On the role of zinc on the formation and growth of intermetallic phases during interdiffusion between steel and aluminium alloys

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ABSTRACT

The effect of Zn – both within Al and as a coating on steel – on the intermetallic phase formation and growth was systematically studied in controlled experiments, simulating the interfacial reactions taking place in dissimilar solid/solid and solid/liquid joining procedures. Independent from the reaction temperature, the addition of 1.05 at.% Zn (2.5 wt.%) to Al had no effect on the reaction layers' build-up with the η phase (Al_5Fe_2) as the dominant component, but accelerated their parabolic growth up to a factor of 13. While Zn-coatings on steel were found to be beneficial for the regular and even formation of intermetallic reaction zones in solid/liquid joining procedures, their role in solid-state processes was found to be more complex and, if no countermeasures are taken, extremely detrimental to the joint properties. Possible reasons for the Zn-induced growth acceleration are discussed, as well as consequences for possible optimisation steps for reducing harmful effects of Zn in dissimilar joints between Al alloys and steel.

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1. Introduction

Dissimilar joining between iron (Fe) based steels and aluminium (Al) alloys is the key to blend the attractive property profiles of these most common structural materials in one hybrid part. Steels are mainly chosen for contributing cost effective strength and high stiffness, Al alloys provide low density, high heat conductivity and excellent corrosion resistance [1]. Examples for such hybrid designs are lightweight body-in-white structures in transportation systems [2,3], protective Al coatings on steel sheets or tubes [4,5], or heat exchangers in energy conversion systems [6,7]. In all those applications an intimate bond between both materials is required, thus necessitating the application of thermal joining procedures opposed to mechanical fasteners such as screws or rivets [8]. Adhesive bondings are typically not only less cost effective, but also require overlapping flanges (which increase weight), are limited in the maximum application temperature and deteriorate the thermal and electrical conductivity [9].

The greatest challenge in the application of thermal joining procedures for the dissimilar joining of steel and Al alloys is the formation of inherently brittle intermetallic reaction layers at the interface. Depending on the reaction conditions determined by the respective joining process (e.g. time/temperature cycle, surface conditions, deformation), the reaction layers are complex in terms of build-up and morphology [10–12]. The η phase (Al_5Fe_2) has been identified as the most prominent component in such dissimilar joints, which is widely acknowledged to be caused by its rapid growth kinetics facilitated by the open and anisotropic crystallographic arrangement [13,14]. This prevalence of the η phase is of great relevance for the dissimilar joining of Al alloys and steel as it has been reported to be one of the most brittle intermetallic phases of the Al–Fe system [15,16]. Many studies have indicated the detrimental effect of growing reaction layers on the mechanical properties and the critical thickness has been found to be in the range of 3 – 10 μm, with different microstructural mechanisms deteriorating the joint strength and ductility [11,17,18]. Consequently, numerous process variations have been developed, both for solid-state joining (e.g. friction welding, diffusion bonding etc. [19–21]) and 'solid/liquid' techniques (e. g. Arc- or Laser-processes, where the Al alloy is molten and wets the solid steel [22,23]), all aimed at minimising and controlling the intermetallic layer thickness and build-up to improve the joint properties.

However, the chemical compositions of the reacting alloy systems – i.e. steel, Al alloy and, if used, filler material – have also a pronounced influence on the intermetallic phase formation and growth. The well-known retarding effect of silicon (Si) additions to Al on the growth kinetics of reaction layers is for example long since exploited in Al dip-coatings on steel, even though the mechanism of the growth suppression is still not completely understood [4,10,24,25]. Gebhardt and Obrowski [26] reported that additions

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of zinc (Zn), on the other hand, have the opposite effect of Si, i.e. leading to rapidly accelerated reaction layer growth up to a factor of more than 50 compared to reactions with pure Al. The growth acceleration was not found to increase linearly with the Zn content, but rather to exhibit a maximum at additions of 10 wt.% Zn [26]. Understanding this effect of Zn is not only important from an academic point of view, but also of enormous technological interest, as Zn-coatings are the most common corrosion protective measures for steels, especially on thin sheet material used in the automotive industry, and thus a common component in the reaction zone in dissimilar Al/steel joints [1]. Many different techniques have been developed to obtain such Zn-coatings, such as galvanic hot dip-coating (as the most commonly applied process), electrolytic deposition, powder/vapour-processes or even organic coatings [27–29]. All of these processes lead to Zn-coatings with thickness values ranging from about five to several hundred μm, and of specific microstructural and chemical characteristics related to the applied treatments. In dip-coating processes for example, small additions of Al (about 0.1 wt.%) are added to the Zn bath, which lead to the formation of a very thin (nm range) layer of an Fe–Al intermetallic reaction layer on the steel substrate [27]. This 'inhibition layer' in between steel and coating is reported to act as a diffusion barrier for Zn, thus suppressing rapid growth of Fe–Zn intermetallic phases ('outbursts') during galvanising, which have been found to strongly decrease the bond quality [30]. Apart from being coincidentally present in the reaction zone stemming from a steel coating during welding, Zn may also be utilised as an alloying element to contribute its cathodic effect for novel Al-based protective coatings on steel [29].

In light of the large variety of joining processes and respective parameters, base materials and types of coatings, it becomes clear that systematic investigations of the underlying phenomena for the intermetallic phase formation and growth are of great interest in order to derive guidelines for the knowledge-based optimisation of dissimilar joining and coating technology.

2. Objective

The objective of this work is to elucidate the role of Zn on the formation and growth of intermetallic reaction layers formed at the interface between steel and Al alloys at elevated temperatures as present in thermal joining procedures. The reaction products are studied in controlled experiments concerning the reaction between pure as well as Zn-containing Al and low C steel with and without different types of Zn-coatings in direct comparison, in experiments above and below the melting point of Al.

3. Materials and methods

3.1. Interdiffusion experiments

The steel samples used for the present study were cut from 3 mm thick sheets of a low-carbon steel (0.08 wt.% C), as used in the automotive industry (type DC04). Three types of steel surface conditions were investigated, namely (i) uncoated, (ii) dip-coated, termed '+Z', and (iii) electrolytic-coated, termed '+ZE'. Two Al alloys were used, namely high purity Al 99.99 as well as Al containing 1.05 at.% Zn (equals 2.5 wt.%), respectively.

Interdiffusion experiments below the melting point of Al were carried out as solid-state diffusion couples. Al samples of $5 \times 5 \times 5$ mm³ and steel samples of $3 \times 5 \times 7$ mm³ were cut by spark erosion. The contacting surfaces were ground and polished to a 1 μm finish except for the Zn-coated steel, which was not ground but only polished for 15 s not to remove the coating. After cleaning in an ultrasonic bath of ethanol and acetone, the samples were clamped together and annealed under Ar-atmosphere at temperatures in the range of 400–640 °C for 1–16 h, respectively. Cooling to room temperature was performed at air.

Experiments with liquid Al alloys were performed as dip-tests. Steel samples of $130 \times 30 \times 3$ mm³ were cut by spark erosion, the surfaces of the uncoated steel ground to 4000 grit, and all specimens cleaned in an ultrasonic bath and thermocouples were attached. The steel sheets were then immersed in Al bath (2 kg charge weight heated by an induction coil) at 750 °C, for 15, 30 and 60 s under an Ar-atmosphere of 400 mbar, and left to cool to room temperature at air afterwards. The steel sheets were pre-heated to 200 °C before immersion by holding them above the melt for 30 s; they reached the experimental temperature within less than 3 s after immersion.

3.2. Characterisation of the reaction zones

Cross sections of the interdiffusion experiments were prepared with standard metallographic techniques. The reaction layers were investigated using optical microscopy (OM; Leica DM4000M) for thickness measurements using a methodology detailed elsewhere [10], and scanning electron microscopy (SEM; Jeol 6450F) for chemical analysis (EDAX energy dispersive X-ray spectroscopy system; EDX) and phase identification (TSL electron backscatter diffraction system; EBSD). Transmission electron microscopy (TEM, Jeol 2200 FS) was performed to characterise the Zn coatings prior to the interdiffusion experiments. Site specific TEM sample preparation was carried out with a focussed ion beam system (FIB, FEI Helios Nano Lab 600i dual beam with Omni Probe manipulator).

4. Results

4.1. Reactions between steel and solid Al alloys

Examples of SEM analysis results from reaction zones formed during interdiffusion between uncoated steel and the Al–Zn alloy at 600 °C are compiled in Fig. 1. Independent from the reaction time, the intermetallic phase seam is protruding finger-shaped into the steel and finely serrated towards the Al alloy (Fig. 1 a and b). EBSD investigations (phase map with image quality data superimposed in grey scale, Fig. 1c) reveal the η phase (green) as its main component, with large columnar grains having grown along the c-axis of the phase, as indicated by green and blue colour-coding in the inverse-pole figure map (right image in Fig. 1c). The much thinner seam between the η phase (right image of Fig. 1a) and the adjacent Al-alloy could be identified as the θ phase ($Al_{13}Fe_4$, red in Fig. 1c) which grew from about 6 to about 11 μm between 1 and 16 h reaction time, while the thin layers between η and steel (white arrows in right image of Fig. 1b) most probably consist of the β′ phase (AlFe) and κ carbide (Fe_3AlC) as shown elsewhere [10]. The formation of pores between η and θ phase layers, the volume fraction of which is increasing with reaction time, can be linked to the Kirkendall-effect during growth of the η phase [11,31]. EDX measurements (Fig. 1d) revealed only traces of Zn incorporated in the θ phase, while the η phase contains about 0.5 at.% close to the Al alloy and about 5 at.% at the interface with steel. In view of the small concentrations and the complex morphology of the intermetallic phase seam, it should be noted that probing the exact chemical composition, especially close to the interfacial regions, requires different techniques such electron probe micro analysis or atom probe tomography. Thickness measurements as function of reaction time (Fig. 2a) showed the intermetallic phase seam to exhibit parabolic growth kinetics with a