Optimizing The Nickel-Zinc Process for Hot Dip Galvanizing

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1.0 Summary

Recent research at Cominco and other zinc producers has led to a better understanding of the effects of nickel levels, bath temperature and other metals on the nickel-zinc galvanizing process. This paper was presented at the 3rd Asian Pacific General Galvanizing Conference, Australia, September 8, 1996.

2.0 Introduction

Use of the nickel-zinc (NiZn) galvanizing process has proven to be the most practical and effective method of dealing with the problems associated with the hot dip galvanizing of silicon-containing steels. These steels, which are commonly referred to as "reactive", exhibit a higher rate of alloy growth during the normal galvanizing process, leading to excessive coating thickness, poor coating adhesion and unattractive grey surface appearance of the galvanized product.

The NiZn process, and its development and commercial use, have been described in a number of comprehensive reviews. [1, 2, 3] The process has been found successful in coping with steels having silicon contents up to 0.20%. (For higher silicon contents, i.e. >0.20%, it is comparatively ineffective). The galvanized coatings produced using the process are generally characterized by smooth, bright surfaces, as opposed to the uneven grey or mottled surfaces which can be encountered on such steels with normal galvanizing. Excessive coating thickness, also, is avoided with a resultant saving in zinc usage.

One of the main advantages of the NiZn process, as compared to other possible ways of dealing with the silicon steel problem, is that it can be operated without any major changes to the normal galvanizing process. Thus, bath temperatures, immersion times and work throughput are typically the same as with common practices. However, higher dross losses can occur which may result in drossing the pot more frequently.
Ni levels ranging from 0.05 to 0.14% have been used, but the tendency in recent years has been towards the lower end of the range. [6] High nickel levels have been found to have a number of disadvantages, particularly high dross losses, rough surfaces and problems with inadequate coating thicknesses on low silicon steels.

Recent research has increased the available knowledge of the Fe-Ni-Zn system and helped clarify the factors influencing the NiZn galvanizing process. There have also been new developments in techniques for alloying and controlling the NiZn bath. This new information, together with data and experience previously reported, provides a basis for optimizing the NiZn process in hot dip galvanizing plants.

3.0 Factors Affecting Efficiency and Cost

3.1 Bath Ni Content vs Control of Coating Thickness

In the interest of process efficiency and economics, it is desirable to determine the optimal nickel level needed to ensure the desired reactivity control. It is of interest, therefore, to examine available information on the effectiveness of lower Ni levels in controlling the coating thickness.

Notowidjojo et al. [4] found that as little as 0.02 % Ni in the bath can partially suppress the reactive coating tendency in steels with Si levels below 0.2%, while 0.1 % Ni can completely suppress it (see Figure 1). Stroud [1] reported that while bath Ni contents in the range 0.07 to 0.12% have been commonly used by galvanizers, a level of 0.05 % are now being used in Australia. In these latter instances, however, a major aim has apparently been just the improvement in surface finish.

![Figure 1](image.png)

**Figure 1.** The effect of Ni addition on the Sandelin curve (450 °C).
Earlier Cominco work showed that most of the reactivity suppression effect can actually be obtained with a Ni level as low as 0.06%, as shown in Figure 2. [5, 6] For example, the results with a reactive steel containing 0.17% Si indicated that a 0.064% Ni bath effected more than 80% of the coating weight reduction achieved by 0.095 and 0.13% Ni baths. Thus, in this case, a doubling of the Ni level in the bath resulted in less than 20% further reduction in the coating thickness. As shown later, this increase in bath nickel level results in significantly increased dross losses and reduced Ni efficiency.

![Figure 2: Coating weights as a function of bath nickel content on steels of varying silicon contents][10].

### 3.2 Intermetallics and Dross

Recently, studies have been carried out on the phase relationships in the Zn-Ni-Fe system. [7, 8, 9] Work at Cominco [10] showed that the solubility of iron in the zinc bath at 450 C decreases from 0.029% in a Ni-free bath to zero at a Ni level of about 0.229%, as shown in Figure 3. Solubility limit curves for other temperatures are also shown. When combined levels of Fe and Ni exceed the solubility limit, intermetallic phases are formed, which then settle to the bottom dross layer or, in some cases, may be trapped in the galvanized coating.
From the phase diagrams developed, and confirmed by observation, it has been established that when the Ni content of the bath is below 0.06 % (at 450°C), the zeta phase is the intermetallic phase formed. When the Ni content exceeds 0.06% a ternary Zn-Ni-Fe phase, gamma 2, is formed. The zeta phase contains less than 1% Ni, while the gamma 2 phase contains Ni in the range 2 to 3% depending on the bath nickel level. Thus, the improved understanding of the phase diagram indicates factors important in affecting the Ni use efficiency. The gamma 2 phase intermetallic, which forms when the Ni is >0.06%, contains a higher level of nickel and adds to the loss of nickel in the bottom dross. Furthermore, if the Ni level is much above 0.06%, the higher level of gamma 2 phase formed can result in intermetallic particles being trapped in the coating, resulting in the surface roughness and excessive coating thickness sometimes encountered.

3.3 Nickel Deportment in the Bath

Plants using the NiZn process have reported typically that about half (40 - 60%) of the nickel added reports to the bottom dross. [1] A small proportion goes to the ash, while the remainder reports to the coating.

The effect of bath Ni level on the loss of Ni from the bath is illustrated in Figure 4. [10] This figure shows a plot of Ni content of two different operating galvanizing baths as a function of time. For Bath No.1, the nickel consumption was 45 ppm per day for a bath Ni above 0.06%, and 11 ppm per day for bath Ni below 0.06%. For Bath No.2, the nickel consumption was 48 ppm per day for bath Ni contents above 0.05 % and 12 ppm per day for bath Ni contents below 0.05%. The reduced rate of Ni loss when the Ni content dropped below about 0.06% is believed to be due to the change in the intermetallic dross particles forming in the bath and the degree of Ni enrichment in the coating. As
noted above, below the 0.06% level the only intermetallic formed would be zeta phase, which has significantly lower Ni content than the ternary gamma 2 phase.

3.4 Alloying Method

Traditionally, nickel is added as a master alloy. NiZn master alloys contain Ni in the form of a NiZn compound (NiZn$^8$) within a zinc-rich matrix. The melting point of the NiZn phase is higher than the normal bath temperature, and therefore, a certain amount of time is required for dissolution of the Ni into the bath. During this time some of the particles will probably settle to the dross layer before they can be dissolved, thus contributing to the dross losses. The extent of this settling effect will be dependent on the size of the intermetallic particles, the temperature of the bath and its turbulence. The use of a pre-alloy (e.g. 0.24% Ni) is advantageous since in this case the proportion of Ni intermetallics is much less and they are more uniformly distributed. The Ni efficiency for additions using a pre-alloy has been reported at 33%, compared to 20% when using a 2% Master Alloy. [11]

A more efficient method of introducing nickel is as a metal powder. This is the basis of Cominco's Direct Alloying Process. [2] In this technique, a nickel powder product is immersed in the zinc bath in a specially designed mixing unit. The high surface area of the powder together with the strong mixing action results in complete dissolution of the Ni powder in a very short period of time. For example, the typical galvanizing kettle can be converted to a NiZn bath within an hour. The Ni efficiency for this method has been found to be about 95%. The Direct Alloying Process has proven to be an easy and efficient means for initial bath alloying and for on-going Ni level maintenance.

3.5 Operating Temperature

As illustrated in Figure 3, the solubility limits of iron and nickel in liquid zinc are greatly
affected by the bath temperature. Reductions in temperature result in reduced solubilities.

Thus, if the temperature of a Ni-Zn galvanizing bath falls significantly, the solubility of Fe and Ni in the bath will decrease, and increasing amounts of intermetallics will form. These will tend to settle to the bottom of the pot contributing to more dross losses. Rises in temperature cause more iron and nickel to go into solution; but if the temperature was later reduced, additional intermetallics will then be produced. It is therefore advisable to avoid wide swings in temperature as much as possible to maximize nickel efficiency.

3.6 Other Alloying Additions (Pb and Al)

Lead additions to the bath are reported to improve its fluidity, thereby helping to achieve smooth uniform coatings. [12] There is some suggestion that lead may, also, have a small beneficial effect in controlling Si-induced reactivity. It is therefore generally agreed that a Pb-containing bath (PW) should be used for the NiZn process.

Aluminum has been found to negate the effectiveness of Ni additions. Aluminum levels should therefore be kept low to improve coating brightness and reduce oxidation of the zinc bath. Levels of 0.002% have been recommended. [13,14]

4.0 Discussion

The NiZn process has been found to be an effective method of coping with the problems associated with the galvanizing of reactive steels. This has been of importance to the galvanizing industry, in view of the ever-increasing proportion of continuous cast silicon killed steels being produced and the severe limitations of the conventional process to produce quality coatings on these materials. The success of the process has been achieved in spite of a relative lack of information on the mechanisms involved and on the important parameters influencing the operation and economics of the process. As further research increases the knowledge of the Fe-Ni-Zn system, and better operating controls and process improvements are more widely used, there is considerable scope for refining the process and making it more cost-efficient.

One of the needs for further documentation of the NiZn process is the development of a model representing the process and showing the relationship of the various input parameters to the process efficiencies and product characteristics. A basic start to such a study would be to establish a materials balance for zinc and nickel in the NiZn process based on carefully monitored production data and analysis from a galvanizing operation. It may be that this has already been done by some galvanizers, but it does not appear to be in the open literature. Steps are being taken to develop a meaningful model, at Cominco, to facilitate studies of material efficiencies and cost/benefits for the process.
5.0 Conclusions and Recommendations

Consideration of the above factors leads to following suggested practices to help optimize the cost effectiveness of the NiZn Process.

1. Maintain bath nickel contents in the range 0.05 to 0.06%. This should give the best balance between product properties and process efficiencies.

2. Make small Ni additions frequently, so that the recommended Ni level can be maintained without large variations above or below the target level.

3. Add Ni to the bath in a form in which it can be readily dissolved in the zinc bath; thus, pre-alloy is preferable to master alloy. Direct alloying using Ni powder is advantageous from the standpoint of rapid alloying and Ni efficiency.

4. Keep the bath temperature within a narrow range, as far as is practical. Wide swings in temperature will contribute to increased dross production.

References


Authors Biography

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