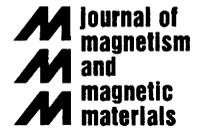




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Letter to the Editor

# A 48% Ni–Fe alloy of low coercivity and improved corrosion resistance in a cyclic damp heat test

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## Abstract

Electric arc 30t melts, deoxidised with Mn and Si, are compared to melts additionally deoxidised with cerium. In a cyclic damp heat test the melts with Ce show better corrosion behaviour.  $\mu_4$  (DC) and  $H_c$  of samples of 1.0 mm thickness after heat treatment at 1080°C vary in the same range of values for both categories of melts. After heat treatment at 1080°C or 1180°C  $\mu_4$  (50 Hz) and  $H_c$  of samples of 0.2 mm thickness are impaired by 20% or more for melts with Ce. For melts with Ce the strong binding of the sulphur to the deoxidiser impedes desulphurization. With small strip thicknesses, the strong binding energy of Ce to oxygen causes additional internal oxidation during heat treatment. Both deteriorate the magnetic properties. At the larger thickness of 1.0 mm there is no noticeable internal oxidation and/or desulphurization in both categories of melt due to the strip thickness. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Ce deoxidised; Damp heat test; Permeabilities; Coercivity; 48% Ni–Fe alloy.

## 1. Introduction

The main property requirements for materials for relay parts are high flux density and high permeability. The force between the poles is proportional to the square of the flux density, so a high flux density is necessary to achieve high forces. A high permeability is necessary to achieve a release of the relay at a low release current. In mains voltage independent ground fault interrupters the energy for the release of the relay is

delivered entirely by the fault current. The permeabilities of normal relay iron are not sufficient and materials with higher permeabilities, such as Ni–Fe alloys, are required. The 48% Ni–Fe alloy has the highest saturation flux density of 1.5 T in the Ni–Fe alloy system. A relay in ground fault interrupters has to pass a damp heat test. If in such a test corrosion on the poles' surfaces occurs, the relay fails. The gap between the surfaces of the poles of the relay has to be as narrow as possible to achieve permeabilities as high as possible in the relay's magnetic circuit. To have an unchanged release current the surfaces of the poles should not be damaged through switching the relay. So the specific property requirements for relays in ground fault interrupters concern not only the magnetic properties, but also corrosion resistance

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and wear resistance properties as well. The corrosion resistance is greatly influenced by melting and deoxidation processes.

## 2. Experimental

The alloys used in this study were commercial electric arc 30t melts, deoxidised and desulphurized with Mn and Si. They consisted approximately of 48 wt% Ni, 0.4 wt% Mn, 0.2 wt% Si, less than 25 ppm S and O<sub>2</sub>, less than 15 ppm Mg, less than 10 ppm Ca and balance Fe. Some of the melts were additionally deoxidised/desulphurized with cerium additions as a mixture of rare earth metals. Hot rolled sheets were cold rolled—with an intermediate anneal at 980°C—to strips of 1.0 and 0.20 mm thickness. The final cold reduction was 70% and 75%, respectively, to avoid secondary recrystallisation [1]. Rings, round blanks (1.0 mm) and M42 laminations (0.20 mm) were stamped. The samples were heat treated at temperatures between 970°C and 1180°C in a hydrogen atmosphere with a dew point of about –60°C and cooled down to 450°C in the furnace. The coercivity  $H_c$  was determined with a Förster Koerzimat 1.095. The DC permeability  $\mu_4$  at 0.4 A/m was determined from the normal magnetisation curve with an electronic fluxmeter. The permeability  $\mu_4$  at 50 Hz was determined by measuring the true root mean square value of the primary current and the average rectified value of the secondary voltage. The samples for the corrosion test—ten round blanks 25 mm in diameter for each test—were cleaned ultrasonically in alcohol before heat treatment. After heat treatment they were tested in a cyclic damp heat test of 8 cycles, each consisting of 3 h at 25°C and 55% humidity and 3 h at 55°C and 95% humidity. They were examined for corrosion points under a stereomicroscope with a magnification factor of at least 15. For the residue analysis the matrix material was dissolved in an organic electrolyte [2]. The residual sulphides were analysed using TEM/EDX. The grain size of the annealed samples was measured by the linear intercept method, counting twins as interfaces similar to grain boundaries.

## 3. Results and discussion

The cyclic damp heat test was carried out after heat treatment at 970°C for 2 h and a second time with new samples after heat treatment at 1030°C for 2 h for one melt with Ce and two without Ce. For the melts without Ce each of the round blanks showed at least several corrosion pits, but none were found in the melt with Ce. In all the pits of the melts without Ce examined by SEM, EDX and EMPA [3], sulphur and often Ca together with S were found. A residue analysis [2] for sulphides showed that these melts with Ce additions contained Ce and La sulphides, whilst those without Ce contained Ca sulphides and possible traces of Mg sulphides. CaS is water-soluble [4] and hence causes corrosion [5]. MgS shows a similar behaviour. Since CeS is not water soluble [6], the water-insoluble binding of S by Ce explains the better corrosion behaviour of the melt with Ce. La has a similar chemical behaviour to that of Ce. The free enthalpy of formation for CaS has a very high (negative) value of –476 kJ per mole S [5]. Only the free enthalpy of formation of CeS (–500 kJ per mole S) is higher and so CeS (and LaS after [2]) is formed instead of CaS in the melts with Ce.

Table 1 shows the coercivity  $H_c$  and the permeability  $\mu_4$  at 0.4 A/m of samples of the thickness  $d$  and heat treatment of 4 h at the temperature  $T$ . With 1.0 mm thickness both— $\mu_4$  (DC) and  $H_c$ —vary in the same range of values for melts with and without Ce. The P(robability)-values for no difference of the means  $x_0$  and  $x_{Ce}$  are much higher than 0.05. So the difference is not statistically significant at the 95% confidence level. For the  $\mu_4$  (50 Hz) of samples of 0.2 mm thickness after 4 h at 1080°C the melts with Ce have a reduced mean of  $\mu_4$  by about 20%. For  $H_c$  the melts with Ce have an increased mean by about 30%. The P-values are under the limit of 0.05 for the 95% confidence level, which means statistical significance at the 95% confidence level. For 0.2 mm thick samples with Ce after 4 h at 1180°C the mean of  $\mu_4$  (50 Hz) is reduced by about one third and the mean of  $H_c$  is increased by about 40%. The P-values are markedly below the 0.05 limit. This is in accordance with the results of [7].

Table 1

Means and standard deviations of  $H_c$  and  $\mu_4$  for melts with and without Ce. The P-value for no difference in the means  $x_0$  and  $x_{Ce}$  was calculated with the statistical program Statgraphics [11]

	$d$ (mm)	$T$ ( $^{\circ}\text{C}$ )	Without Ce		With Ce		$x_{Ce}/x_0$	P-value
			Mean $x_0$	St. dev.	Mean $x_{Ce}$	St. dev.		
$H_c$ (A/m)	1.00	1080	2.62	1.11	2.72	1.01	104%	0.87
$H_c$ (A/m)	0.20	1080	2.85	0.27	3.79	0.75	133%	0.030
$H_c$ (A/m)	0.20	1180	2.72	0.24	3.80	0.49	140%	0.0024
$\mu_4$ (DC)	1.00	1080	10440	1860	11631	2460	111%	0.31
$\mu_4$ (50 Hz)	0.20	1080	7220	550	5986	658	83%	0.35
$\mu_4$ (50 Hz)	0.20	1180	9790	210	6478	820	66%	0.0006

Table 2

Means and standard deviations of  $\mu_4$  (50 Hz) for strip thickness 0.20 mm. The P-value for no difference in the means  $x_{T1}$  and  $x_{T2}$  was calculated with the statistical program Statgraphics [11]

	$T$ ( $^{\circ}\text{C}$ )	Mean $x_T$	St. dev.	$x_{1180}/x_{1180}$	P-value
Without Ce	1080	7220	550		
	1180	9790	210	1.36	0.33
With Ce	1080	5986	658		
	1180	6478	820	1.08	0.0017

There,  $\mu_4$  (50 Hz) of 0.10 mm thick samples of melts with Ce is about  $\frac{2}{3}$  of the value of melts with Mn and Si but without Ce after 5–6 h at 1100 $^{\circ}\text{C}$  (dew point  $-45$  to  $-60^{\circ}\text{C}$ ). This is also in accordance with the observation that the highest permeabilities are observed when no strong deoxidisers are present [8].

With the melts without Ce there is an increase in  $\mu_4$  (50 Hz) at 0.2 mm thickness with increasing temperature in accordance with [8,9], which was due to further desulphurization. For the melts with Ce, however, no significant increase with temperature is observed (Table 2). All samples of 0.20 mm thickness of both categories of melts after heat treatment at 1080 $^{\circ}\text{C}$  and 1180 $^{\circ}\text{C}$ , respectively, had the same grain diameter of about 150  $\mu\text{m}$ , counting twins as interfaces similar to grain boundaries.

For some melts, additional analysis [10] after heat treatment was done for O and S, which mainly influence  $\mu_4$  [8,9] and  $H_c$ , respectively. The accuracy of the S analysis was 2 ppm, that of the O analysis 1 ppm. For the melt without Ce and 7 ppm S before heat treatment the S content was the same for the sample of 1.0 mm thickness after heat treatment at 1080 $^{\circ}\text{C}$ , but was reduced to 2 ppm for

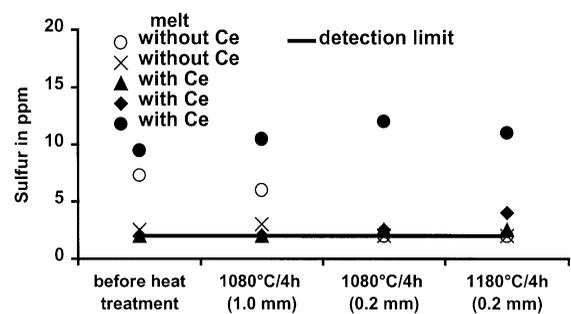


Fig. 1. Dependence of sulphur content on heat treatment and strip thickness.

the sample of 0.2 mm thickness after heat treatment at 1080 $^{\circ}\text{C}$  (Fig. 1). So the expected further reduction of the S content for 0.20 mm thickness at higher temperature could not be detected. For the melt with Ce and 10 ppm S before heat treatment the S content was the same for the sample of 1.0 mm thickness after heat treatment at 1080 $^{\circ}\text{C}$  and for the samples of 0.2 mm thickness after treatment at 1080 $^{\circ}\text{C}$  or 1180 $^{\circ}\text{C}$ . The other analysed melts without Ce and with Ce already had 2–3 ppm S before heat treatment. The oxygen

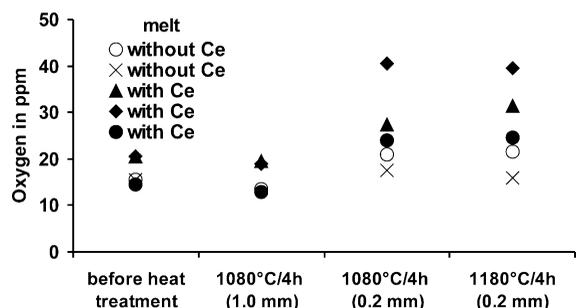


Fig. 2. Dependence of oxygen content on heat treatment and strip thickness.

content remained constant after 1080°C for the samples of 1.0 mm thickness for both categories of melts (Fig. 2), but for the samples of 0.2 mm thickness the oxygen content increased up to twice this value for melts with Ce. For melts without Ce no marked increase was analysed. The carbon content of the melts before heat treatment varied between 40 and 140 ppm. After all heat treatments for samples of both thicknesses the C content varied between 5 and 10 ppm, so C has no influence on magnetic properties.

For melts with strong deoxidisers like Ce the strong binding of the sulphur to the deoxidiser impedes desulphurization. Additionally the strong binding energy of Ce to oxygen causes additional internal oxidation during heat treatment at small strip thicknesses and can reduce  $\mu_4$  and increase  $H_c$ . These are both typical effects of strong deoxidisers [7,8]. At the larger thickness of 1.0 mm there is no noticeable internal oxidation and/or desulphurization in both categories of melts due to strip thickness.

#### 4. Conclusions

Most of the relay parts are thicker than 1.0 mm and temperatures lower than 1100°C are preferred in production. So deoxidation with Ce is an excellent method of improving the corrosion resistance of 48% Ni–Fe in a damp heat test with unchanged magnetic properties.

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#### References

- [1] G.W. Rathenau, J.F.H. Custers, Philips Res. Rep. 4 (1949) 241.
- [2] K.H. Waldöfner et al., Examination Report P9798/156, Thyssen Krupp Stahl, 1997.
- [3] P. Willich, U. Schiffmann, Analysenbericht, IST-Fraunhofer-Institut, 1997.
- [4] R.C. Weast et al., Handbook of Chemistry and Physics, Boca Raton, Florida, 1985.
- [5] G. Wranglen, Corrosion Sci. 14 (1974) 331.
- [6] G. Czack et al., Gmelin Handbook, Rare Earth—C7, Springer, Berlin, 1983.
- [7] A. Hoffmann, Z. angew. Physik 32 (1972) 236.
- [8] D.A. Colling, R.G. Aspen, J. Appl. Phys. 41 (1970) 1040.
- [9] D.A. Colling, R.G. Aspen, J. Appl. Phys. 40 (1969) 1571.
- [10] H.-J. Frieg, K. Vogt et al., Revierlabor Essen, 1999 and 2000.
- [11] Statgraphics Plus Standard Edition, Manugistics, Rockville, USA, 1998.