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LIQUID PHASE TECHNOLOGIES FOR SURFACE TREATMENT OF Al AND Mg ALLOYS[1]

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Abstract

The paper describes specific requirements to be met by the beam guiding systems for geometry and material related surface treatment of Al and Mg alloys. For different EB technologies (remelting, densifying, alloying, dispersing) the influence of beam parameters and energy transfer conditions (single- and multi-process technologies) on microstructure of the materials and its properties will be discussed. Under optimum conditions fine grained and homogenous layers with a thickness up to 1.5…5 mm without pores or cracks and with a very good metallurgical contact to the basic material without gaps can be produced. Using multi-process technology in case of EB alloying the maximum hardness of layers on Al alloys AlZnMgCu1.5, AlSi10Mg, as well as AlSi21Ni7Cu3 and AlSi30 achieved values up to 500HV0.1 and wear rate decreases by a factor of 10. The scratch energy density by EB alloying achieves a maximum improvement of factor 10…25. The EB alloying of Mg alloys MgAl9Zn1 and MgAl3Zn1, performed by single- and double-staged processes results in layers thickness up to 3 mm and noteworthy changes of mechanical properties (hardness by factor 4 up to 300HV0.3). In this case corrosion resistance is nearly comparable to those of a rapid solidified Al alloy.
Key words: Electron beam; Multi-process technologies; Alloying; Surface treatment; Al alloys; Mg alloys.

Resumo

Este artigo descreve os requisitos específicos necessários aos sistemas orientadores de feixe para a geometria do material relacionado com o tratamento de superfícies de ligas de Al e Mg. Será discutida a influência dos parâmetros do feixe e as condições de transferência de energia (tecnologias de processos simples e múltiplos) na microestrutura dos materiais, e as suas propriedades para as diferentes tecnologias de feixe de electrões (refusão, densificação, liga, dispersão). Em condições ideais é possível produzir camadas de granulação fina e homogénea, com uma espessura até 1.5…5 mm sem poros ou rachas e de bom contacto metalúrgico com o material básico sem fendas. Com a utilização de uma tecnologia de processos múltiplos no caso da liga do feixe de electrões, a resistência das camadas das ligas de Al AlZnMgCu1.5, AlSi10Mg, bem como das ligas AlSi21Ni7Cu3 e AlSi30 alcançam valores até 500HV 0.10, e a taxa de desgaste desce para um factor de 10. A densidade de energia por danos de liga de feixe de electrões alcança um melhoramento de factor 10… 25. A liga de feixe de electrões da liga de Mg MgAl9Zn1 e MgAl3Zn, levada a cabo por processos de fase simples e dupla resulta num espessamento das camadas até 3 mm e em alterações de propriedades mecânicas (resistência de factor 4 até 300 HV 0.3). Neste caso, a resistência à corrosão é aproximadamente comparável à da solidificação rápida da liga de Al.
Palavras-chave: Feixe de electrões; Liga; Tecnologias de processos múltiplos; Tratamento de superfícies; Ligas de Al; Ligas de Mg.

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1 INTRODUCTION

The worldwide demands for environmental protection and energy-saving solutions as well as the competitive situation induced great efforts to develop recyclable lightweight construction solutions and hybrid material designs with high strength and adequate corrosion and wear properties. Thus, light weight materials are essential in many industrial fields.[1,2]

EB surface technologies are characterized by a high productivity, high efficiency, excellent flexibility and technological diversity as well as by the high reproducibility of the treatment results. And they are used, in particular, for enhancing wear and/or corrosion resistance. EB technologies are preferably carried out in vacuum which is an advantage for the treatment of Mg and Al alloys because it avoids oxidation processes and causes positive effects like the reduction of pores as well as the evaporation of impurities. In general, EB technologies are environmentally friendly and highly efficient energy-saving processes.[3-5]

New demands create new solutions. So in the last 10…15 years in connection with electron beam (EB) were developed new surface heat treatment technologies with a high innovation potential.

A promising option to protect the functional surface against wear is provided by electron beam (EB) liquid phase surface treatments with/without the use of additions. These technologies allow the local specific change of microstructure and characteristics in a basic material layer.[6-8]

Because of the almost inertia-less formability and deflectability of the electron beam (EB) beam guiding techniques were developed allowing the energy input within a deflection field to be adapted almost at will. It is possible to implement defined local temperature time regimes. This is advantageous for surface treatment but also for other thermal EB technologies.[3,9-11]

EB liquid phase surface treatment is one possible solution for an additional modification of the functional surfaces according to the stress, especially to tribological or/and corrosive requirements. Local properties (friction coefficient, wear and corrosion behavior, thermal properties) can be influenced positively and adjusted for specific applications[12-16] especially in combination with additional elements (e.g. Co, Cu, Fe, Ni) and hard material particles (e.g. TiC, WC) which are inserted into the surface layer in a controlled way. Known studies[11,13,14,17,18] demonstrated that surface alloying with Fe and Ni (400 HV0.1), Co (450HV) as well as Cu (600HV0.1) can lead to significantly higher hardness in the surface layer of Al alloys that mostly contributes to the improvement of wear behavior. Thereby, the increase in hardness depends on the fraction of additional alloying elements, i. e. the degree of mixture between base material and additives. As a result of layer thickness decreasing, an increased hardness is noticed (more than 800HV0.1, however with cracks in the layer) because of the higher amount of additives. Beside cracks, other effects like porosity, inhomogenities and heavy surface deformations have to be overcome and a satisfying metallurgical connection between base material and surface layer should be reached[11,13-18].

The modification of microstructure and properties of the surface layers is caused by rapid solidification and cooling on the relatively cold substrate. This leads to over saturation of Θ-Al solid solution, very fine segregation structures and also non-equilibrium phases.[12-15,18]

Up to now, Mg alloys are used for construction solutions only to a minor degree. Although their specific density properties are the best among light materials, its insufficient corrosion behavior (galvanic corrosion) among others lead to the fact that the use of Al alloys is preferred by the industry.[19,20]

When lightweight Mg alloys, are applied in highly loaded systems, wear and corrosion call for additional modification of the functional surfaces according to the loading conditions. Liquid phase surface treatment is one possible solution for these requirements. Local properties (e.g. wear and/or corrosion behavior) can be positively influenced and adjusted for specific applications.[10,21,22] Thermal surface technologies like EB remelting and EB alloying in connection with additives (e.g. Al, Ti (Ni), Si) and EB dispersing by inserting hard material particles (e.g. SiC, TiC) are particularly suitable to meet these demands.

Different studies[23,24] demonstrated that surface remelting leads to an increase of hardness (2...3-fold) and a weak improvement of corrosion behavior resulting from the finer microstructure and the precipitation of new phases ($Mg_{17}Al_{12}$) due to rapid self-cooling.

Surface alloying with the above mentioned additives can lead to significantly higher hardness of the surface layer of Mg alloys (up to 350HV0.1) that mostly contributes to the improvement of the wear behavior.[23-26] The increase of hardness depends on the fraction of additional alloying elements, i.e. the degree of mixture between base material and additives. In terms of corrosion, only Al additives effectuated satisfactory results.[25]

Dispersing of hard particle materials also in combination with Al additives (e.g. AlSi12/SiC) leads to the best wear properties. However, optimization is needed to reach a fine dispersion of the particles. Although a homogeneous and very high level of layer hardness is attainable due to high-volume contents of hard particles, there are no noticeable effects with regard to the corrosion behavior.[27,28]

2 ELECTRON BEAM GUIDING AND DEFLECTION TECHNIQUES

A modern generation of beam deflection techniques allows the development of thermal EB technologies which cannot be carried out by other energy sources.[5] High-frequency 3D beam deflection serves as a basis for EB multi-field, multi-spot and, finally, multi-process technologies for surface treatment and welding which result in higher productivity and new property combinations.[3,9,29] Figure 1 summarizes the beam guiding techniques in connection with the motion between EB and component concerning EB welding and EB surface treatment. In case of CI-techniques the component and/or the EB are moving relatively to each other during interaction of beam. Beam splitting in case of multi-spot beam deflection technique means that the EB is jumping with high frequencies (up to 100 kHz) between the different spots.

A selection of these beam guiding techniques is the basis for new EB technologies that form the subject of this paper.

3 APPROACHES AND EXPERIMENTAL PROCEDURES

The experiments were carried out on a multiple-purpose electron beam facility with an acceleration voltage of 60 (80) kV. The working pressure in the vacuum chamber was 10^{-3} mbar.

For energy transfer, different beam deflection techniques (Figure 1), such as one-spot and multi-spot technique, were used. The beam current (Ib: 5 - 50 mA) and the

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feeding rate (vx: 5 - 60 mm/s) were changed expediently in combination in order to reach different treatment depths.

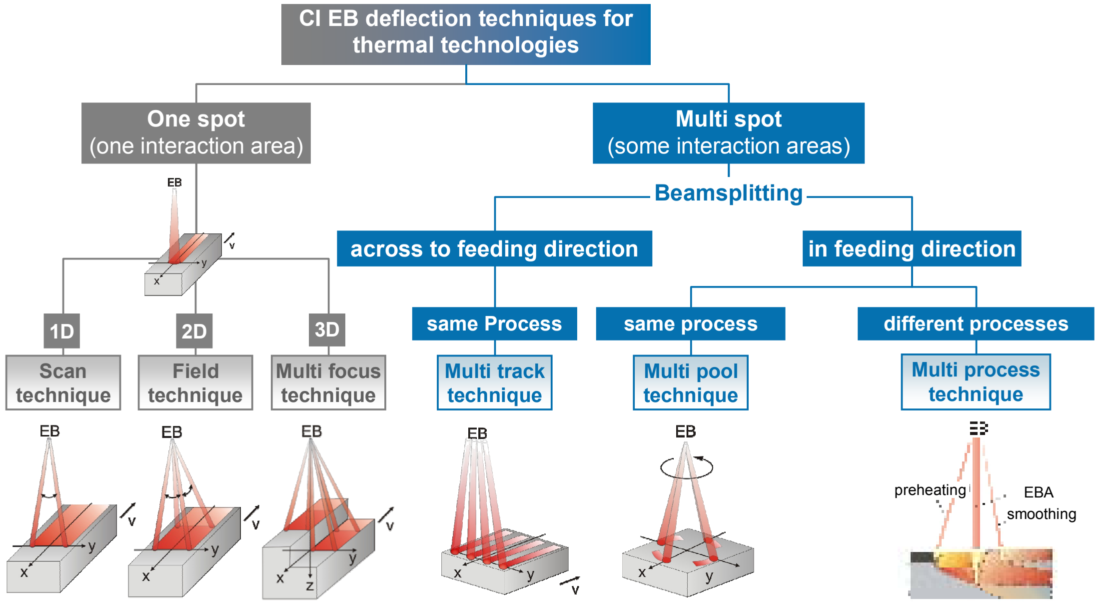
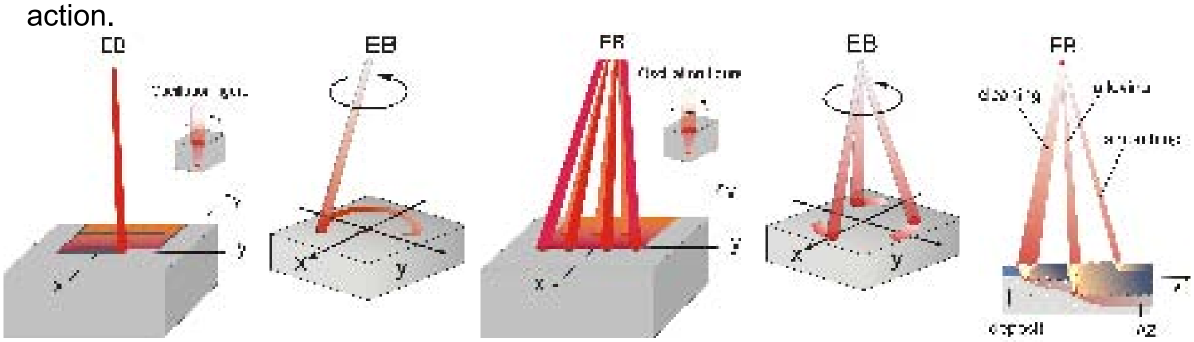


Figure 1. EB guiding techniques for **c**ontinuous **i**nteraction (CI techniques).

The one-spot options included meander technique and rotating beam (Figure 2a, b). There, the EB only acts in one position. With multi-spot techniques, the EB simultaneously affects many different positions. Therefore on the one hand, the multi-track technique (Figure 2c) on the other hand the multi-pool technique (Figure 2d) was used. In situ it is possible to generate in additional special oscillation figure, deflected with high frequency (e.g. loops, ellipses et al.) for every point of EB action.



a) meander b) rotating beam c) multi-track d) multi-pool e) multi-process

Figure 2. EB surface treatment with a, b) one- and c, d) multi-spot technique or e) multi-process technique.

The spot pattern with the generated oscillation figure (loops) is shown schematically in Figure 2a, c). When the EB acts in several positions to perform different tasks, it is a so called multi-process technique. Here, a combination of cleaning, alloying and smoothing was tested (Figure 2e).

As Mg alloys MgAl9Zn1 and MgAl3Zn1 and as Al alloys AlMgCu1.5, AlSi10Mg, as well as AlSi21Ni7Cu3 and AlSi30 were selected for the EB alloying processes. In case of Mg alloys additional material was AlSi12. In connection with Al alloys additives followed were used Ni-Cr17-Si4-B4, Cu-Ni38, Co-Cr28-Mo5-Fe4-Ni3-Si1.

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The results have been characterized by the following methods of investigation:

- Microscopic investigations (optical microscope, scanning electron microscope, EDX).
- Hardness measurements (surface hardness: HV5, hardness-depth-profiles: HV0.10).
- Scratch tests with constant load (50 N), determination of scratch energy density.
- Fretting wear/fatigue investigations under oil-lubricated conditions at T = 80 °C.

4 RESULTS AND DISCUSSION

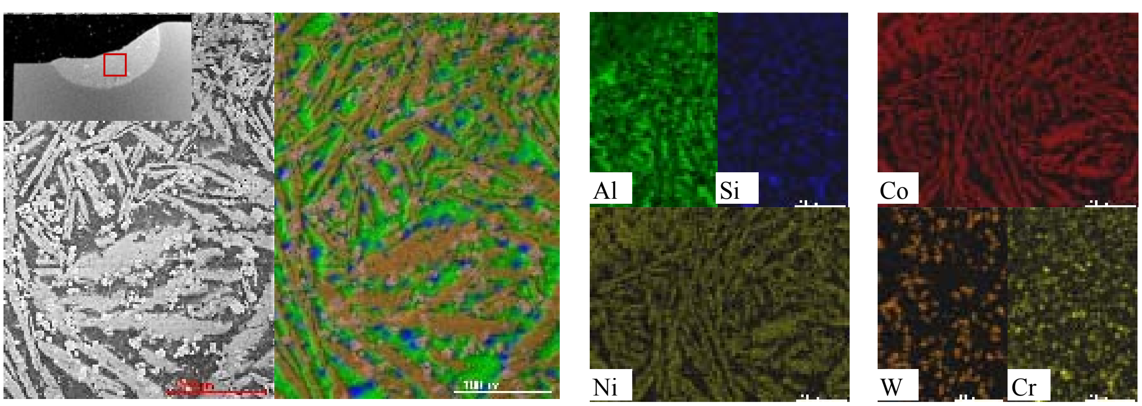
The additives were remelted together with the surrounding base material and an alloying layer was produced. In case of application of single- and multi-pool technique with rotating EB a 5 mm wide track was the result. The EB surface treatment in all other cases was performed with track widths of 10 and 20 mm, respectively.

Liquid phase surface treatment of Al and Mg alloys causes in a surface layer a modification of microstructure by fast melting and fast solidification due to self-quenching as well as phase transformations, especially in connection with the additives. The thickness of these layers connected by fusion metallurgy can be controlled by the energy input. Its geometry depends on the applied EB deflection technique. Below the interface to the base material, a more or less wide heat-affected zone (HAZ) is created.

4.1. Electron Beam Alloying of Al Alloys

In case EB surface alloying of Al materials with optimum parameters are caused crack free layers without or poor in pores with a thickness of 0.5 to 5 mm.

Figure 3 exemplarily shows the microstructure of an EB alloyed layer without cracks and pores and with acceptable hardness of about 450 HV0.10.



a) EDX analysis of EB alloyed microstructure   b) distribution of each element (colour)

Figure 3. EB alloyed layer with Co additive (base material: AlSi21Ni7Cu3).

As a result of the optimized EB technology, the distribution of deposited and alloyed additives is relatively homogenous inside the EB alloyed zone (Figure 3a). The alloyed microstructure consists of oversaturated Al solid solution (green), Si_P

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particles with a diameter < 20 µm (blue), elongate Co and Ni containing compounds (red, yellow) and finely dispersed W and Cr containing compounds (Figure 3b).

The mechanical properties exemplarily are summarizes, both layer representative properties for AlSi10Mg and AlSi35 for base material and EB treated layers in Figure 4. By EB alloying surface hardness and scratch energy density can explicitly increased (hardness: AlSi10Mg → 2- to 3-fold, AlSi35 → 3- to 6-fold; scratch energy density: AlSi10Mg → 3- to 4-fold, AlSi35 → to 5-fold). EB alloying with Cu38Ni especially leads to higher hardness. In general, cracks were found below layer depths of 1.2 ... 1.5 mm because of the high alloying addition.

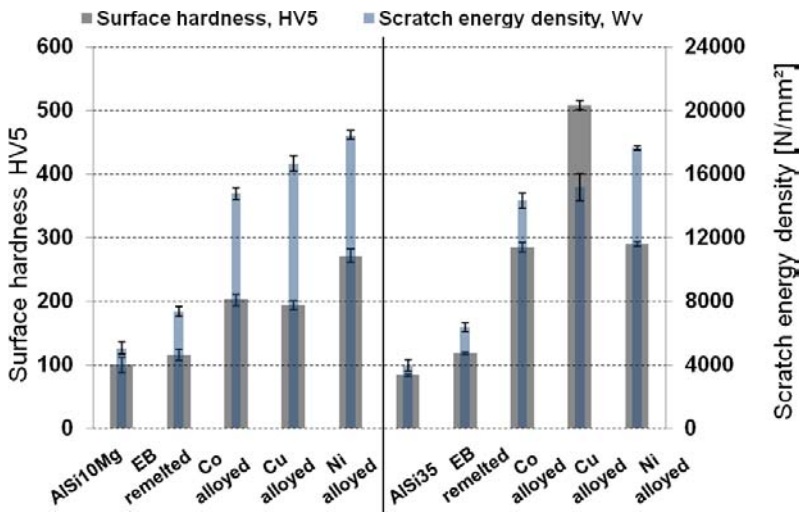

Figure 4. Maximum surface hardness and scratch energy density of AlSi10Mg and AlSi35 untreated and remelted state and in dependence of alloying additives.

For AlSi35 (Figure 5), the wear rate k declines clearly in comparison with the base material. EB remelting decreases k by a factor of 4.5. EB alloying with Co and Ni additives decreases the wear rate by a factor of 10.

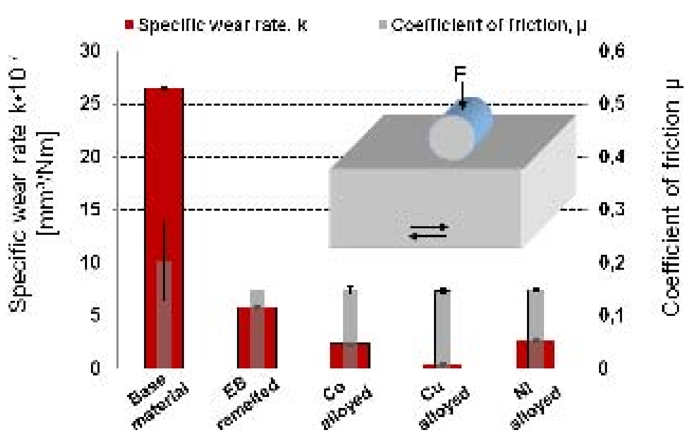

Figure 5. Results of fretting wear tests of AlSi35 under oil-lubricated conditions at T = 80 °C.

Analogical to hardness and scratch energy density, EB alloying with Cu additive achieves the largest improvement of k by a factor up to 25. The main wear mechanism noticed is abrasion by building a synclinal track.

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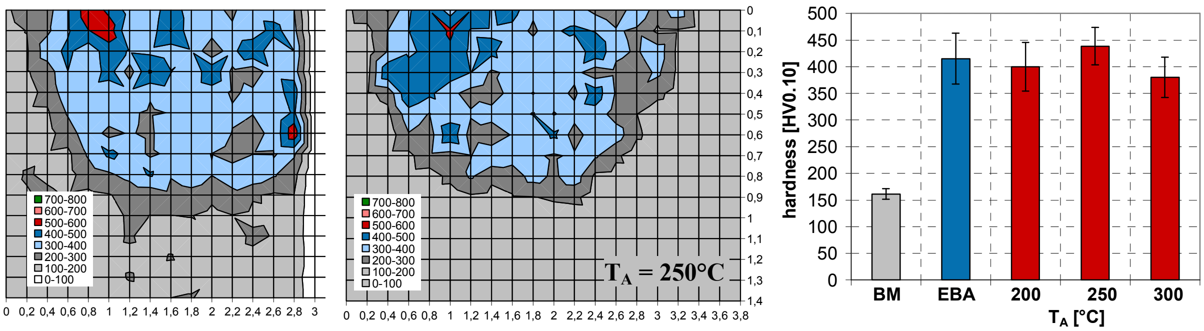
The friction coefficient μ can be reduced from 0.2 to approximately 0.15 (semi-fluid friction) irrespectively of the EB technology.

Often the real loading conditions are in the temperature range of 150 to 250°C (engine components). Therefore, the thermal resistance of the EB alloyed layers with respect to the base material (BM) was tested at annealing temperatures (TA) of 200, 250 and 300 °C for 24 h. EB alloying and annealing at these temperatures tends to influence layer hardness marginally (Figure 6c) considering the dispersion of hardness values measured afterwards (Figure 6a, b). A detailed evaluation of the microstructure is relatively difficult because of morphology differences (Figure 3a) inside the EB alloyed layer (e.g. centre, boundary) that depend on the cooling rate.



a) after EB alloying b) after EB alloying and annealing c) macro hardness of different states

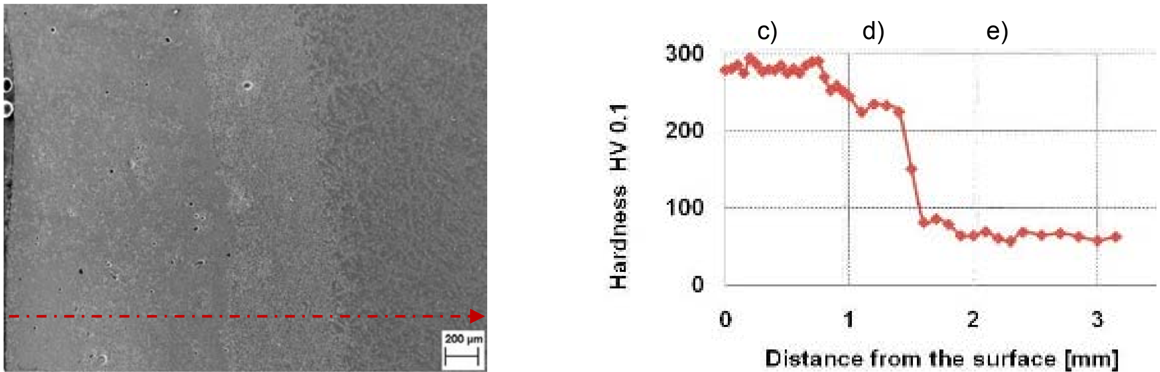
Figure 6. Hardness distribution [HV0.10] of EB alloyed layer (EBA) with Co additive (AlSi21Ni7Cu3).

4.2 Electron Beam Alloying of Mg Alloys

EB alloying of MgAl9Zn1 was performed in two steps with spraying material powder (AlSi12) followed by EB liquid phase surface treatment. The commercial powder was pre-deposited using plasma spraying to prepare a coating with a thickness of about 150 µm and 300 µm, respectively. Afterwards EBA was performed with track widths of 10 mm. Depending on the energy input, different layer depths between 0.3 and 3.0 mm with microhardness values ranging between about 120 and 280HV0.1 according to the mixture of base and additive material were obtained.

Particularly in regard to EB multi-spot techniques, layers with good metallurgical fusion bonding to the substrate and minimized porosity in comparison to the base material were achieved. By means of rapid self-quenching, a very fine microstructure consisting of α-Mg solid solution, globular and acicular Mg17Al12 and the facetted phase Mg2Si was obtained.

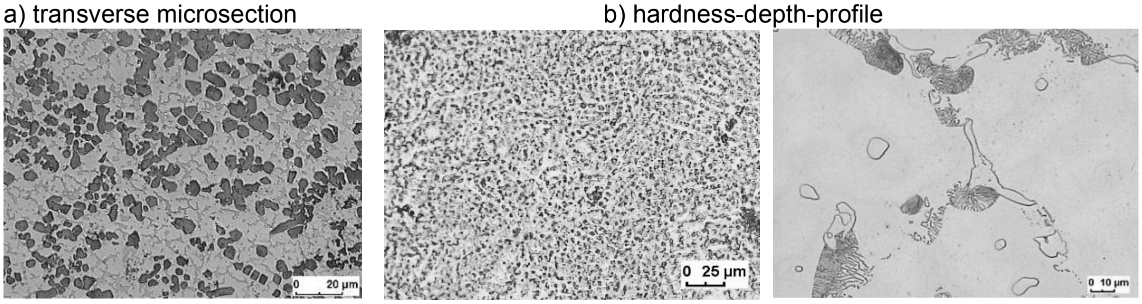
In terms of corrosion behavior, the strategy to reduce the content of Mg in direction to the surface was followed. After the single EBA has been carried out in the layer, Mg declines to 60 wt.-%. In order to achieve a lower content of Mg in this area, This EBA was designed as a double 2-step EBA process. The layer of the first double step is the same as described above. After the second EBA double step, a second surface layer with good metallurgical bonding between both layers is produced. It is possible to decrease the content of Mg in the surface layer to 10 wt.-% thereof. The fine-grained microstructure in the second layer consists of α-Al solid solution, an Mg-Al eutectic and the intermetallic phase Mg_2Si with globular morphology (Figure 7).



step 2 (c) | step 1 (d) | base material (e)

a) transverse microsection

b) hardness-depth-profile



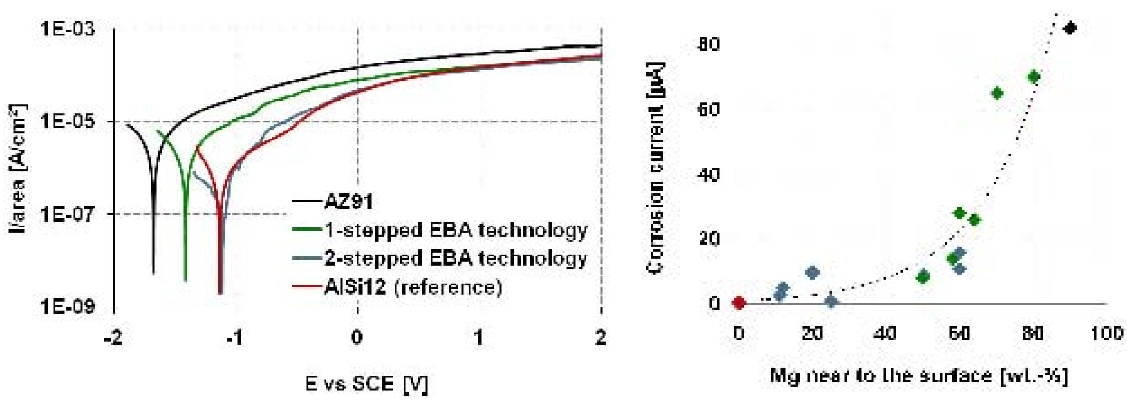
c) Step 2: external EBA layer

d) Step 1: internal EBA layer

e) base material

Figure 7. Local microstructure and microhardness profile after a two-step EBA double process.

The surface layer that is rich of Al (Figure 7c) reaches a microhardness of about 300HV0.1 (Figure 7b) and shows corrosion properties close to an Al-Si cast alloy (Figure 8a). Using potentiodynamic polarisation curve measurements in NaCl solution (0.0001 M) at 20 °C, the base material MgAl9Zn1 and the layers obtained with 1-step and 2-step double EBA were compared to the reference material AlSi12. Figure 8b shows the influence of the Mg content in the surface layer on the corrosion current.



a) potentiodynamic polarisation curves (NaCl solution)

b) influence of the Mg content

Figure 8. Corrosion behavior – influence of EB technology / content of Mg near to the surface.

5 CONCLUSIONS

In order to extend the use of Al and Mg alloys for components, especially in the automotive industry, it is necessary to protect functional surface areas against wear and/or corrosion.

One of the promising possibilities to realize these demands is the application of EB surface technologies, especially EB alloying by using technical and economical advantageous multi-spot beam deflection techniques as well as multi-process technologies with variable and very precise energy input. Thus, a locally defined treatment of the functional surface areas can be achieved.

In the case of EB surface alloying of Al materials in layers free of cracks and pores clear modifications of properties based on the changes of the microstructure can be achieved. The advantageous multi-spot and/or multi-process beam deflection techniques/ technologies support these positives effects.

The results of the EB surface alloying of Mg alloys show that also improved properties based on the changes of the microstructure can be initiated.

Especially with regard to the 2-step EB processes in the surface layer hardness as well as corrosion resistance were impressively increased.

It can be expected that more fields of application will be established for EB surface technologies within the coming years, notably in automotive industry but also in other industrial fields.

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