Recycling of AMCs and Aluminium Foams

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Abstract

In a government supported project, recycling concepts for SiC-particle reinforced AMCs (aluminium-matrix-composites) and aluminium foams are examined at IME Institute of Process Metallurgy and Metal Recycling. The AMC material is treated by centrifuge and conventional salt. The aluminium foams are treated in a salt based process. The results presented show that the recycling of these AMCs as well as the examined Al-foams is feasible by the investigated recycling routes and lead to sufficient recycling yields for aluminium. Remaining problems that have to be solved are the concentration of SiC-particles in the aluminium melt after treatment and the titanium content in the recycled aluminium that originates from the foaming agent TiH_2. Concerning the results of the tests SiC-particle reinforced MMCs as well as TiH_2 foamed aluminium have to be recycled separately from other aluminium scrap.

1 Introduction

In aerospace as well as in the automotive industry light materials are used in order to reduce weight and thereby fuel consumption. These materials are often utilized in form of light metals. But even as alloys, they often have insufficient mechanical properties like strength. This resulted in the development of new materials combining the required properties with low density. For example metal-matrix-composites (MMCs) combine the positive properties of metals and ceramics and constitute a very hard and light material. MMCs find their applications e.g. in motor construction, as break disks, in tail rotors or in nuclear technology.

A recent outcome of materials research is aluminium foam that is stiff and ultra light because of its porous structure. The use of foamed aluminium has big advantage in large sandwich constructions and in the stiffening of hollow aluminium profiles or sometimes even steel profiles. Other application possibilities are present in the automobile and construction industry and in aerospace industry.

It can be expected that the demand for such materials will grow also in other sectors as soon as the production and processing costs can be reduced. Parallel to the growing demand the development of suitable recycling concepts is necessary to save raw material resources due to increasing requirements concerning environmental protection. Until now, only a part of production scrap of these complex materials is recycled and returned directly into the process. This process needs clean scraps and is not practicable with contaminated material that usually consists of several different alloys and probably non-metallic parts. For impure materials only a few recycling concepts exist that yet are not applied industrially.

Due to this in a government supported project IME Process Metallurgy and Metal Recycling together with Hydro Aluminium Deutschland GmbH are searching for recycling concepts for advanced materials like composite materials, special alloys with lithium or scandium contents, iron containing cast parts and as well aluminium foams and AMC. Test runs in laboratory scale and investigations on metallurgical basics are done at IME, scale up test runs in pilot scale and material characterisation are done at Hydro Aluminium Deutschland GmbH.

Within this project recycling concepts for SiC-particle reinforced AMCs and aluminium foams are examined at IME. The AMC material is treated by centrifuge and conventional salt to regain the aluminium and possibly the reinforcing SiC-particles as well. In a successful recycling process the particle content in the recycled aluminium melt has to be reduced to zero, because if the aluminium is charged into a conventional recycling route remaining particles might cause damages in workpieces or tools. Also the regained particles have to be very pure to be reused in AMC production to guarantee the production of an isotropic material.

The aluminium foams are treated in a salt based process to regain the aluminium that possibly can be added to conventional aluminium recycling processes. Special attention has to be paid on the titanium content in foams that had been produced with TiH_2, because the titanium enrichment in the aluminium matrix can reach values of about 0.7 %. This material has to be diluted with pure aluminium to decrease the titanium content to less than 0.1 %.

2 AMC Recycling

2.1 Definition of AMCs

Apart from natural formed fiber composites like eutectic structures, MMCs are material combinations of a metal matrix and reinforcing ceramic particles or fibres respectively whiskers. If the metal matrix consists of aluminium or an aluminium alloy the composites are called AMCs.

The fraction of the dispersed ceramic phase is about 15-25 % for particles and fibres. The particles have a diameter of 5-50 µm, short fibres possess a diameter of 3 µm and a length of 0.5-10 mm. For whiskers and long fibres the diameter is about 0.1-0.5 µm and they are 20-200 mm long.

2.2 State of the Art of Recycling Process Chains for AMC

Production scraps are already recycled by remelting them and adding them to the production process again. This process however needs very pure scraps and the amount of scrap can only reach 15 % of a charge if a good quality of the product shall be guaranteed. For old scraps this purity is not given and other recycling processes have to be utilised. Up to now only some recycling concepts exist. These are the salt bath- rotary drum type kiln-process [1], the pot melting extraction [2] and a melt treatment with gases [1]. They are not yet industrially used.

For the salt bath-rotary drum type kiln-process the principle of chemical elimination of the ceramic particles from the metal melt is used. The process is similar to conventional rotary drum type kiln processes of aluminium recycling. Referred to the input of MMCs 20-50 % NaCl/KCL are charged into the furnace. Disadvantages of this process are the big time exposure of 3-4 h for a treatment and the formation of large quantities of salt slag.

The treatment with gases is based on the same principle as the treatment described before and is often combined with an addition of salt. The salt phase can be added either as salt melt or as a reactive gas like chlorine mixed with an inert gas like argon. The salt separates the particles from the metal melt and they are transported to the surface by the gas jet [1].

The pot melting extraction is based on the phenomenon that impurities in the aluminium melt are pushed back into the remaining melt during solidification of the metal. Because of this also materials in which hardly any difference in densities of the metal matrix and the reinforcing particles exists can be recycled. In addition no other aggregates or auxiliary materials are necessary. Fine fibres or flakes are regained from the basic metal that can be processed in a powder metallurgical way [2].

2.3 Test Runs at IME (Proof of Principle)

2.3.1 Removal of Particles by Centrifugation

These tests were made to evaluate the possibility to separate the reinforcing SiC-particles from the aluminium matrix of MMCs, so that the metal can be processed in conventional aluminium recycling and the SiC-particles can be reused as well to produce new MMCs.

3 kg MMC material, that was charged without salt addition under air into a graphite crucible and molten in a resistance heated furnace, consisted of an aluminium alloy A356 reinforced with about 20 vol.-% of SiC-particles. The chemical analysis made by Hydro Aluminium Deutschland GmbH is shown in Table 1. In every test run the material was treated about 3 minutes by centrifuge. Afterwards the centrifuge was taken out of the melt and the remaining metal melt was catapulted out of the rotor through the filter cake at maximum speed. Afterwards the filter cake was taken out of the centrifuge.

Table 1: Chemical analysis of MMC (Hydro Aluminium Deutschland GmbH)

Al / %	Mg / %	Fe / %	Ti / %	Cu / %	Mn / %	Si / %	SiC / %
72.0	0.33	0.11	0.059	0.014	0.0067	5.37	22.0

Parameters in these test runs were the temperature of the melt T, the frequency of the centrifuge in the melt n_1 and time and frequency of throwing the remaining metal melt off the centrifuge outside the melt, t and n_2. The experimental set up is shown in Figure 1.

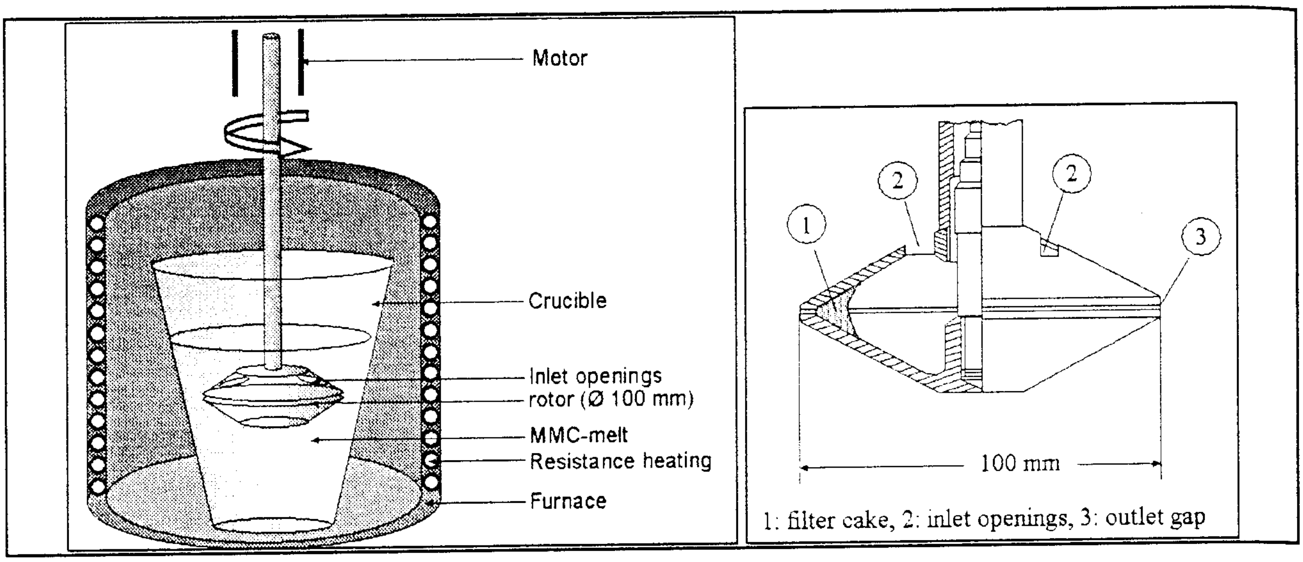

Figure 1: Experimental set up (left), rotor (right)

A typical filter cake is shown in Figure 2. A compact phase at the edge (small box) and a porous phase at the inner part of the centrifuge (bigger box) can be seen.

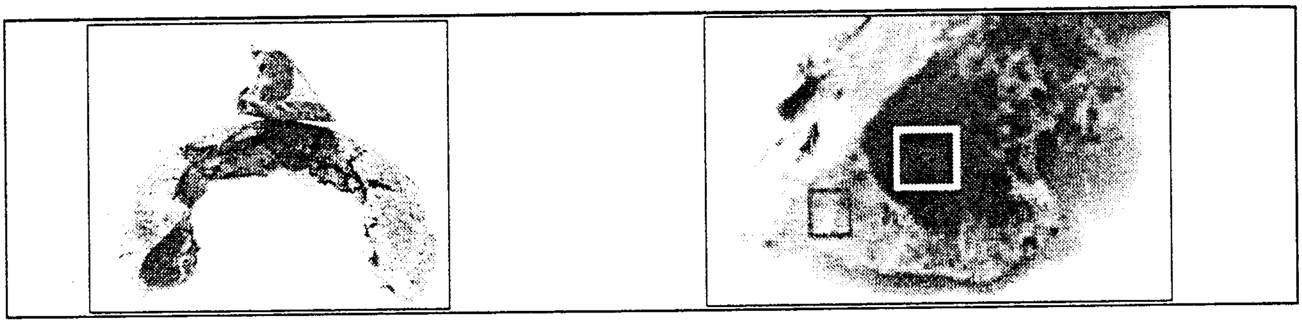

Figure 2: Typical filter cake after test runs with centrifuge

To define the distribution of the SiC-particles in the filter cakes, micrographs of the inner (big box) and outer zone (small box) have been made (Figure 3, a), b)). They show that the particles have been enriched in the filter cake. For comparison, Figure 3 c)shows a micrograph of the original MMC, where the concentration in particles is lower than in the outer zones of the centrifuge.

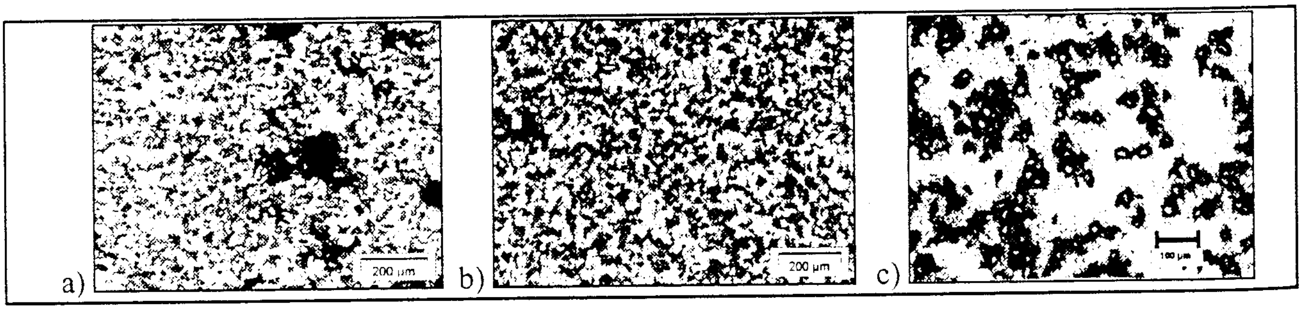

Figure 3: Filter cakes inner zone (a) and outer zone (b); initial AlSi7Mg with SiC-particles (c)

The chemical analyses of the refined aluminium samples proof as well that the concentration in SiC-particles decreases during centrifugation (Figure 4).

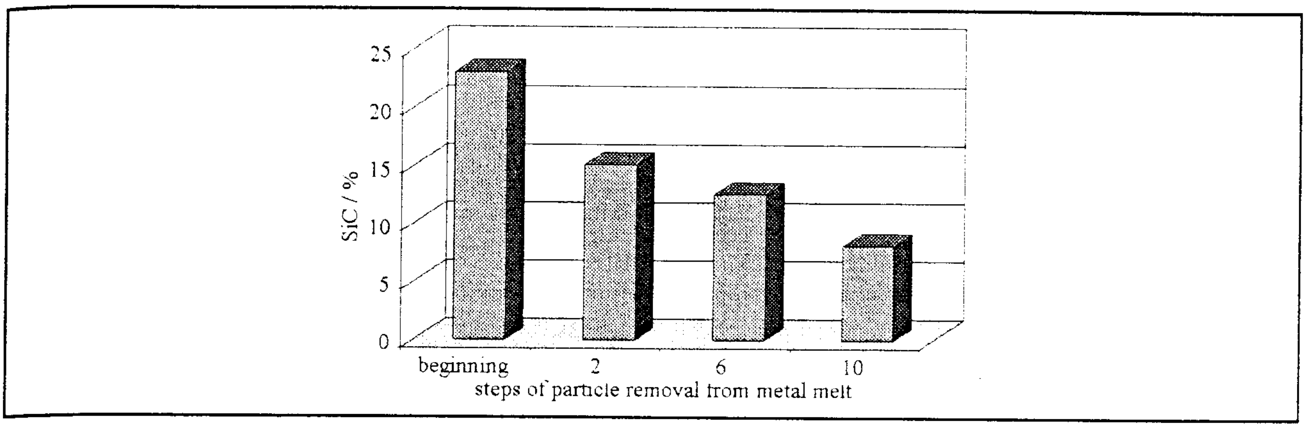

Figure 4: SiC contents in the metal samples during the first 10 removal steps

The further evaluation of the test runs was done by statistic methods. For this an appropriate mathematical model was checked (Figure 5). R^2 shows the adjustment of the model to the test run results. It should have a value near 1. In this case it has a value of 0.889, which represents an adequate adjustment. Q^2 designates the predictability of the model. It should be over 0.4 and at least half of the R^2 value. In this model both conditions are fulfilled and the model can be used. The adjustment of the model is also shown in Figure 5. The differences between observed and predicted values are quite small.

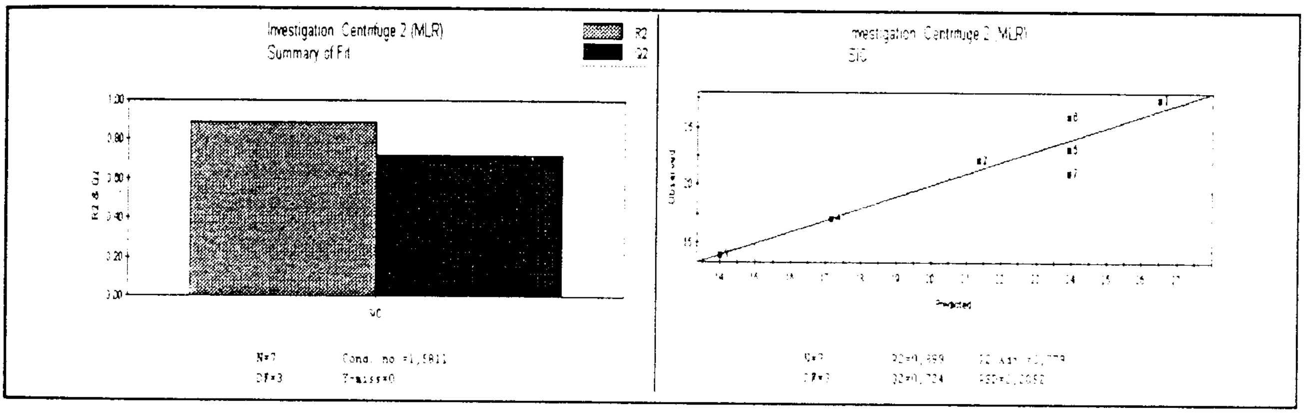

Figure 5: Summary of fit for the mathematical model, differences between observed and predicted values

Concerning the model, the SiC-content in the filter cake can be described by the following equation:

$$y = f(T, n, T^*n) \qquad (1)$$

n : frequency, T : temperature

The graphical evaluation of the results shows that the temperature has hardly any influence on the particle concentration in the filter cake. The only significant influence on it has the frequency of the centrifuge rotor outside the melt because the confidence interval remains below zero, whereas the confidence intervals of the other coefficients reach from the negative into the positive area which suggests that one coefficient might have contrary influences at the same time.

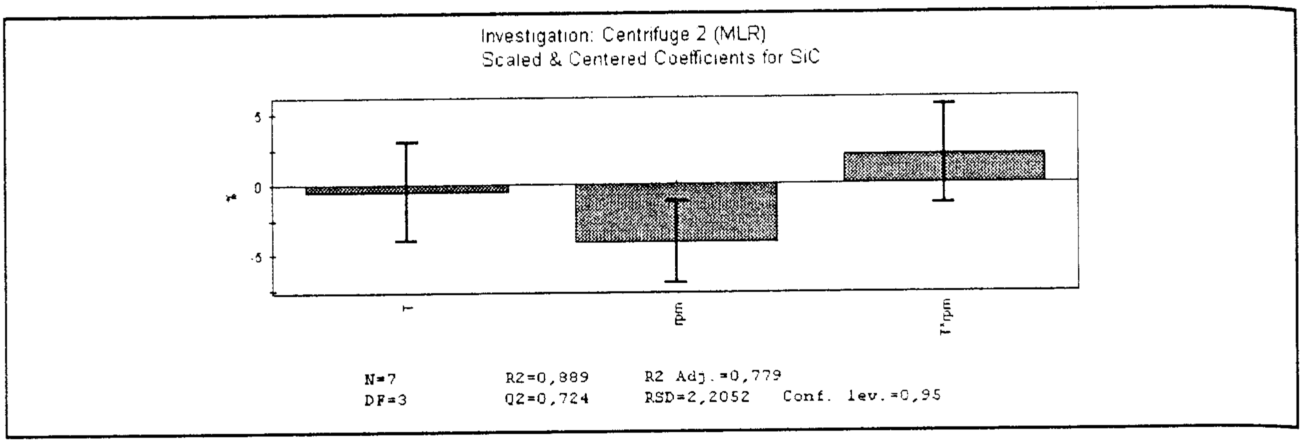

Figure 6: Influence of the parameters on the SiC-concentration in the filter cake

The results of the test runs that have been carried out until now indicate that the particle concentration in the filter cakes decreases with increasing rotor frequencies (Figure 7). With very high frequencies the particles can be taken out of the rotor with the metal melt because of the strong centrifugal forces.

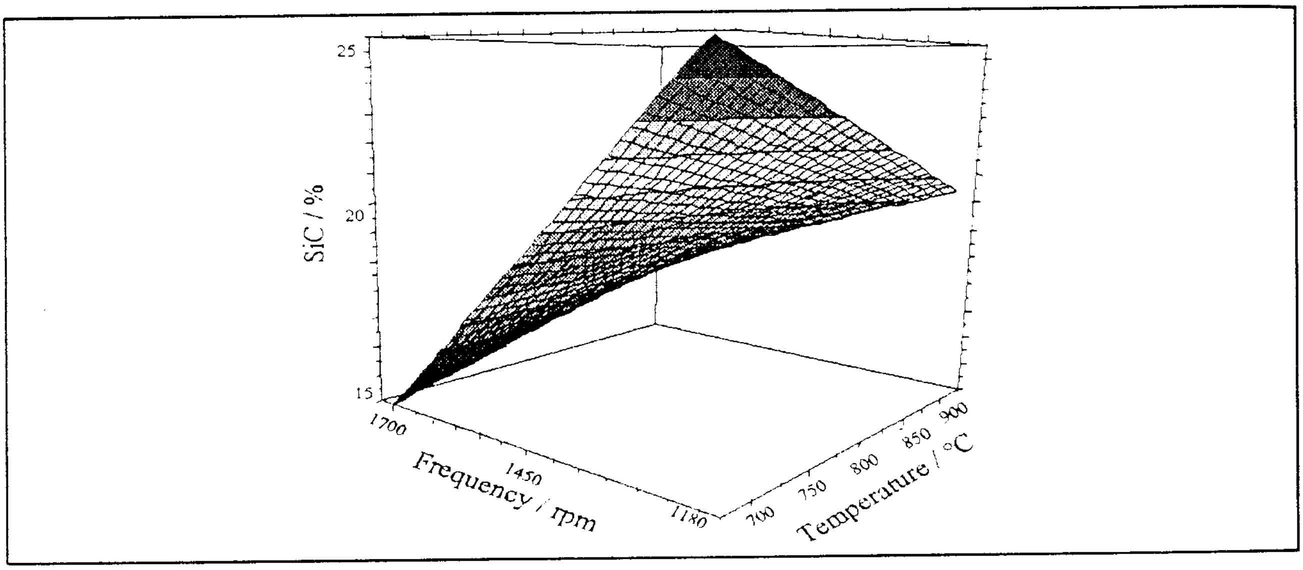

Figure 7: Process window: influence of temperature and rotor frequency on the SiC-concentration

The particles that are taken out of the metal melt in this process cannot be reused at once. There is still very much metal in the filter cake that has to be separated from the particles. There will be further examinations to solve this problem within the recycling project at IME.

2.3.2 Removal of Particles by Salt Dispersion

These test runs should demonstrate that the SiC-particles can be separated from the aluminium melt with the help of salt according to the separation of oxides and other impurities from aluminium melts. The experimental set up was basically the same as in the centrifugation test runs. 1.5 kg of metal were charged together with salt into a glazed graphite crucible and molten in a resistance heated furnace. The MMC melt with the salt was stirred by a graphite agitator. The added salt was a mixture of NaCl and KCl (70/30 up to 50/50) with additions of CaF_2 or NaF (5-15 %). Other parameters were the process temperature and the frequency of the agitator.

Table 2: Process parameters

	min	max
Ratio salt to metal	0.2	0.5
NaCl/KCl	50/50	70/30
CaF_2 addition / %	5	15
NaF addition / %	5	15
Agitator frequency / rpm	200	450

The salt melt that was clear and thin fluid in the beginning of the test runs became always dark grey and highly viscous. After casting the salt slag separates itself into a white layer on top and a dark grey layer at the bottom. Yet in the test runs with NaF addition this separation is not so distinct.

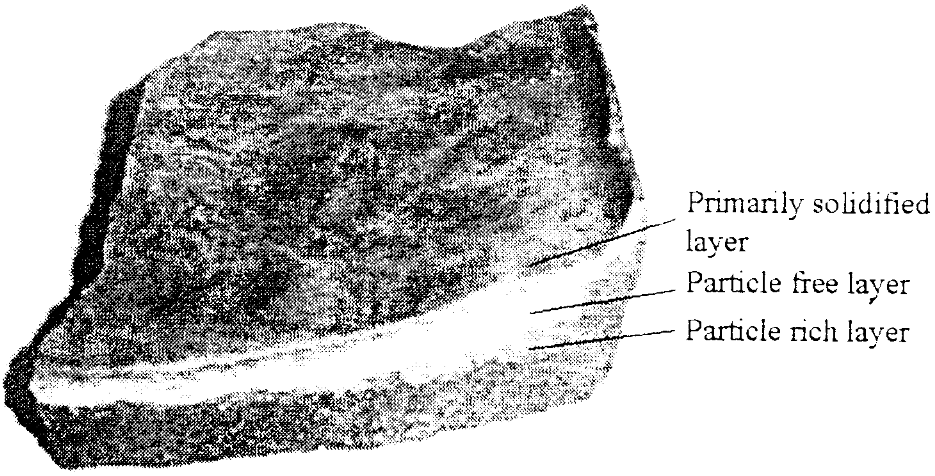

Figure 8: Casting of the salt phase

In all the test runs with CaF_2 addition in the salt melt the metal yield was very low. The aluminium for the biggest part was dispersed in the salt slag and did not drop off again. Better results could be achieved with the addition of NaF instead of CaF_2. In this case the metal yields reached up to 80 %.

The metal yield was calculated concerning to the following equation:

$$x = \frac{(m_2) \cdot (1 - \%SiC_{output} / 100)}{m_1 \cdot (1 - \%SiC_{input} / 100)} \quad (2)$$

x-metal yield; m_2-mass of metal casting; m_1-mass of charged AMC; $\%SiC_{input}$-SiC-concentration in the metal before test run; $\%SiC_{output}$-SiC-concentration in metal casting

The analyses of the salt slags show that the SiC concentration increased during the test runs like the concentrations of other impurities did. In some test runs, however, the particle concentration in the salt slag decreased at the end (Figure 9). So it can be suggested that the SiC-particles did not stay in the salt melt but fell back to the metal phase accumulated at the surface of the dispersed aluminium and dropped off the slag with them.

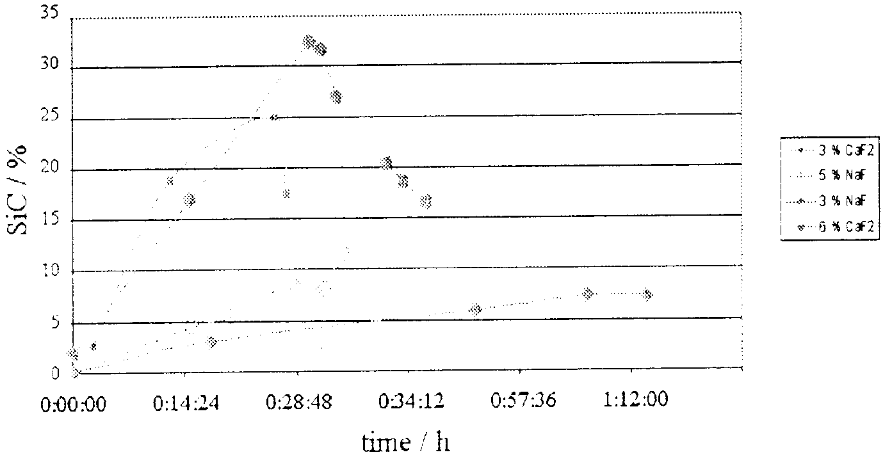

Figure 9: Concentrations of particles in the salt slag during test runs

This way they inhibit the aluminium drops from coagulation. This behaviour of the SiC-particles explains why the dispersed metal and also the metal castings have a grey and dull surface after the test runs (Figure 10).

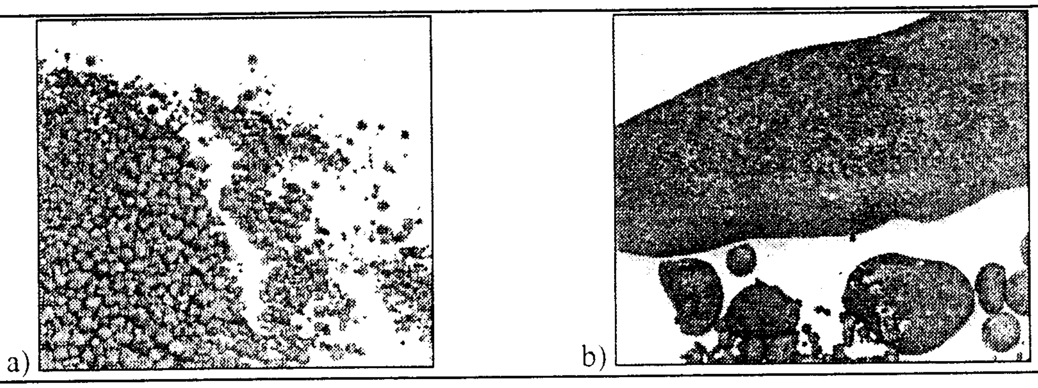

Figure 10: Aluminium phase after test runs with CaF_2 (a) and NaF addition (b) in the salt

An evaluation of the micrographs indicates that the SiC-particles are nearly completely eliminated from the metal phase (Figure 11). The microstructure is similar to a conventional AlSi7Mg alloy that is not reinforced with ceramic particles. The primary solidified aluminium dendrites and the eutectic Al-Si-phase between them can clearly be identified. Particles like in the micrograph of the MMC cannot be found any more.

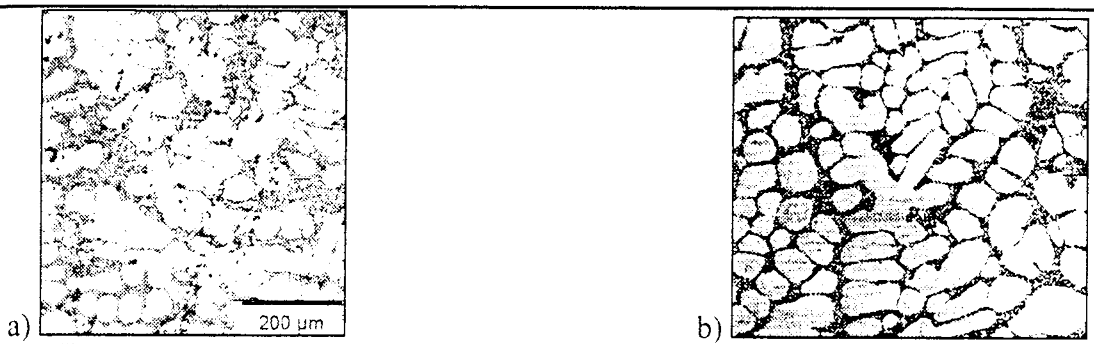

Figure 11: Micrographs of recycled aluminium from MMCs, IME (a) and AlSi7Mg alloy [3] (b)

A micrograph of the surface of an aluminium drop that did not coagulate with other aluminium drops dispersed in the salt slag shows that the SiC-particles accumulated at the surface of the aluminium drops. The SiC-particles are not wetted neither by aluminium melt, nor by salt melt because of too high surface tensions. They are separated from the aluminium melt by the salt but they do not stay in the salt slag. Because of a higher density they drop out of the salt slag again and accumulate at the aluminium drops dispersed in the salt slag or at the surface of the aluminium melt. Due to this they form an insuperable layer between the aluminium drops and inhibit them from coagulation.

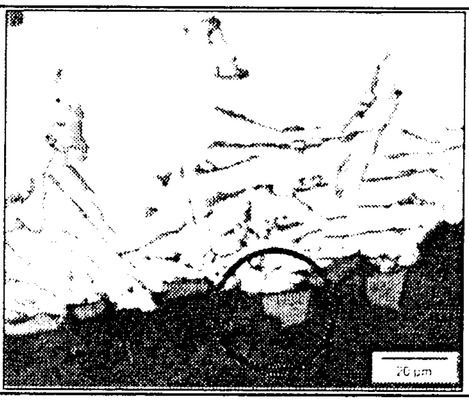

Figure 12: Micrograph of an aluminium drop with SiC-particles on its surface

An addition of NaF to the salt melt lowers the surface tensions of the salt slag and the SiC-particles can be kept in the salt slag. This way they do not accumulate at the surface of the aluminium drops dispersed in the salt slag and the aluminium can drop off the slag. The metal yield increases with growing NaF concentration in the salt,because hardly any aluminium rests dispersed in the slag. Another proof that the SiC-particles are better kept in the salt slag is the fact that the split of the salt into to phases after casting is far smaller than in the test runs with CaF_2 addition. In the test runs with NaF addition as well as in the test runs with CaF_2 addition, the SiC-particles are nearly completely eliminated from the aluminium phase.

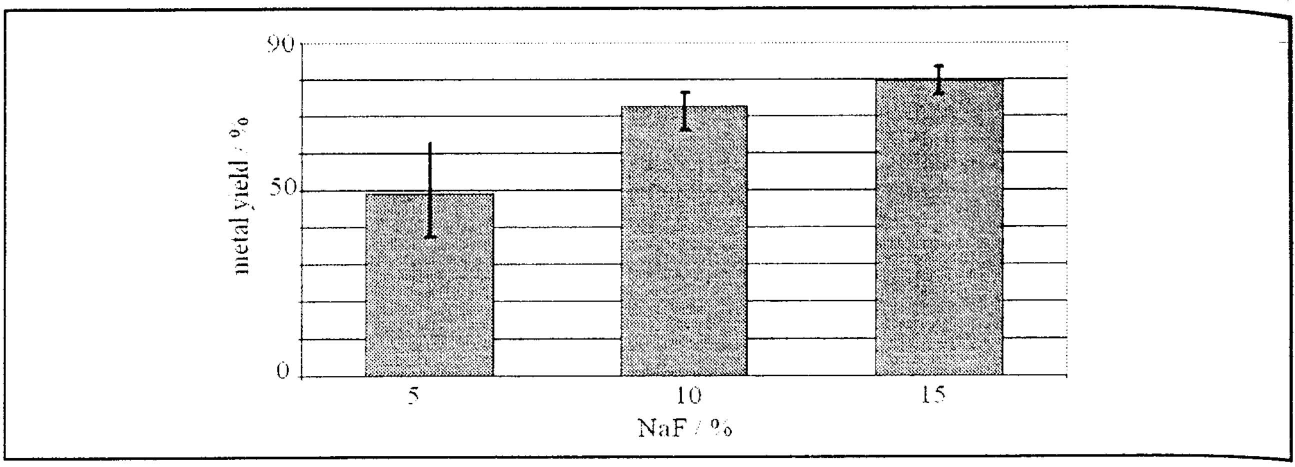

Figure 13: Metal yield in dependence from NaF addition

The influences of temperature, frequency of the agitator and quantity of added salt are very small. The metal yield decreases a little bit with higher temperatures. It decreases as well with higher frequencies of the agitator. The higher the frequencies the stronger is the turbulence of the melt, so metal dispersed in the salt slag cannot drop out of it again and is lost for the metal casting.

An influence of the ratio of NaCl to KCl cannot be proved from the test runs. The results vary significantly and do not show any tendencies to higher or lower ratios of NaCl to KCl (Figure 15).

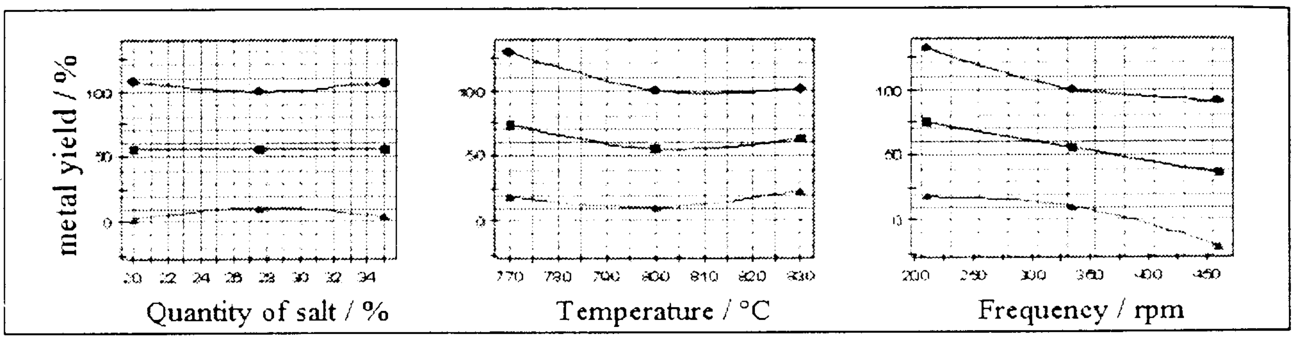

Figure 14: Dependence of metal yield from salt quantity, temperature and agitator frequency

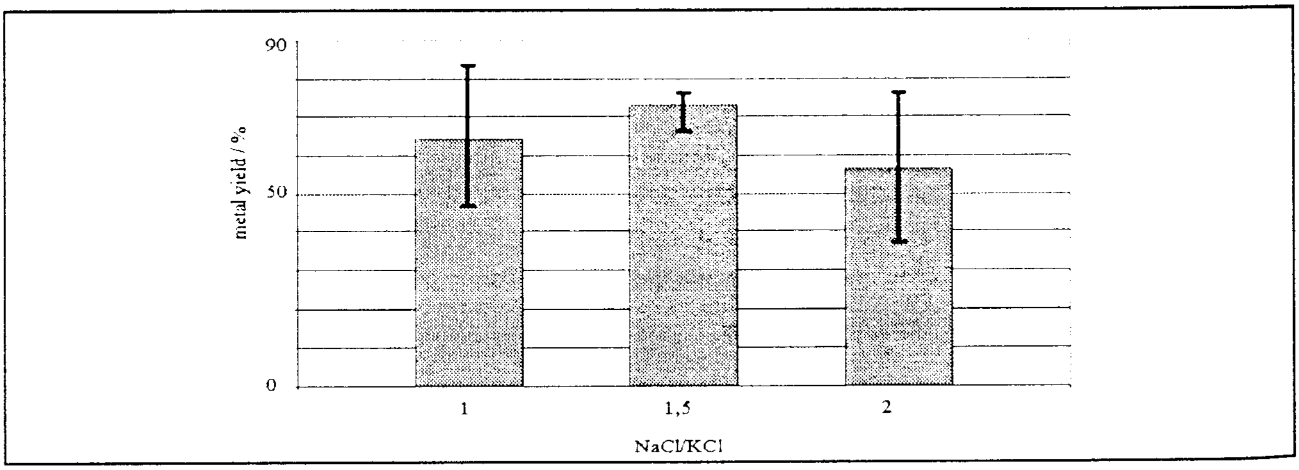

Figure 15: Metal yield depending on the NaCl/KCl ratio

A remaining topic for the project is the recycling of the ceramic particles from the salt melt. First leaching tests have shown that it is possible to dissolve the salt with water and recover the insoluble fraction with ceramic particles and oxides by filtration. The content of ceramic particles in the filter cake amounts to 60 %. The particles do not agglomerate but remain separate, so it seems to be possible to regain them and put them back to AMC production again [4]. In further tests it has to be examined how the ceramic particles can be separated from the oxides. A high purity of the particles must be guaranteed for a reuse in AMC production to assure a high quality of the products.

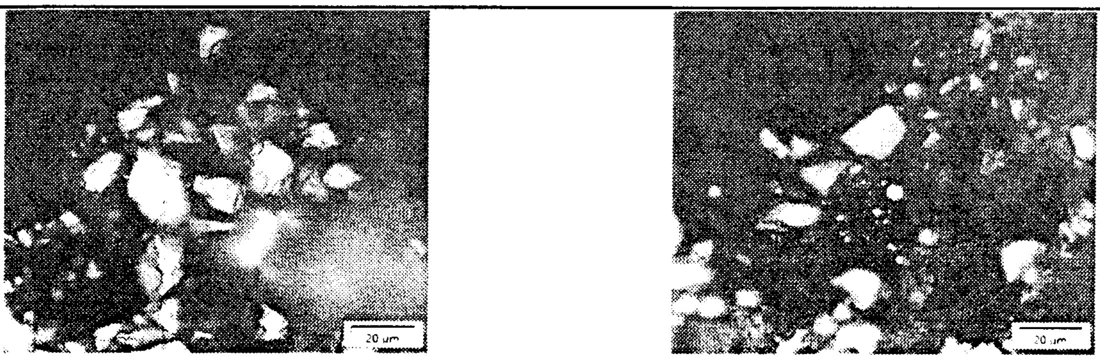

Figure 16: SiC-particles in filter cake after dissolution and filtration of salt slag [4]

3 Aluminium Foam Recycling

3.1 Definition of Foam

Foams are systems of two phases that are thermodynamically not stable. Mostly they consist of a big gas volume that is dispersed in a small liquid or solid volume. The gas bubbles are normally divided from each other by thin films of the second phase. Pure liquids normally do not form foams. There has to be a substance that inhibits the coalescence of the gas bubbles. In case of aluminium foams, these stabilising agents are oxides, ceramic particles, carbides or intermetallic compounds, depending on the production method.

The gas bubbles can be spherical or polyhedral. Their form depends on the porosity of the foam. With a porosity of more than 74 % they are polyhedral, otherwise they are spherical. The reason for this is the surface tension. In a smaller porosity the surface tension is higher than in bigger porosity, so the bubbles are spherical to possess a surface energy as small as possible.

The cells of a closed cell structure are bordered by very thin films of the liquid or solid phase. The edges of the cell walls that are connected by nodes form the web of the cell structure. If the cell walls are damaged or if they flow into the edges at the end of the foam formation, an open cell structure is formed [5].

3.2 Foam Production Methods

Foam production methods are for example the gas injection technique, the place holder technique or the foam production with foaming agents. In the gas injection technique, air or inert gas is blown into a particle stabilized aluminium melt. The gas forms bubbles, which float to the surface and form the foam. In the place holder technique, aluminium melt is cast into wax moulds or moulds filled with polystyrene balls. Afterwards the place holders are burned and an aluminium foam remains. In the last production method, aluminium powder is mixed with foaming agents like metal hydrides or carbonates. In a following sintering and foaming process, the foaming agents volatilise and form bubbles in the aluminium phase that form the foam.

In the first and in the last mentioned methods, closed cell structures are produced, open cell structures are produced by place holder methods.

3.3 State of the Art of Recycling Possibilities

Up to now only a few examinations concerning the possibility to recycle aluminium foams have been published. Mainly these tests are limited up to the addition of particle stabilised foams produced with gas injection into the MMC production or to recycle them to new foams [6]. Aluminium foams produced with metal hydrides are recommended to be recycled in the conventional aluminium recycling processes according to laboratory tests [6].

3.4 Test runs at IME

Within the scope of this project, it was examined under which circumstances aluminium foams produced with TiH_2 can be added to conventional aluminium recycling processes. With this intention several test runs were done to evaluate the influences of salt quantity (0-50 % of the charged foam mass) and composition (0-15 % CaF_2 in the salt) on metal yield, alloying element concentrations and porosity of the recycled metal.

The foam material was charged into a graphite crucible with salt consisting of NaCl and KCl (70/30) and up to 15 % CaF_2 and melted in a resistance heated furnace.

Table 3: Chemical analyses of two industrial foams (Hydro Aluminium Deutschland GmbH)

	A	B
Al / %	93.3	89.5
Ti / %	0.50	0.72
Oxides / %	6.5	10.4

After melting the material, it was stirred with different agitator frequencies for about 20 min to evaluate the influence of the stirring conditions on the porosity of the recycled aluminium ingot.

Table 4: List of test series executed with aluminium foam

Test series	1	2	3	4	5
Salt / $\%_{foam}$	0	20	50	50	50
CaF_2 / $\%_{salt}$	-	-	-	15	15
agitation / rpm	100	100	100	150	250

In the test runs without salt addition the metal yields were very low, because a lot of dross appeared. The more salt was given to the aluminium melt, the better were the results for the metal yield. An addition of CaF_2 improved the metal yields once more (Figure 17).

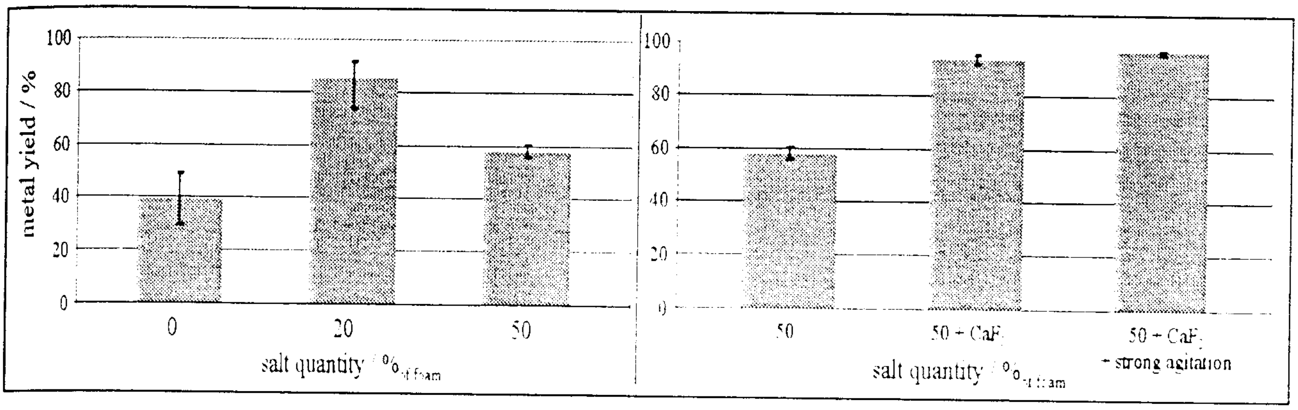

Figure 17: Metal yield in dependence from salt parameters and agitating conditions

The presented results prove the possibility to reach metal yields of more than 95 %, when CaF_2 is added to the salt and the melt is well stirred (Figure 17, right side). CaF_2 in the melt lowers the surface tension of the salt melt and enables metal drops dispersed in the salt slag to coagulate and to settle down to the rest of the metal phase again. In test runs, where the quantity of the added salt was big in comparison to the metal quantity and no CaF_2 was added the metal, yield was quite low, because most of the metal remained dispersed in the salt slag (Figure 17, left side). That is why the metal yields are better in test runs with only 20 % salt. The quantity of metal that can be dispersed in the salt slag is smaller and due to this the metal yields are bigger. Also a stronger agitation of the melt in addition to a CaF_2 addition in the salt leads to a better coagulation of the dispersed aluminium drops and so to a better metal yield (Figure 17, right side).

All ingots of recycled aluminium show macroporosity in the middle, independent from agitating conditions or salt quantity and composition. Figure 18 shows an ingot and these pores.

During foam production with TiH_2 the titanium enriches in the aluminium phase but also a big part of the titanium remains as precipitations at the surfaces of the pores in the foam [7]. This titanium, that is not already solved in the aluminium, however cannot be eliminated completely from the aluminium matrix during recycling of the foam but can only partly be transferred to the salt slag. Micrographs of the pores prove that it precipitates in the pores that are visible in the castings and in the metal matrix as high-tensile Al-Ti-phases (Figure 19). The rest of the titanium is supposed to be dissolved in the aluminium matrix referring to the chemical analyses in Table 5.

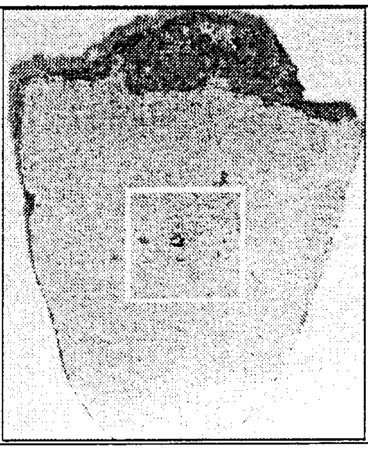

Figure 18: Aluminium ingot with pores

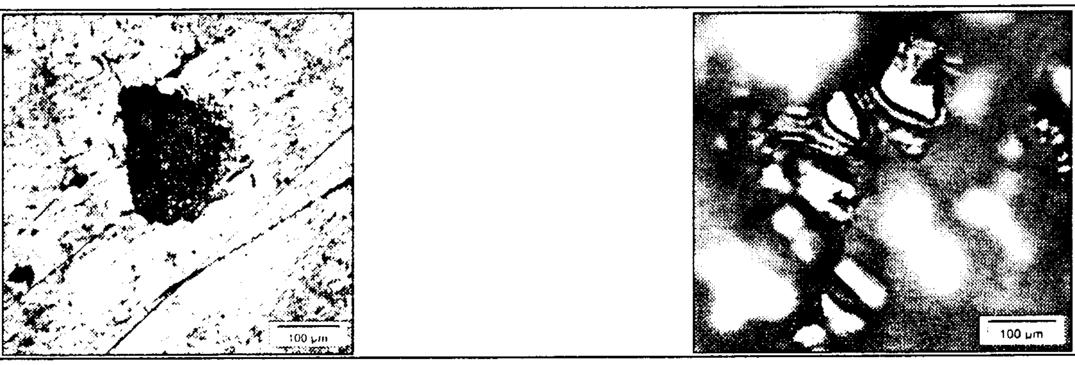

Figure 19: Precipitated Ti-Al-phases in the aluminium matrix (left) and in the pores (right)

Table 5: Chemical analyses of the recycled aluminium ingots (average values)

Test series	1	2	3	4	5
Al_{Oxide} / %	0.64	0.66	0.43	0.54	0.1
Ti / %	0.5	0.46	0.56	0.22	0.49
Si / %	9.96	8.32	9.38	9.8	10.1

A problem for the recycling of aluminium foams, that were produced with TiH_2, is the elevated content of titanium in the aluminium. The titanium concentrations in the aluminium foam amount about 0.5 to 0.7 %. Nevertheless, the titanium content can be lowered to about half of the initial content in aluminium. As a result of these test runs, care shall be taken to add aluminium foams foamed with TiH_2 into conventional aluminium recycling processes. The titanium concentration in the aluminium is very high and due to this the produced recycling aluminium would have to be diluted with pure aluminium to diminish the titanium concentration under an acceptable value for other alloys. As another solution, the recycled aluminium from foams can be used as master alloy for titanium alloys.

4 Conclusion

The test runs concerning the recycling of MMCs in a centrifuge until now only have been conducted on a in laboratory scale. Nevertheless they demonstrated that an elimination of SiC.-particles from the aluminium matrix is principally possible. Further test runs on a bigger scale have to show to which concentrations the SiC content can be reduced in the aluminium melt. On those results an introduction of this method into the market depends. Only if it is possible to remove the particles from the melt completely. there will be any chances to introduce the centrifuge method into the market. Centrifuges are more expensive in operation and more complex than for example rotary kilns. The particles that are taken out of the metal melt in this process cannot be reused directly. There will be further examinations to separate the particles from the remaining metal within the recycling project at IME.

The test runs concerning the recycling of MMCs with salt melts have given very satisfactory results. The particles can be removed from the metal melt to concentrations of 0.1 %. If it is possible to eliminate the particles completely from the metal melt with the help of injected gases like argon or chlorine, this method will have good chances to be introduced into the market. It is a cost effective method that can be executed in conventional furnaces.

For the recycling of the ceramic particles from the salt melt first leaching tests have shown that it is possible to dissolve the salt with water and recover the insoluble fraction with ceramic particles and oxides by filtration. The particles do not agglomerate but remain separate so it seems to be possible to recover them and return them to AMC production again. In further tests it has to be examined how the ceramic particles can be separated from the oxides to reuse them in AMC production and to assure a high quality of the products.

The test runs that have been done until now for the recycling of aluminium foams show that high metal yields can be reached by the recycling with salt melts. Problems are given as a result of the high titanium concentrations in the aluminium phase. For industrial application there is only the possibility to dilute the recycled aluminium from foams with pure aluminium or conventional recycling aluminium or to use foam scrap to form titanium containing master alloys. But for the dilution with other recycling materials there has to be taken care of the entire concentration of alloying elements in the aluminium that must not reach too high values.

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