

# Surface Segregation of Phosphorus, Carbon, and Sulfur in Commercial Low-Carbon Grades of Steel

V. RANGARAJAN, R. TONCHEFF, and L.L. FRANKS

Surface segregation behavior of solute atoms has been studied on low-carbon steels used in producing galvanized sheet steels for automotive body panel applications. Samples of cold-rolled low-carbon steels with different amounts of carbon and phosphorus in solution were heated in a vacuum chamber and their surface chemistries analyzed by Auger electron spectroscopy. For the steels studied here, one or more of the elements carbon, phosphorus, and sulfur accumulated significantly at the surface within a temperature window of 300 to 973 K. As the temperature was increased, carbon appeared on the surface first, followed by phosphorus, and then sulfur. Each succeeding segregating element displaced the previous one from the surface. The free solute concentration in the bulk and the temperature were critical factors controlling the amount of solute accumulation at the surface. Once segregated, the solute atoms remained on the surface as the samples cooled. Carbon and/or boron in steels retarded the transport of phosphorus to the surface. The implications of these findings in understanding the galvanizing behavior of these steels are discussed.

## I. INTRODUCTION

Galvanneal coatings are zinc-iron alloy coatings produced by dipping sheet steel in a molten zinc bath and, subsequently, annealing the coated sheet steel in a furnace.<sup>[1]</sup> Galvanized sheet steels are used extensively in the automotive industry for exposed and unexposed body panel applications.<sup>[2,3]</sup> The function of the coating is to provide extended corrosion resistance for the body panels.<sup>[4]</sup>

Steel chemistry plays a critical role in determining the intermetallic composition of the galvanneal coating.<sup>[5]</sup> In particular, the phosphorus in the steel has a profound effect on the galvanizing process and the galvanized product. Rephosphorized steels require greater galvanizing heat input in order to be satisfactorily alloyed. The phosphorus in the steel influences the evolution of the coating structure as well as the final properties of the coating.<sup>[6]</sup> It has been postulated that phosphorus, which had segregated to the sheet steel surface during recrystallization annealing, affected the kinetics of the Fe-Zn reaction as the sheet steel was subsequently dipped in a molten zinc bath of a continuous galvanizing line.<sup>[7,8]</sup>

Surface chemistry changes occurring during annealing of sheet steels have been studied extensively.<sup>[9-13]</sup> Some of these studies examined the selective oxidation behavior of manganese and silicon in steels as a function of oxygen potential, time, and temperature in industrial annealing atmospheres (N<sub>2</sub>/H<sub>2</sub> gas mixtures). Particles of manganese and silicon oxides were formed on grain boundaries intersecting the surface, as well as on free surfaces away from the boundaries, during batch annealing in N<sub>2</sub>-H<sub>2</sub> atmospheres.<sup>[9,10,11]</sup> The annealing cycles in these studies typically ran for several hours, and the peak temperature attained was

around 973 K.<sup>[9,10]</sup> The oxide particles were shown to interfere with the wetting of the steel surface when steel was dipped in a molten zinc bath.<sup>[9]</sup> In other studies, the annealing experiments were extended to 1123 K, and the different factors leading to external vs internal oxidation of manganese and silicon were explained.<sup>[11]</sup> Further, an accelerating influence of boron on the external oxidation of manganese was presented, particularly for an annealing cycle very typical of the recrystallization annealing step in a continuous hot-dip coating line.<sup>[11]</sup>

While selective oxidation of Mn and Si have been shown to interfere with the galvanizing reaction, this phenomenon alone is insufficient to explain the anomalous galvanizing behavior of phosphorus-bearing sheet steels. Surface segregation of elements such as carbon, phosphorus, and sulfur can also occur during these annealing treatments, and some studies have measured two distinct layers forming on the surface after annealing in industrial N<sub>2</sub>-H<sub>2</sub> atmospheres.<sup>[12]</sup> The outer sublayer was 20-nm thick and consisted of carbon, phosphorus, sulfur, and sodium, as well as manganese and chromium. The inner sublayer was 120-nm thick and was primarily enriched in oxygen, manganese, and chromium.<sup>[12]</sup> Thus, both surface segregation and selective oxidation can play vital roles in modifying the steel surface chemistry as it enters the zinc bath after recrystallization annealing.

That phosphorus in the steel has a strong effect on the galvanizing process and the galvanized product is well known. Producers of galvanized rephosphorized steels have had to adapt their processes to accommodate this effect. A mechanism by which phosphorus might act in the galvanizing process suggests that segregated phosphorus on the steel surface alters the composition of the initial alloy layer that forms on the sheet steel when it comes in contact with the zinc bath, which then has a significant impact on the subsequent alloying rate.<sup>[7]</sup> However, the segregation of phosphorus and other solute elements in these specific steel grades has not been analyzed to support such a mechanism.

The primary purpose of this work was to examine the

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**Table I. Typical Compositions of Automotive Sheet Steel Grades Selected for This Study (Weight Percentages)**

Element	ELC Grade	ULC Grade (Ti/Nb Stabilized)	ULC + P Grade (Ti/Nb Stabilized)
C	0.02 to 0.03	≤0.004	≤0.003
Mn	0.20	0.16	0.25
P	≤0.02	≤0.02	0.035 to 0.06
S	≤0.015	≤0.015	≤0.012
Si	—	—	—
Cr	—	—	—
Nb	—	0.03 to 0.04	0.03 to 0.04
Al	0.04 to 0.05	0.05	0.04
N	≤0.008	≤0.004	≤0.004
B	—	—	—
Ti	—	0.015 to 0.025	0.015 to 0.025

**Table II. Chemistries of Specific Nonautomotive Steels Analyzed in This Work (Weight Percentages)**

Element	ELC + B	ULC + P (Lab Produced)	ELC + P + B
C	0.0234	0.0025	0.0062
Mn	0.19	0.7	0.3
P	0.014	0.069	0.063
S	0.013	0.017	0.014
Si	0.006	0.26	—
Cr	0.02	—	—
Nb	0.0021	—	0.002
Al	0.041	0.19	—
N	0.0067	0.0048	0.0028
B	0.0059	—	0.0006
Ti	—	—	0.013

segregation behavior of phosphorus and other steel constituents, to determine the degree to which phosphorus segregation can occur prior to and during the galvannealing process. A second purpose was to determine how other steel constituents interact with the phosphorus segregation, possibly diminishing or enhancing its extent. This work examines the surface segregation behavior in a temperature range from 300 to 973 K for low-carbon steels, including stabilized ultralow-carbon steels, which are of particular interest in coated automotive body panel applications. Further, the effect of boron additions to low-carbon steels on the surface segregation of phosphorus is examined, to a limited extent.

## II. EXPERIMENTAL PROCEDURES

### A. Materials

The sheet steel grades selected for this study include an extra-low-carbon steel (ELC) grade with a total carbon between 200 and 300 ppm by weight, an ultralow-carbon steel (ULC) grade with a total carbon of less than 40 ppm by weight in the steel, and a rephosphorized ultralow-carbon steel (ULC + P) with a phosphorus addition of up to 0.06 wt pct. The samples were analyzed in the cold-rolled condition. The cold-rolled samples were degreased in a solution of acetone and methanol and were subsequently sputter cleaned in the Auger chamber prior to conducting the experimental heating cycles. In going from grade ELC to

ULC + P, the carbon/phosphorus concentration ratio in the steel continually decreases and the concentration of sulfur is nearly constant. The ultralow-carbon steels were stabilized with additions of titanium and niobium (Ti-Nb-stabilized ultralow-carbon steels). Typical compositions for these sheet steel grades are listed in Table I. Manganese was added to all of the steels to control the amount of sulfur in solution. For the specific purpose of illustrating the role of boron on segregation behavior in ELC- and ULC-type steel chemistries, use is made of limited surface segregation results generated on steels from other (nonautomotive) applications. The specific chemistries of these other steels, denoted as ELC + B, ULC + P (lab-produced), and ELC + P + B, are given in Table II. The ULC + P (lab-produced) sample was ELC-grade steel that had been subjected to a decarburizing heat treatment as part of another study, resulting in a final carbon of 25 ppm by weight. This particular sample was not stabilized with titanium and niobium additions.

### B. Surface Analysis

A PHI 548 Auger/ESCA system with a double-pass cylindrical mirror analyzer was used to obtain Auger spectra from the steel surfaces. An electron-bombardment heater was installed in the vacuum chamber for heating the sample. The electron-bombardment heater was mounted on the opposite side of the vacuum chamber from the double-pass cylindrical mirror analyzer. This configuration was necessary for achieving high temperatures and rapid heating rates while protecting the analyzer from high-energy electrons generated by the heater. The sample holder was rotated, between heating and analysis, in the vacuum chamber. Since the sample was not being heated during the Auger scans, it cooled continuously while the scan was being collected. No detectable surface chemistry changes occurred during cooling over the period of time needed to acquire the scan ( $\approx 2$  minutes). Chromel-alumel thermocouples were spot welded to the backs of the sheet samples (which were anywhere between 2 and 6 cm<sup>2</sup> in area). This formed the hot junction of the thermocouple. The cold ends of the thermocouple were attached to feedthroughs on the vacuum chamber. The other ends of the feedthroughs were connected to a thermocouple meter, which displayed the temperature.

The maximum sample temperature that could be obtained in the Auger system with the experimental setup previously described was 973 K. Beyond this temperature, the outgassing in the vacuum chamber was sufficient to shut the Auger system down. Two types of heating cycles were conducted in this study. The first was a stepped-ramp heating cycle, in which the sample was heated to a series of increasing temperatures and held for 5 minutes at each temperature. At the end of each 5-minute hold time, the surface composition was measured before continuing the heating to the next-higher temperature. The purpose of this procedure was to monitor surface composition as a function of temperature. The 5-minute time period was also helpful for stabilizing the temperature. No significant surface chemistry differences were observed between Auger scans that were started as soon as the sample reached the desired temperature and those that were started after a 5-minute hold time. The second type of heating cycle involved long hold times

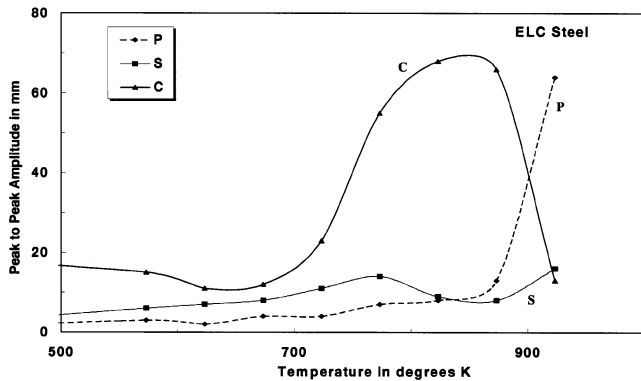


Fig. 1—Measured Auger peak amplitudes of carbon, phosphorus, and sulfur on ELC steel sample surface as a function of temperature for a fixed hold time of 5 min at each temperature.

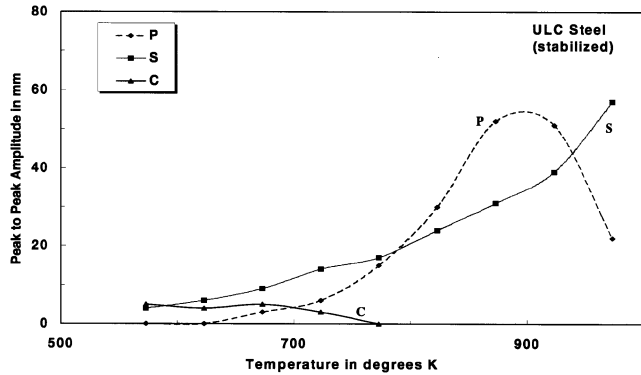


Fig. 2—Measured Auger peak amplitudes of carbon, phosphorus, and sulfur on ULC steel sample surface as a function of temperature for a fixed hold time of 5 min at each temperature.

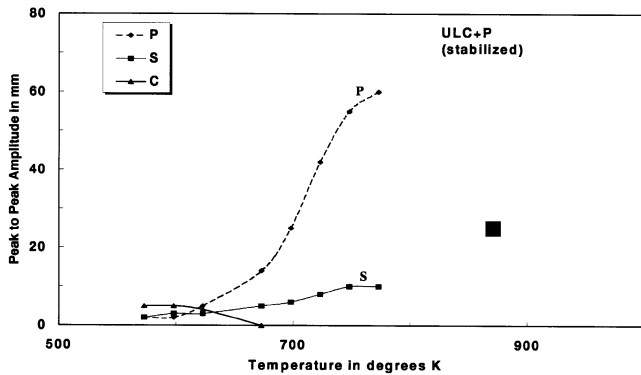


Fig. 3—Measured Auger peak amplitudes of carbon, phosphorus, and sulfur on ULC + P steel sample surface as a function of temperature for a fixed hold time of 5 min at each temperature.

(45 to 60 minutes) at specific temperatures, with several measurements of surface composition at each temperature. The purpose of this cycle was to monitor the surface composition at a given temperature as a function of time. It must be noted that, in these isothermal heating cycles, the sample was heated from ambient temperature to the target temperature within a few minutes ( $\approx 5$  minutes). In contrast, during a stepped-ramp heating experiment, the sample could take as long as 1 hour to heat up to, for example, 973 K. Such differences in heating rates resulted in some

differences in observed peak amplitudes, primarily at short hold times (less than 10 minutes).

The usual method for determining surface compositions from Auger data is to divide the measured amplitudes of differentiated peaks by elemental sensitivity factors and to normalize the sum of the modified amplitudes to 100 at. pct. In most cases in this article, amplitudes of the differentiated Auger peaks (denoted in the figures as “Peak-to-Peak Amplitude in Millimeters”) from the elements are presented directly, without converting them into normalized atomic concentrations. The use of sensitivity factors gives compositions homogenized over the Auger sampling depth (approximately 5 nm of material) and underestimates the extent of surface segregation that has occurred on the sample. However, using unconverted peak amplitudes poses the problem that changes in instrumental conditions between samples may result in changes in the observed peak amplitudes. Therefore, in those few cases where a single element’s concentration on the surface was followed across various samples, normalized atomic concentrations (using bulk sensitivity factors) are presented.

### III. RESULTS

#### A. Surface Segregation as a Function of Temperature

Surface chemistry changes as a function of temperature are presented in Figures 1 through 3 for ELC-, ULC-, and ULC + P-grade steel samples, respectively. The data are in the form of Auger peak amplitudes measured during stepped-ramp heating. For the ELC sample (Figure 1), carbon was the predominant element on the surface at temperatures between 700 and 900 K. Above 900 K, phosphorus accumulation on the surface became significant. Sulfur segregation was not significant at temperatures up to 923 K. In contrast, for a stabilized ULC steel sample with lower amounts of carbon in solution, no significant carbon segregation was observed (Figure 2). Phosphorus segregation in the ULC steel, however, started becoming significant at temperatures above 700 K and reached a peak near 900 K. Above 900 K, sulfur accumulation became significant at the surface. For the rephosphorized ULC steel sample (ULC + P), phosphorus accumulation started below 700 K and reached a high concentration at temperatures below 800 K (Figure 3). No accumulation of sulfur was noted for the ULC + P steel sample. Accumulation of phosphorus on the surface of the ULC + P-grade steel was significant, even without a hold time, at temperatures above 700 K. Figure 4 presents data from a ULC + P sample, where Auger scans were collected immediately after the sample reached the desired temperature (as opposed to a hold time of 5 minutes in a stepped-ramp heating cycle). The onset of phosphorus at the surface is similar in both cases (Figures 3 and 4) for the ULC + P samples. In going from ELC to ULC + P steel samples, with increasing phosphorus in solution and decreasing carbon in solution, the onset of phosphorus accumulation at the surface is shifted to lower temperatures.

The behavior of segregated atoms during cooling in the Auger chamber was also monitored. Figure 5 plots an Auger scan obtained on the surface of a ULC + P steel sample that had cooled to 373 K after being held at 773 K for 5 minutes. The scan shows the presence of phosphorus and

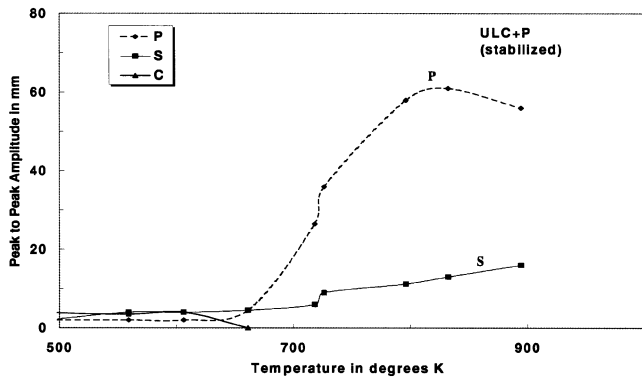


Fig. 4—Measured Auger peak amplitudes of carbon, phosphorus, and sulfur on a ULC + P steel sample surface as a function of temperature. There was no hold time at any of these temperatures.

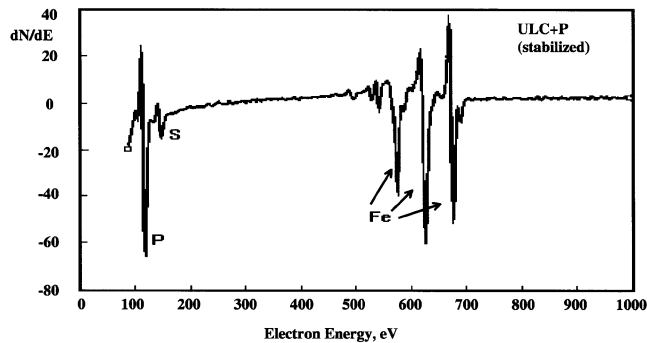


Fig. 5—Auger scan on the surface of a ULC + P steel sample after it had cooled down to 373 K from a temperature of 773 K (sample was heated to 773 K and held for 5 min as part of a heating cycle).

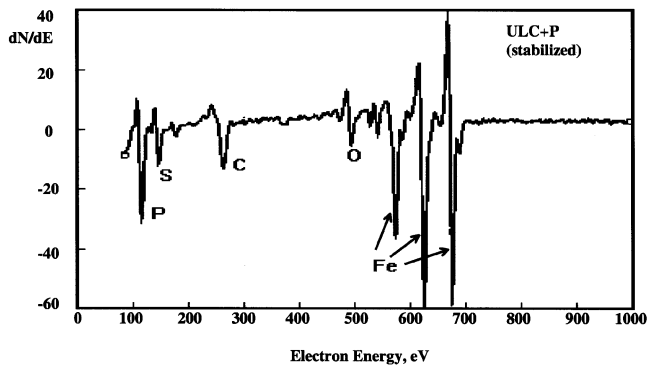


Fig. 6—Auger scan on the surface of a ULC + P steel sample after it had cooled overnight to room temperature. The sample had been heated to 773 K and held there for 5 min as part of a heating cycle prior to cooling overnight.

sulfur on the surface. Figure 6 shows an Auger scan taken from the same sample after it had further cooled overnight in the Auger vacuum chamber. The surface still had the segregated phosphorus and sulfur atoms, along with some adsorbed carbon and oxygen from vacuum contaminants. A depth profile was done on this surface to determine the thickness of the segregated layer. Figure 7 plots the depth profile obtained on the surface by sputtering with 1 kV Ar<sup>+</sup> ions at a 5 mA current spread over the area where the ion beam hits the sample. For similar conditions, 0.6 to 0.7 nm of SiO<sub>2</sub> is removed per minute of sputtering. Figure 7 shows that the adsorbed and segregated layers of atoms on

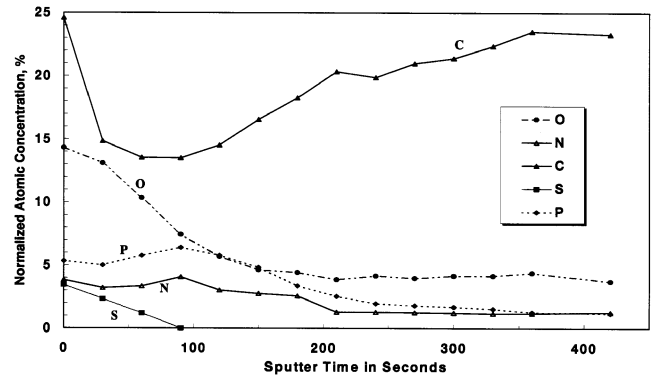


Fig. 7—Sputter depth profile on the surface of a ULC + P sample after it was subjected to a heating cycle and cooled overnight. Sputtering was done with 1 kV Ar<sup>+</sup> ions at an ion current of 5 mA (sputtering rate of 0.6 to 0.7 nm of SiO<sub>2</sub> per minute).

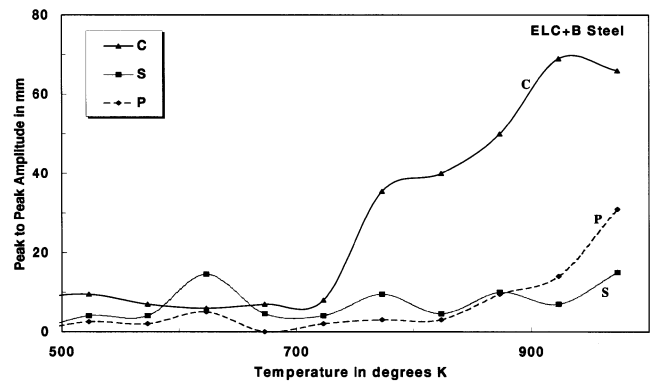


Fig. 8—Measured Auger peak amplitudes of carbon, phosphorus, and sulfur on ELC + B sample surface as a function of temperature for a fixed hold time of 5 min at each temperature.

the surface of the steel were sputtered away in approximately 4 minutes. The increase in carbon signal after the initial depletion in Figure 7 is the result of the electron beam hitting a carbide particle. Some residual carbon and oxygen are typically observed on sample surfaces, even after a considerable amount of sputtering.

The effect of boron on the surface segregation behavior of phosphorus was studied in stepped-ramp heating of the ELC + B sample. The results from this experiment are presented in Figure 8, where the surface concentrations of carbon, phosphorus, and sulfur are plotted as a function of temperature. The carbon concentration on the surface was strong, even at a temperature of 973 K. Comparing Figure 8 with Figure 1, it is clear that phosphorus accumulation on the surface is retarded by the presence of boron in the steel. Further, in related experiments it was observed that, even after 60 minutes of hold at 973 K, the phosphorus concentration did not significantly increase and carbon was still dominant on the surface.

In summary, for the steels studied, carbon accumulates on the surface first, followed by phosphorus, and then by sulfur. Stabilized ULC steels exhibit negligible carbon segregation to the surface. Studying the accumulation of phosphorus on ELC, ULC, and ULC + P steel surfaces, it is clear that the phosphorus concentration in the steel matrix has a significant influence on the accumulation of phosphorus at the steel surface. Comparing results from the ELC

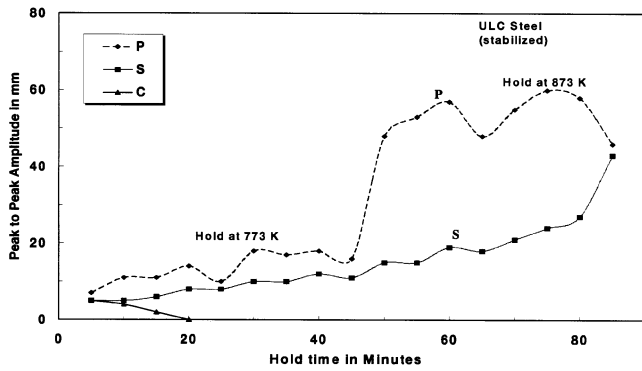


Fig. 9—Measured Auger peak amplitudes of carbon, phosphorus, and sulfur as a function of hold time on an ULC steel sample.

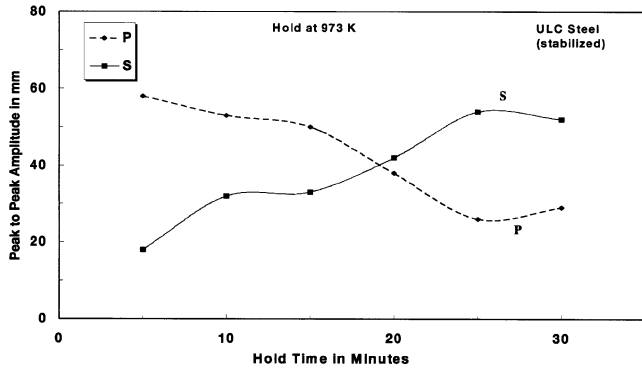


Fig. 10—Measured Auger peak amplitudes of phosphorus and sulfur as a function of hold time at 973 K on an ULC steel sample.

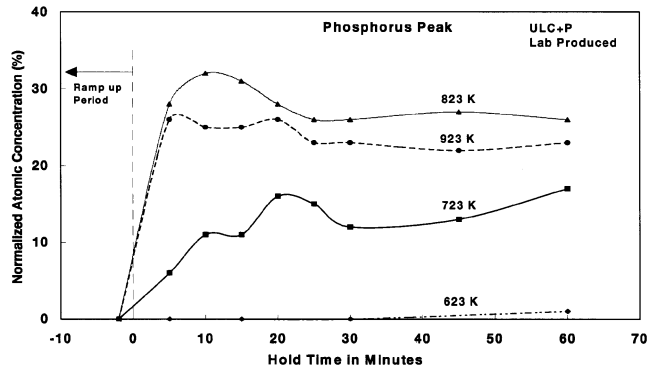


Fig. 11—Phosphorus concentration on the surface of ULC + P (lab produced) sample as a function of hold time at different temperatures.

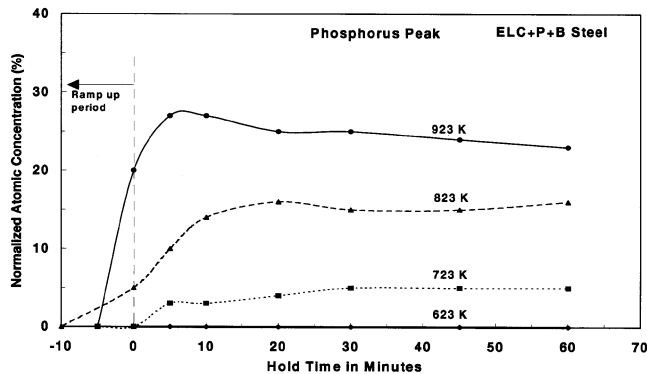


Fig. 12—Phosphorus concentration on the surface of ELC + P + B sample as a function of hold time at different temperatures.

steel and ULC steel, it also appears that carbon retards the surface segregation of phosphorus in ELC steels at temperatures  $<900$  K. In addition to carbon, the presence of boron seems to further retard the accumulation of phosphorus in ELC steel at temperatures  $\leq 973$  K.

### B. Surface Segregation as a Function of Time

Figure 9 presents surface concentrations of carbon, sulfur, and phosphorus on the ULC steel sample as a function of time, at hold temperatures of 773 and 873 K. In this experiment, the sample was initially heated to 773 K and held for 45 minutes, then further heated to 873 K. With the 45-minute hold time at 773 K, the carbon initially on the surface was replaced by phosphorus and sulfur. However, the accumulation of phosphorus and sulfur at the surface proceeded slowly. When the temperature was raised to 873 K, there was an immediate jump in the phosphorus concentration at the surface, while the sulfur concentration continued to increase only gradually. When the ULC steel sample was heated directly to a temperature of 973 K and held at that temperature, sulfur gradually took over as the dominant element of the surface, as shown in Figure 10. The results confirm the lack of carbon segregation to the surface in ULC steels. The results also point out that, at these temperatures, the controlling factor of the surface segregation of phosphorus and sulfur is the kinetics of the process. The kinetics of phosphorus accumulation at the surface appears to be fairly insensitive to hold time. However, an increase in temperature of 100 K affects the diffusion rates significantly enough to affect the surface accumulation of phosphorus.

The effect of boron on the surface segregation of phosphorus can be inferred from the results of isothermal experiments conducted at 623, 723, 823, and 923 K for the ULC + P (lab-produced) steel sample with 25 ppm of carbon and for the ELC + P + B steel sample with 62 ppm of carbon and 6 ppm of boron. The results from these experiments are presented in Figures 11 and 12. In these figures, the surface concentrations of elements are expressed in normalized atomic percentages. At 623 K, there was no accumulation of phosphorus at the surface of either sample. At 723 and 823 K, the rate of accumulation of phosphorus at the surface of the ULC + P (lab-produced) steel was significant, as expected, because of the increased temperature and the available phosphorus in solution. In contrast, the phosphorus accumulation on the boron-containing ELC + P + B steel surface at 723 and 823 K was clearly lower than the ULC + P (lab-produced) steel surface. At 923 K, however, the accumulation of phosphorus was similar in both the ULC + P (lab-produced) and the ELC + P + B steels. The retarding effect of minor amounts of carbon and boron on phosphorus segregation appears to be valid at the lower temperatures of 723 and 823 K. In all of these steels, an increase in sample temperature by 100 K increases the surface accumulation of phosphorus far more than holding the sample at any given temperature for an extended period of time (here, up to 1 hour).

## IV. DISCUSSION

The data presented clearly suggest that the controlling factor in determining the extent of solute accumulation is

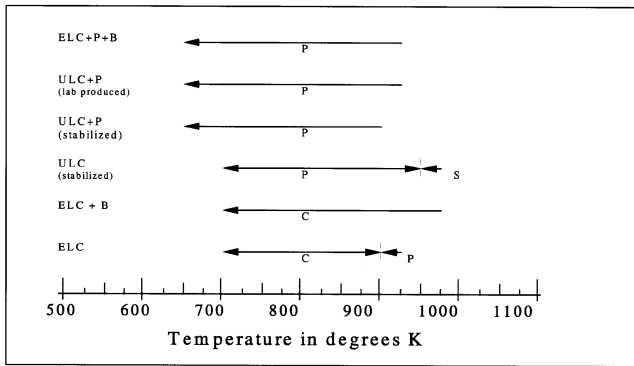


Fig. 13—Temperature ranges over which carbon, phosphorus, or sulfur accumulates on the surface of the steel samples analyzed in this work.

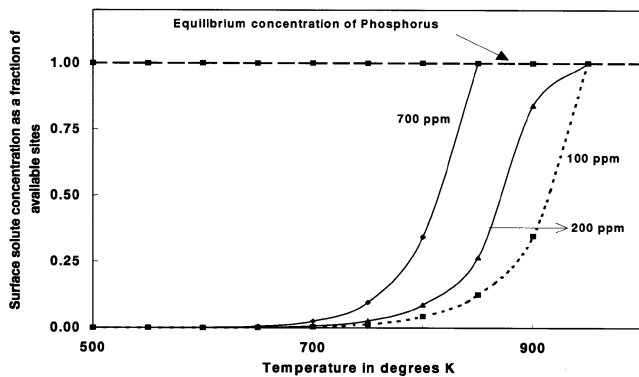


Fig. 14—Calculated accumulation of phosphorus (per Eq. [1]) on the surface of steels with different amounts of phosphorus in solution.

the kinetics of the segregation process. Further, the effect of temperature is far more significant than the effect of hold time on affecting surface accumulation. Upon cooling, the solute atoms do not desegregate, as it is thermodynamically unfavorable for the system and kinetically unfavorable for the solute. Practically, this implies that once segregated, the element stays on the surface unless the steel is heated to higher temperatures. (Experimentally, it has been observed that adsorption occurs during cooling). The material property affecting the kinetics of the process is the concentration of solute atoms in the bulk that are free to segregate. Atomic interactions between solute atoms do seem to affect the kinetics of segregation to the surface.

Taking into account the fact that solute concentration and temperature are the key factors controlling surface accumulation, Figure 13 summarizes the findings for the six different samples analyzed, by presenting temperature ranges where carbon, phosphorus, or sulfur are dominant on each of these steel surfaces within the window studied. Below 650 K, no significant surface accumulation of solute elements occurred on these steel sample surfaces. For the ELC steels, the dominant element on the surface from 700 to 900 K is carbon. Beyond 900 K, phosphorus displaces carbon. However, if boron is also present to retard phosphorus segregation kinetics, then carbon stays on the surface until higher temperatures, as shown by the ELC + B sample. For the stabilized ULC steel, with no carbon in solution, there is no carbon segregation to the surface and phosphorus accumulation begins at lower temperatures. Phosphorus remains dominant from 700 to 950 K, beyond

which sulfur becomes dominant. Thus, the onset of phosphorus accumulation is pushed from near 900 K in ELC steel to just above 700 K in ULC steel. With the ULC + P steel, the onset of phosphorus accumulation is pushed to even lower temperatures. It is not known when sulfur takes over as the dominant element, but, looking at the build up of sulfur on ULC steel and a ULC + P steel, it is possible that sulfur would not be the significant element on the ULC + P steel surface at temperatures  $\leq 973$  K. Therefore, phosphorus remains on the surface from 650 K to at least 973 K.

The maximum measured atomic concentration of phosphorus normalized over a sampling depth of 5 nm is 30 pct for a ULC + P-grade steel. In LEED studies on single crystals of Fe-Si alloys, it has been identified that phosphorus occupies the center sites (in between four iron atoms) on a Fe(001) surface.<sup>[14]</sup> At saturation coverage on the Fe(001) surface, only half the available center sites are occupied, which amounts to an atomic concentration of 1 solute atom for every 2 iron atoms, or an atomic concentration of approximately 0.33.<sup>[14]</sup> Using this number for saturation coverage, the kinetics of phosphorus accumulation to the surface as a function of temperature, in a simulated stepped-ramp cycle (50 degree step) with a hold time of 5 minutes at each temperature, is plotted in Figure 14. The equation used to calculate the accumulation as a function of temperature is<sup>[15]</sup>

$$C_s^t = [2/(d\sqrt{\pi})] (C_b^0) [\sqrt{Dt}] \quad [1]$$

where  $C_s^t$  is the surface solute concentration at time  $t$ ,  $C_b^0$  is the solute concentration in the bulk,  $d$  is the thickness of a monolayer of segregant, and  $D$  is the effective diffusion coefficient. The bulk diffusion coefficient of phosphorus in  $\alpha$ -iron is given as  $1.58 \exp(-52,300/RT)$ , where the activation energy is in calories.<sup>[16]</sup> For a fixed hold time at any temperature, Eq. [1] can predict the concentration buildup as a function of temperature. The value of  $C_s^t$  is converted from an atomic concentration to a fraction of the available sites occupied. At an atomic concentration of 0.33, the available sites are saturated. Figure 14 shows that, with increased solute activity in the matrix, the onset of phosphorus accumulation is pushed to lower temperatures.

Comparing the calculated behavior in Figure 14 to the experimental results, it is seen that phosphorus segregation in ELC steel is very close to that predicted for 100 ppm of phosphorus in solution. Bulk diffusion of phosphorus appears to be the primary contributor to surface accumulation. Perhaps carbon blocks the high diffusivity paths in this grade of steel. In contrast, comparing the observed phosphorus segregation behavior on ULC steel to Figure 14, it appears that high diffusivity paths do play a role in phosphorus build-up at the surface, at temperatures below 850 K. Above this temperature, the bulk diffusion of phosphorus is rapid enough to saturate the surface. For the rephosphorized steel, it is clear that high diffusivity paths contribute to surface accumulation at temperatures below 750 K.

To illustrate the effect of boron and carbon on phosphorus segregation, Figure 15 replots the isothermal data for ELC + P + B steel (Figure 12) by taking the data points after a hold time of 30 minutes at each of the temperatures, along with the stepped-ramp cycle data on ULC + P-grade

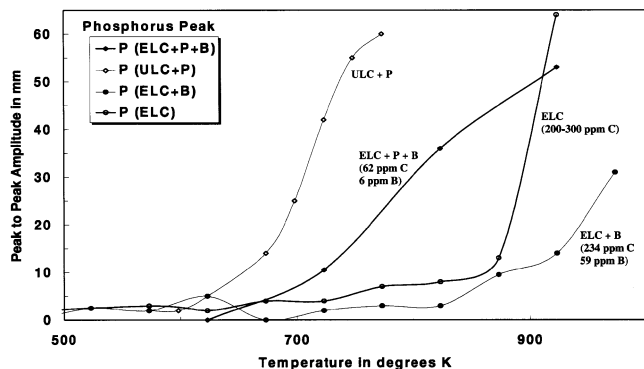


Fig. 15—Measured amplitudes of phosphorus Auger peak as a function of sample temperature on the surfaces of selected steel samples analyzed in this work.

(stabilized), ELC-grade, and the ELC + B samples. The effect of small additions of boron (only a few parts per million by weight) is to retard the kinetics of phosphorus segregation primarily at temperatures lower than 923 K. Thus, the small amounts of carbon and boron in the ELC + P + B sample did not change the temperature range over which phosphorus is dominant on the surface, but lowered its concentration at the lower temperatures. In contrast, when significant amounts of carbon with or without boron are present, as in the ELC + B and ELC samples, the retarding effect on phosphorus segregation is significant and extends to higher temperatures. Carbon segregates to the surface significantly at the lower temperatures. Compared to the ELC sample, the retardation of phosphorus accumulation on the ELC + B sample surface is extended further, to at least 973 K. Segregation of boron to the surfaces was not observed.

In a commercial, continuous hot-dip galvanizing line, sheet steels are subjected to recrystallization annealing prior to dipping in the zinc bath. During recrystallization annealing, stabilized ultralow-carbon steels are heated to a peak temperature somewhere between 1000 and 1123 K (depending on the steel chemistry and prior processing history) for a short period (about 1 minute).<sup>[17]</sup> It was not possible to reach such high temperatures in the Auger chamber used in this study. Further, the lab studies did not achieve the rapid heating rates encountered in commercial coating lines, where the sheet steel is heated from ambient temperature to the peak recrystallization anneal temperature in less than 1 minute. But the results presented thus far suggest that, in most of the steels, the likely element to be present on the surface, at the peak annealing temperature, is sulfur. In the case of rephosphorized steels, it is possible that some phosphorus remains on the surface. As the steel cools from this temperature to the zinc bath entry temperature of approximately 723 K, there will be no further change in surface chemistry due to segregation from bulk. The small amount of phosphorus on the steel surface could contribute toward altering the reaction kinetics between the ULC + P steel and the molten zinc bath.<sup>[7]</sup> It must be noted that aluminum additions are made to the zinc bath to control the reaction between steel and zinc.<sup>[18]</sup> Therefore, the effect of phosphorus could vary with the level of aluminum additions in the bath. The additions of small amounts of boron to rephosphorized steel affects phosphorus segregation be-

havior only at lower temperatures and, therefore, is not expected to have an effect on reducing the phosphorus effects on the Fe-Zn reaction in rephosphorized steels. This was illustrated in a recent study on galvannealing behavior of stabilized ULC + P + B-type steel with 0.07 wt pct phosphorus and 8 ppm of boron.<sup>[19]</sup>

The present work suggests that carbon is displaced from the surfaces of ELC and ULC steels by phosphorus and sulfur. Therefore, surface-segregated carbon is not expected to influence galvanneal microstructure development. Even though sulfur is the most likely element to be present on the surfaces of ELC and ULC steels as a result of segregation, there is no known effect of sulfur on Fe-Zn reaction kinetics during continuous hot-dip galvanizing. The main element of interest for the galvanizing industry is phosphorus.

During commercial production of galvannealed sheet steels, it is necessary to provide a higher galvannealing heat input to produce a fully alloyed coating (with an average iron content of 9 to 10 pct by weight) on ULC + P steel. Further, the distribution of iron in commercial galvannealing coatings on ULC + P steel is different from the distribution of iron found in coatings on ULC and ELC steels, in two ways.<sup>[5,20]</sup> First, the iron content near the steel interface is lower for the coating on galvannealed ULC + P steel than for the coatings on galvannealed ULC and ELC steels. Second, the iron content in the body of the coating is higher for galvannealed ULC + P steel than for galvannealed ULC and ELC steels. The increased iron content in the main body of the coating, which is made up of the Fe-Zn intermetallic phase  $\delta$  ( $\text{FeZn}_{10}$ , 7 to 12 wt pct Fe), can contribute to increased powdering (disintegration) of the coating during forming, which is undesirable.<sup>[21]</sup> The presence of surface-segregated phosphorus on ULC + P steel has been suggested as the cause for the increased inhibition of Fe-Zn reactions and the modification of the iron distribution within the galvannealing coating on this steel.<sup>[7]</sup> Mechanism(s) for the greater inhibition of steel-zinc reactions in the presence of segregated phosphorus are not known at present. A possible explanation for the change in iron distribution within the coating is discussed next. It should be noted here that the Fe-Zn intermetallics that can form in a galvannealing coating include  $\zeta$  (zeta,  $\text{FeZn}_{13}$ ),  $\delta$  (delta,  $\text{FeZn}_{10}$ ),  $\Gamma_1$  (gamma-1,  $\text{Fe}_3\text{Zn}_{21}$ ), and  $\Gamma$  (gamma,  $\text{Fe}_3\text{Zn}_{10}$ ), listed in order of increasing iron content. The  $\Gamma$  and  $\Gamma_1$  phases are typically present at the steel-coating interface, while the  $\delta$  phase constitutes the main body of most commercial galvanneal coatings. Frequently, some  $\zeta$  is detected on the surface of the coatings.

Aluminum additions are made to the zinc bath to control the reaction between the iron and zinc, and the first alloy layers to form during hot dipping are Fe-Al alloys. The Fe-Al layer acts briefly as an inhibition layer, preventing contact between the liquid zinc and steel. Typically, the Fe-Al ( $\text{Fe}_2\text{Al}_5$  and/or  $\text{FeAl}_3$ ) alloy layer breaks down while still in the hot-dipping stage, leading to subsequent Fe-Zn alloying. Remnants of the Fe-Al layer were observed at the steel-coating interface, along with Fe-Zn intermetallic particles, immediately after hot dipping.<sup>[7]</sup> The reactions occurring between steel and liquid zinc in the first few seconds of dipping in a continuous galvanizing line are the subject of current research efforts.<sup>[22,23,24]</sup> After a few seconds of gal-

vannealing following dipping, a continuous layer of  $\Gamma_1$  forms at the steel-coating interface.<sup>[7]</sup> This is followed by the nucleation of a thin  $\Gamma$  layer at the steel- $\Gamma_1$  interface and the solidification of  $\delta$  crystals on top of the  $\Gamma_1$  layer. For ULC steel, the iron-rich  $\Gamma$  ( $\text{Fe}_3\text{Zn}_{10}$ ) grows at the expense of  $\Gamma_1$  ( $\text{Fe}_5\text{Zn}_{21}$ ), aided by the flux of iron atoms into the coating. However, for a ULC + P steel, the nucleation of the  $\Gamma$  phase at the steel- $\Gamma_1$  interface is retarded, possibly due to the presence of segregated phosphorus,<sup>[7]</sup> and the influx of iron atoms causes an increase in the iron content of the bulk of the coating, made up of the  $\delta$  phase. This suggests that the iron concentration near the steel-coating interface will be lower (lack of  $\Gamma$  phase) and that the iron content in the  $\delta$  phase of the galvannealing coatings will be higher for ULC + P steels.<sup>[5,20]</sup> The higher iron content in the  $\delta$  phase can lead to poor forming characteristics for the galvannealing coating.<sup>[21,25]</sup>

Our observations in this study suggest that surface chemistry changes due to segregation occur as sheet steels are heated to the peak recrystallization temperature prior to dipping in the zinc bath. No further changes in surface chemistry due to segregation occur as the sheet steel cools from the peak recrystallization temperature to the zinc bath entry temperature. For all the steel grades studied in this work, it appears that sulfur would be the element segregated significantly to the surface as the steel enters the zinc bath. In the case of ULC + P steel, some amount of segregated phosphorus may also be present, along with sulfur, on the surface as the steel enters the zinc bath. The presence of phosphorus could then hinder the nucleation of the  $\Gamma$  phase, as described previously. With an increase in the dissolved sulfur content, the presence of phosphorus at the surface may be largely reduced, thereby preventing its effects of retarding  $\Gamma$  nucleation and enriching the  $\delta$  phase in the coating with iron.

## V. CONCLUSIONS

1. For all steels studied, the free solute concentration in the bulk and the temperature are the primary factors controlling solute accumulation at the surface.
2. The temperature affects surface solute accumulation far more significantly than hold times, within the window of temperatures and times studied.
3. Once segregated, solute atoms remained on the surface as the steel was cooled. Changes to surface chemistry due to surface segregation occur primarily as the steel is heated to higher temperatures and not during cooling.
4. For the ELC steel, carbon segregation to the surface became significant at temperatures above 700 K. Carbon was replaced by phosphorus at temperatures above 900 K.
5. For stabilized ULC steel, no carbon segregation was observed. Phosphorus segregated significantly to the surface above 700 K and was replaced by sulfur at temperatures above 950 K.
6. For rephosphorized ULC steel, phosphorus segregated significantly to the surface at temperatures above 650 K and reached a peak concentration at 800 K.
7. Small amounts of carbon and boron in the ELC + P + B steel (62 and 6 ppm, respectively) reduced the phosphorus concentration at the surface, for temperatures be-

low 923 K. Boron at such low levels (6 ppm) did not prevent phosphorus segregation to the surface.

8. With moderate amounts of carbon and boron present in the ELC + B steel sample (234 and 59 ppm, respectively), no significant accumulation of phosphorus was observed on the surface, even at a temperature of 973 K.
9. The surface chemistry created at the peak recrystallization anneal temperature will prevail as the sheet steel is cooled to the zinc bath entry temperature in continuous galvanizing lines. In rephosphorized steels, the presence of phosphorus on the surface could affect the Fe-Zn reaction. Small additions of boron to rephosphorized steels are not expected to alter the Fe-Zn reaction kinetics for these steels.

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