Experimental and computer thermodynamics evaluations of an Al-Si-Coating on a quenchable steel

http://dx.doi.org/10.1590/0370-44672016700080

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Abstract

High-strength steels are commonly used in the automobile industry in order to reduce the weight of the vehicles. However, a technical difficulty appears due to the need of hot stamping of the components, which leads to oxidation. Therefore, the application of a coating on the substrate to avoid high-temperature oxidation is used. In this work, experimental analysis and computer thermodynamic calculation were used to describe the phase transformations within an Al-Si coating on a quenchable high strength steel. The Al-Si coating was deposited by hot dipping and its characterization was done using SEM and XRD techniques. Computer thermodynamics calculations were done using the commercial software FactSage using the Calphad methodology. It demonstrated a good relationship between the experimental results and the computer calculations of phase stabilities for the as-deposited condition and after diffusion experiment at 920°C for 7 minutes, which simulates the thermal cycle of hot stamping of the quenchable steel used.

Keywords: Al-Si coating, hot stamping, computer thermodynamics, interdiffusion, ultra-high-strength steel.

1. Introduction

The demand for weight reduction in mechanical structures and at the same time, car safety improvement require the use of ultra-high-strength steels of high toughness and good deformability. Usually, high-strength steel components with complex geometries are deformed at high temperatures. In the case of quenchable steels, the deformation temperature would be around 920°C in the austenite stability field. After deformation, cooling should be fast enough to form the martensitic structure. However, iron forms very stable oxides at high temperatures, especially above 570°C due to the fast growing of wustite (FeO). The formation of oxide should be avoided in order to keep a good surface condition of the component and to conserve the good spot weldability of the steel. Therefore, ultra-high-strength steel plates are often hot-dip coated with the Al–Si alloy (Grauer *et al*., 2015; Borsetto *et al*., 2009). The coating is deposited using an eutectic composition, which melts at 577°C (Paar *et al*., 2008) and the diffusion of iron from the steel substrate into the molten Al–Si layer forms intermetallic phases (Al–Si–Fe) with a melting temperature around 1200°C (Grauer *et al*., 2015; Engels *et al*., 2006; Gui *et al*. 2014), which is higher than the temperature used during hot stamping (around 920°C).

The information about phases coexisting at given conditions can be obtained from the phase diagrams of multicomponent alloys, which are therefore a useful tool for the understanding of processes taking place in complex materials. Calphad (Dinsdale, 1991) method allows the theorectical modelling of phase diagrams taking advantage of the current development of powerful computers and sophisticated softwares. A powerful commercial software using the Calphad methodology is the FactSage (Bale *et al*., 2002; Trindade *et al*., 2009), which was used in this work for the thermodynamics calculations for the binary Al-Si, Fe-Al and Fe-Si systems as well as the ternay Fe-Al-Si and quaternary Fe-Al-Si-O systems.

The aim of this work is to evaluate the phase transformations occurring in the coating during deposition and during simulated hot stamping, by means of computational thermodynamics calculations and XRD measurements.

2. Material and method

In this study, quenchable steel alloyed with boron was used. The chemical composition is presented in Table 1. A very high strength can be reached with this steel by forming martensite even during a low cooling rate. A tensile strength of 1600MPa can be achieved combined with good ductility.

C	Si	Mn	Cr	Mo	P	S	Ti	Al	B	Fe
0.20	0.15	1.10	<0.35	<0.35	<0.025	<0.005	0.020	0.020	0.020	Bal.

Table 1
Nominal chemical composition (in wt.%) of the martensitic steel used.

The deposition of the Al-Si-coating is done according to the DIN EN 10292 Standard. The Al-Si system has an eutectic point at 577ºC and 12.5wt.% of Si as shown in Figure 1. The dipping temperature was 950ºC for 0.5 minute. The coating used has a composition of 12wt.% of Si. From the melt, a eutectic is formed between aluminum solid solution and virtually pure silicon. The eutectic is comprised of large plates of silicon in the aluminum matrix.

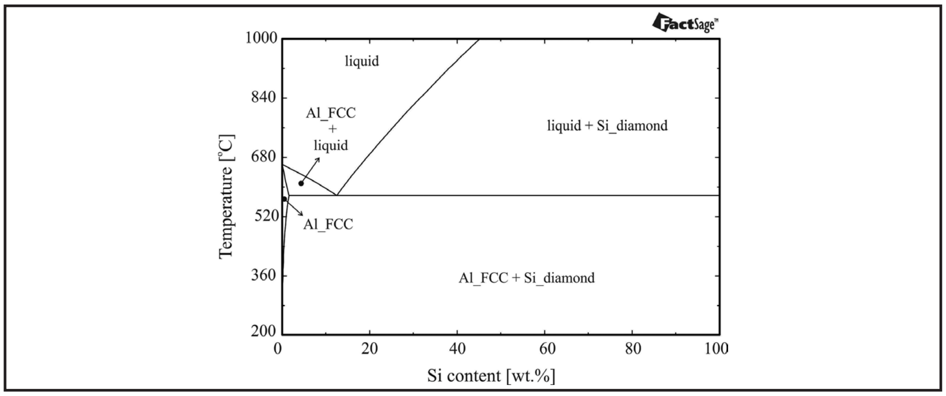

Figure 1
Binary phase diagram for the system Al-Si. The calculation was performed using the software FactSage.

The studied samples are from a hot-dipping industrial process. A thermal cycle representing the hot-dip aluminizing was performed in a laboratory furnace. Figure 2 schematically shows the complete thermal cycle of the studied samples: (a) as-deposited – sample after hot dipping and (b) after diffusion heat treatment – sample after simulated steel hot stamping.

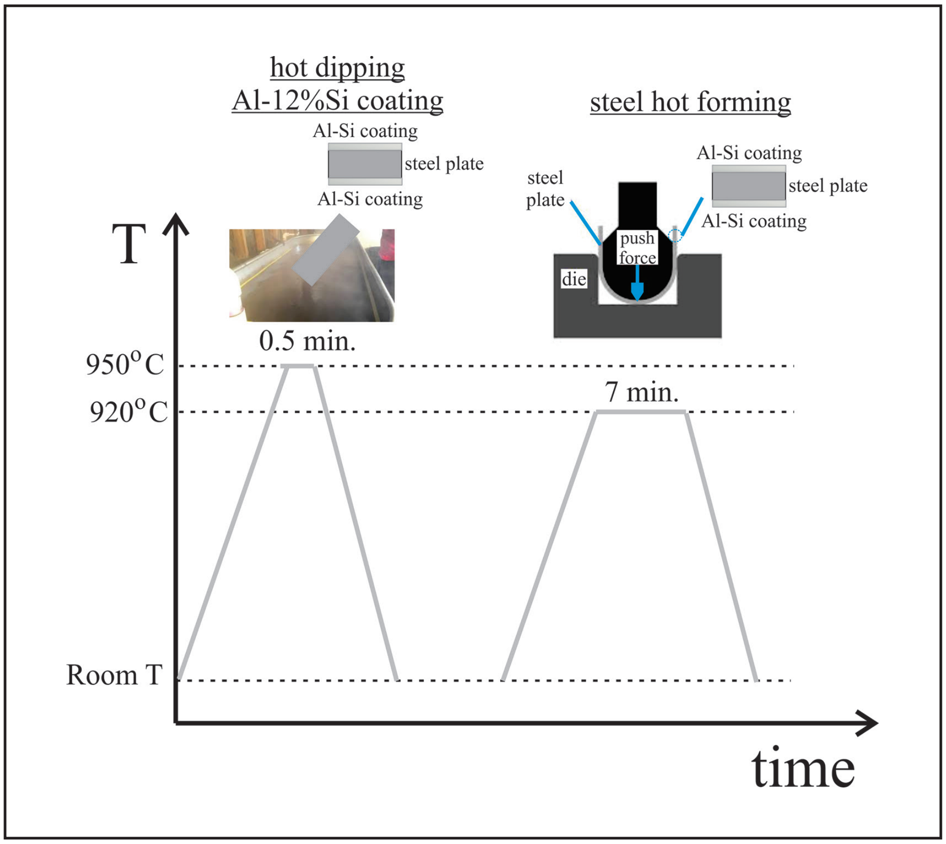

Figure 2
Schematic representation of thermal cycles during hot dipping and simulated steel aluminizing.

The microstructure of the deposited coating was analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) after diffusion heat treatment at 920ºC in laboratory air for 7 minutes attempting to simulate the conditions during aluminizing.

3. Results and discussion

Figure 3a shows that the coating consists of two layers: an outer layer and an inner layer. The outer layer is predominantly eutectic-Al-Si alloy (see Figure 3b and Figure 1) and the inner layer (or diffusion layer) is enriched on Fe (Figure 2b).

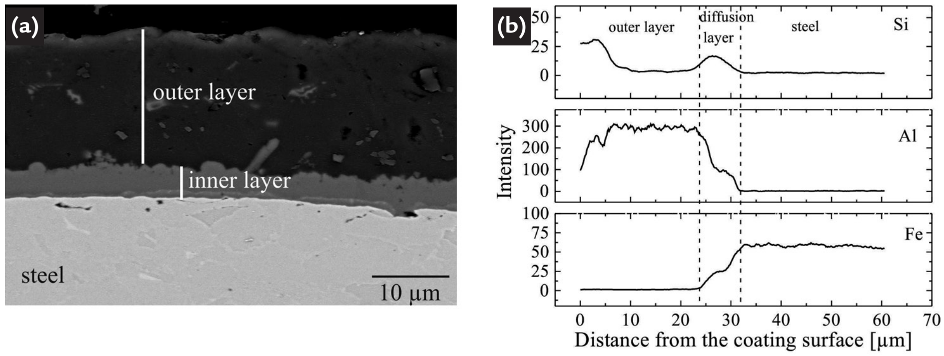

Figure 3
Cross section SEM observation of the coating in the as-deposited condition: (a) formation of outer layer and inner layer (=diffusion layer) and (b) EDS element profiles.

The Fe-Si phase diagram has been the subject of controversial considerations for a long time. A generally accepted Fe-Si phase diagram is shown in Figure 4a, which was calculated using the commercial software FactSage. The main phases at higher Fe content are Fe_5Si_3, Fe_2Si and FeSi. The Fe-Al phase diagram is as complex as the Fe-Si system (see Figure 4b). The solubility of Al in Fe is significantly higher than that of Si in Fe. The main intermetallic phase is $FeAl_2$ at high Fe content and Fe_2Al_5 for intermediate Fe content. Figure 4c shows the one-dimensional phase diagram for the ternary Fe-Al-12wt.%Si system, which presents a large number of phases (more than 40 phases).

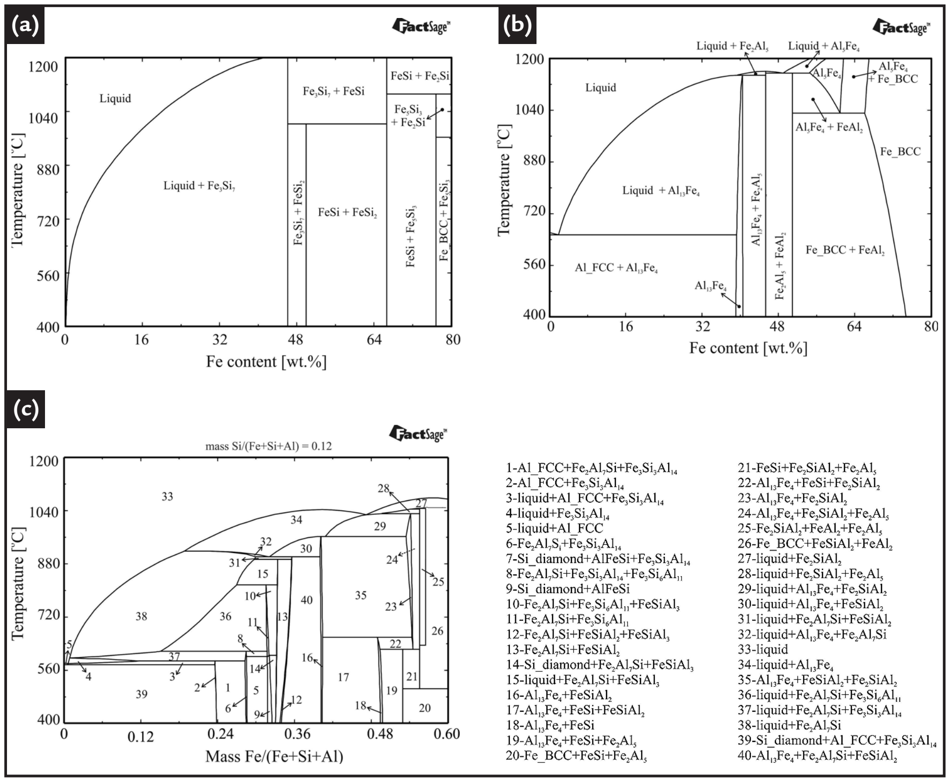

Figure 4
Calculation of phase diagrams using the software FactSage for the systems: (a) Fe-Si, (b) Fe-Al and (c) Fe-Al-12wt.%Si.

In order to simulate the hot stamping condition, the coating/steel was heated up to 920°C and held 7 minutes. After this diffusion treatment, the coating could still be observed. However, some major modifications compared to the as-deposited condition can be pointed out: (i) the outer and the inner layers could not be distinguished (see Figure 5a). Interdiffusion occurs causing Fe diffusion outwards and Al and Si diffusion inwards (see Figure 5b). Furthermore, a huge amount of Kirkendall voids is observed as consequence of interdiffusion mechanisms (see Figure 5a).

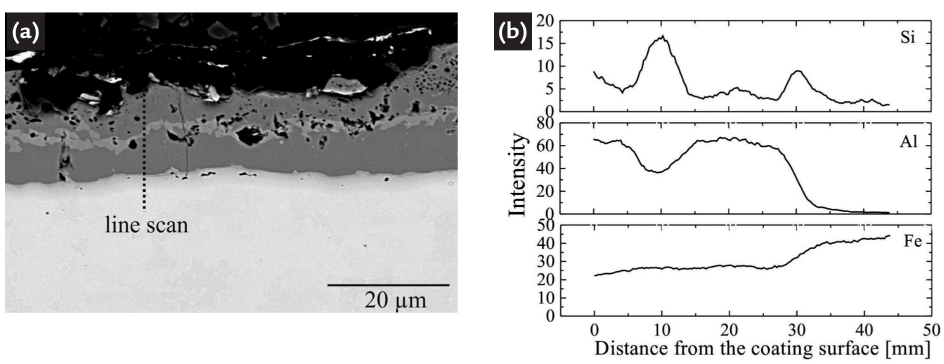

Figure 5
Cross section SEM observation of the coating after 7 minutes diffusion treatment at 920°C: (a) formation of a new coating due to interdiffusion phenomenon and (b) EDS-line scan elements profile.

XRD measurements after the diffusion process, identified the main phases formed as: oxide formed on the outer surface (Al_2O_3, SiO_2, FeO, $AlFeO_3$, Al_2SiO_5) and intermetallic phases along the coating cross section (Al_5Fe_2, Al_8Fe_2Si, Fe_3Si, Al_2Si, $FeAl_3$, $AlFe_3$). These results are in line with the predicted phases by thermodynamic calculations (see Figure 4).

During the heat treatment of the substrate steel/coating system a Fe-gradient is established across the coating. This leads to the formation of different FeAlSi-phases due to different Fe concentration. For high Fe content (close to the coating/substrate interface) and low temperature, the phases are FeSi and Fe_2Al_5 and Fe_2Al_7Si. For low Fe content (close to the coating surface) and low temperature, the original eutectic structure (Al/Si) is in equilibrium with the ternary phase $Fe_3Al_3Si_{14}$. The major problem that appears due to the formation of silicides as well as pores within the Al-Si coating is the decreasing on the electrical conductivity of the coating. Consequently, the spot weldability of the component is strongly affected by the presence of Fe-Al-silicides within the coating.

4. Conclusions

From the present study, it is possible to draw the following conclusions:

(1) SEM analysis allowed the characterization of the coating structure in the as-deposited condition and after a simulated thermal cycle representing the hot forming. In the as-deposited condition a two layer coating was observed. The outer layer is enriched in the Al-Si eutectic phase and Si in the inner layer forming Fe-Si intermetallic phases.

(2) Computer thermodynamic calculations allowed the prediction of all possible phases in this complex system, taking into account binary systems (Al-Si, Fe-Al and Fe-Si), a ternary system (Fe-Al-Si) and a quaternary system (Fe-Al-Si-O).

(3) XRD measurements demonstrated the excellent relationship between experiments and predicted phases by computational thermodynamics.

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Received: 7 June 2016 - Accepted: 13 September 2016.