Formation of an Aluminide Coating on Hot Stamped Steel

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The degradation of type 1 aluminized coating during hot stamping leads to the coating cracking due to the formation of a brittle FeAl_2 intermetallic phase. The formation of an aluminide coating prior to hot stamping was investigated as a method to simultaneously improve the coating ductility and achieve a good hot corrosion resistance of the hot stamped parts. A formable aluminide coating was obtained when the coating alloying was achieved during the pre-heating of the steel and an Fe content higher than 70 at% (83 wt%) was reached. The coating was identified as Fe_3Al phase at room temperature. The formation of this aluminide coating on 22MnB5 hot stamping steel was investigated in detail. The effect of this alternative hot stamping thermal cycle on the room temperature mechanical properties of the steel was also investigated.

KEY WORDS: aluminide; coating; hot stamping.

1. Introduction

Hot stamping is one of the most effective methods to produce ultra high strength steels (UHSS) for automotive bodies. Hot stamped steels are mainly used in the production of side impact beams, bumpers, B-pillars, roof rails, and tunnels. The use of hot stamped steel parts in body-in-white construction can significantly increase the passenger safety, contribute to vehicle mass containment and reduce fuel consumption.

At present, the type 1 aluminized coating (Al–10wt%Si) is used as a shield coating for the hot stamped steels. It protects steel from surface oxidation and decarburization, and enhances its corrosion resistance. Currently the 22MnB5 steel coated with 25–30 μm thick type 1 aluminized coating is widely used. In the hot stamping process, the coated steel blank is heated in a furnace to a temperature in the range of 900–950°C for 3–10 min. In the heating process, the steel becomes fully austenitic. The aluminized coating melts and reacts with the substrate steel to form solid intermetallic phases. After being transferred into press forming equipment, the steel blank is press formed in the temperature range of 600–800°C and simultaneously quenched by the water-cooled dies until the temperature reaches about 200°C. During the deformation at high temperature, the coating is broken into segments which adhere to the steel substrate. The cracked coating deteriorates the surface appearance and exposes the steel to corrosion.¹⁾ It is therefore necessary to explore possible solutions for the coating deterioration on hot stamped steels. These solutions should lead to a steel surface with a high temperature oxidation resistance and an adequate formability without cracking.

Aluminide coatings are commonly used as thermal barrier coatings on work pieces for elevated temperature service. Two methods are used to form iron aluminide coatings.

In the calorizing process, the work piece is covered with a Fe–Al alloy powder, sintered alumina and NH_4Cl . The NH_4Cl acts as a halide activator which transports the Al in gaseous form to substrate. The work piece is then heated at 850–1 000°C for several hours. A Fe–Al solid solution or an intermetallic compound is formed at the surface.²⁾ In the second process, the steel is coated with metallic Al or an Al alloy by hot dip aluminizing. During heating at 700–1 100°C, the substrate steel diffuses into the coating and iron aluminide phases are formed.^{2,3)}

In previous work,^{3–5)} iron aluminide coatings were produced by heat treating aluminized steels. The ductile FeAl or Fe_3Al phase was found to be preferred as a shield coating instead of the brittle FeAl_2 or Fe_2Al_5 phase. The formability of the iron aluminide coating was not an issue in those studies, because the coated parts did not need to be deformed subsequently. In the hot stamping process, the steel blanks are plastically deformed at high temperature, and the formability of the coating is an essential aspect of the process.

2. Experimental Procedure

The material used in the present study was a 22MnB5 steel sheet, which was hot dip coated on both side with a type 1 aluminized coating (Al–10wt%Si). The steel composition had 0.22 wt% C, 1.2 wt% Mn and 20 ppm B as main alloying elements. Two coating thicknesses were used: 25 μm and 10 μm .

In the present work, the coated steel sheet was heated in a box furnace in the 930–1 050°C temperature range with an air atmosphere to simulate the heat treatment of hot stamping. The steel was also tested on a Gleeble 3500 thermo-mechanical tester to simulate the hot deformation during the hot stamping process. The specimens were de-

formed to 30% engineering strain with a strain rate of 0.5/s in the temperature range of 600–800°C. The coating cross sections were polished with diamond suspension down to 1 μm . The specimens were observed in a Zeiss Ultra55 Field Emission Scanning Electron Microscopy (FE-SEM) operated at 20 kV and analyzed by Energy Dispersive Spectroscopy (EDS). The fracture surface of cracked coating was also analyzed. Specimens were prepared using Focused Ion Beam (FIB) method and observed in a JEOL 2100F Transmission Electron Microcopy (TEM) operated at 200 keV. The Vickers hardness of the steel was measured with a load of 0.5 kg and a dwell time of 10 s. The specimens were polished, etched with 2 vol% Nital and observed in the FE-SEM. The prior austenite grain size was measured by using intercept method according to ASTM standard E112.

3. Results and Discussion

3.1. Coating Degradation in Conventional Hot Stamping Process

In the hot stamping process, some parts of the steel, such as those in the corner areas of the hot stamped parts, are severely deformed at 600–800°C. 22MnB5 steel sheet coated with type 1 aluminized coating was thermo-mechanically tested in a Gleeble 3500 to simulate the hot stamping process. In the present study, the specimens were heated at 930°C for 5 min, and then cooled to 800°C with a cooling rate of 20°C/s. The specimen was then isothermally deformed uniaxially to 30% engineering strain at 800°C.

During the deformation at 800°C, the coating broke into segments, which remained adherent to the steel substrate. This is shown in **Fig. 1(a)**. Bare steel was exposed between the broken coating segments. The lengths of coating segments and gaps between the segments were found to be shorter when the strain rate increased. The coating fracture pattern of the coating became finer at higher strain rates (**Fig. 1(b)**). The cracking of the coating caused by plastic deformation was reported previously by Denner *et al.* for a type 1 aluminized coating heat treated at 816°C.⁶⁾

Fig. 1. (a) The cross section and (b) the surface of the cracked coating on 22MnB5 steel. (c) The FE-SEM micrograph of coating segment in edge and (d) FE-SEM micrograph of the cracked coating cross section after hardness indentation at room temperature.

The cracked coating was identified as a layer of FeAl_2 intermetallic phase (**Fig. 1(c)**). A thin layer of thermal oxide, approximately 1 μm thick, was present between the coating and steel substrate. A small gap can be observed between this layer and substrate steel, which implies that this layer might easily peel off. The EDS analysis revealed that this layer was FeO_x . These exposed areas are expected to be much more susceptible to corrosion compared with the areas still covered by the intermetallic layer.

Figure 1(d) shows the coating cross section of the 0% strained sample after heat treatment. Its thickness is same as the 30% strained one in **Fig. 1(c)**, which implies that the coating did not plastically deform during the hot deformation.

A hardness indent with a load of 0.1 kg was made in the coating and observed in the FE-SEM (**Fig. 1(d)**). It can be clearly seen that cracks were formed in the indent area and propagated in a brittle fashion into the coating. This implies that the FeAl_2 coating is brittle both during hot forming and at room temperature. Hence the coating can easily be damaged during service.

From the above, it is clear that, during conventional hot stamping type 1 aluminized coating reacts with the steel substrate to form the FeAl_2 intermetallic phase, which is brittle both at high temperature and at room temperature. In addition, the cracked coating deteriorates the surface appearance and makes the exposed segments of steel susceptible to corrosion. The coating is also susceptible to cracking during service. It is therefore necessary to explore alternative heat treatments for Al–Si coated hot stamped steels, so that the coating may provide a high temperature oxidation resistance and display an adequate formability during hot stamping.

3.2. Criteria for Coating Ductility

An aluminized steel specimen was heated for 4 min at 1050°C and deformed uniaxially 30% at 800°C at a strain rate of 0.5/s. It was found that the coating cracked during the hot deformation. In **Fig. 2(a)** the fracture surface of a coating crack is shown. The top surface of the coating consisted of an oxide layer. The region beneath the coating was the steel surface which was oxidized when the crack formed at high temperature. It can be clearly seen that the coating consisted of two distinct layers, each with a characteristic fracture morphology. The upper part of the coating crack surface was faceted due to brittle fracture, and it is labeled as region 1. The lower half of the coating crack surface had a ductile fracture appearance, and it is labeled as region 2. It is very likely that region 1 cracked initially dur-

Fig. 2. (a) The fracture surface of the cracked coating, (b) the cross sectional composition profile of the coating obtained by EDS.

ing plastic deformation and that the crack propagated into the region 2 causing the final failure of the entire coating. If the entire coating had been composed of region 2, it is expected that the coating would have been able to deform plastically with the substrate steel without cracking.

Between region 1 and 2, there are some voids, which are indicated with circles in Fig. 2(a). These voids are very likely Kirkendall voids formed due to the different diffusivities of Fe or Al in regions 1 and 2. In the composition profile shown in Fig. 2(b), the regions 1 and 2 are separated by a dashed line. Region 1 had a Fe content in the range of 50–70 at%. Region 2 had a Fe content in the range of 70–98 at%. The Si content was about 5 at%. In the present study, Si was considered to have same behavior in the coating as Al, and the coating was treated as a binary Fe–Al system. This is reasonable as Si has an atomic radius and molecular weight very similar to that of Al, and it is also a strong ferrite stabilizing element.

The alloyed coating covered the range of 50 to 98 at% Fe after heating at 1050°C for 4 min. The Fe–Al binary phase diagram is shown in Fig. 3(a).⁷⁾ The transition between ordered B2 FeAl phase and the disordered α -Fe phase with Al in solid solution occurs at 1050°C for an Fe–Al alloy

Fig. 3. (a) The Fe–Al binary phase diagram (reproduced from Ref. 7)) and (b) comparison between conventional hot stamping process and proposed alternative hot stamping process.

with 70 at% Fe. This is the same as the composition of the interface between regions 1 and 2 in Fig. 2(b). From Fig. 3(a) it can be estimated that region 1 was very likely the ordered B2 FeAl phase. Region 2 was disordered α -Fe with Al in solid solution at high temperature. According to the Fe–Al phase diagram this phase transforms to the ordered D03 Fe₃Al phase at low temperatures.

Regions 1 and 2 were observed and analyzed at high resolution by TEM. Figures 4(a) and 4(b) are the $\langle 110 \rangle$ lattice image and the corresponding diffraction pattern of region 1, which was identified as the ordered B2 FeAl phase. The inter-planar distances d_{002} and d_{110} were measured to be 0.144 nm and 0.206 nm, respectively. The calculated lattice parameter was 0.290 nm. Figures 4(d) and 4(e) are the $\langle 110 \rangle$ lattice image and diffraction pattern of region 2, which was identified as ordered D03 Fe₃Al phase. The inter-planar distances d_{004} and d_{220} were measured as 0.145 nm and 0.209 nm respectively. The calculated lattice parameter was 0.585 nm. These measured values are in agreement with the reported lattice parameter values of 0.291 nm for FeAl and 0.579 nm for Fe₃Al, respectively.⁸⁾ The diffraction patterns of regions 1 and 2 are shown in Fig. 4(b) and 4(e). They are the characteristic diffraction patterns for the B2 FeAl and D03 Fe₃Al phases with $\langle 110 \rangle$ zone axis.

The diffraction spots in italics are forbidden in the disordered bcc phase, but they are allowed superlattice reflections in the ordered B2 FeAl and D03 Fe₃Al phases (Figs. 4(c) and 4(f)). For example the $(1\bar{1}1)$ diffraction spot in Fig. 4(b) is caused by the Al atoms which occupy the central position in the B2 unit cell (Fig. 4(c)). The $(1\bar{1}\bar{1})$ diffraction spot in Fig. 4(e) is caused by the Al atoms which form a central tetrahedral unit in the D03 unit cell (Fig. 4(f)).

From the above analysis, it is clear that there are two criteria to obtain a formable coating: the Fe content in the coating should be above 70 at% (83 wt%) at 1050°C. And the coating should have a disordered bcc structure at high temperature and an ordered Fe₃Al D03 structure at low tem-

Fig. 4. (a) Lattice image, (b) corresponding diffraction pattern and (c) crystallographic structure for the ordered B2 FeAl phase in region 1. (d) Lattice image, (e) corresponding diffraction pattern and (f) crystallographic structure for the order D03 Fe₃Al phase in region 2. The zone axis is $\langle 110 \rangle$ in both cases. The inserts in (a) and (b) are the corresponding unit cells.

perature. This Fe_3Al aluminide coating is desired for the hot stamping process and it can be easily be obtained by using an adapted pre-heating process.

In the hot stamping process, the steel sheets are usually deformed in the temperature range of 600–800°C. In the present study, the samples were pre-heated at 1 050°C and deformed at 800°C. On the basis of the equilibrium Fe–Al binary phase diagram (Fig. 3(a)), it is expected that from 1 050 to 800°C, the disordered bcc α -Fe phase should partially transform to B2 FeAl. The α -Fe/FeAl phase boundary is approximately 76 at% (87 wt%) Fe at 800°C. This transformation was however not observed in the present study. This implies that the disordered α -Fe phase remained present in the undercooled state at 800°C. A cooling rate of 20°C/s therefore effectively suppresses the transformation of the disordered α -Fe phase to the ordered FeAl phase.

It has been reported that the FeAl phase, alloyed with Cr, Ti, Zr, or B, was ductile in tensile and compressive deformation at temperature above 700°C,^{9,10)} and that it could be super plastic at high temperature when tested at low strain rates even for a large grain size microstructure.¹¹⁾ Baker *et al.* mentioned that a Fe–40at%Al alloy had no elongation and a transgranular cleavage fracture surface when deformed in the temperature range of 950–1 100°C at relatively high strain rates. The ductile to brittle transition showed a clear dependence on the Al content and the deformation temperature.¹²⁾ In the present study the FeAl phase was found to be brittle when tested at strain rate of 0.5/s in the temperature range of 600–800°C. In this case the FeAl phase contained 5 at% Si. It is presently unknown if this Si content may cause the FeAl to be brittle. This phenomenon needs further investigation.

3.3. Formation of a Ductile Coating for Hot Stamping

From the previous paragraphs, it is clear that the disordered bcc α -Fe phase with Al in solid solution is the desired coating during the hot stamping process. In order to make the initial Al–Si coating transform to a disordered bcc α -Fe phase, the Fe content in the coating must be higher than the threshold value of 70 at% at 1 050°C. Two methods can be considered to increase the Fe content in the surface layer.

First, a steel coated with a thick type 1 aluminized coating needs to be heated for a longer time or at a higher temperature. This process will increase the diffusion time or the diffusivity of Fe in order to increase its content in the coating. The other method is to reduce the coating thickness *i.e.* the diffusion distance, so that the Fe content can reach 70 at% in a shorter time or at a lower temperature. In the present study, specimens coated with 25 μm and 10 μm

type 1 aluminized coating were tested at a temperature of 1 050°C for different time. The thermal cycles are shown schematically in Fig. 3(b). After the heat treatment, cross sections of the samples were observed in the FE-SEM. Their composition profiles are shown in Fig. 5.

For the specimen coated with a 25 μm thick coating, the coating thickness increased to about 93 μm after heating at 1 050°C for 30 min (Fig. 5(a)). The Fe content in the coating was slightly more than 70 at%. For the sample with a 10 μm thick coating, the coating thickness increased to about 30 μm after heating at 1 050°C for only 4 min (Fig. 5(b)). The Fe content in the coating was also higher than 70 at% in this case.

Figure 6 shows the cross-sectional images of the 25 μm coated specimens. In Fig. 6(a) the initial coating consisted of an Al matrix layer in which eutectic Si was formed. An intermetallic layer was present at the steel/coating interface, which was identified as the Fe_2SiAl_7 phase by EDS. After a heat treatment at 1 050°C for 30 min, the Fe diffused into the coating and its content at the coating surface increased to 70 at%. The thickness of the coating increased to 93 μm . The Kirkendall voids coalesced and formed a more or less continuous cavity, which retarded the Fe diffusion into the upper side of the coating (Fig. 6(b)). This phenomenon very likely resulted in a longer time to increase the Fe content in the entire coating. During deformation the voids were extended and formed larger gaps in the coating (Fig. 6(c)). The thickness of the coating was reduced to 75 μm due to plastic deformation. No delamination or powdering of the coating was observed during deformation. And the coating remained strongly adherent to the substrate steel.

The formation of an aluminide coating from a thick aluminized coating by diffusion treatment has already been reported in literatures. In the work of Kobayashi *et al.*,³⁾ a 60 μm thick pure aluminum coating was reported to have transformed to a 100 μm thick Fe_3Al coating after heating at 1 100°C for 1 h. The existence of FeAl_2 phase was ob-

Fig. 5. The compositional depth profiles of (a) a 25 μm coated specimen after 30 min at 1 050°C and (b) a 10 μm coated specimen after 4 min at 1 050°C.

Fig. 6. FE-SEM micrographs of the cross section of the 22MnB5 steel coated with thick Al–10wt%Si coating (a) as hot dipped, (b) heat treated at 1 050°C for 30 min and (c) heat treated at 1 050°C for 30 min and 30% strained at 700°C.

Fig. 7. FE-SEM micrographs of the cross section of the 22MnB5 steel coated with thin Al-10wt%Si coating (a) as hot dipped, (b) heat treated at 1050°C for 4 min and (c) heat treated at 1050°C for 4 min and 30% strained at 700°C.

served in the final coating. In the work of Chang *et al.*,⁴⁾ a 25 μm Al-7wt%Si coating was heat treated at 850°C for 24 h. The final thickness was almost 90 μm . FeAl, FeAl₂, and Fe₂Al₅ were found to be present in the final room temperature alloy coating. The formation of voids was also reported. The formability of the diffusion treated coating was however not discussed in these previous reports.

Figure 7 shows the cross sections of the 10 μm coated specimens. The original thin coating structure was similar to that of the 25 μm coating (Fig. 7(a)). After heat treating at 1050°C for 4 min, the Fe content at coating surface increased to 70 at%. The thickness of the coating increased to 30 μm . Due to the shorter duration of the thermal cycle, the number and the size of voids were much smaller than in the case of thicker coating, and they had a less retarding effect on the Fe diffusion into the topmost layer (Fig. 7(b)). During deformation the voids were extended and became larger (Fig. 7(c)). The coating thickness was reduced to 25 μm .

The tests shown that, both the 25 μm and 10 μm coatings alloyed to form a disordered bcc phase, were formable and did not crack or delaminate during deformation tests. Considering the distribution of voids in the coating and the efficiency of the process, the 10 μm thin coating heated at 1050°C for 4 min is preferred. It is estimated that the heating time or temperature can be reduced further if the initial coating thickness is decreased.

As the coating thickness varied and the coating/steel interface was unclear after alloying, it was difficult to precisely measure the coating thickness. Nevertheless the coating thickness strain could be evaluated, and compared to the thickness strain of the substrate steel. The thickness of substrate steel decreased from 1.65 to 1.41 mm after 30% tensile deformation. The thickness strain was about 0.15. The thicknesses of the thick coating before and after deformation were 93 μm and 75 μm . This corresponds to a strain of about 0.19. The thicknesses of the thin coating before and after deformation were 30 μm and 25 μm . This corresponds to a strain of about 0.17. These similar thickness strains imply that the coatings were completely plastically deformed together with the substrate steel.

The coating layer hardness after a conventional thermal cycle and the new thermal cycle are compared in Fig. 8. The hardness of the layer was 769 after the conventional cycle. In contrast, the hardness of the 25 μm thick coating obtained after heating at 1050°C for 30 min was only 311. The hardness of the 10 μm coating obtained after heating at 1050°C for 4 min was also low, *i.e.* 222. As shown in Fig. 1(d), the hardness test also resulted in the formation of brittle cracks in the layer formed during the conventional HPF

Fig. 8. The hardness comparison of coating obtained in conventional process and the ductile coatings formed in the new thermal cycles.

Fig. 9. Comparison of hardness and prior austenite grain size of 22MnB5 steel after different thermal cycles.

process. The cracks caused variations in the measured indent size. This is the reason for the larger error bars associated with the hardness data for the conventionally processed coating. Figures 6(b) and 7(b) show the hardness indents in the 25 μm coating heated 30 min to 1050°C and the 10 μm coating after heating 4 min at 1050°C, respectively. No cracks were observed in both cases. The indent in Fig. 7(b) showed a pronounced asymmetry in the coating thickness direction, which implied that the hardness decreased in the direction from the surface to the bulk. This is due to the hardness gradually decreasing with increasing Fe content towards the steel substrate. From the hardness measurement and indents morphology, it is clear that the coatings formed during the new thermal cycle were ductile both at high temperature and at room temperature.

3.4. The Influence of the Thermal Cycle on the Mechanical Properties

The hardness of 22MnB5 steel after heating at 1050°C was shown in Fig. 9 and compared with the hardness of the

steel after heat treatment in the conventional HPF thermal cycle. All the specimens had a martensitic microstructure. Compared with the steel produced in a conventional hot stamping process (930°C, 5 min), the steel hardness decreased slightly after heating at 1 050°C for 4 min. The high heating temperature resulted in coarsening of the prior austenite grain size and this, in turn, lead to coarsening of packet size in the quenched martensite. As a consequence, the hardness of martensite decreased. This implies that the heating time at 1 050°C should be kept to a minimum and that thin coatings are preferred. The influence of the new thermal cycle on the steel mechanical properties at room temperature should also be taken into account when the hot stamped parts are designed.

4. Conclusion

It was found that the ordered B2 FeAl phase was brittle and that the disordered α -Fe phase with Al in solid solution was ductile during high temperature deformation. The two criteria for obtaining a formable coating on a hot stamped steel is that the Fe content in the coating should be above 70 at% and that the disordered α -Fe phase with Al in solid solution should be formed. This high temperature disordered α -Fe phase transforms to the ordered D03 Fe₃Al phase during cooling to room temperature.

A 10 μ m aluminized 22MnB5 steel can be used to form this aluminide coating after heating at 1 050°C for only 4 min. The coating has a good formability at high temperature. Compared to the conventional hot stamping method, the use of a thinner coating and a higher heating temperature make it possible to avoid the formation of cracks dur-

ing the hot stamping process. This ordered D03 Fe₃Al aluminide layer is ductile at room temperature as well.

The decreased steel strength caused by higher temperature pre-heating should however also be considered when hot stamped parts are designed.

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