ARCHIVES OF METALLURGY AND MATERIALS
Volume 53 2008 Issue 4

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EFFECT OF CHROMIUM ON THE EARLY STAGE OF TEMPERING OF HYPEREUTECTOID STEELS

WPŁYW CHROMU NA WCZESNE STADIUM ODPUSZCZANIA STALI NADEUTEKTOIDALNYCH

The article presents a quantitative evaluation of chromium influence on transformations during early stage of tempering of hypereutectoid steels. The tests have been conducted on a C110 carbon steel and a 115Cr5 steel containing 1.15% C and 1.23% Cr. The characteristic temperatures of early stages of tempering have been determined using dilatometric method on the basis of digitally recorded dilatograms of heating from quenched state at various rates, which have been subsequently differentiated.

It has been pointed out that dissolution of 1.23% chromium in austenite has practically no influence on the temperature of contraction ε_s (most probably connected with precipitation of ε carbide) taking place during early stage of tempering, while it increases both the temperature of contraction ε_f, and the maximum of its intensity ε_{max} as well. Furthermore, it has been revealed that fracture toughness (K_{Ic}) for the low-tempered (200°C) C110 steel, after previous quenching from homogeneous austenite range, is higher than that for the 115Cr5 alloy steel.

Keywords: tempering, dilatometer, phase transformations, heating rate, fracture toughness, hypereutectoid steel

W artykule dokonano ilościowej oceny wpływu chromu na przemiany zachodzące we wczesnym stadium odpuszczania stali nadeutektoidalnych. Badania wykonano na stali niestopowej C110 oraz stali 115Cr5 zawierającej 1,15% C i 1,23% Cr. Temperatury charakterystyczne wczesnego stadium odpuszczania określono metodą dylatometryczną na podstawie zarejestrowanych cyfrowo dylatogramów nagrzewania z różnymi szybkościami ze stanu zahartowanego, które poddano różniczkowaniu.

Wykazano, że rozpuszczenie 1,23% chromu w austenicie praktycznie nie wpływa na temperaturę początku skurczu ε_s (najprawdopodobniej związanego z wydzielaniem węglika ε) zachodzącego we wczesnym stadium odpuszczania, natomiast podnosi zarówno temperaturę końca skurczu ε_f, jak również maksimum jego intensywności ε_{max}. Ponadto wykazano, że odporność na pękanie (KI_c) niskoodpuszczonej (200°C) stali C110, po uprzednim zahartowaniu z zakresu jednorodnego austenitu, jest większa niż stali stopowej 115Cr5.

1. Introduction

The process of martensite tempering consists of a few stages: carbon segregation, precipitation of carbides, transformation of retained austenite, recovery and recrystallization of matrix [1÷6].

During the first (or early) stage of tempering taking place below 200°C [4, 6, 7] transition carbides may precipitate in the structure of martensite. One of them is ε carbide with hexagonal close packed (HCP) structure and formula $Fe_{2.4}C$. In steels containing less than 0.2% of carbon the precipitation of this type of carbides does not take place, because significant part of carbon atoms is trapped at dislocations [1, 2]. In high-carbon steels tempered in the temperature range of 200÷300°C the Hägg's carbide having $Fe_{2.2}C$ formula and the monoclinic lattice is usually formed [4, 6], while at lower temperatures (i.e. about 150°C) the η carbide with orthorhombic lattice and the Fe_2C formula may also appear [6].

The transformations occuring during tempering of steel are dependent not only on carbon content in martensite and amount of retained austenite but also on alloying elements. According to Ref. [5, 8] the influence of carbide-forming elements, including chromium, on the early stage of tempering depends mostly in maintaining the supersaturation of α solution with carbon, i.e. delaying of martensite decomposition by decreasing the diffusion rate of carbon in iron. Chromium increases also the thermal stability of ε carbide, what results in the increase of start temperature of cementite precipitation [8].

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The Ref. [7] contains a quantitative evaluation of influence of alloying elements: manganese, chromium, silicon, vanadium and nickel, on the early stage of tempering of hypereutectoid steels containing 0.3÷0.5% C, while in Ref. [9] there is an evaluation, in a quantitative manner, the effect of carbon, within the concentration range from 0.10 to 1.25%, on tempering in steels with constant concentration of chromium, silicon and nickel. The results have shown the complexity of an impact of the alloying elements on this stage of tempering. This influence has been dependent not only on carbon content but also on a "background" of the other alloying elements.

The research [7, 10] has proved that at carbon concentrations about 0.5% and increasing chromium concentration from 0.33 to 17.20%, together with a weak "background" from other alloying elements, the temperature of contraction start (ε_s) associated with the first stage of tempering (likely due to the beginning of ε carbide precipitation) changes from about 45 up to 60°C. The temperature of the end of this contraction (ε_f) changes within the range from 240 to 275°C. The higher is the concentration of chromium the wider is the temperature range of ε carbide precipitation. The temperature of the highest precipitation intensity during the first stage of tempering (ε_{max}) changes within fairly narrow range, i.e. from 150 to 160°C. Along with an increase of chromium concentration from 0.33 to 17.20% the intensity of precipitation during the first stage of tempering systematically and significantly decreases.

The study carried out on the second group of alloys containing about 0.3% of carbon and the chromium concentration within the range from 0.3 to 1.18% together with strong "background" from silicon, manganese, nickel and molybdenum has shown that, when these elements are present, the chromium practically has no influence on the early stage of tempering. The appearance of contraction is determined primarily by carbon concentration, while chromium seems to increase this contraction, however only in alloys with strong "background" from other elements.

The present paper, is the continuation of our previous research [7, 9, 10]. On the basis of dilatometric examinations and fracture toughness tests, a quantitative evaluation of chromium influence on the early stage of tempering of two steels with the same carbon content (about 1.1%), different concentration of chromium, 0.10 and 1.23% respectively, and constant concentration (weak "background") of other alloying elements has been examinated.

The results of dilatometric examinations of hypereutectoid steels supported with the results of their fracture toughness tests (K_{IC}) for selected tempering temperatures might be used for a correct design of chemical compositions and heat treatment technology of new grades of tool steels, which are anticipated to be subjected to low-temperature tempering only.

2. Research material

Two hypereutectoid steels have been selected for the present investigation. The first was a C110 carbon tool steel while the other one was a 115Cr5 steel [10], which differed from the first one in chromium content mainly.

The steels have been prepared by Metallurgical Experimental Plant "Mikrohuta" in Dąbrowa Górnicza. The material for tests has been received from 40 kg ingots melted in an open industry furnace and forged subsequently into rods with 25×35 mm cross section.

Chemical compositions of steels selected for tests are presented in Table 1.

TABLE 1

Chemical composition of the investigated steels, % by mass

Element / Steel	C	Cr	Si	Mn	P	S	Ni
C110	1.10	0.10	0.20	0.02	0.015	0.015	0.02
115Cr5, [10]	1.15	1.23	0.21	0.03	0.009	0.014	0.02

3. Experimental procedure

The examination of chromium influence on the early stage of tempering of hypereutectoid steels has been carried out with dilatometric method using Adamel DT1000 dilatometer.

The ϕ2×12 mm samples of tested alloys have been first heated in argon atmosphere at the rate of 3°C/s to austenitizing temperatures $T_A = A_{Ccm}+50°C$, i.e. 950°C – for the C110 steel and 930°C – for the 115Cr5 one (that is within homogeneous austenite), than sustained at these temperatures for 20 minutes, and after that cooled at the rate higher than critical one (in water) down to the room temperature.

The samples quenched like that were then heated in dilatometer to the temperature 700°C at the following rates: 35; 15; 5; 1; 0.5; 0.1 and 0.05° C/s.

Digitally recorded dilatograms of heating have been differentiated, what resulted in the possibility of quite precise determination of the temperatures of the beginning and the end of the first stage of contraction during tempering, i.e. ε_s and ε_f depending on the rate of heating.

In order to increase the analysis accuracy of temperature range, in which the first stage of contraction occurs, the analysis of dilatograms was limited to the temperatures from 20°C to 500°C. Within this range there were visible on dilatograms were two contraction ranges, i.e. the first one – connected with precipitation of ε carbide from martensite and the second one – connected with cementite precipitation. Only the first stage of contraction has been analyzed.

Three characteristic temperatures of this contraction have been determined numerically:

- temperature of contraction start (beginning of differential decrease) – ε_s;
- temperature of highest intensity of contraction, i.e. a point at which the first derivative reaches minimum, and on dilatograms there is a point of inflexion – ε_{max};
- temperature of a point at which the first derivative reaches maximum again, i.e. the temperature of the end of first contraction stage – ε_f.

For both alloys there were constructed original dilatograms of heating (at the heating rate 0.05°C/s) in configuration $\Delta L/Lo = f(T)$ along with corresponding differential curves in configuration $\Delta L/Lo/\Delta T = f(T)$.

In order to analyze more precisely the early stage of tempering also the fracture toughness of both steels at selected tempering temperatures has been examined, i.e. 200°C – for C110 steel and 205°C – for 115Cr5 steel, after previous quenching the samples from a temperature of 930°C – 115Cr5 steel and 950°C – C110 steel (i.e. from homogeneous austenite range). The austenitizing time of the samples for these tests was 45 minutes, and the quenching have been conducted in water. Tempering time was 2 hours. Austenitizing and tempering has been performed in Carbolite RHF 16/19 induction furnace.

Fracture toughness of C110 and 115Cr5 steels has been determined by means of linear elastic fracture mechanics (K_{Ic} test). Fracture toughness test was performed in accordance with ASTM Standard EI 399-74. During the test the force as a function of notch edges spacing has been recorded. The test has been conducted on three-point bent samples with dimensions of 7.4×14.7×70 mm having a 1 mm wide notch in the middle of the length and 5.3 mm deep. The samples have been made with heat treatment allowance, which was flat leveled using a grinder. On the mechanical notch tip a 2 mm fatigue precrack has been made. The samples prepared in this manner have been bent until fracture, in special grip jaw, of computer controlled Instron testing machine. On the basis of diagrams recorded during the test the values of K_{Ic} has been determined, verifying each time if the sample met the requirement for plain strain state.

For the measurement of total depth of mechanical and fatigue notch an optical microscope has been used.

The fractographic study has been performed on fractures of samples used for K_{Ic} determination. The fracture surfaces have been observed using Hitachi 3500N type SEM microscope.

Hardness of samples in quenched state and of the samples used for determination of fracture toughness (K_{Ic}) has been Vickers tested, using the load of 294 N (30 kG).

Microscopic observations of C110 steel samples in quenched state have been preformed using Zeiss Axiovert 200MAT optical microscope.

4. Results and discussion

Figure 1 presents the microstructures of C110 and 115Cr5 steels after quenching in water from homogeneous austenite range. There are martensite plates and bright areas of retained austenite visible in the C110 steel structure (Fig. 1a). Macroscopic hardness of the sample quenched in that way is 780HV30.

The structure of 115Cr5 steel sample [10] (Fig. 1b) is also composed of martensite with retained austenite and its hardness after quenching from homogeneous austenite range (T_A=930°C) is 752 HV30.

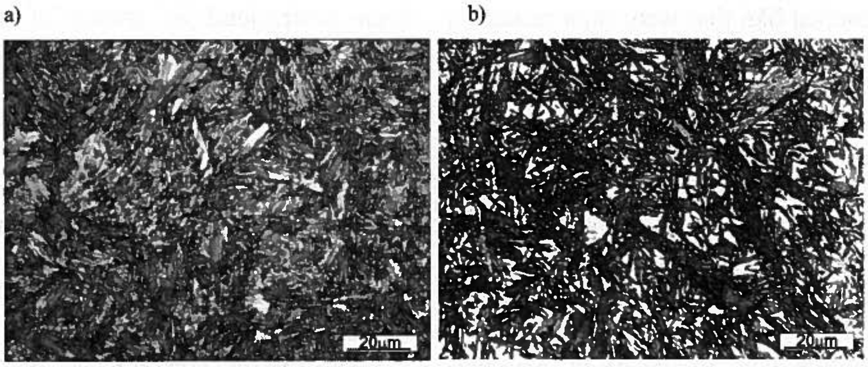

Fig. 1. Microstructures of water-quenched steels: (a) C110 – austenitizing temperature 950°C, (b) 115 Cr5 – austenitizing temperature 930°C

Figures 2 and 3 present heating dilatograms (at the rate of 0.05°C) to 500°C along with corresponding differential curves of C110 steel (Fig. 2) previously quenched from 950°C and 115Cr5 steel (Fig. 3) previously quenched from 930°C.

The analyzed heating dilatograms and the corresponding differential curves (Fig. 2, 3) have similar nature. For both steels, during the first stage of tempering, on heating dilatograms there has been noticed a strong contraction of the samples, probably connected with ε carbide precipitation, what is typical for medium- and high carbon steels. The temperature of precipitation start has been denoted as ε_s, and the temperature of the end as ε_f.

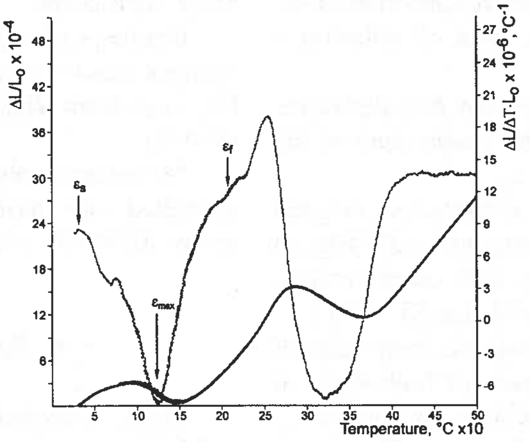

Fig. 2. Example of the dilatogram $\Delta L/L_0=f(T)$ recorded during heating up step (V=0.05°C/s) of a tempered specimen made of the C110 steel, first differentiate curve $(\Delta L/\Delta T)/L_0=f(T)$ and method of determination of the ε_s, ε_f, ε_{max} temperatures

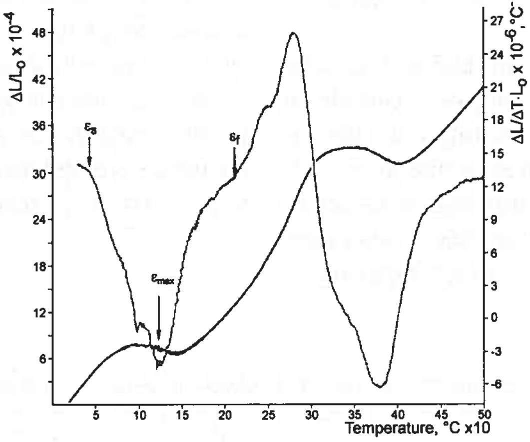

Fig. 3. Example of the dilatogram $\Delta L/L_0=f(T)$ recorded during heating up step (V=0.05°C/s) of a tempered specimen made of the 115Cr5 steel, first differentiate curve $(\Delta L/\Delta T)/L_0=f(T)$ and method of determination of the ε_s, ε_f, ε_{max} temperatures

Table 2 contains the temperatures of start and the end of ε carbide precipitation (ε_s and ε_f) read out from heating dilatograms (within the whole test range of heating rate, i.e. 0.05 – 35°C/s) and the temperature of highest intensity of precipitation during early stage of tempering (ε_{max}) of C110 and 115Cr5 steel.

TABLE 2

ε_s, ε_f and ε_{max} temperatures at the early stage of tempering as a function of the heating rate of the quenched C110 and 115 Cr5 steels

Heating rate [°C/s]	C110			115Cr5		
	ε_s, ε_f and ε_{max} temperatures [°C]					
	ε_s	ε_{max}	ε_f	ε_s	ε_{max}	ε_f
0.05	50	120	200	50	130	205
0.1	50	125	205	50	140	230
0.5	50	130	205	–		
1	60	155	225	60	165	255
5	70	170	250	75	185	270
10	80	190	260	85	195	280
15	–			95	200	290
35	100	205	280	100	215	320

In the case of C110 steel (compare Fig. 2 and Table 2) for heating rate of 0.05°C/s the beginning of sample contraction, which has been assumed as precipitation start of the carbide is observed at 50°C, while for the rate of 35°C/s at 100°C. The temperature of carbide precipitation end (ε_f) is 200°C (for the lowest heating rate) and 280°C (for the highest heating rate) respectively. The highest intensity of ε carbide precipitation during early stage of tempering of this steel (measured as sample contraction magnitude) is observed for heating rate of 0.05°C/s and it occurs at 120°C (Fig. 2). With the increase of heating rate the intensity of precipitation (contraction magnitude) decreases, however, the temperature corresponding to the maximum of precipitation intensity rises. For the highest heating rate (35°C/s) it is about 205°C (Table 2).

In the case of 115Cr5 steel containing 1.23% of Cr heated with the rate of 0.05°C/s the beginning of ε carbide precipitation is observed, like in C110 steel, at 50°C, while for the rate of 35°C/s at 100°C (Fig. 3, Table 2). The temperature of ε carbide precipitation end (ε_f) is 205°C for the lowest and 320°C for the highest heating rate, respectively. The highest intensity of ε carbide precipitation during early stage of tempering of 115Cr5 steel is observed for heating rate of 0.05°C/s and it occurs at the temperature of 130°C (Fig. 3). With the increase of heating rate the intensity of precipitation (measured as for C110 steel i.e. contraction magnitude) decreases, however, the temperature corresponding to the maximum of precipitation intensity rises. For the highest heating rate (35°C/s) it is about 215°C (Table 2).

As the Table 2 shows, with the increase of heating rate, for both steels, there is observed a shift towards higher values of temperatures: start, end and of highest precipitation intensity of ε carbide, present during early stage of tempering.

Within the heating rate range from 0.05 to 1°C/s the temperatures of precipitation beginning of ε carbide in both steels are similar. For each of heating rates the increase of chromium concentration in austenite to the value of 1.23% results in the shift towards higher values of highest intensity temperature (ε_{max}) and the temperature of ε carbides (ε_s) precipitation end during tempering.

Table 3 shows the results of hardness (HV30) and fracture toughness tests (K_{Ic}) of C110 and 115Cr5 steel samples, quenched in water from homogeneous austenite range, and subsequently low-temperature tempered at selected temperatures corresponding to the temperature of ε carbide precipitation end during heating (at the lowest rate of 0.05°C/s) from quenched state.

TABLE 3

Results of hardness measurements and fracture toughness after heat treatment of investigated steels

Steel	Heat treatment	Hardness	Fracture toughness (K_{Ic}) [$MNm^{-3/2}$]
		*HV*30	k_{Ic}
C110	950°C/45min./quenched in water + 200°C/2h/cooled in air	730	19.20
115Cr5	930°C/45min./quenched in water + 205°C/2h/cooled in air	720	14.90

The analysis of the data from Table 3 indicates that higher resistance to crack propagation after quenching from T_A=950°C and subsequent tempering at 200°C was obtained for the C110 carbon steel. With the hardness of 730 HV (on the sample surface) the fracture toughness (K_{Ic}) for this steel was 19.20 $MNm^{-3/2}$.

Figures 4 and 5 present fracture micrographs of samples used for determination of fracture toughness (K_{Ic}) of C110 steel quenched in water from homogeneous austenite range following by tempering for two hours at 200°C (Fig. 4) and of 115Cr5 steel also quenched from homogeneous austenite range and further tempered at 205°C (Fig. 5).

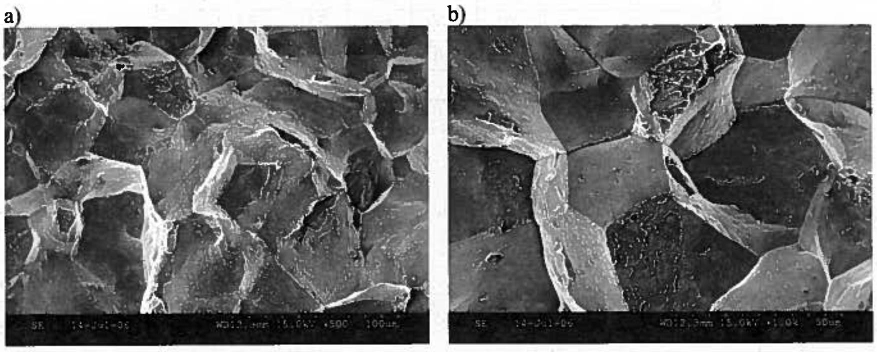

Fig. 4. Fractographs of the fracture toughness C110 steel specimen, water-quenched from 950°C and tempered for 2 hours at 200°C (Magnification: a – 500×; b – 1000×)

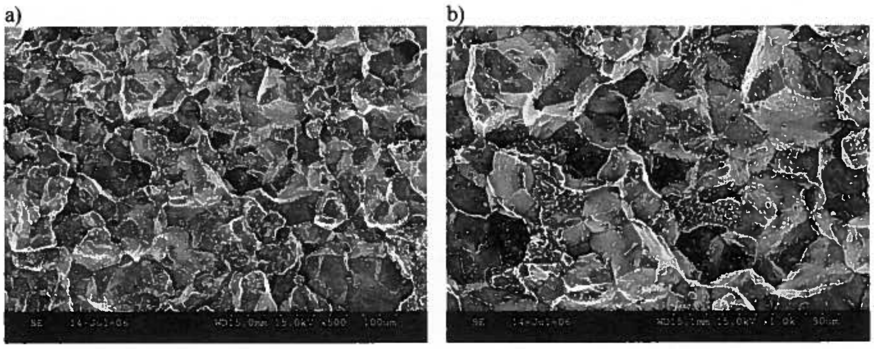

Fig. 5. Fractographs of the fracture toughness 115Cr5 steel specimen, water-quenched from 930°C and tempered for 2 hours at 205°C (Magnification: a – 500×; b – 1000×)

The fractures of C110 and 115Cr5 steel samples quenched in water from homogeneous austenite range and after that low-temperature tempered presented in Fig. 4 and 5 demonstrate similar characters. They are intergranular with small fraction of quasi-cleavable transcrystallic fracture. The presence of quasi-cleavable transcrystallic fracture is particularly well visible in the 115Cr5 steel. Fracture comparison of C110 and 115Cr5 steel samples points out to the significant differences in grains size of former austenite in both steels.

5. Conclusions

The results obtained allowed to formulate the following conclusions:

1. Dissolution of 1.23% of chromium in austenite practically does not have any effect during tempering on the temperature of the sample contraction start (most likely connected with ε carbide precipitation (ε_s)).
2. The increase in the concentration of chromium in the solution to 1.23% shifts the maximum of precipitation intensity of ε carbide (ε_{max}) and the end of it precipitation (ε_f) towards higher temperatures.
3. Fracture toughness (K_{Ic}), determined in the static bend test, is higher for low-temperature tempered (200°C), previously quenched from homogeneous austenite range C110 carbon steel.
4. The fracture surfaces of C110 (0.10% Cr) and 115Cr5 (1.23% Cr) steel samples used for KIc examination demonstrate similar characters. They are intergranular with small fraction of quasi-cleavable transcrystallic fracture.
5. In order to more precisely investigate the transformations occurring during early stage of tempering one should carry out analogous research on model alloys, applying to the influence of carbon in steels with low chromium concentration (i.e. 1.23%). It is intended to carry out such research in the future.
6. The results obtained in this paper have very high cognitive significance and in the future it may be possible to use them for elaboration of detailed heat treatment technology of new tool steels, which are anticipated to be subjected to low-temperature tempering only.

REFERENCES

[1] R. W. K. Honeycombe, H.K.D.H. Bhadeshia, Steels, Microstructure and properties, 2nd ed., London, 1995.

[2] M. Blicharski, Inżynieria Materiałowa. Stal, WNT, Warszawa, 2004.

[3] W. C. Leslie, The Phisical Metallurgy of Steels. International Student Edition, 1982.

[4] Y. Hirotsu, S. Nagakura, Acta Metallurgica **20**, 645 (1972).

[5] Steel – A Handbook for Materials Research and Engineering, V1 Fundamentals, VDE, Berlin-Heidelberg-New York- London-Paris, 2004.

[6] A. K. Sinha, Physical Metallurgy Handbook, The McGraw-Hill Companies, Inc., 2003.

[7] J. Pacyna, P. Bała, R. Dąbrowski, Wpływ pierwiastków stopowych na wczesne stadium odpuszczania stali – Materiały Konferencyjne "Polska metalurgia w latach 2002-2006", Kraków, 2006.

[8] J. Nutting, Hutnik **12**, 623 (1969).

[9] R. Dąbrowski, J. Pacyna, P. Bała, Hutnik. Wiadomości Hutnicze **10**, 449 (2006).

[10] M. Dubiel, Phase transformation in model alloys with chromium imitating the matrix of quenched construction and rustless steels, Ph.D. Thesis, AGH University of Science and Technology, Kraków, 1996.

Received: 17 March 2008.