



ALUMINIUM DIVISION

RECYCLING – THE EFFECT ON GRAIN REFINEMENT OF COMMERCIAL ALUMINIUM ALLOYS

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ABSTRACT

It has been known for many years that aluminium alloys refined with TiBAl benefit from partial regeneration of the refining effect after remelting. Little appears to have been published on a subject that is gaining in importance with increased recycling within the industry.

The use of various TiBAl grades and carbon enhanced TiAl refiners brings into question the effects mixing these alloys have on quality and consistency.

This paper examines the effect of recycling grain refined aluminium alloys. In particular the interactions between the different nuclei, TiB₂ and TiC are studied. Recommendations for industrial practice are given.

INTRODUCTION

Recycling of aluminium alloys, in particular in-house generated scraps and returns, has for many years been an integral part of the production process. However, in more recent times, environmental pressures have increased and this, combined with the escalating costs of producing virgin aluminium, has led to an ever increasing usage of scrap aluminium alloys in much the same way as the steel industry operates.

It has been known for many years that the effects of grain refinement are, in general, re-activated during the remelting process. Although many papers have been written on the grain refinement of wrought aluminium alloys; it appears, from literature searches, that little or no work has been published on the effects of remelting/recycling on grain refinement. Only one reference could be found (1) and this looked at the effect of only one recycle with different quantities of scrap.

The work in this paper was undertaken on four common wrought alloys using three grain refiners; two containing TiB₂ and one TiC based refiner. The refiners were chosen to cover as wide a range of Ti:B/C ratio as possible. The aim of the study was to observe the effect of repeatedly recycling alloys treated with different refiners and also to look at the effects, if any, of remelt temperature and mixing TiB₂ with TiC based refiners. The implications of the results on the scrap loop in commercial practice will also be considered.

EXPERIMENTAL PROCEDURE

The refiners used and the alloys tested are listed below in Table I along with the respective addition rates. The addition rates were chosen to reflect typical addition rates used within the wrought aluminium industry.

The grain refiners were all produced on a production scale either at London & Scandinavian Metallurgical Co Limited (LSM) or Shieldalloy Metallurgical Corporation (SMC), whilst the aluminium alloys were produced in house from 99.7 aluminium and the appropriate aluminium binary master alloys.

Each combination of alloy and grain refiner was recycled three times using a modified TP-1 test at 730°C and 800°C (2). After the final recycle cumulative additions of refiner were made to assess the recovery of refinement. The exact procedure is described in detail in Appendix 1.

To assess the effect of mixing alloys refined with boron or carbon, the above procedure was repeated but the recycled metal was half boron refined/half carbon refined. The top up with refiner was carried out firstly using boron then carbon in a second series. Only two refiners were used, 5/0.2 TiBAl and 6TiAl. The work was undertaken at 730°C and 800°C.

Table I – Alloys, Refiners and Addition Rates Used

Alloy	Refiner and Addition (kg/t)		
	3/1 TiBAl	5/0.2 TiBAl	6 TiAl 0.02C
1070	1.0	2.0	4.0
6063	0.5	1.0	2.0
3004	0.5	1.0	2.0
7050	1.0	2.0	4.0

RESULTS

The chemical analyses of the alloys tested and the grain refiners used are shown below in Tables II and III. The results of the grain refining tests are given in Tables IV - IX.

Table II – Analysis of Alloys (in wt. %)

Alloy	Ti ppm	Fe	Si	Mg	Mn	Cu	Zn	Zr
1070	50	0.15	0.02	-	-	-	-	-
6063	50	0.17	0.37	0.75	-	-	-	-
3004	50	0.16	0.04	1.06	1.24	-	-	-
7050	50	0.16	0.04	2.4	-	2.2	6.4	0.12

Table III – Analysis of Master Alloys

Refiner	Ti	B	C
3/1TiBAl	3.10	1.07	-
5/0.2 TiBAl	5.47	0.20	-
6 TiAl	5.93	0.003	0.02

DISCUSSION

Effect of Recycling

In general all three refiners showed a certain amount of fade, despite the melt being stirred two minutes before sampling, which discounts loss of grain refinement due to the known phenomenon of settling which was the subject of work by Birch and Fisher (3). The fade in this case must have been caused by another phenomenon such as slight poisoning with recycling, a gradual destruction of the surface layer of the nuclei or coarsening of the particles.

Figure 1 – Effect of temperature on TiC nuclei.

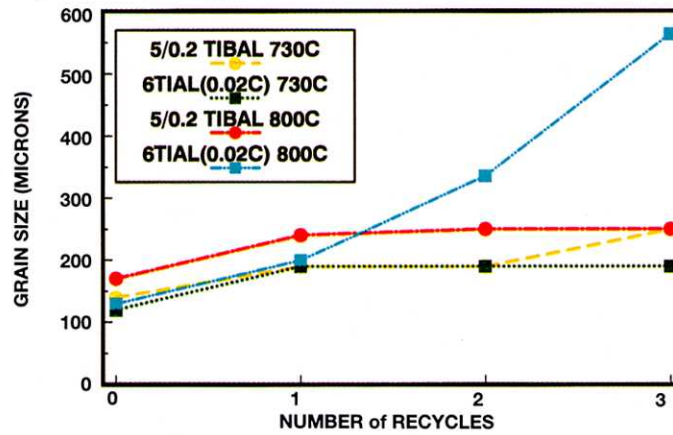


Figure 2 – 1070 Alloy at 730°C showing fade due to recycling and rejuvenation by further additions.

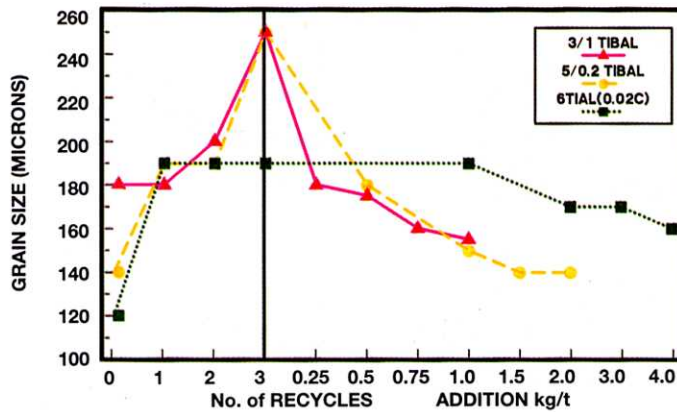


Figure 3 – 1070 Alloy at 730°C showing lack of Recovery with extra TiC Additions in mixed system

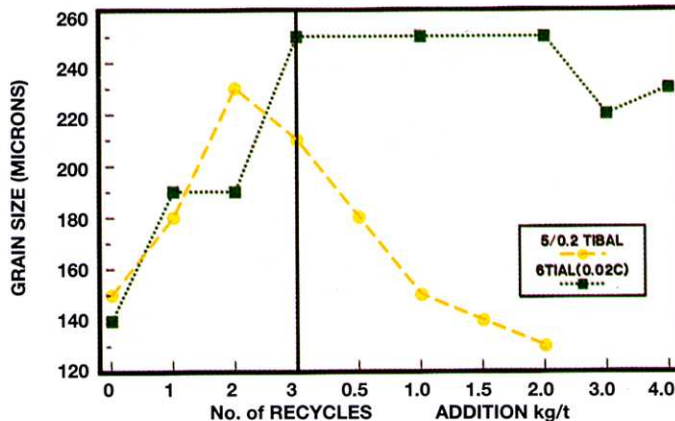


Table IV – Showing the Effects of Temperature and Grain Refiner on 1070 Alloy

Sample	Grain Size (Microns)					
	3/1 TiBAl 1Kg/t		5/0.2 TiBAl 2Kg/t		6 TiAl 4Kg/t	
	730°C	800°C	730°C	800°C	730°C	800°C
Blank	1260	2326	960	3680	1818	1960
2 min	180	160	140	170	120	130
End 1st Recycle	180	170	190	240	190	200
End 2nd Recycle	200	220	190	250	190	336
End 3rd Recycle	250	250	250	250	190	564
25% Addition	180	220	180	190	190	200
50% Addition	175	180	150	170	170	160
75% Addition	160	150	140	150	170	140
Full Addition	155	150	140	140	160	110

Another interesting feature of the recycling part of the tests was the much more rapid loss of refining effect at 800°C when using the carbide containing TiAl alloy, compared to the results at 730°C. The TiBAl alloys on the other hand were not affected by temperature (see Figure 1). Banerji et al (4) also observed a loss of grain refinement when holding melts for two hours which had been inoculated with a TiC based refiner at 800°C. It is believed that this may be caused by the carbides dissolving around 800°C. Jarfors and Fredriksson (5) have shown that TiC can transform to Al_4C_3 when held at 900°C but not at 700°C. They also state that reprecipitation of TiC is a function of time and titanium content and under the conditions of this work both factors were unfavourable.

It is well known that zirconium poisons the effect of TiB_2 as a grain refiner (6). In the case of 7050 alloy however, the carbon based alloy is more resistant to poisoning by zirconium (7) as can be seen in Table VII. It is difficult at this stage to put forward a theory as to why this may be happening. However, it may be due to the carbides being less reactive than borides with zirconium. The possibility that there are many more sub micron particles of carbides and hence more nucleation sites seems unlikely as work by Campbell and Fisher (8) showed that a similar level of boron/carbon was the key factor in determining the refining effect.

Effect of Rejuvenation

The effect of adding further quantities of refiner at 730°C to alloys recycled at 730°C and 800°C was a rapid rejuvenation, even with the 7050 alloy which was badly poisoned by zirconium. (Table IV -VII). All three refiners were effective in recovering the original grain size by adding just half the original refiner addition with obvious commercial benefits. This is represented graphically for 1070 alloy (Figure 2).

This statement however, is only true for systems containing purely borides or carbides. When alloys are mixed 50:50 with both nucleants present, a very interesting situation arises; the borides continue to rejuvenate as per the pure systems (Table VIII and Figure 3) but the carbides effect little or no recovery of refinement except in the case of 7050 alloy.

It is currently believed that the lack of recovery by carbides added to recycled metal already containing borides at 730°C may be due to an under-cooling effect which is shown schematically in figure 4. If the borides have a lower degree of under-cooling than the carbides then, provided there are sufficient potent borides still in the melt, nucleation will be nearing completion before the less effective rejuvenator carbides can act as nucleation centres. In the case of boride rejuvenation, there is a combined effect of the recycled borides and the rejuvenator borides. The borides in the 7050 alloy on the other hand, are poisoned by zirconium thus allowing the added carbides or added borides to rejuvenate grain refinement (see Figure 5). This argument is strengthened by the partial rejuvenation of 3004 alloy which contains manganese, a minor poison to borides (Table VIII). A more detailed discussion of nucleation theory is given by D. G. McCartney (9) and Maxwell and Hellawell (10) among others. Here again there are commercial implications due to choice of scrap returns, i.e., if boride and carbide refined scraps are mixed, in a 50:50 ratio at least, then it is

Figure 4 – Schematic representation of undercooling effect for different nuclei

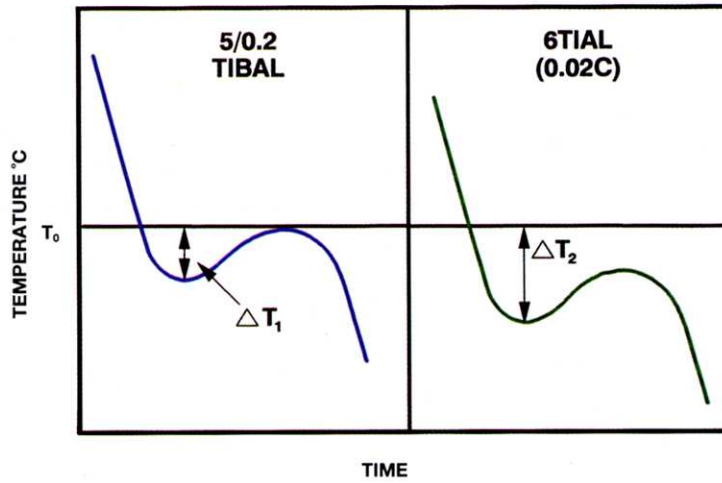


Table V – Showing the Effects of Temperature and Grain Refiner on 6063 Alloy

Sample	Grain Size (Microns)					
	3/1 TiBAL 0.5Kg/t		5/0.2 TiBAL 1Kg/t		6 TiAl 2Kg/t	
	730°C	800°C	730°C	800°C	730°C	800°C
Blank	888	772	702	748	748	610
2 min	150	140	180	140	120	150
End 1st Recycle	180	160	180	200	180	150
End 2nd Recycle	220	220	230	245	160	230
End 3rd Recycle	240	230	240	230	160	408
25% Addition	190	160	220	200	160	250
50% Addition	160	160	140	160	180	220
75% Addition	150	150	140	160	180	160
Full Addition	150	140	140	145	150	140

Table VI – Showing the Effects of Temperature and Grain Refiner on 3004 Alloy

Sample	Grain Size (Microns)					
	3/1 TiBAL 0.5Kg/t		5/0.2 TiBAL 1Kg/t		6 TiAl 2Kg/t	
	730°C	800°C	730°C	800°C	730°C	800°C
Blank	798	502	1042	960	960	725
2 min	140	150	150	150	140	130
End 1st Recycle	160	140	190	150	190	250
End 2nd Recycle	240	200	190	200	240	372
End 3rd Recycle	250	240	250	240	200	1000
25% Addition	180	190	190	190	180	240
50% Addition	155	180	160	150	170	180
75% Addition	130	150	150	145	160	160
Full Addition	120	150	130	145	150	140

Table VII – Showing the Effects of Temperature and Grain Refiner on 7050 Alloy

Sample	Grain Size (Microns)					
	3/1 TiBAL 1Kg/t		5/0.2 TiBAL 2Kg/t		6 TiAl 4Kg/t	
	730°C	800°C	730°C	800°C	730°C	800°C
Blank	594	TCG	748	TCG	1142	TCG
2 min	140	120	150	160	125	110
End 1st Recycle	2324	1260	1090	820	150	250
End 2nd Recycle	1586	2126	1960	2126	180	360
End 3rd Recycle	2324	TCG	1260	TCG	1198	TCG
25% Addition	160	185	180	160	140	130
50% Addition	150	160	160	165	130	120
75% Addition	150	150	140	150	130	120
Full Addition	150	150	140	150	110	115

impossible to re-grain refine with a carbide containing alloy unless it is used in an alloy system which poisons the borides.

If however, we mix the alloys 50:50, recycle at 800°C, and rejuvenate as before, some form of poisoning appears to take place. If the results in Table IX are compared to those in Table VIII it is clear that recycling produces a considerable loss of refinement at 800°C compared to 730°C (see Figure 6). Moreover the recovery of refinement is slowed when 5/0.2 TiBAL is used as the rejuvenator.

In the case of 6TiAl (0.02C) some recovery is seen when compared to the 730°C results (see Figure 6). Again 7050 alloy performs differently to the other alloys and full rejuvenation occurs with both refiners at the 50% addition level.

A possible explanation for these differences again lies in the dissolution of carbides. If this effect occurs between 730°C and 800°C then it is possible that on cooling they poison sufficient borides to reduce the rejuvenation powers of added TiBAL. Carbides also appear to achieve some rejuvenation but it is very slow and could be due purely to the borides being poisoned and the high titanium level of 0.04% having a constitutional effect.

Commercial Considerations

Extreme care should be taken before choosing a carbide containing refiner if the recycled scrap contains carbides and borides. Where recycling occurs and carbides are used as the nucleant, great caution must be exercised to avoid contamination by borides either from the recycle material or furnaces which may contain traces of borides. On a weight addition basis and hence cost basis, the more concentrated boron refiners are more economical. The 6TiAl (0.02C) alloy however, is more resilient to poisoning by zirconium and in this case it rejuvenates grain

refinement even in the presence of borides. This refiner may therefore be a suitable choice on alloy systems such as 7050 provided good scrap segregation practices are maintained.

Future Considerations

The work has generated some very interesting aspects regarding the mechanism of grain refinement and a more fundamental study of the effects of under-cooling using both borides and carbides as the nucleants will be undertaken.

Conclusions

1. All grain refiners lose some effectiveness with repeated recycling.
2. Borides are more efficient nuclei than carbides when the two species are mixed during recycling.
3. Borides are much less susceptible to changes in process temperatures than carbides.
4. Carbides are more resistant to zirconium poisoning than borides.

Figure 5 – Rejuvenation of 7050 alloy at 730°C with mixed carbides and borides in recycle material

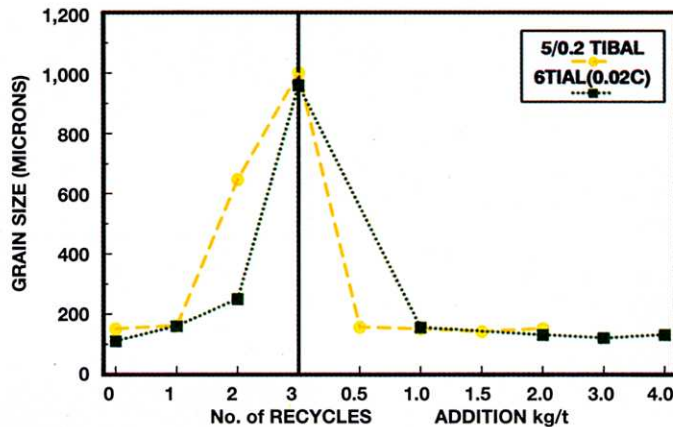


Figure 6 – Rejuvenation of 1070 alloy at 730°C and 800°C with mixed carbides and borides in recycle material

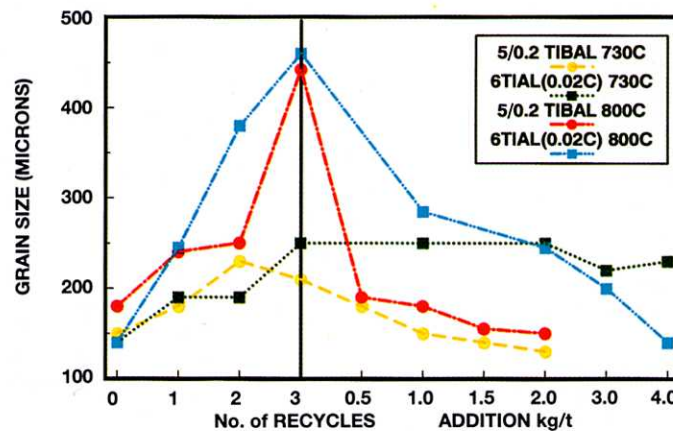


Table VIII – Mixed TiB₂ and TiC Recycled at 730°C and Rejuvenating with either TiB₂ or TiC at 730°C

Sample	Grain Size (Microns)							
	5/0.2 TiBAL				6 TiAl (0.02C)			
	1070 2kg/t	6063 1kg/t	3004 1kg/t	7050 2kg/t	1070 4kg/t	6063 2kg/t	3004 2kg/t	7050 4kg/t
Blank	2126	856	820	250	1696	856	596	TCG
2 min	150	180	170	150	140	140	120	110
5 min	150	180	180	150	140	150	145	110
1st Recycle	180	240	250	160	190	220	245	160
2nd Recycle	230	220	280	646	190	240	220	250
3rd Recycle	210	280	280	1000	250	250	250	960
25% Addition	180	230	240	155	250	245	240	155
50% Addition	150	200	180	150	250	250	230	130
75% Addition	140	150	160	140	220	225	190	120
Full Addition	130	140	150	150	230	245	190	130

Table IX – Mixed TiB₂ and TiC Recycled at 800°C and Rejuvenated with either TiB₂ or TiC at 730°C

Sample	Grain Size (Microns)							
	5/0.2 TiBAL				6TiAl (0.02C)			
	1070 2kg/t	6063 1kg/t	3004 1kg/t	7050 2kg/t	1070 4kg/t	6063 2kg/t	3004 2kg/t	7050 4kg/t
Blank	1042	922	1090	TCG	1328	960	856	TCG
2 min	180	155	170	170	140	145	185	130
5 min	180	150	170	170	140	155	180	130
1st Recycle	240	230	299	265	245	200	416	526
2nd Recycle	250	314	310	TCG	380	245	564	TCG
3rd Recycle	442	366	310	TCG	460	372	502	TCG
25% Addition	190	245	240	180	285	250	502	160
50% Addition	180	200	200	160	245	230	250	145
75% Addition	155	180	160	140	200	190	240	140
Full Addition	150	160	175	150	140	190	200	130

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APPENDIX 1

1. Carry out a TP-I two minute test taking a blank and two minute sample.
2. Stir the melt and cast.
3. Remelt the cast material, take up to required temperature (730°C or 800°C).
4. Hold one hour, stir (30 secs), wait two minutes and sample.
5. Repeat steps 2-5 until the metal has been recycled three times.
6. For tests being recycled at 800°C, the following modification to procedure was carried out; The alloy was remelted to 800°C and then allowed to cool to 730°C gradually over the one hour hold period.

This was done to simulate what would generally happen in practice.
7. After the final recycle further quantities of refiner were added, before casting, to give the following fractions of the original addition rate:- 25%, 50%, 75%, full. These additions were made to assess the amount of extra refiner needed to rejuvenate the grain refining performance back to its original level. After each addition the melt was stirred for thirty seconds and samples taken after two minutes. Each combination was carried out at 730°C and 800°C.



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