Singer, A.R.E., "Aluminium and Aluminium Alloy Strip Produced by Spray Deposition and Rolling", J. Inst. Metals, 100, 185-190, 1972.