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Characteristics in Paintability of Advanced High Strength Steels

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It is expected that advanced high strength steels (AHSS) would be widely used for vehicles with better performance in automotive industries. One of distinctive features of AHSS is the high value of carbon equivalent (Ceq), which results in the different properties in formability, weldability and paintability from those of common grade of steel sheets. There is an exponential relation between Ceq and electric resistance, which seems also to have correlation with the thickness of electric deposition (ED) coat. Higher value of Ceq of AHSS lower the thickness of ED coat of AHSS. Some elements of AHSS such as silicon, if it is concentrated on the surface, affect negatively the formation of phosphates. In this case, silicon itself doesn't affect the phosphate, but its oxide does. This phenomenon is shown dramatically in the welding area. Arc welding or laser welding melts the base material. In the process of cooling of AHSS melt, the oxides of Si and Mn are easily concentrated on the surface of boundary between welded and non welded area because Si and Mn could be oxidized easier than Fe. More oxide on surface results in poor phosphating and ED coating. This is more distinctive in AHSS than in mild steel. General results on paintability of AHSS would be reported, being compared to those of mild steel.

Keywords *: phosphate, AHSS, ED coating, welding*

1. Introduction

One of the main issues in automotive industries is the improvement of fuel efficiency to decrease exhaust gas. In material side, one of the solutions is to make lightweight body by adopting high strength steel. Auto body is very important part directly related to safety of passenger. Therefore, how to secure passenger's safety should be considered at first to realize lightweight body. Recently, many carmakers is tend to use high strength steel (HSS) more and more in order to make the car body safer and lighter. Application rate of HSS at present is around 40% and would be supposed to be up to 70% in a few years.[1)] ULSAB AVC (Ultra Light Steel Auto Body - Advanced Vehicle Concept), of which project promote to use steel material for car body, use 100% of HSS, and especially more than 85% of advanced high strength steels (AHSS) with tensile strength of 590 MPa and over.[2)] Even though AHSS are used more and more for car body and all car body are joined by welding and finally painted because of corrosion protection and appearance, paintability of AHSS and the effect of welding of AHSS on paintability are not well known yet. In this report, general paintability of AHSS and its characteristics will be presented. Effect of arc welding to AHSS on paintability will be also given in brief.

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2. Results and discussion

2.1 Paintability of AHSS

One of distinctive features of AHSS compared to mild steels is high Ceq, which may affect phosphating and paintability. General results on paintability of AHSS are shown in Table 1, being compared to those of mild steel.

Thickness of two AHSS, DP590 and TRIP780 GA, is 1.4 mm and that of EDDQ GI and EG is 0.65 mm. Properties of phosphate and ED coat of four steels in Table 1 were evaluated by the method and procedure of engineering standard of GMDAT. Differences in paintability between AHSS and mild steels, even though metal coatings of AHSS and EDDQ are different, are not found in Table 1 except corrosion properties shown in salt spray test (SST) for 480hours. Furthermore, one of most rigorous adherence test, which is Erichsen cupping test in cross hatched ED coat specimen, gives different results between them similar to the results of SST. This phenomenon is obvious in Fig. 1.

Table 1. Paintability of various steels

Materials	Phosphate		ED coat						
	Weight (g/m^2)	Crystal size (㎛)	Thickness (㎛)	Adherence	Impact resistance	Chipping	Water resistance	Humidity resistance	SST 480h
DP590 GA	2.1	5	20.9	++	++	++	++	++	1.8mm
TRIP780 GA	4.0	4	13.6	++	++	++	++	++	1.7mm
EDDQ GI	3.0	5	20.3	++	++	++	++	++	5.1mm
EDDQ EG	2.1	5	18.2	++	++	++	++	++	6.1mm

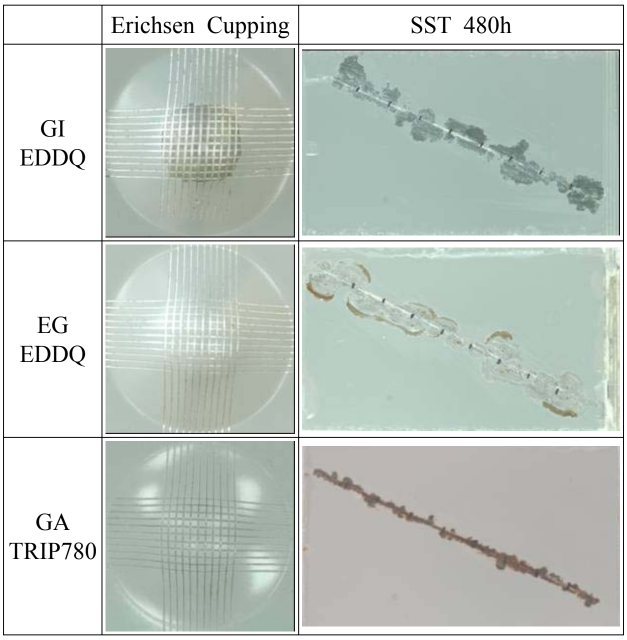

Fig. 1. Comparison of Adherence and Corrosion Properties of GI/EG/GA

Adhesion of ED coat on EG and GA is much stronger than that on GI. These results are consistent with that done in Corus. It is guessed that Al on surface of GI is main factor to deteriorate adhesion of ED coat. In general, Zn is apt to go to cosmetic corrosion. On the other hand, Fe and Fe-Zn alloy to perforation corrosion. Therefore, width of blister of GI and EG is much larger than that of GA.

2.2 Behavior of thickness of ED coat on AHSS

Dependence of thickness of ED coat on ED voltage is shown in Fig. 2. Two kinds of dual phase (DP) 590 Mpa grade galvanealed (GA) and two AHSS, DP590 cold roll (CR) and 780 Mpa grade of TRIP GA steel, as references, were studied. Two DP590 GA have different value of Ceq. One is commercially available at present, which is denoted as Nor., the other is newly under the development, denoted as New. All materials show the increase of thickness of ED coat to the applied voltage for ED coat. However, the thickness of ED coat decrease according to the order of New DP590 CR>Nor. DP590 GA>New DP590 GA~ TRIP780 GA at the same applied voltage. It is guessed that this comes from the difference in Ceq between materials. Normally, Ceq of mild steels is similar to each other because it is in the small range of Ceq. However, as one of most distinctive features of AHSS is the high value of Ceq, there is big difference in Ceq's of the various grades of AHSS. Ceq comes from the chemical contents of steels such as C, Mn, Si etc, which have different electric resistance from pure iron. Therefore, different value of Ceq can result in the difference in electric resistance of steels. If a steel has high value of Ceq, its electric resistance will be also high, which result in the decrease of current on the surface of steel at the same applied voltage during electro deposition and finally the decrease of thickness of ED coat. This assumption can be supported by the result in Fig. 3 and Table 2 which show the relationship between Ceq and specific resistance of various automotive steels. Specific resistances of materials were measured in Korea Research Institute of Standards and Science. Table 2 and Fig. 3 show the exponential increase of specific resistance as Ceq of steels go up, of which fitting result are denoted in Fig. 3 and its equation is following.

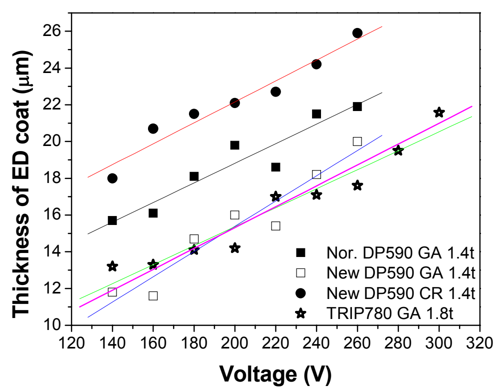

Fig. 2. Dependence of thickness of ED coat on ED voltage

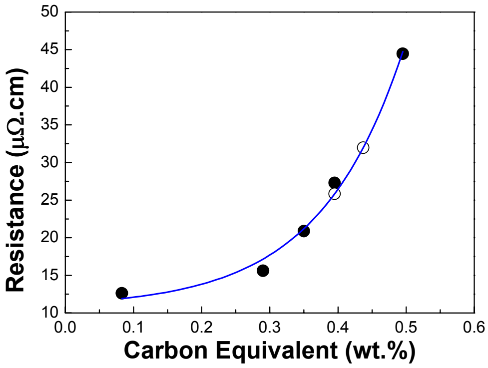

Fig. 3. Relationship between Ceq and Specific resistance of Automotive Steels

Table 2. Electric properties of automotive steels

Material	Specific resistance (・Ωμcm)	Conductivity (MS/cm)	Ceq*
SAPH270	12.61	0.0793	0.083
SAPH440	15.60	0.0641	0.29
DP590 GA	27.30	0.0366	0.40
FB590	20.87	0.0479	0.35
TRIP780	44.46	0.0225	0.50

*Ceq(JIS) = C + Mn/6 + Si/24

$$\text{Specific Resistance } (\Omega\mu cm) = 10.7 + 0.61 * \exp(Ceq/0.12) \quad (1)$$

Even though Nor.DP590 GA and New DP590 GA are the same grade, its Ceq's are different each other. Ceq of Nor. DP590 GA is 0.395 and New DP590 GA is 0.437. Therefore, New DP590 GA has higher specific resistance, 31.97 Ωμcm, than that of Nor. DP590 GA, 27.10 Ωμcm, if they are calculated from eq. 1. In Fig. 3, open circles are the assumed value from its Ceq's of Nor. and New DP590 GA. In this region of specific resistance, it changes very rapidly to Ceq. Although two steels have the similar mechanical properties, the reason why two similar DP590 GA have different thickness dependence on the voltage could be understood based on the above discussion. Combining the dependence of thickness of ED coat on the applied voltage and the behavior of specific resistance of AHSS to its Ceq, dependence of thickness of ED coat shown in Fig. 2 could be well explained. Higher value of Ceq of material gives the smaller thickness of ED coat at the same voltage. Although TRIP780 GA has the highest Ceq and specific resistance, its thickness dependence of ED coat on the voltage is very similar to that of New DP590 GA. This might suggest the limited effect of specific resistance to the thickness of ED coat. Similar situation is also found in the case of New DP590 CR. Even though its Ceq is the same as that of New DP590 GA, the dependence of thickness of ED coat on the voltage of New DP590 CR is totally different from that of New DP590 GA. In this case, the existence of metal coating layer play an important role. That is, interfacial resistance between GA coating layer and its base steel could be high. Therefore, comparison of same GA series could be reasonable, and further experimental study for CR should be required.

2.3 Paintability in area of weld

There are so many weld area in Body In White (BIW). Most of them are exposed and should be protected from corrosion by painting. Weld area can be divided into two region, weld part and haz part which is the area affected by welding heat. The mechanical and chemical properties of weld area may be determined by welding condition. In this report, mainly arc welding and brirefly laser welding effect will be addressed. In Table 3, arc welding conditions are given. General condition for arc weld which is widely used in automotive industry was used. In order to check the only welding effect, welding is done by bead-on-plate .

Table 3. Arc Welding Condition

Material	Condition (weld material, direction, method)	Current (A)	Speed (m/min)
DP590 CR 1.0t	SM70, backward, MAG, But	80	1.0
DP590 GA 1.4t	SM70, backward, MAG, But	100	1.0

2.3.1 Paintability of CR in weld area

Results of phophating on arc welding area of DP590 CR are given in Fig. 4. Surface of weld part is not clean, some precipitates are found and some of pore are shown in the interface.

Phosphates in weld part itself are very well formed and it has very good coverage. However, the shape of phosphate is slightly different from typical phosphophylite, which is formed on CR. Some of part, specifically in white rectangle, show good and typical phosphophylite, but in the other area mixed phosphate crystal between hopeite and phosphophylite are observed. This may come from the change in the composition of element on surface of weld part. This phenomenon is much clearly observed in the interface. In the area between weld part and haz part, large pores are observed and none of phosphate crystals are formed, which make interface without phosphate crystal. EDS result on interface shows that lots of Al, Si and Mn are observed on the surface at the interface.

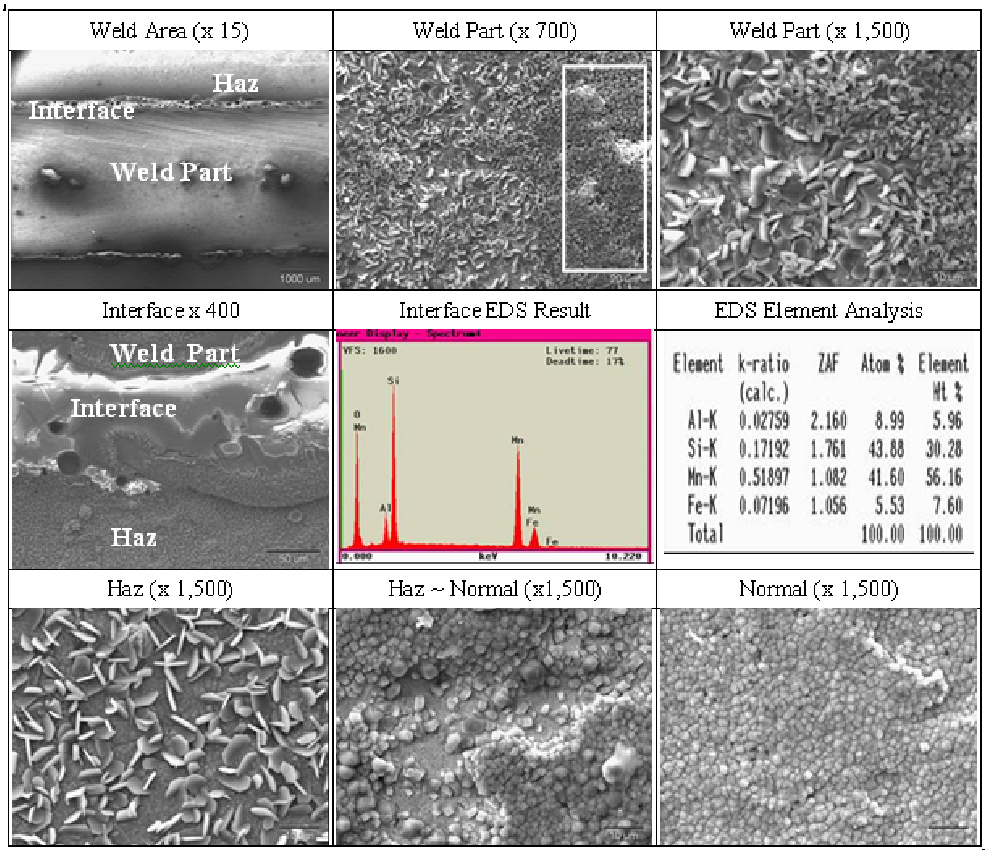

Fig. 4. Phosphate on arc weld area of DP590 CR. Number in ( ) is magnification of SEM.

Mn and Si are the main components on the surface even though its content in base steel are at most below 2%, even for Al below 0.1%. Most of them formed at the surface are oxide and Si oxide is well known as the deteriorate elements for phosphate, therefore, it could be explained why any phosphate crystal are not formed at the interface. This behavior of formation of oxide of Mn, Si and Al at the interface might be guessed that during welding process the metal in the weld area melted, then for the cooling some of elements, which can form oxide much easier and faster than iron, comes up to the surface of the interface from weld part. This is consistent with that the amount of element on the surface is the same as the order of formation energy of oxide, Al>Si>Mn>Fe.[3] It may be plausible inference that the concentration of Si oxide on the surface would decrease from the weld part to the unaffected area. In the haz part near to the interface, coverage of phosphate crystal is not good and shape of crystal is different from phosphophylite, which is typically formed on CR. As going from interface to far away, crystal shape is recovered to phosphophylite even though its coverage is not 100% yet. At about 1 cm apart from the interface, fully recovered phosphophylites are observed and 100% coverage is gotten back. From the above observation of formation of phosphate in weld area, we can expect the weak adhesion of ED coat and bad corrosion property in this area because of bad phosphating.

Results of paintability on weld area of DP590 CR are shown in Fig. 5. ED coating for those is made at 180 V. Its appearance was good and no pinhole is observed in weld area at this voltage, which is much below rupture voltage for CR. Adhesion seems to be good, but this test is least discriminative even though it is most basic and widely used. The exfoliation of ED coat around weld area is observed in the other adhesion tests such as water and humidity resistance, impact test, Erichsen cupping and chipping. These results suggest that in the weld area, the formation of phosphate is not good, which result in poor adhesion of ED coat to phosphate layer.

Therefore, water cam penetrate through ED coat to phosphate layer, make the adhesion of ED coat weak and finally ED coat peeled off. Mechanical deformation of weld area of ED coated specimen also result in peeling off ED coat from phosphate layer in weld area. Even though deformation of specimen is little by impact test because the strength of base steel is high, the exfoliation

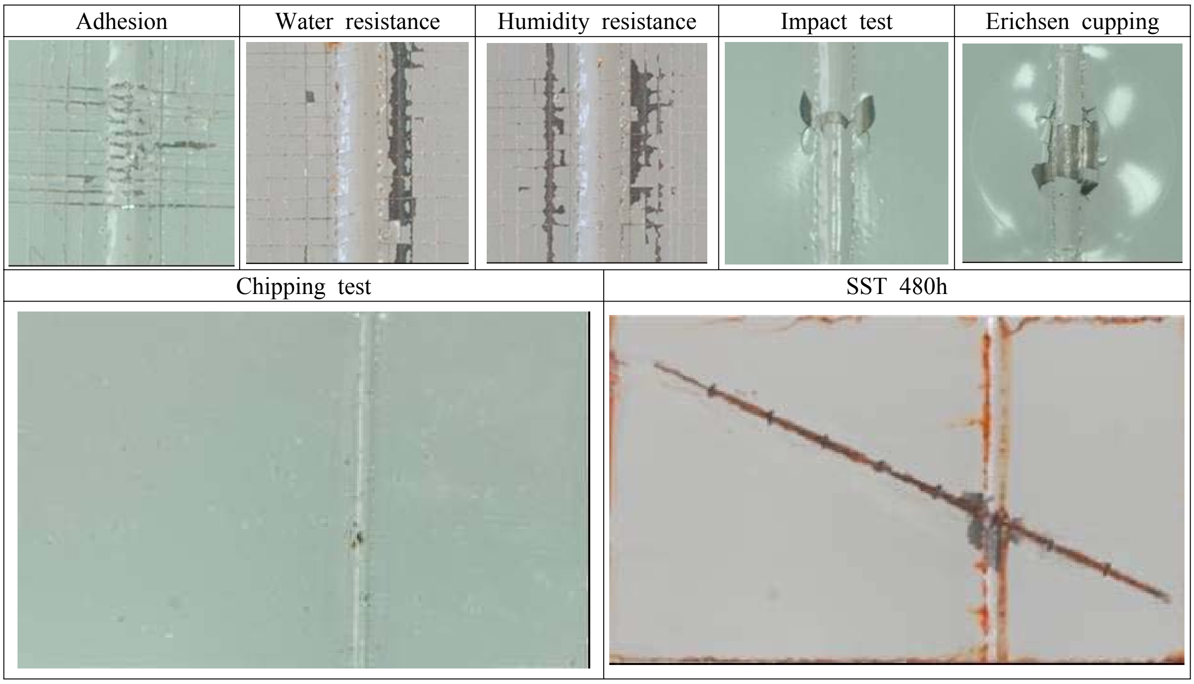

Fig. 5. Paintability in arc weld area of DP590 CR

of weld area is the same as that shown in the other test. Chipping in normal part of the specimen is very good but not in weld area. Corrosion test also show the similar result to chipping. Width of blister in normal part is very good, 0.3 mm but larger blister in weld area and red rust along the weld line, which means that the weak adhesion is apt to corrode easily. In summary, by arc welding, many easily oxidized elements such as Mn and Si are accumulated on the surface of weld area, specifically welding interface. Oxide interfere the formation of phosphate or make bad phosphate crystal, resulting in the weak adhesion between ED coat and phosphate layer.

2.3.2 Paintability of GA in weld area

Results of phophating on arc welding area of DP590 GA are given in Fig. 6. On the whole, characteristics of phosphate layer on weld area of DP590 GA is very similar to that of DP590 CR. In this section, only some difference between GA and CR will be presented. Arc weld area of DP590 GA also show the clearly defined weld part, interfaceand haz part. Even though phosphate itself is well formed on weld part, shape of phosphate crystal is far different from typical hopeite which is formed on GA surface. In the case of GA, the situation is more complicated than in CR because of the existance of GA coating layer. Phosphate itself are well formed in this area, but a few kinds of phosphate crystals are mixed such as phosphophylite-like, disk-like and large lump of crystal, of which phosphate crystals are far from the typical phosphate crystal on GA, that is, hopeite crystal. The formation of complex crystals may come from the newly formed complex alloy in weld part resulting from mixing base metal with coating metal during welding. Interface between weld part and haz part are also observed and Al, Si and Mn are detected at interface by EDS similar to CR's result. Zn shown in interface came from metal coating layer. Metal oxide on the surface of interface obstruct the formation of phosphate, resulting in the interface. Distinctive features of weld area for GA come from the existence of Zn metal coating layer. This is obvious in haz part. Crystal shape in Haz A and Haz B of Fig. 6 is very peculiar and different from each other even in the same haz part. Even though its results was not shown in here, qualitative analysis by EDS on phosphate in Haz A and B gave very normal results similar to hopeite's. This results suggest that chemical composition on surface affect the formation of phosphate and its reaction, which means further study would be required. Normal phosphate, hopeite in this case, was observed in very far away, at least 1 cm, from the interface.

As phosphating in weld area for GA is also very bad similarly to CR's, it is inferred that paintability in this area would be not good. Paintability on weld area of DP590 GA is reported in Fig. 7. ED coating for those is made at 220 V in order to match the thickness of ED coat with that of DP590 CR.

Appearance of ED coat was good as much as that of

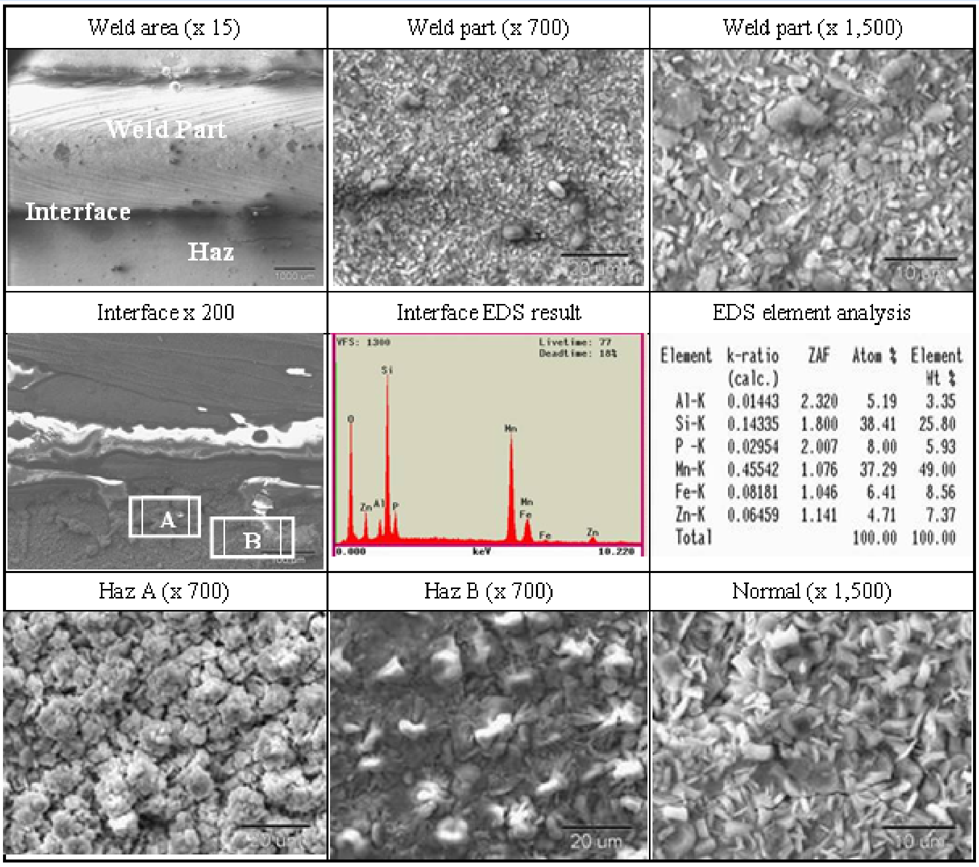

Fig. 6. Phosphate on arc weld area of DP590 GA. Number in ( ) is magnification of SEM.

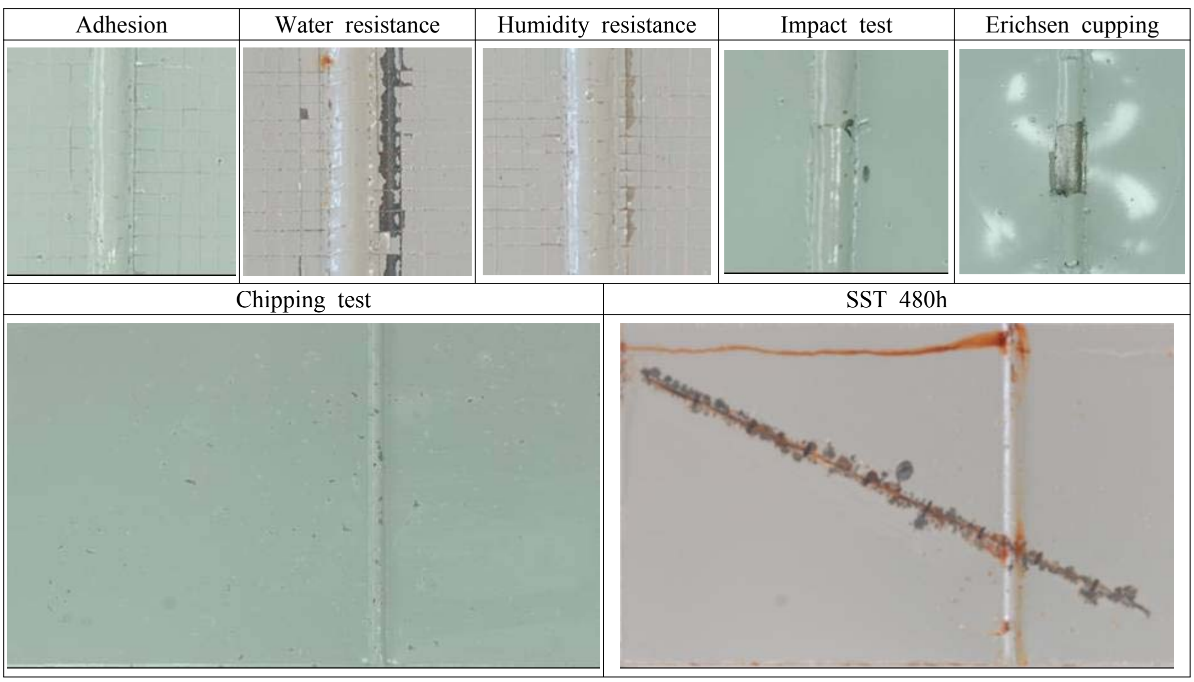

Fig. 7. Paintability in arc weld area of DP590 GA

DP590 CR and no pinhole was observed in weld area at this voltage. Adhesion seems to be good, but the exfoliation of ED coat around weld area is observed in water and humidity resistance, impact test, Erichsen cupping and chipping. These results are very similar to those shown in DP590 CR because of bad phosphates in weld area. Overall adhesion tests seem to show better results in DP590 GA than in DP590 CR. This may come from better coverage of phosphate in weld area of DP590 GA, which means the form of phosphate crystals is not important to adhesion between ED coat and phosphate layer, but phosphate itself is. Corrosion property in weld area of DP590 GA is also as good as in normal area of GA except small red rust in weld area.

In summary, adhesion and corrosion property in weld area of GA is not good because of bad phosphate and formation of interface, but better than that of CR due to better coverage and formation of phosphate and narrow interface between weld part and haz in GA.

3. Summary

Overall paintability of AHSS is good as much as that of mild steel. In general, adhesion and cosmetic corrosion property of coated steels such as GA, GI and EG is unrelated to base steel, but to coating characteristic. That is, GA's adhesion and cosmetic corrosion is better than that of EG and GI. Specific resistance of steel have strongly related to its Ceq. Different value of specific resistance of AHSS result in the different thickness dependence of ED to applied voltage. However, there seems to be limit of specific resistance of AHSS to affect thickness dependence of ED coating. Welding also affect significantly paintability and formation of phosphate through the formation of oxide of Mn, Al, and Si during cooling after melting the base material and coated metal. Width of interface formed between weld part and haz part is narrower in GA than in CR, which result in better adhesion and corrosion in GA's weld area than in CR's.

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