

High-Resolution Microstructural Investigations of Interfaces Between Light Metal Alloy Substrates and Cold Gas-Sprayed Coatings

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Interfaces between light metal alloys, aluminum AA7022, and magnesium AZ91, and optimized cold gas-sprayed zinc-based coatings are characterized. The analyses include scanning electron microscopy (SEM) as well as transmission electron microscopy (TEM). Investigations by SEM show a seam with intensive mixing of the substrate and coating material, which is indicated by different values of gray due to element contrast. In energy-dispersive spectroscopy analyses, increased zinc concentrations compared with the substrate material are detected in <1 μm thick vortexes inside the seam. The TEM investigations prove that these areas consist of a homogeneous solid solution and submicron-sized or nanosized intermetallic phases with different concentrations of aluminum, zinc, and magnesium. Because diffusion processes cannot result in the observed microstructure, local melting followed by precipitation of intermetallic phases is concluded as the consequence of the intensive mechanical interaction at the substrate-coating interface during particle impact during the cold gas spraying of zinc on magnesium or aluminum substrates.

Keywords AA7022, aluminum substrate, AZ91, cold gas spraying, interface, magnesium substrate, zinc coating

1. Introduction

Cold gas-sprayed (CGS) coatings show a high density and a low content of dissolved gases. The formation of reaction products like oxides during the spraying process is usually negligible. These features make cold gas spraying interesting for the coating of defined component surface areas with materials capable of acting as a filler for brazing processes. Especially for the complex geometry of the brazing joint, technological and economic advantages can be exploited. Also, the use of flux agents is not generally necessary due to an effect of substrate surface prewetting, as proved in previous studies (Ref 1-3). Thereby, harm to the corrosion resistance of joint components and to the environment can be avoided.

To clear up the basics of the observed prewetting phenomenon, detailed high-resolution microstructural investigations on the interfaces between CGS zinc-based filler coatings and aluminum as well as magnesium light metal alloy substrates were carried out. The high kinetic energy of CGS particles results in an intensive interaction between the spray particles and the substrate surface at impact, and between the individual particles

during the build-up of the coating. It is proposed that the strong interaction causes local melting and the formation of thin metallurgical reaction zones. Thereby, strong cohesion and adhesion of CGS coatings to their substrates are achieved (Ref 4-6). Also, the observed prewetting phenomenon could be explained by the formation of metallurgical reaction zones. However, when using nitrogen as the process gas, the occurrence of melting has not been proved until now.

2. Experimental

Zinc-based coatings were deposited on specimens of aluminum alloy AA7022 and magnesium alloy AZ91 with dimensions 50 × 80 × 8 mm and 50 × 50 × 7 mm, respectively. The process parameters are optimized by the design of experiments with the aim of achieving simultaneously a high deposition rate, deposition efficiency, and density (Table 1) (Ref 1). For CGS coating production, the Kinetic 3000 system by CGT (Ampfing, Germany) using nitrogen as the process gas was used.

The AZ91 and AA7022 substrates were coated with pure zinc and Zn5Al that was mechanically blended from pure zinc and pure aluminum powders. Both zinc and aluminum powder particles showed the irregular shape that is typical of the gas-water

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Table 1 Cold gas spraying parameters

Parameters	AA7022	Az91
Coating	Zn5Al	Zn
Nitrogen pressure, MPa	3	3
Nitrogen temperature, °C	250	250
Nitrogen flow, m ³ /h	78	86
Powder feed rate, g/min	31.5	32.5
Gun traverse velocity, m/s	0.35	0.35
Spraying distance, mm	20	40

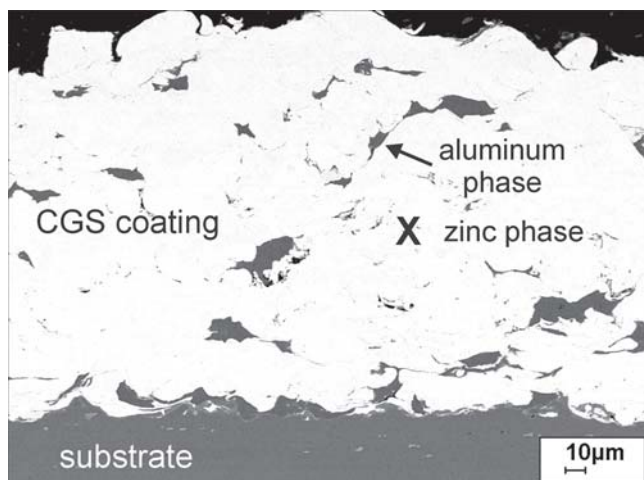


Fig. 1 A CGS Zn5Al coating on an AA7022 substrate (SEM micrograph, cross section)

melt atomization process. Coatings were sprayed with a maximum thickness of 200 µm.

Cross sections were prepared as polished bulk for scanning electron microscopy (SEM) investigations of coated specimens. Additionally, conventional ion thinning is applied to produce cross sections for transmission electron microscopy (TEM) investigations. Overview microstructure studies by SEM were the basis for detailed TEM analyses. Both electron microscopes (SEM LEO 1455VP, Cambridge, U.K.; TEM Hitachi 8100, Tokyo, Japan) were equipped with energy-dispersive x-ray spectrometers for local analyses of the chemical composition. The spatial resolution of elemental analyses is especially high in the case of thinned TEM specimens. Thereby, phases with sizes down to 100 nm can be analyzed.

3. Results

3.1 Scanning Electron Microscopy Investigations

Both Zn5Al coatings on AA7022 substrates and pure zinc coatings on AZ91 substrates show typical low porosity and cover the substrate surface completely (Fig. 1, 2). In the interface zones, there is a high density of zinc material penetrating into the substrates and forming vortexes. This results in a strong mixing of coating and substrate material in seams with ~10 µm thickness.

For AA7022 substrates at high magnification, the gradual transition from the coating zinc phase to the substrate aluminum phase was observed. Due to the strong difference in atomic number between zinc and aluminum, the differentiation of pure zinc and zinc-rich areas ~1 µm thick within the transition zone is possible (Fig. 3). The quantification of energy-dispersive spectroscopy (EDS) point analyses is restricted, because in bulk material investigations the minimum size of the analyzed volumes is between 1 and 2 µm in diameter. However, small-area EDS analyses show a significantly higher zinc content within the bright-appearing zones inside the transition zone compared with that in the substrate material underneath (Table 2).

The SEM investigations on the interface between CGS pure zinc coatings and AZ91 substrates showed comparable results to

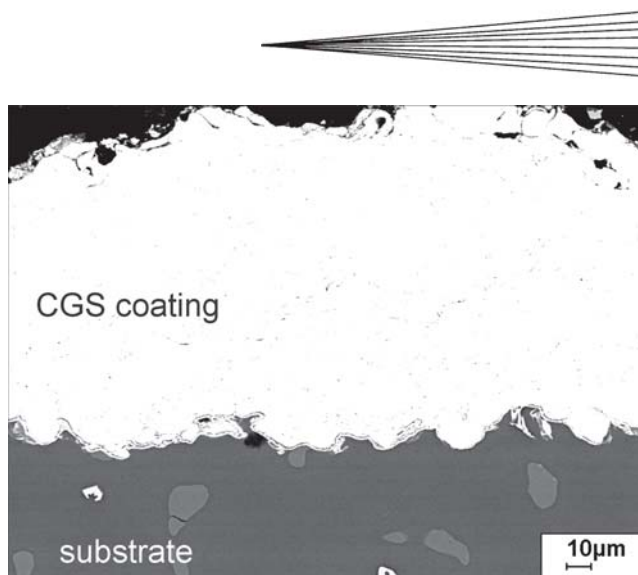


Fig. 2 A CGS pure zinc coating on an AZ91 substrate (SEM micrograph, cross section)

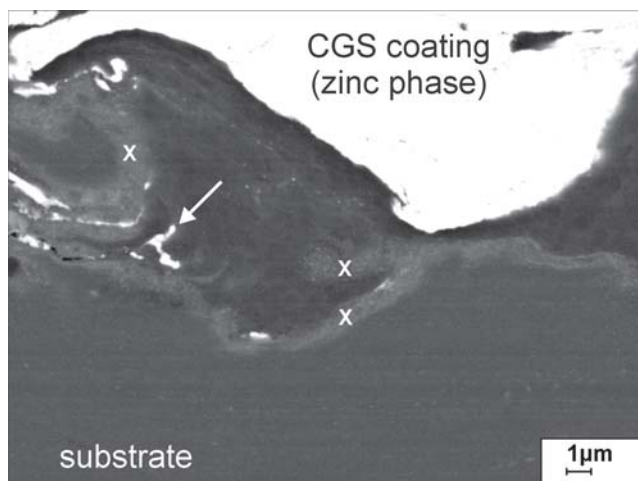


Fig. 3 An SEM micrograph showing zinc particles (arrow) and zinc-rich zones (x) at the interface between the CGS Zn5Al coating and the AA7022 substrate

Table 2 Chemical composition of different areas in specimens with cold gas-sprayed Zn5Al coatings on AA7022 substrates

According to energy-dispersive spectroscopy analyses of a polished bulk section

Variables	Composition, at. %		
	Zn	Al	Mg
CGS coating (Zn phase)	97	3	0
Bright area in transition zone	>10	<86	4
Substrate material (AA7022)	2	94	4

those for Zn5Al coatings on AA7022 substrates. A roughly 10 µm thick transition zone at the magnesium alloy surface affected by the impinged zinc particles was found (Fig. 4). First, a discontinuous oxygen-containing film at the substrate surface with a thickness of approximately 100 nm was observed. Underneath, there were several submicron-sized zinc-rich layers. Due to the

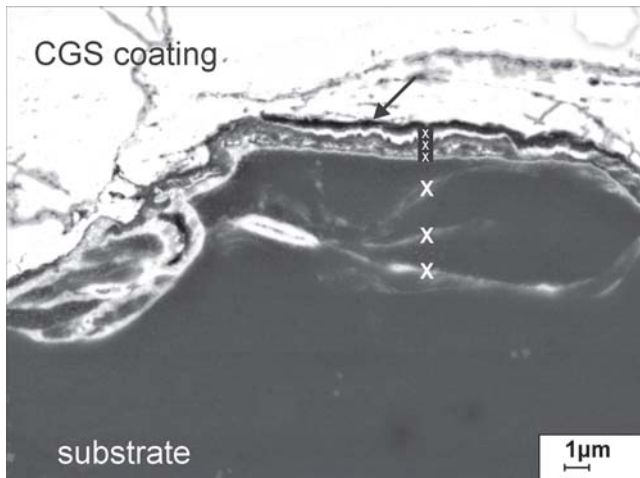


Fig. 4 An SEM micrograph showing an oxide film (arrow) and zinc-rich zones (x) at the interface between the CGS pure zinc coating and the AZ91 substrate

small dimensions of the different layers, EDS analyses on the bulk sections do not contribute to the accurate determination of the occurring phases.

For both combinations of substrates and CGS coatings, mechanical alloying due to the penetration of spray particle material jets into the substrate was observed. However, SEM investigations alone cannot give clear evidence for the occurrence of local melting.

3.2 Transmission Electron Microscopy Investigations

The TEM studies on coating-substrate interfaces verified the results of SEM investigations and gave further insight. The vortices within the transition zone of CGS Zn5Al coatings and AA7022 substrates documented by SEM show a different microstructure and composition compared with the substrate (Fig. 5). The average zinc content was 13 at.%. In this zone, the zinc content is significantly higher than that in the aluminum solid solution crystals of the substrate (i.e., 2 at.%). There is a high density of submicron-sized and nanosized particles embedded in an aluminum matrix that contains <1 at.% Mg and 4 at.% Zn (Fig. 6). In EDS point analyses of the particles with submicron size, densities of 27 at.% Mg, 57 at.% Zn, and <16 at.% Al were found. The chemical composition of the nanosized phases cannot be determined quantitatively by EDS due to their small size. However, the precipitates in the vortices showed a significantly different composition compared with those present in the AA7022 substrate underneath.

Based on the results of the investigations of both the coating-substrate interface and the substrate itself, it can be concluded that besides the mechanical alloying that is proved by the existence of zinc vortices, thermally induced reactions between impinging CGS zinc particles and the AA7022 substrate take place locally. As the atomic ratio of magnesium and zinc in precipitates with submicron size is approximately 1:2 and $MgZn_2$ is known to exist with a significant amount of dissolved aluminum, the formation of the so-called η -phase is proposed (Ref 7). As

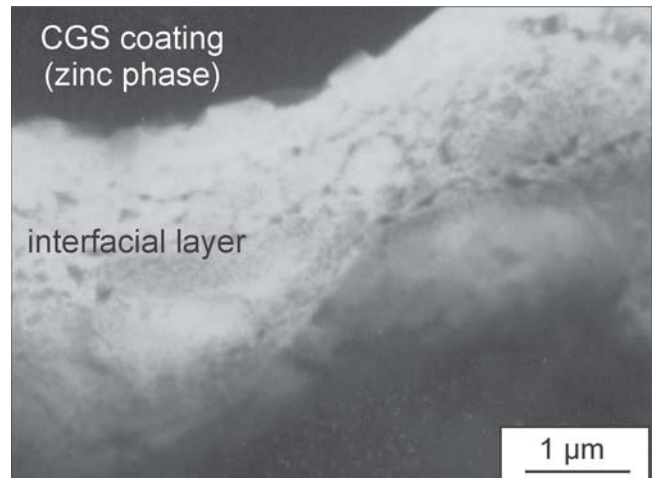


Fig. 5 A TEM micrograph of the interface between the CGS Zn5Al coating and the AA7022 substrate

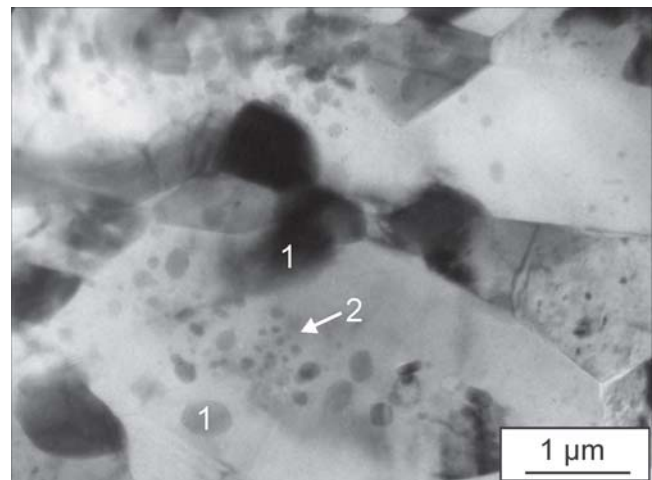


Fig. 6 A TEM micrograph showing Mg-Zn-based submicron-sized (1) and nanosized (2) precipitates within the interfacial layer shown in Fig. 5

the matrix phase inside the vortices shows decreased magnesium content in comparison to the substrate underneath, local melting with the subsequent precipitation of intermetallic phases including $MgZn_2$ can be deduced. The formation of the finely dispersed intermetallic phases due to diffusion-controlled reactions after mechanical alloying during the spraying process can be excluded because both the general substrate temperature and the time the specimen spends at increased temperature due to heating by the spraying gun are not sufficient.

The formation of magnesium-rich intermetallic phases causes the decrease of magnesium content in the aluminum matrix phase. At the same time, alloying by CGS zinc and extremely high cooling rates result in the formation of an aluminum solid solution with increased zinc content compared with that of the aluminum solid solution of the substrate material.

The TEM investigations on CGS zinc-coated AZ91 also confirm the results of the SEM analyses. The vortices consist of at

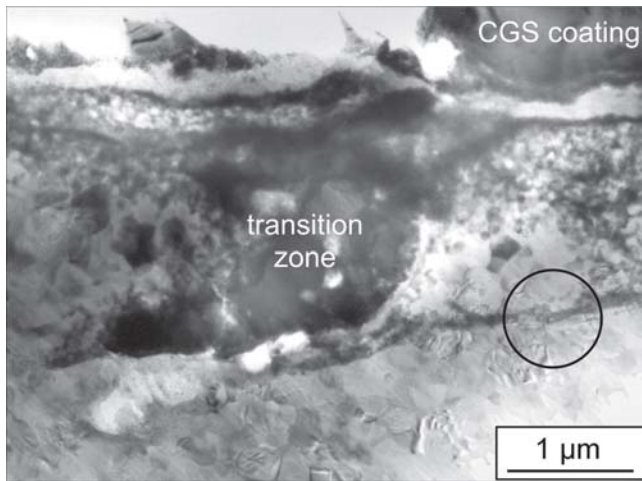


Fig. 7 A TEM micrograph of the interface between the CGS pure zinc coating and the AZ91 substrate; only fragments of the CGS coating remain after preparation (the marked region is shown in detail in Fig. 8)

least one nanosized, finely dispersed precipitate phase besides magnesium with a submicron-sized phase and Al content of up to 9 at.% (Fig. 7, 8). The EDS analyses of the precipitate groups revealed two types of composition (i.e., zinc-to-magnesium ratio inside the precipitates of roughly 1:2.6 and 1:1.3, respectively). On the basis of the ternary Mg-Zn-Al phase diagram, the existence of the two ternary phases $Mg_5Zn_2Al_2$ and $Mg_{11}Zn_{11}Al_6$ is proposed. The plastic deformation of the substrate material below the transition zone is indicated by the flattened $Al_{12}Mg_{17}$ precipitates. The oxide layers observed at the interface between the coating and the transition zone are attributed to the sample preparation procedure prior to microstructural investigations, which include grinding and polishing with water-based lubricants. This explanation is supported by the observation that during brazing, no dewetting occurs and also, in the produced brazing joints, no oxide phases are detected.

4. Summary and Conclusions

The evolution of zones showing intensive mechanical alloying at the interface of CGS zinc or Zn5Al coatings and AA7022 or AZ91 substrates was proved by high-resolution electron microscopy investigations. Transition zones contain vortexes that are due to the mixing of coating and substrate material. In addition, reaction phases are detected for both combinations of substrate and coating materials, which point at the short-term existence of the melt due to the conversion of kinetic energy to heat during the impact of CGS particles on the substrates. Reaction phases were detected within the transition zones in the vicinity of vortexes. Several submicron-sized or nanosized intermetallic precipitates with different compositions were observed. For Zn5Al coatings on AA7022, the formation of $MgZn_2$ is proposed, and for zinc coatings on AZ91 formation of ternary phases $Mg_5Zn_2Al_2$ and $Mg_{11}Zn_{11}Al_6$ is proposed. Both effects (i.e., mechanical alloying in vortexes and metallurgical reac-

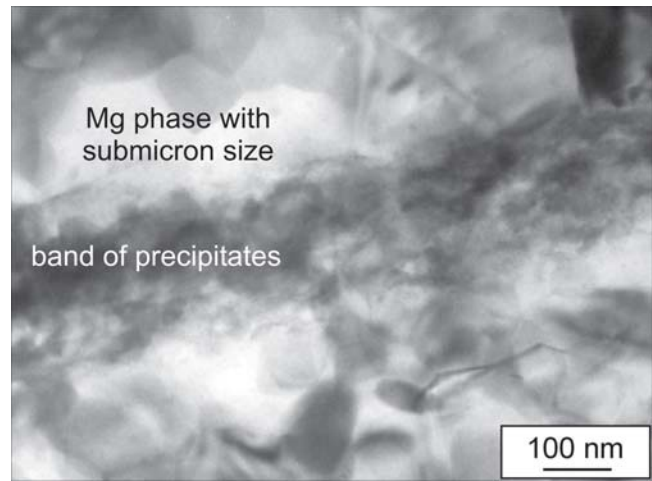


Fig. 8 A TEM micrograph showing the transition zone marked in Fig. 7 at high magnification

tions in their vicinity) cause the strong bonding of CGS zinc-based coatings on the light metal substrates. Also, the prewetting of light metal surfaces by the CGS filler coatings can be attributed to these metallurgical interaction processes. Oxide layers observed at the interface between CGS zinc coatings and AZ91 substrates are attributed to corrosion processes during the preparation of specimens.

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