Effect of Zirconium on the Magnetic Properties of Nonoriented Semiprocessed Electrical Steel Sheet

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(Submitted 7 June 2000)

The effects of zirconium precipitates on the magnetic properties of nonoriented semiprocessed electrical steel sheets were investigated. Core loss of the test specimens declined for zirconium contents of 0.01 wt.%, whereas the magnetic induction did not change due to the addition of zirconium less than 0.133 wt.%. Precipitates and texture studies revealed that the zirconium precipitates had no effect on the grain coarsening at hot rolling and after final annealing after being cold rolled.

Keywords grain size, magnetic properties, semiprocessed nonoriented electrical steel, textures, zirconium precipitates

1. Introduction

Electrical steel sheets are consumed in millions of tons annually as the core materials of small motors and ballast.[1] Reducing total carbon dioxide emission is an important issue identified in the 3rd Conference of Parties (COP3) of the United Nations Framework Convention on Climate Change (UNFCCC) in Kyoto in 1997. Thus, much attention is now paid to developing magnetic properties through the control of chemistry, grain size, and texture, and several new products with low core loss and high induction have been developed.[2,3] This improvement has been achieved with the advances in steel-making technology, which turn out to be the relationship between structure and magnetic properties. Control of impurities or tramp elements is one of the most important technologies in the steel-making process. Nakayama and Takahashi[4] and Nakayama and Tanaka[5] investigated the effect of vanadium and titanium on the magnetic properties of semiprocessed nonoriented electrical steel sheets, respectively, and concluded that vanadium carbonitrides or titanium carbonitrides inhibited grain coarsening at recrystallization and lessened the magnetic induction and core loss.

At the point of processing, hot rolling, cold rolling, annealing, and temper rolling strongly affect the magnetic properties. Yashiki and Okamoto[6] and Park and Woo[7] investigated the effect of hot-band grain size and magnetic properties of nonoriented electrical steel sheet and concluded that the core loss decreased with an increase in hot-band grain size by high-temperature annealing. Kawamata *et al.*[8] studied cold reduction with texture controlling and concluded that magnetic induction or permeability were strongly affected by the cold-rolling condition.

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In this study, we investigated the effect of zirconium on the magnetic properties of semiprocessed nonoriented electrical steel sheets.

2. Experimental Procedure

Various zirconium-bearing steels were prepared in a 50 kg vacuum induction furnace. Table 1 lists the chemical composition of the steels. The proportions of zirconium were 0.001, 0.004, 0.007, 0.008, 0.014, 0.021, 0.040, 0.083, and 0.130 with 0.0011 to 0.0020 wt.% nitrogen, denoted Z1-1, Z1-4, Z1-7, Z1-8, Z1-14, Z1-21, Z1-40, Z1-83, and Z1-130, respectively, and the proportions of zirconium were 0.001, 0.003, 0.004, 0.005, 0.008, 0.015, 0.043, 0.095, and 0.133 with 0.0027 to 0.0036 wt.% nitrogen, denoted Z2-1, Z2-3, Z2-4, Z2-5, Z2-8, Z2-15, Z2-43, Z2-95, and Z2-133, respectively. The steel ingots were machined to 45 mm thickness and reheated at 1450 K, then hot rolled to 4.5 mm thick sheets at a finishing temperature of 1103 K. After being air cooled to 943 K, the hot-rolled sheets were kept at 943 K for 5 h, then furnace cooled. These sheets were uniformly ground to 2.3 mm in thickness to remove any scale and cold rolled to 0.5 mm thick by a four-high-pilot cold-rolling mill with a total reduction of 78%. The continuous annealing was performed with a Shinku-Riko (Tokyo, Japan) ULVAC CCT-QB simulator along the time-temperature schedule shown in Fig. 1. Continuous annealed sheets were cut to 30×100 mm in dimension, either longitudinally or transversely to the rolling direction, for 10 cm miniature Epstein frame specimens. These specimens were annealed at 1023 K for 2 h in nitrogen gas (for stress relieving) and furnace cooled. Magnetic properties, including core loss and induction, were measured on a 10 cm miniature Epstein frame (Yokogawa Electric Works Measuring System (Tokyo, Japan)). Texture examinations were performed by x-ray diffraction (Material Analysis and Characterization Inc., MXP-3); the system had a molybdenum target operated at 46 kV and 16 mA. Precipitate investigation was done by an extraction replica method using a transmission electron microscope (TEM) attached to an EDAX for chemical analysis (Hitachi HU-700H operating at 100 kV).

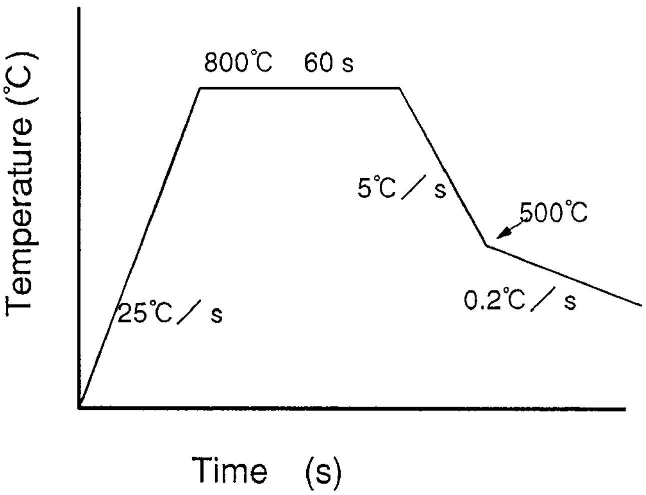


Fig. 1 Heat diagram of final annealing of cold-rolled sheets

Table 1 Chemical composition of the steels (wt.%)

Steel	C	Si	Mn	P	S	Acid-soluble Al	N	Zr
Z1-1	0.001	0.28	0.30	0.081	0.005	0.29	0.0020	0.001
Z1-4	0.001	0.29	0.30	0.077	0.005	0.28	0.0020	0.004
Z1-7	0.001	0.32	0.29	0.075	0.004	0.29	0.0011	0.007
Z1-8	0.001	0.31	0.30	0.078	0.005	0.26	0.0020	0.008
Z1-14	0.001	0.33	0.30	0.080	0.005	0.23	0.0014	0.014
Z1-21	0.001	0.33	0.30	0.071	0.005	0.26	0.0020	0.026
Z1-40	0.001	0.29	0.30	0.065	0.005	0.25	0.0019	0.040
Z1-83	0.001	0.30	0.30	0.081	0.005	0.24	0.0019	0.083
ZI-130	0.001	0.30	0.31	0.066	0.005	0.35	0.0011	0.130
Z2-1	0.001	0.30	0.30	0.082	0.005	0.32	0.0035	0.001
Z2-3	0.002	0.30	0.30	0.083	0.005	0.32	0.0036	0.003
Z2-4	0.001	0.31	0.30	0.083	0.005	0.32	0.0036	0.004
Z2-5	0.001	0.30	0.32	0.085	0.004	0.32	0.0027	0.005
Z2-8	0.001	0.30	0.32	0.084	0.003	0.32	0.0030	0.008
Z2-15	0.001	0.30	0.31	0.083	0.003	0.30	0.0030	0.015
Z2-43	0.001	0.30	0.32	0.084	0.003	0.32	0.0028	0.043
Z2-95	0.001	0.30	0.31	0.084	0.003	0.32	0.0030	0.095
Z2-133	0.001	0.30	0.31	0.083	0.003	0.32	0.0030	0.133

3. Results and Discussion

Figure 2 shows the relationship between core loss at 1.5 T and 50 Hz (W15/50) and zirconium content after stress relief annealing. Core loss is almost unchanged in steels containing zirconium $<$0.01 wt.%, whereas in steels containing zirconium $>$0.01 wt.%, the core loss increases drastically due to the numerous precipitates both along the grain boundaries and in grains. Precipitates generally increase hysteresis loss; therefore, in the case of steels with zirconium more than 0.01 wt.%, the core loss was drastically increased by these precipitates. The effect on core loss of numerous precipitates is the same as that in steels with $>$0.01 wt.% titanium by (Fe,Ti)P.[5]

These numerous precipitates in steels with $>$0.01 wt.% zirconium were analyzed by the TEM replica method with EDAX and proved that they are Zr_3Fe (Fig. 6b). Although Zr_3Fe is known to be an unstable intermetallic phase,[9] it occurred at

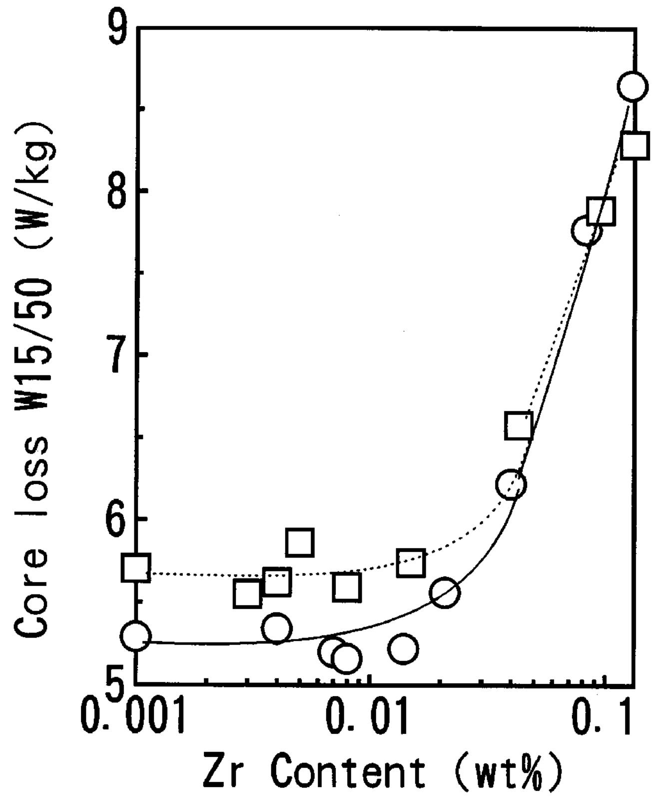


Fig. 2 Effect of zirconium addition on core loss W15/50 after stress relief annealing. (N = 0.0011 to 0.0020 wt.%; and N = 0.0027 to 0.0036 wt.%)

the crystallization of amorphous Zr-Fe alloy; the diffraction pattern was fit to Zr_3Fe.

In steels with $<$0.01 wt.% zirconium, no zirconium nitrides or carbonitrides were observed, but AlN was observed along the grain boundaries.

It is well known that zirconium is one of the easiest elements to form nitrides[10] or carbonitrides. To make ensure the effect of nitrogen, we increased the nitrogen content (Z2 steels); however, the trend of core loss is almost the same as in the lower nitrogen-bearing steel, Z1 steels. The microstructure study revealed that the grain size of Z2-3 was smaller than that of Z1-4, and the grain boundaries were pinned down by small AlN precipitates by TEM observation; however, no zirconium nitrides or carbonitrides were observed.

This AlN effect is the same as the results of the previous study. Nakayama and Honjou[11] investigated the effect of aluminum and nitrogen on the magnetic properties of semi-processed nonoriented electrical steels, and concluded that the core loss in the steels with AlN $>$0.0024 is changed by "harmful AlN." The Z2 steels in this study contained this harmful AlN.

Although zirconium is the element that most easily forms a nitride,[10] no zirconium nitrides or carbonitrides are formed in this study. Shinomiya *et al.*[12] reported that the zirconium nitrides observed in commercial silicon steels, which inhibit grain growth during final continuous annealing, also deteriorated the magnetic properties.

Vanadium or titanium forms nitrides as precipitates in silicon steels. Nakayama and Takahashi[4] investigated the effects of

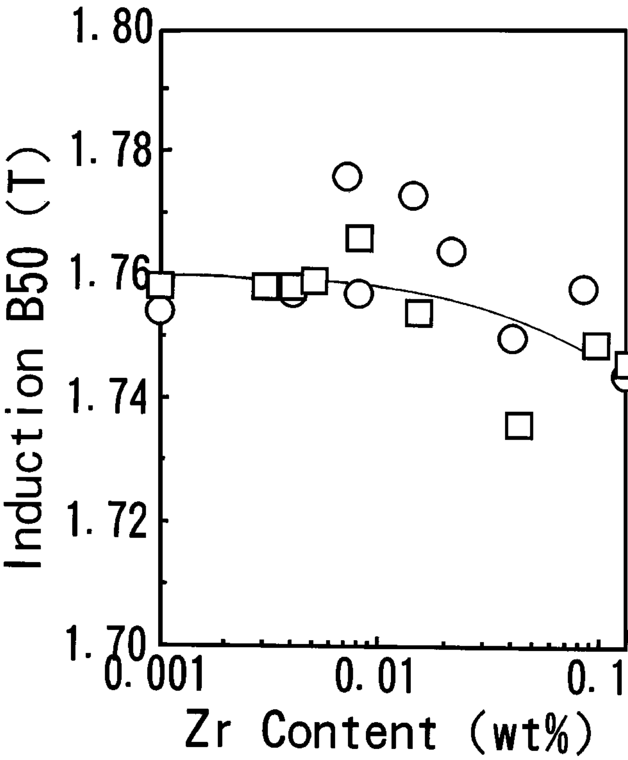


Fig. 3 Effect of zirconium addition on induction B50 after stress relief annealing. (N = 0.0011 to 0.0020 wt.%; and N = 0.0027 to 0.0036 wt.%)

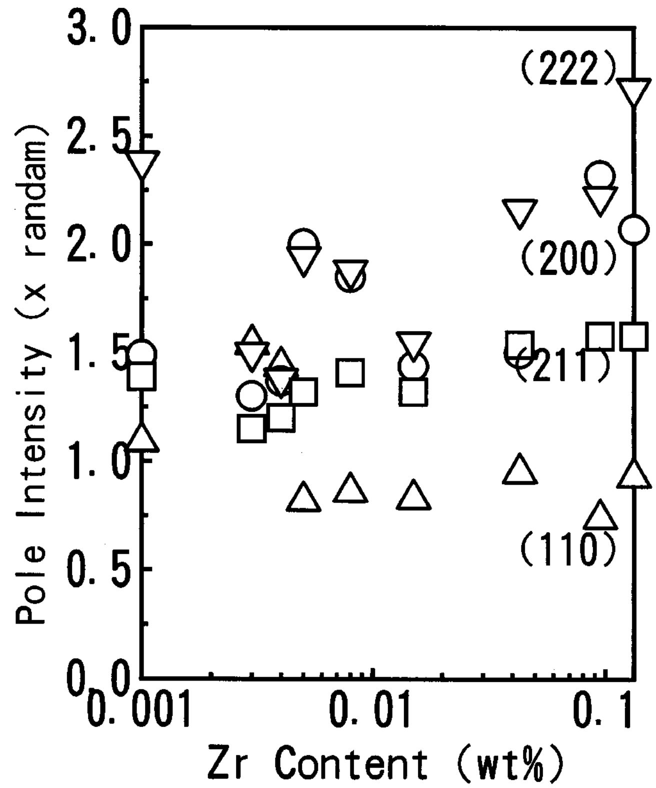


Fig. 4 Effect of zirconium addition on grain size of hot bands (N = 0.0027 to 0.0036 wt.%)

vanadium on the magnetic properties of nonoriented semi-processed electrical steel sheets and concluded that the fine vanadium carbonitride precipitates pinned down the grain boundaries during recrystallization in hot rolling and annealing; therefore, the grain size was smaller and magnetic properties deteriorated with an increase in vanadium content $<$0.016 wt.%. However, in this study of zirconium additions, no zirconium nitrides or carbonitrides are formed and the zirconium precipitates as Zr_3Fe had little effect on the grain growth.

Yashiki and Okamoto[6] studied how the grain size of hot bands affects magnetic induction B50, how that of final annealed cold-rolled sheets affects the core loss, and how the large grain size of the hot band improves the magnetic induction. In our study, Fig. 3 shows that the induction at 5000 A/m (B50) is slightly lower as zirconium increases. This magnetic induction is decreased by the numerous precipitates of Zr_3Fe in the steels bearing zirconium $>$0.01 wt.%.

To make this effect clear, the grain size and texture of hot bands as a function of zirconium addition are shown in Fig. 4 and 5, respectively. This effect is the same as in steels with $>$0.01 wt.% titanium, where (Fe,Ti)P formed in the previous study.[5]

The effects of a "nitriding-easy" element in 0.3% silicon steel are summarized in Table 2.

4. Conclusion

The effects of zirconium on the magnetic properties of semi-processed nonoriented electrical steel sheets are as follows.

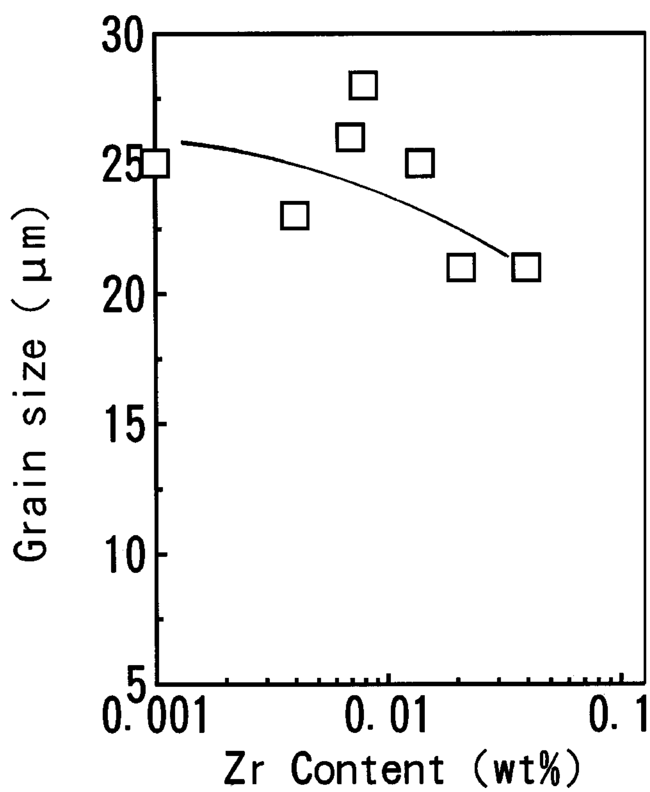
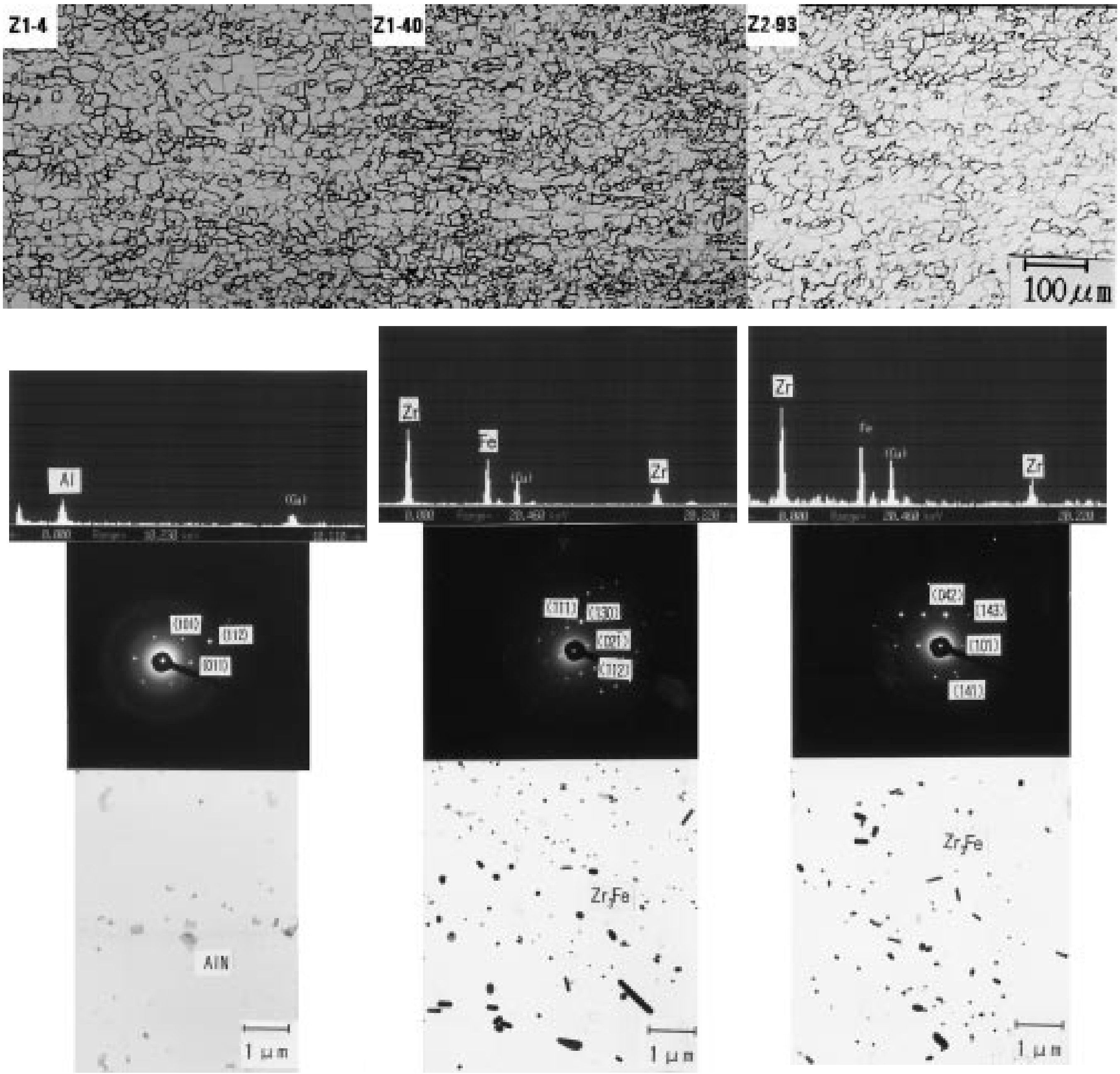


Fig. 5 Effect of zirconium addition on the pole intensity of hot bands (N = 0.0027 to 0.0036 wt.%)



Z1-4 Z1-40 Z2-93

Fig. 6. Microstructures and precipitate observation by TEM in cold-rolled sheets after stress relief annealing. (Z1-4, Z1-40, Z2-95)

Table 2 Effect of the nitriding-easy element on the magnetic properties in 0.3 wt.% silicon steel[4,5]

Element	Range	Core loss	Magnetic induction	Precipitates
V	0.001 wt.%–0.01 wt.%	Deteriorate	Deteriorate	V(C, N)
Ti	⋯	Deteriorate	Deteriorate	Ti(C, N)
Zr	⋯	No change	No change	⋯
V	0.01 wt.%–0.1 wt.%	Deteriorate	Deteriorate	V(C, N)
Ti	⋯	Deteriorate	Deteriorate	(Fe, Ti)P
Zr	⋯	Deteriorate	No change	Zr_3Fe
V	>0.1 wt.%	Improve	Improve	V(C, N)
Ti	⋯	Deteriorate	Deteriorate	(Fe, Ti)P
Zr	⋯	Deteriorate	Deteriorate	Zr_3Fe

- The magnetic properties such as the core loss W15/50 and the induction B50 are not affected by the zirconium precipitates in the range of Zr <0.01 wt.%. The major deterioration in this range is by aluminum nitride.
- In steels containing Zr ranging from 0.01 to 0.13 wt.%, the core loss increases with an increase in zirconium content by the numerous precipitates, but not zirconium nitrides. Zr_3Fe was identified by TEM observation. This Zr_3Fe does not pin down the grain boundary to inhibit the grain growth, but forms inside the grain and increases the core loss by increasing hysteresis loss. However, there is less effect on the magnetic induction B50 because of the small effect on the hot-band grain size and texture by those precipitates.

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