The New Look of Sheet Steels

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In 1968 I presented the Campbell Memorial Lecture to the National Metals Congress in Detroit under the title "Sheet Steel—Micrometallurgy by the Millions". My theme proposed: Small changes in composition and processing have large effects on the metallurgical structure and mechanical properties of the product. Nevertheless, sheet steels were being produced in tremendous quantities to exacting standards for more than twenty different markets. In fact the value of finished manufactured products in which sheet steel was a major component accounted for about 9% of America’s Gross National Product in 1968, making it the commodity material of first importance in the economy.

Since then many changes—both negative and positive—have occurred. Some sheet steel markets have grown: For example, the pre-engineered-prefabricated buildings market has doubled in 15 years. But some major markets for sheet declined (even before the onset of the recession), these being containers and automotive. The decline in sheet consumption in the American automotive market is attributed to many causes, the major one being the import of automobiles. Another was the dramatic increase in the price of fuel, which led the automobile companies to reduce the size and weight of their products.

One action was the substitution of lighter weight materials for steel, principally aluminum and plastics. In addition, the mass of steel components has been reduced by substitution of higher strength steel for ordinary sheet steels. And in response to consumer demand the automobile industry has taken actions to improve the durability of the car, including protection of the exterior body parts from premature corrosion.

In response to these market changes, the steel industry throughout the world has made many technical advances in sheet steel products and production processes. Indeed, sheet steel technology continues to by dynamic, complex, and fascinating. I think it appropriate to again discuss the subject. It is even more appropriate in this lecture honoring the late Mr. Yukawa, one of the builders of the modern Japanese steel industry, where so many of these advances in sheet steel have taken place.

Back in 1968 the main technical requirement for sheet steels for many markets was good formability. My Campbell Lecture and the subsequent monograph published by ASM focused principally on the mechanics of press-forming sheet steel, the metallurgical characteristics that influence formability (composition, microstructure and crystallographic texture), and the effects of processing (steelmaking, rolling, and annealing) on these characteristics.

Good formability is still a most important property. Other properties and characteristics have increased in importance: properties such as high strength, weldability, paintability, and corrosion protection. Optimizing them while maintaining good formability has given sheet steel producers some interesting challenges. They have come forth with new processes, like secondary or ladle steelmaking, continuous casting, and continuous annealing; new steel compositions and new coatings. Taken together, these developments have resulted in major technical changes that have given sheet steel a new look. In the remainder of this lecture, I will describe some of the changes and the fundamental knowledge they have provided that I am confident will lead to further advances.

I. Review of Old Knowledge

To set the stage for our discussion it is helpful to review briefly some basic principles I described in the Campbell Lecture.

There are two modes of deformation in press forming of sheet: stretching and drawing. The measure of stretchability is the uniform elongation as measured in a simple tension test.
The measure of drawability is the plastic strain ratio, \( r \), which is the ratio of the width to thickness strains in a tensile specimen. Because this parameter varies around the rolling direction, the value is determined by the average of the plastic strain ratios measured in tensile specimens taken from the rolling direction, transverse to the rolling direction, and 45 deg to the rolling direction. This is called the average strain ratio, \( r \).

The principal metallurgical feature that affects uniform elongation (i.e., stretchability) is the grain size of the sheet, with larger grain size being beneficial (see Fig. 1). Alloy elements dissolved in the ferrite reduce uniform elongation to a minor extent, although when combined as excess phases they may have significant indirect effects on grain size.

The major metallurgical characteristic that affects \( r \) is the crystallographic texture of the steel. Body centered cubic iron is strongest in the cube diagonal direction. Thus compositional and processing effects that promote the cube diagonal to be oriented in the thickness direction of the sheet increases the strength in this direction and increases the average strain ratio, or drawability.

Crystallographic texture forms and develops from recrystallization and grain growth during annealing of cold reduced sheet steel (hot-rolled sheet steel has almost a random crystallographic texture). The mechanism by which this occurs is complex. It is sufficient to say here that the amount of cold rolling strongly influences the texture after annealing (see Fig. 2). Also, the desired texture is enhanced by grain growth, which, of course, occurs with longer annealing times and/or higher annealing temperatures (see Fig. 3). As mentioned, uniform elongation is higher at coarser grain sizes so, as a general rule, drawability and stretchability both improve with larger grain sizes.

In ordinary sheet steels, annealing is restricted to temperatures below that at which austenite will form (730 °C in steels containing more than 0.01 % C). However, in very low carbon sheet steels, austenite forms at higher temperatures. Thus, by decarbu-

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**Fig. 1.** Relationship between uniform elongation and grain size. 

**Fig. 2.** The effect of prior cold reduction on the average strain ratio and texture of annealed sheet steel. 

**Fig. 3.** The effect of annealing temperature on average strain ratio and grain size of aluminum killed steel decarburized before cold rolling and annealing.
rizing the steel before cold rolling and annealing, or by adding elements like titanium which tie up the carbon as carbides or carbonitrides that are stable at high temperatures, the annealing temperature can be raised without the interference of austenite formation, thereby obtaining more grain growth of the ferrite, a stronger cube-on-corner texture and higher average strain ratios. The data shown in Fig. 3 were obtained with a decarburized steel, but for reasons I will mention, the addition of strong carbide formers is the preferred way to reduce soluble carbon in sheet steel. The effect was described in my Campbell Lecture. I like to think it was the basis for the commercial introduction in the early 1970's of interstitial-free (I-F) steels with very high average strain ratios and very good drawability.

Recrystallization and the development of the desired crystallographic texture is also strongly affected by fine particles of excess phases such as nitrides, carbides, and carbonitrides present before cold rolling and are stable during subsequent annealing. Small additions of aluminum, titanium, or niobium are commonly added. Also, as mentioned, titanium and niobium have the added benefit of reducing dissolved carbon. Figure 4, taken from the Campbell Lecture, illustrates the extra benefit that alloy additions have on average strain ratio. Note, for instance, that at a given grain size, the \( f \) of aluminum-killed and titanium containing steels exceeds that of unalloyed steel with the same grain size. Also note that for each grade of steel \( f \) is higher with larger grain sizes.

During the late 60's and early 70's, the major thrust in sheet steel development was drawability improvement. As mentioned, the principles just described were, at least in part, the basis for the development of some of the "super-deep-drawing" grades.

Then came the energy crisis. To improve vehicle fuel economy, the auto industry turned its attention to reducing vehicle weight, partly by using thinner sheet steel for body parts. To do this, sheet with higher strength was required. Metallurgists in the steel industry were faced with the challenge of developing sheet steels with good formability and high strength, properties which do not go hand-in-hand. The engineers have been remarkably innovative and successful in finding solutions to the dilemma. The new look of sheet steel includes a variety of new grades that provide combinations of these disparate properties. Automakers now have great flexibility in selecting the most cost effective grade for a particular part.

II. High Strength Sheet Steels

A number of well-known metallurgical principles have been applied to increase the strength of either or both hot-rolled and cold-rolled sheet steels, these being:
- Solid solution strengthening
- Dislocation strengthening
- Grain refinement
- Precipitation strengthening
- Dispersion strengthening

Except for solid solution strengthening, the application of all of these techniques to cold-rolled sheet is greatly aided by continuous or rapid annealing.

The simplest grades of high strength hot- or cold-rolled sheet contain controlled additions of P, Mn, and Si to achieve different degrees of strengthening. Furthermore, strengthening by this method can be additive to strengthening by the other methods. But there are limits to the amounts of these elements that can be added. For example, despite the small effect the usual residual amounts of these elements have on sheet formability, the rather large additions required to obtain significant strengthening reduces formability appreciably. Also, spot weldability limits P to under 0.10%.

Stress relief annealing of unalloyed cold-rolled sheet produces yield strengths in the range 80 to 100 KSI (550~700 MPa) without impairing weldability. In annealing at low temperatures, dislocations from the prior reduction partially annihilate each other and regroup to form cells or subgrains. In effect, a very fine grain size is produced. However, the annealing temperature must be closely controlled.

Temperatures within coils in a batch annealing furnace can only be controlled to ±40°C, which makes it difficult to obtain uniform properties. This can be alleviated by limiting prior cold reduction to less than 40%, which however is uneconomical and restricts the minimum sheet thickness that can be produced. Continuous annealing, on the other hand, provides good temperature control and excellent
uniformity without gage limitation. But because the "grain size" of stress relief steels is so small, their formability is poor whether produced by either annealing process. However, they are inexpensive to produce and are used for some parts that require only limited formability.

The well-known Hall–Petch relationship of yield strength to grain size (see Fig. 5) shows that high strength can be achieved by refining the grain size of fully annealed; i.e., recrystallized cold-rolled steels. Standard sheet steel with a grain size of about 25 microns has a yield strength of 25–30 KSI (170–205 MPa). This value can be increased to 80 KSI (550 MPa) by refining grain size to about 2 microns. Such a fine grain would be uneconomical to produce, requiring very heavy rolling reduction (over 95%). (In fact, that grain size is comparable to the subgrain size of a recovery annealed steel). And, as mentioned, the formability of a steel with such a fine grain is poor.

However, fine grain sizes on the order of 5 to 10 microns can be obtained by alloying the steel with small amounts of the carbonitride forming elements, Nb, Ti, and V. Such microalloyed steels (called high strength low alloy, or HSLA steels) are also strengthened by the carbonitride precipitates of these elements. As shown in Fig. 5, for example, the added increment of precipitation strengthening makes it possible for a yield strength of 80 KSI (550 MPa) to be obtained with a grain size of 5 to 10 microns.

The fine grain size and the carbonitride precipitation in microalloyed steels are both developed during hot rolling. Thus microalloying has the extra advantage that it can be applied to hot-rolled as well as cold-rolled sheet steel. The mechanisms of strengthening was clarified a few years ago by Hansen and Cohen. Though their findings are probably well-known to many in this audience, I will briefly summarize them because they illustrate the complexity of sheet steel technology.

During hot rolling the grain size of austenite is reduced by the repeated deformation and recrystallization in the successive stands of the hot strip mill. But there is a practical limit to the refinement of the grain size that can be obtained this way. Refinement beyond this limit requires that the recrystallization of the austenite be retarded—subsequent reductions are then cumulative and the grain size of the austenite continues to become finer. Precipitation of carbonitrides in the deformed, unrecrystallized austenite does this by precipitation at the grain boundaries, which retards recrystallization, and within the matrix, which retards growth.

The temperatures at which carbonitrides of niobium, titanium, and vanadium precipitate rapidly in austenite depends on their concentration in the steel. If the steel contains over 0.03% Nb, niobium carbonitrides precipitate rapidly at 1050 °C and below. Hence, austenite grain refinement can easily be obtained during hot strip rolling of such steels. Because titanium carbonitride is more soluble in austenite than niobium carbonitride, greater concentrations of Ti are required than of Nb to obtain precipitation at 1050 °C. Or to put it another way, at equal concentrations of Ti and Nb, precipitation of Ti carbonitrides occurs at lower temperatures. And because vanadium carbonitride is the most soluble of the microalloying elements, much more vanadium must be added to the steel, or much lower rolling temperatures must be used, to retard austenite recrystallization.

Hansen and Cohen showed that fine austenite grains transform to fine ferrite grains even on slow cooling of a coil off the hot mill. Thus microalloying increases the strength of hot-rolled sheet by the combined effect of grain size refinement and carbonitride precipitation. (By the way, these principles also apply to plate steels.)

It is a well-known metallurgical principle that the finer the grain size of a metal before cold reduction and annealing, the finer will be the grain size after annealing. Therefore, microalloyed steels, properly processed during hot rolling, will also have a fine grain size after cold rolling and annealing.

Again, continuous annealing assists in obtaining fine grain sizes as well as retaining precipitation hardening. Continuous annealing time is so short that no appreciable coarsening of the precipitates can occur,
and effective precipitation strengthening is retained in the annealed steel.

Batch annealing involves a long soak time. The carbonitride precipitates are, nevertheless, effective in restricting grain growth and thus maintain a good degree of grain size strengthening, although the final grain size may be slightly coarser than with continuous annealing. But the long soak time coarsens the precipitates which, therefore, lose some of their effectiveness as true precipitation strengtheners.4

Of course the formability of cold-rolled high strength microalloyed steels, because they are fine grained, is not as good as that of traditional sheet steels: For example, their uniform elongation is in the range 13 to 17 %, and the average strain ratio is about 1.0 to 1.3.

High strength with formability approaching that of the traditional soft unalloyed steel has been achieved in a class of steels commonly called dual phase steels. They can be considered a special subgroup of steels strengthened by a second phase, i.e., dispersion strengthened steels. But dual phase steels are unique. Their structure consists of ferrite and martensite rather than ferrite and pearlite.

Martensite, of course, is a much more potent strengthener than pearlite, the usual second phase in sheet steel. About 45 % pearlite is required to provide a tensile strength of 80 KSI (550 MPa). To get that much pearlite requires a high carbon content which is impractical because the steel can not be welded. On the other hand, the same strength can be obtained at low carbon contents with only 15 % martensite in the structure.

The dual phase structure is formed by cooling the steel rapidly enough from a temperature in the intercritical austenite-ferrite region to transform the austenite to martensite. The cooling rate from the intercritical temperature is very important. Figure 6 schematically shows three cooling curves from the intercritical annealing temperature superimposed on a continuous cooling transformation diagram. At the most rapid cooling rate the amount of martensite formed is the same as the austenite that was present at the higher temperature. At the intermediate rate ferrite starts growing and reduces the remaining austenite, thus less martensite ultimately forms. This new ferrite is called epitaxial ferrite or secondary ferrite. It has been suggested that the epitaxial ferrite may contribute to improved ductility. And finally at the slowest rate the austenite transforms to pearlite.

Needless to say with slower cooling rates like those obtained in a coil of hot-rolled sheet, or in batch annealing, significant amounts of alloying elements—such as Mn, Si, Cr, Mo and V—must be added to increase hardenability. Since alloying adds appreciably to cost, batch annealing is not the favored way to produce dual phase steel. And temperature control in finish hot rolling and cooling after hot rolling is not precise. The preferred method of producing dual phase sheet steel is by continuous or rapid annealing after cold rolling. The annealing temperature can be precisely controlled and the cooling rate is rapid.

In Fig. 7, the stress strain behavior of a dual phase steel in a simple tensile test is compared with that of other steels. The standard sheet steel containing about 0.08 % C has a low yield strength of 25~30 KSI (170~205 MPa) and a uniform elongation of about 25 %. It exhibits a yield point and, therefore, plastically deforms by discontinuous yielding. Also shown are the stress strain diagrams for 50 KSI (350 MPa) and 80 KSI (550 MPa) microalloyed steels, each having a yield point. Note that the elongation (uniform and total) decreases with increasing strength. Also note that the dual phase steel has the same ultimate strength as the 80 KSI (550 MPa) microalloyed steel but exhibits both continuous yielding and higher uniform and total elongation. Because of this, these steels work harder more during forming, require less energy to form, and can be used in more severe forming operations than other types of high strength steels.

The unique properties of dual phase steels—high ultimate strength, good uniform and total elongation, and continuous yielding—are the consequence of the martensite-ferrite structure. The martensite provides the high strength. The austenite-martensite
transformation introduces dislocations into the surrounding ferrite; and because the ferrite is essentially free of dissolved C and N there is no yield point; i.e., the steel yields continuously. Some also contend that retained austenite contributes to continuous yielding.

Continuous annealing lines have design differences that involve different cooling rates from the annealing temperature; some cool in the range of 10 °C/sec while others quench very rapidly in the range of 1000 °C/sec. With the most rapid cooling, ferrite-martensite structures can be obtained in sheet steels of relatively low alloy content. Such lean alloy dual phase steels in the as-quenched condition contain ferrite that is supersaturated with C, and the martensite is untempered. This combination results in high strength, low ductility and low aging resistance. However, because the steel is tempered as it passes through the overaging section of the continuous annealing line, the C dissolved in the ferrite is reduced and the martensite is tempered. This brings about a desirable combination of strength and ductility. On the other hand, a yield elongation appears which must be eliminated by subsequent tension leveling or temper rolling.

Different strength levels can be obtained in these steels by changing the amount of martensite in the structure, which is accomplished by increasing the carbon or manganese content of the steel, by increasing the annealing temperature, or by increasing the soak time. Figure 8 shows the linear dependence of yield and tensile strength on the percentage martensite. Also solid solution strengthening by additions of P and/or Si can supplement the martensite strengthening.

The uniform elongation of lean alloy dual phase steels is slightly higher (15 to 18 %) than precipitation strengthened cold-rolled steels and the \( f \) value is about the same.

To obtain the desired ferrite-martensite structure in continuous annealing lines that use a slower quench rate (e.g., 15 °C/sec), it is necessary to increase the hardenability of the steel by additions of Mn, Cr, Mo, or B. Slower cooling allows the C to diffuse from the ferrite to the austenite regions, resulting in less than 30 ppm C in ferrite at room temperature. This leads to a smooth, continuous yielding tensile behavior. Thus no tempering treatment is required, and temper rolling or tension leveling is done only to improve shape, not to eliminate the yield point. The strength of high alloy dual phase steels is also controlled by the amount of martensite, which is accomplished in these steels by changing the carbon content of the steel. Untempered high alloy dual phase steels have a uniform elongation of about 20 %, which is better than lean alloy dual phase steels. But the \( f \) values are not outstanding (about 1.0).

Another aspect of formability, called edge formability, is inherent in all high strength sheet, especially hot rolled. It depends on the cleanliness (inclusion content) of the steel. Manganese sulfides adversely affect edge formability. Desulfurization in the steel-making operation, and the addition of rare earths to control sulfide shape alleviate this problem.

### III. Continuous Annealing

The development and implementation of new sheet production processes have been among the outstanding technical advances in the steel industry during the past 15 years. In fact, automatic control of the BOF, secondary steelmaking processes to reduce concentrations of residual elements like S, P, O, N, and C, continuous casting, and continuous annealing often have been essential ingredients to the “new look” of sheet steels. Although I do not have time in this lecture to discuss all of these, I would like to discuss very briefly one process that is close to my heart—continuous annealing.

In my early years as a researcher at Bethlehem Steel Corporation—in the early 50's—my colleagues and I conducted laboratory and mill trial experiments to determine if cold-rolled sheet steel with excellent formability could be produced by rapid annealing rather than batch annealing. We found, for example, that the carbon taken in solution during a short time recrystallization anneal below the critical temperature could be reduced by a 1-min carbide precipitation treatment at 370 °C, which we carried out by reheating to that temperature (see Fig. 9). And we found that by adjusting the hot strip mill finishing and coiling practices and the amount of prior cold reduction it was possible to obtain grain sizes comparable to batch annealed sheet. With makeshift equipment we successfully made tonnage quantities of low strength product, suitable for many autobody parts such as doors and quarter panels.

But my colleagues and I were unable to convince the management of our company to appropriate funds to develop the process even to a semiworks plant.

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**Fig. 8.** The effect of percentage martensite on yield and ultimate strength of tempered lean alloy dual phase sheet.\(^{10}\)
As matters turned out, that was a mistake. I must commend the Japanese steel industry, particularly Nippon Steel, and subsequently Nippon Kokan and Kawasaki Steel, for their boldness and tenacity in developing continuous annealing as a production-worthy process. Not only does the process provide advantages in producing ordinary low strength sheet, but it has opened doors to the production of some new grades, like high strength sheet, and to cost reductions by consolidating the annealing step with downstream and upstream operations.

I will pass over further discussion of the technology of continuous annealing: It is a large subject in itself and an excellent review of the subject by Dr. Peter Mould has been published recently. Also, considerable research is currently being conducted on continuous annealing throughout the world which will result in improvements, changes and new applications. For example, there will be four technical sessions about continuous annealing at the National Metals Congress in Detroit in September of this year.

**IV. Coated Sheet Steels**

Precoating to improve appearance and durability is another new look of sheet steel. In the long run, developments in this field may prove to be more important than developments of those mechanical properties that I have just described. That's because sheet steels compete with other materials in many markets, notably aluminum and plastics. These competitive materials have some disadvantages, usually strength and sometimes cost. But they also have the advantage of better resistance to corrosion.

A protective or appearance-enhancing coating is almost always applied to sheet steels. The coating has usually been applied on a bare steel surface by the manufacturer of finished products—home appliances, automobiles, etc. But many of these products are increasingly being made from sheet steels that have been precoated with a metallic or non-metallic material to further improve their durability.

Precoated sheets often must retain the many traditional attributes of steel itself. For example, an unblemished surface, good paintability in the existing finishing systems, good formability, good weldability, and low cost. Retaining these properties while improving durability or corrosion resistance has increased the technical sophistication of sheet steels.

I did not discuss corrosion resistant coatings in my 1968 Campbell Memorial Lecture nor in my subsequent monograph. However, I did recognize that the nature of the surface of sheet steel was important to its ultimate applications. For instance, the mechanism by which contaminants formed on the surface during box annealing was described in some detail in my monograph. That information probably was useful to American producers during the 70's in developing practices to meet new specifications of the automobile industry for clean, carbon-free sheet surfaces. (Japanese sheet producers, who customarily washed cold-rolled sheet before annealing and used nitrogen-hydrogen protective atmospheres during annealing did not experience this problem, and, of course, continuous annealing avoids the problem.)

I also reported in my Campbell Lecture the intriguing observation of my colleagues at Bethlehem Steel Corporation that carbon and manganese in the base steel tended to concentrate in the surface layers of the sheet during box annealing.

The original data described in that lecture are shown in Fig. 10. The data were obtained on sheet made from an ingot cast rimmed steel using one of the first models of a secondary ion mass spectrometer (SIMS). I suggested then that such surface concentrations may affect the rust resistance and the adherence of surface coatings on sheet steel. I also suggested that the phenomenon might be deliberately exploited to attain improved surface properties.

But those speculations were illusory. More recent studies with improved SIMS have shown that the manganese and carbon are not uniformly distributed in the surface layers of the steel. They are concentrated in spots on the surface, the manganese probably as an oxide and the carbon as elemental carbon. Furthermore, it has been found that the manganese has no effect on the adherence of surface coatings. And while the surface carbon adversely affects coating...
adherence, it is avoided by the proper rolling and annealing practices that I have just mentioned.

I also discussed the deleterious effect of oxide inclusions that stem from steelmaking and ingot casting practices on surface appearance. Today advanced steelmaking processes such as combined blowing, vacuum deoxidation, and inert gas stirring (not to mention improved continuous casting practices), have made surface imperfections from oxide inclusions almost a thing of the past.

Hot dipped galvanized and aluminized sheet were discussed in monograph, but only in the context of the influence of these processes in formability. Corrosion protection by these coatings was not discussed, partly for brevity, but mainly because the technology seemed well established at that time and there was little new that I could report.

Since then there have been some very significant developments in mill-coated sheet products. The first of these was an electro-deposited chromium oxide coating for container applications, called tin-free steel-chrome type (TFS-CT). This product was developed as a lower cost substitute for tinplate to compete with aluminum for beer and beverage can ends. As it turned out, TFS-CT at best only delayed the eventual change to the all-aluminum can with a drawn and ironed body and an easy open end. However, electroplated chromium oxide coatings on top of zinc coatings have recently been investigated for other applications.

The second important development in coated steels during the seventies was Bethlehem Steel Company’s “Galvalume”, their tradename for sheet hot dip coated with an alloy of 55 % Al, 43.5 % Zn, and 1.5 % Si. This product is well established for many applications in competition with both galvanized and aluminized sheet. Principal markets are roofing and siding of industrial buildings.

The third major change in coated sheet steels was brought about by a new requirement of the automobile market in North America. Increased use of salt to deice roadways in the Northern regions of U.S.A. and in Canada was causing autobodies to corrode at an alarming rate, thereby not only losing their attractive appearance but actually perforating after a short period of service. Automobile owners began to demand cars that would withstand this extremely corrosive environment for a period at least equal to the life of the engine and drive train. Dr. Shigetosi Ishihara, Executive Vice President of Nippon Steel Corp., recently wrote an excellent review of the problem and the efforts by the automotive industry and their suppliers to solve it. His paper appears in Transactions of the Iron and Steel Institute of Japan.6

Among the first of many measures taken by the North American automobile manufacturers to solve the problem was to improve the adherence and quality of the finishes applied to the autobody. Also “clean” sheet, free of carbonaceous surface deposits, was demanded from sheet producers; and as mentioned earlier, they were successful in meeting this requirement by adjusting their rolling and annealing practices.

The automotive industry also installed equipment for dip application of the phosphate conversion coating and for the electrophoretic deposition of the primer to the entire autobody. Initially electrophoretic deposition was done with the autobody as the anode. But it was found that under these conditions metal ions dissolved in the primer, which adversely affected the durability of the finished film of paint. This problem was solved by electrodепositing the primer cathodically, i.e., with the autobody as the cathode. Today cathodic deposition of the primer has gained worldwide acceptance.

Unfortunately, cathodic deposition of the primer on zinc-rich surfaces has displayed a tendency to form “crater-like” features in the primer film. Hart and Townsend7) have shown that the formation of craters is caused by localized dielectric breakdown of the film during cathodic deposition. However, cratering occurs only above a threshold potential that is different for different metal surfaces, the potential being lower for zinc surfaces than for steel. Although reducing the electrocoat voltage avoids the cratering problem, it also reduces the rate of deposition of the
primer and, in turn, the speed of the coating line. One alternative to avoid this problem is to search for a way to increase the dielectric breakdown voltage of the primer film on coated surfaces containing zinc. Other alternatives are to modify existing lines, build new lines, or use special over-coatings, such as electrodeposited chromium metal or Fe rich Fe-Zn alloys, on the surface of the zinc coatings.

Nevertheless, cathodic electrocoated primer on clean surfaces of bare sheet steel has significantly improved the adherence and corrosion resistance of the painted autobody, especially of the exposed or outer surfaces. On the other hand, cathodic electrocoat only provides barrier protection which is not sufficient for the inner surfaces of the autobody where salty, muddy water can become trapped. To protect these surfaces the automobile industry decided to use sheet steels precoated with a material that provides sacrificial protection.

It was realized that although standard hot dip galvanized sheet (275 g/m², two sides) would assure the required corrosion resistance, the normal surface appearance of this product was not satisfactory for most exterior autobody parts. Electroplated zinc had the disadvantage of requiring expensive facilities and high power consumption to produce coatings of adequate thickness to provide sufficient protection to both sides. Accordingly, the automobile industry pressed steel suppliers to develop and produce sheet with a suitable protective coating on one side, the other side being the unblemished bare steel surface. Other properties and characteristics were required too—formability, spot weldability, and compatibility with the manufacturers’ paint systems.

In response, some companies devised modifications to the hot dip galvanizing process (Armco, National, USINOR, Bethlehem and others) and U.S. Steel installed a one-side zinc electroplating process. But most of the steel industry in America chose to supply a product coated on one side with a material called “Zincrometal”, the coating usually being applied by coil coating companies. Zincrometal is a two-layer coating consisting of a thin inorganic underlayer containing a zinc-filled chromate passivating agent and an outer organic layer containing 50 to 60 vol % zinc powder. The inner layer is cured (baked) at 260 °C and the outer layer at 175 °C, which reduces the formability of some steels.

One-side Zincrometal coated sheet has performed well in improving the corrosion resistance of the autobody, especially the roof and hood. Whether the product will prove to be adequate for autobody parts that encounter more severe corrosion conditions remains to be established.

Meanwhile, many sheet steel producers have been conducting R & D on coatings that they hope will prove to be superior to Zincrometal, one-side hot dipped galvanized, or one-side electrogali-vanized sheet. Most of the attention has been directed to electrodeposited coatings of zinc alloys. The objective of these developments is to obtain corrosion resistance equal to standard 275 g zinc/m² hot dipped galvanized but with a much thinner coating, thereby holding down electroplating costs, minimizing stamping and welding problems, and preserving the appearance of the bare sheet surface. Also, because the temperature of the sheet is not raised in electroplating, mechanical properties are not altered. This is an especially important factor in coating some of high strength sheet steel grades mentioned earlier.

Much of the development work on electroplated zinc alloys has been done in Japan, possibly because Japanese sheet producers or their subsidiary companies already had production electroplating facilities. However, researchers in U.S.A. did much of the initial research that led to the discovery of these alloys, and due credit should also be given to them.8-10,12-14

It is not appropriate in a lecture like this to express an opinion about the relative merits of the various electroplated alloys that have been or are being developed. Rather it is better to leave such judgments to the marketplace.

But it is appropriate to discuss the fundamental knowledge that new alloy coatings are providing about the mechanisms by which they protect sheet steel against corrosion. Often science follows practice which, in turn, starts a new round of practical advances. Perhaps, therefore, an examination of the corrosion mechanisms of alloy coatings may help in the development of still better coatings in the future.

V. Mechanisms of Corrosion Protection of Sheet Steel

Coatings protect steel from corrosion by one or more of three basic mechanisms:

1) Primary barrier protection by the original coating. This is a static mechanism and requires coating integrity.

2) Sacrificial protection by the original coating. This is an active mechanism and protects steel exposed at defects in the coating, cut edges, etc.

3) Barrier protection by the corrosion products from the coating, or inhibitors. This is an active mechanism by which defects are healed by the formation of a secondary barrier.

Aluminum provides primary barrier protection in most environments because it has a durable surface of aluminum oxide. In chloride environments aluminum also provides some sacrificial protection to steel. Zinc itself corrodes in most environments and thus provides barrier protection as long as it covers the surface of the steel. Being more reactive than steel, it also provides sacrificial protection wherever the steel is exposed. The duration of protection by a bare zinc coating is directly proportional to the amount of zinc present; i.e., it is a linear function of the coating thickness. The corrosion products of bare zinc, ZnO, and Zn (OH)₂, may not remain in place, particularly in acidic environments, and thus may not provide secondary barrier protection.

Organic coatings without active additives (inhibitors or zinc dust) provide only primary barrier protection.

These mechanisms of corrosion protection of steel
by single metal or organic coatings have been extensively studied and are described in elementary textbooks on corrosion. As might be expected, the behavior of metal alloy coatings—or organic coatings with active additives—is more complex. Thus, alloying a metal coating may change the electrochemical behavior of the primary component of the alloy relative to the base steel. Or the alloy may have more than one phase in the coating with different electrochemical potentials relative to the base steel and relative to each other. Or the behavior of the corrosion products may be changed. And additives to an otherwise inert organic film can impart some degree of activity to it either through the formation of a barrier-forming substance at defects (e.g., an inhibitor), or by the formation of corrosion products that remain embedded in the organic film or precipitated on exposed steel to provide secondary barrier protection (e.g., from zinc dust).

The important factors are the phase or phases in the coating; their electrochemical position relative to the steel substrate (and if more than one phase is present, their electrochemical position relative to each other); their corrosion characteristics in the environment; the corrosion products that form; and the amount, size and distribution of the various phases in the coating (i.e., the structure of the coating).

Investigations at Bethlehem Steel have shown that all of these factors seem to have a role in the corrosion protection mechanism of hot dipped aluminum-zinc-silicon alloys (Galvalume). As mentioned, the optimum composition of this alloy system for both marine (chloride containing) and industrial (SO2 containing) environments is about 55 % Al, 43.5 % Zn, 1.5 % Si. This composition has proved to be two to four times better than conventional hot dipped galvanized sheet (275 g/m² two sides of equal thickness). In fact, in industrial and rural atmospheres the long-term corrosion rate is similar to that of an aluminum coating (see Fig. 11).

But unlike aluminum coating, the alloy provides galvanic or sacrificial protection against the formation of rust at the bare edges of steel in industrial atmospheres. In other words the alloy provides a combination of both sacrificial and barrier protection.

This dual characteristic arises from the microstructural phases in the alloy coating. Viewed in a plane parallel to the sheet surface, the alloy coating, when cooled in still air, is seen at the left in Photo. 1 to consist of a cored structure of aluminum rich dendrites (light etching phase) and a zinc-rich interdendritic phase (dark etching phase). When cooled from the melt more rapidly (by forced air cooling after jet wiping), the spacing between the dendrites is reduced appreciably (right photomicrograph in Photo. 1). As I will discuss later, the finer structure is important to the superior performance of the coating.

The light etching phase is a solid solution of zinc in aluminum (alpha) and the dark etching phase is a very dilute solid solution of aluminum in zinc (eta). Metallographic examination of the coating in a plane perpendicular to the sheet shows silicon particles in the interdendritic spaces and a thin interfacial layer, which has a composition of about 48 % Al, 24 % Fe, 14 % Zn, 11 % Si, and the crystallographic structure of Al₅₃ Fe₄ (see Photo. 2).

Electron probe, ion microprobe, and scanning Auger analyses have shown that most of the silicon associated with the inter-metallic layer is concentrated at the overlay/interfacial layer interface.

The corrosion potential in aqueous sodium chloride...
solutions after different times of exposure is shown in Fig. 12. After first immersion the coating exhibits a corrosion potential close to that of an unalloyed zinc coating exposed under identical conditions. During this first stage the zinc-rich interdendritic portion of the coating dissolves preferentially; i.e., it is anodic to steel. This corrosion behavior persists until this zinc-rich phase in the coating is consumed. Following depletion of this phase the corrosion potential rises, approaching that of an aluminum coating. Thereafter the coating behaves like an aluminum coating; i.e., it is cathodic to steel in sulfate environments but anodic to steel in chloride environments.

During the first stage of corrosion in which the zinc-rich phase is consumed, zinc corrosion products fill the interdendritic interstices. Thus the coating becomes a composite of an aluminum-rich matrix with zinc corrosion products mechanically keyed into the interdendritic labyrinth. These zinc corrosion products probably restrict the corrodant from contacting the lower layers of the coating. Thereafter the coating behaves like an aluminum coating; i.e., it is cathodic to steel in sulfate environments but anodic to steel in chloride environments.

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So we see that a number of corrosion protection mechanisms are operative in Galvalume sheet. The zinc-rich phase in the structure provides sacrificial protection in industrial atmospheres while the aluminum-rich phase provides barrier protection. In marine atmospheres, the aluminum-rich phase as well as the zinc-rich phase provide sacrificial protection and the interfacial layer provides barrier protection. The corrosion products from the zinc-rich phase (probably zinc hydroxide chloride, $\text{Zn}_5 (\text{OH})_8 \text{Cl}_2$) are trapped in the interstices between the aluminum-rich alpha phase and also provide barrier protection.

The morphology of the aluminum-rich alpha phase has an important role in the retention of the corrosion products within the coating. In the slowly cooled, coarse structure the corrodant tends to penetrate to the interfacial layer, then spread out along the interface lifting off the overlying coating. This kind of corrosion phenomenon is called exfoliation and is analogous to delamination of paint coatings (see Photo. 3).

Rapidly cooled Galvalume does not exhibit this behavior, presumably because the fine structure of the coating traps the corrosion products more effectively to prevent the corrodant from reaching the interfacial layer.

It is noteworthy that alloys with lower aluminum content, e.g., 5 to 10 % Al, either do not contain the alpha aluminum-rich phase or contain lesser amounts of it than Galvalume. Nor do they seem to have the iron-aluminum interfacial phase (see Photo. 4). Although the zinc-rich phase in these low aluminum alloys does provide sacrificial protection to the steel
substrate, the alloys evidently do not have a sufficient amount of finely distributed alpha phase to provide long term barrier protection or to trap the corrosion products.

The corrosion protection mechanism of electrodeposited zinc–nickel alloys is also more complex than that of an unalloyed metal coating. At the optimum composition of about 13 % nickel, these coatings consist only of a single phase—the gamma phase of the zinc–nickel system. In a NaCl solution, this phase is anodic to steel, but to a lesser degree than zinc—in other words it is less active than zinc. Perhaps this property is the principal attribute of the Zn–Ni coating. However, this alloy also provides corrosion protection by other mechanisms.

One mechanism is the result of dezincification of the gamma phase during corrosion. Thus as corrosion proceeds in NaCl solutions the coating gradually becomes richer in nickel and, hence, more electro-positive.

An additional protection mechanism is that the residual stresses in the coating become strongly tensile during dezincification, leading to the formation of microcracks in the coating. It has been suggested that the corrosion products from dezincification become trapped in these microcracks, preventing the transfer of the corrodant to the base steel.

It has also been proposed that the corrosion product that forms in zinc–nickel alloys is zinc hydroxide, Zn(OH)_2, which in itself is effective in suppressing the oxygen reduction rate.

Thus, although zinc—13 % nickel electrodeposited alloy initially has a simple, single-phase structure, the corrosion protection mechanism is complex, involving the reduced activity of the coating, the gradual change of the coating from sacrificial to barrier protection and secondary barrier protection provided by the corrosion product, possibly by entrapment within microcracks in the coating that form during corrosion.

Another electrodeposited coating that has received considerable attention is that of an alloy of zinc and iron, typically containing 15 to 25 % iron. Electro-deposited coatings over this range of iron content all contain δ1, the intermetallic compound FeZn7. However, ε1, (essentially pure zinc) is the dominant phase at the lower end of the range. At higher iron concentrations gamma phase (FeZn13) and epsilon phase (Fe3Zn10) also appear. The amounts of these phases in the structure also depend on the plating conditions.

I was not able to find any published information about the mechanism of corrosion protection by zinc iron alloys. However, Dr. Stavros Fountoulakis at Bethlehem Steel's Research Laboratories, who is investigating the corrosion mechanisms of these and other electro-plated alloys, has informed me that his investigations have shown that the mechanism is not at all like that of Zn–Ni alloys, in that the coating does not dezincify in sodium chloride solutions. Instead, in the unpainted condition red rust forms on the surface in a rather short period of time, which is not the result of corrosion of the base steel, but corrosion of the iron in the coating. Thus it appears that sacrificial protection of steel by Zn–Fe alloys is not only provided by the zinc in the coating but also by iron in the δ1 phase. Dr. Fountoulakis has observed the δ1 phase to be less anodic to steel than pure zinc; i.e., like the phase in zinc nickel alloys, it does not corrode as rapidly as zinc but still provides sacrificial protection.

The mechanisms of corrosion protection of the various alloy coatings that I have described apply to unpainted surfaces, which are the conditions in which galvanized or aluminized steel have been traditionally used. But in automobile body applications a decorative coating is also applied by the manufacturer consisting of a phosphate conversion coating, an organic primer applied by electrocoating (generally cathodically) and a finish paint applied mainly on the exterior surfaces. This paint system, of course, provides an added degree of corrosion protection to the steel. However, the paint coating is subject to service damage (nicks, scratches, etc.) and the underlying coating must protect the base steel from corroding at those damaged areas, as well as protect the degradation of the paint film by cathodic delamination and filiform corrosion.

In other words, interactions among components of the entire corrosion protection system—the mill applied coating on the steel, the phosphate film, the primer, the paint, and the process by which these are applied—affect the ultimate corrosion resistance of
the painted autobody. An important component of this system is the phosphate film, the main function of which is to enhance the adherence of the primer-paint films to the surface and to reduce underfilm corrosion at the interface between the paint and the metal surface.

The technology of phosphate coatings applied to steel is well established. But, not surprisingly, it has been found that phosphate coatings on some of the new alloy coatings lack the performance of such coatings on bare steel. For example, Nomura et al. have shown that the formation of an iron containing compound, phosphophyllite, \( Zn_4Fe(PO_4)_3 \cdot 2H_2O \), enhances the adherence of the primer to the metal surface. This compound is not formed in phosphate conversion coatings on zinc or zinc–iron alloys containing up to 20 % iron. But it does form on high iron–zinc alloys. Therefore, to further improve the performance of the phosphate film on zinc alloys, a thin layer (4 g/m²) of a high iron–zinc alloy (about 80 % Fe) has been electroplated over the base zinc–iron alloy.

It was mentioned earlier that cathodic electrocoating of primers, when applied above a certain threshold voltage, can result in the formation of craters in the primer film. The threshold voltage is different for different substrates: high for steel, lower for zinc–nickel and lowers for the Zn–low Fe alloy. Operating conditions of cathodic electrocoat systems vary from one producer to another: some companies operate with voltages well below the threshold voltage of cratering on zinc–iron surfaces; others operate at voltages well above the threshold voltage for any zinc alloys.

These ancillary problems of phosphatability and cathodic electrocoatability illustrate the difficulties in developing a mill coated sheet for automobiles. It probably will be fortuitous if a single alloy coating will be found that universally meets the requirements of each producer in the automotive industry, let alone alone applications for coated steels in other markets. Rather, sheet steel producers will probably have to produce a number of variations of a basic product to meet the needs of different customers in a market. Consequently, coating processes that provide the flexibility to adjust the coating composition and other characteristics, while still achieving low cost, may be required.

**VI. Some Thoughts about the Future of Sheet Steel Technology**

One of the pleasures of being retired and invited to give a notable lecture like this is the opportunity it provides to forecast the future without being held accountable if the prediction proves to be wrong. Also, I am encouraged to do so by a comment made by Dr. Isaac Asimov, one of America's most popular science fiction writers (he is the author of over 290 science fiction books) who had this to say about forecasting:

"In many small and unexpected ways there have been and undoubtedly will continue to be surprises that no science fiction writer—or scientist for that matter—has thought of. It is these surprises that are the excitement and glory of the human intellectual adventure."

So my first forecast about sheet steel is that there will be surprises: Surprises in science, technology, and the marketplace.

New technologies sometimes create markets. A good example is the personal computer market created by the technical advances in integrated circuits. But technical advances in commodity products, like sheet steels, are generally pulled by the market. Thus the changed requirements of the automotive market led to the development of many of the new sheet steels that I have described in this lecture. So to forecast the future of sheet steels, it is probably best to start with a forecast of the markets for this product, recognizing of course that surprises will occur.

From my viewpoint the major change in most of the markets for sheet steel will be stronger attention to full life-cycle costs: Not just the initial cost and efficient use of the raw materials from which a manufactured product is made, and the manufacturing costs; but reliability in service, the life expectancy of the product and the cost of scrapping and recycling the product. This will place greater emphasis on design engineering, manufacturing methods to assure product quality, and the selection of materials for durability and recyclability as well as aesthetics.

For instance, aluminum replaced tinplate for beer and beverage cans partly because of its high value in recycling. The growing market for pre-engineered, prefabricated industrial buildings owes part of its success to more corrosion resistant coated sheet. And we are all aware of the efforts of the automobile manufacturers to improve the reliability and durability of their products.

As mentioned previously in this lecture, other materials, notably aluminum and plastics, are vying for many of the markets in which sheet steel is used. To some extent they have been successful—the Pontiac Fiero with plastic outer body parts is a recent example. New materials that are presently being developed, such as engineered ceramics, metal and nonmetal matrix composites and new processing technologies, will join the list of competitive materials to sheet steel.

As a consequence of these trends, sheet steel producers will have to maintain the flexibility to tailor properties to user needs. Powder injection to reduce S and P, vacuum carbon deoxidation, and inert gas stirring provide flexibility to attain low residuals needed for certain applications. Continuous annealing provides greater flexibility that batch annealing. And coating by electrodeposition is more flexible than hot dip coating. Consequently, these processes will be used more widely, not just to produce sheet products for the automotive market, but for other markets too.

Continuous annealing has recently been combined with the upstream process of cold rolling to provide operating efficiencies. And right from the beginning,
it was combined with the downstream process of skin rolling. In the future it seems likely that continuous annealing will also be combined with a coating process. That is not new, of course: hot dip coating has been combined with a rudimentary form of continuous annealing. However, other processes that could be used to apply a greater variety of metal alloy compositions than hot dip coating or even electrodeposition have the potential to be integrated with the modern continuous annealing process. There are many relatively new coating processes—sputtering, ion plating, vapor deposition, plasma spraying, cladding and electron beam and laser beam melting of materials on the surface. Except for vapor deposition, all of these have been used for batch coating; i.e., they have not been applied to continuous coating of the large surface area of moving strip. However, two of the new processes—sputtering and electron beam melting of surface material—appear to have that potential.

These two processes have the capability of coating a wide variety of metals and alloys. Indeed, virtually any material is a candidate for coating by sputtering. Metallic alloys, oxides, polymer's and even amorphous metal coatings have been successfully deposited by this method.

Electron beam melting is also a well established technology. It can be carried out in air or in controlled atmospheres, and it will melt surfaces to a depth of 15 microns at the rate of a meter per second.

There has been so much recent progress in metal alloy coatings on steel that it is probable that other alloys will be found that will be superior to those applied to date by hot dip coating and electrodeposition. Sputtering and electron beam melting, because of their great versatility and potential applicability to coating moving sheet, seem to be the best candidates to be combined with continuous annealing for the application of new coatings. It is conceivable that these processes could be inserted at some location in the continuous annealing process, either where the sheet is hot or where it is cold, i.e., after it emerges from the line.

Another sheet steel production process that is attracting attention throughout the world is that of casting either thin slabs or thin sheet directly from the melt. A variety of methods have been proposed to do this, these being 1) casting between two water-cooled moving belts (e.g., the Hazelett process), 2) casting between a moving belt and a rotating roll, 3) casting between two rotating rolls, and 4) casting on a single rotating roll. The latter is an outgrowth of recent developments in producing rapidly solidified, thin sheet of special metals with a amorphous structure. Casting a sheet of comparable thickness to hot rolled sheet, which could subsequently be cold rolled to final gage and annealed, would, of course, eliminate hot rolling. Clearly that would have significant cost benefits. And just as clearly it has formidable technical obstacles.

Casting a thin slab, say 4 to 5 cm thick, has fewer technical obstacles and, though hot rolling would still be required, would enable the mini mill concept to be used to produce sheet. Thus, if a cast thin slab could be coiled to keep it hot, then hot rolled on a reversing hot mill, capital costs for the hot mill per ton of capacity would be reduced appreciably. The New York Times reported recently that some of the mini mills are very interested in this prospect.

My prediction is that continuous casting of thin slabs will be accomplished within the next 5 to 10 years. Although this may directly impact existing large integrated sheet steel producers, it seems more likely that prospects are greatest in the less developed countries which do not have, and probably can not afford, large sheet rolling facilities.

To sum up, the technology of sheet steel has been dynamic and will continue that way in the future. During my career I have enjoyed and have been mentally stimulated by my involvement with sheet steel products. I am such the present and future generations of those whose career involves this product will similarly find it exciting, interesting, and rewarding.

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