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CeMn/AlSiO ceramic layers on metallic supports for high-temperature catalytic processes

WŁODZIMIERZ TYLUS[*]

Institute of Inorganic Technology and Mineral Fertilizers, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław

The CeO_2–$Mn/SiO_2Al_2O_3$ coating (also as γ-Al_2O_3 or $AlOOH \cdot H_2O$) on metallic supports was found to be best suited for high-temperature catalytic oxidation of diesel soot. With a thickness of 15–20 μm, the ceramic layer coated by the sol-gel method showed no cracks either before or after a thermal shock. Scanning micrographs revealed a tight contact between coating and substrate. The crystallites of active cerium oxides were uniformly distributed in the top part of the layer. No segregation of Cr or Fe from substrate bulk to surface was evidenced, but – advantageously – it was Al that segregated (surface concentration rose from 14 to 24 wt. %), forming a protective layer on the metal surface and a bond with SiO_2/Al_2O_3 coated by the sol-gel method. Making use of DTA and DTG techniques, the catalytic activity of the coating in the diesel soot oxidation reaction was determined. Two temperature peaks (at 350 °C and 470 °C) corresponding to the maxima of the soot oxidation rate were distinguished.

Key words: *sol-gel; ceramic layer; high-temperature corrosion*

1. Introduction

Three-way catalysts have long been used in spark ignition engines. A major element of such a catalyst is a ceramic washcoat deposited onto a metallic monolith support by the sol-gel method. With compression-ignition engines, however, where emission of particulates (especially from heavy duty engines) creates serious hazards, the problem is far more sophisticated [1–3]. The key point is the need of combining two functions in one device which has to act as a particulate filter and a catalyst reducing the ignition temperature from 550 °C to at least 400 °C [4]. During regeneration, when the soot depositing in the filter undergoes catalytic combustion, the process conditions are extremely harsh (thermal shocks, exhaust gas temperature above 1000 °C).

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[*] E-mail: tylus@itn.pwr.wroc.pl.

The response of the ceramic catalytic coatings to the harsh conditions of regeneration was investigated. The application of the heat-resisting metal foam made of FeCrAl alloy increased noticeably the strength of the filter as compared to the conventional ceramic monolith [5]. Owing to a better thermal conductivity, metal monoliths become easier heated and are easier to handle. This metallic support was covered with ceramic and catalytic layers by the sol-gel method.

A certain part of the study, which was carried out to obtain a catalytic layer resistant to a harsh external environment, involved the following procedures: preparation of the metallic surface of the support [6], preparation of coating mixtures, deposition of the ceramic layer and active substances, as well as laboratory tests and physicochemical characterization of the layers obtained in this way. In the present study, a CeMn/$Al_2O_3SiO_2$ coating is described, which meets relevant requirements and has been prepared by mixing silica sols with Ce- and Mn-impregnated aluminium powders. The layers obtained were tested for resistance to high-temperature corrosion and for catalytic performance (DTA, DTG). The surface was analyzed with AES, XRD and electron scanning techniques.

High-temperature corrosion resistance of both uncoated and ceramic-coated FeCrAl foils was determined by thermal shocks, a well-known method dealt with in metallurgy. The samples were treated by approximately 3000 cycles of alternating heating (10 s at 1200 °C) and cooled to room temperature. The measured weight increment of a sample resulting from the oxidation of the material was regarded as a measure of the resistance to high-temperature corrosion. The oxidation of the metallic substrate is the lesser, the tighter is the contact between the coating and the substrate.

2. Experimental

2.1. Preparation of silica sols

Silica sols were obtained from TEOS (tetraethoxysilane >98%) made by FLUKA. They differed in SiO_2 content, which was achieved by adding appropriate portions of water and ethanol. The best starting compound was found to be the partly hydrolyzed $Si(OC_2H_5)_4$. Following the water addition, some part of the ethoxy groups hydrolyzed to form Si–OH groups. Of these, a certain portion condensed to produce Si–O–Si compounds. Another portion preserved its reactive groups.

$$(\mathrm{Si-OC_2H_5}) + \mathrm{H_2O} \xrightarrow{\mathrm{H^+}} (\mathrm{Si-OH}) + \mathrm{C_2H_5OH} \tag{1}$$

$$(\mathrm{S-OH}) + (\mathrm{HO-Si}) \xrightarrow{-\mathrm{H_2O}} \mathrm{Si-O-Si} \tag{2}$$

On changing the proportion of water, it is possible to obtain products of various storage lives or gelation rates. For example, a sol with a low water content and a 20%

SiO_2 ingredient did not gelify within a 12-month period. The hydrolysis was carried out with a solvent of choice. Water-miscible solvents, e.g. ethanol, ethyl glycol or isopropanol, can be used in a wide range of proportion. The rate of coating, the duration of drying and viscosity depend on the type of the solvent applied. Methanol and ethyl glycol accelerated crosslinking, while isopropanol or butanol retarded it.

2.2. Preparation of catalytic powders

Alumina sols were obtained from aluminium isopropanolate which was synthesized under laboratory conditions via the following reaction:

$$2Al + 6(CH_3)_2CHOH = 2((CH_3)_2CHO)_3Al + 3H_2 \tag{3}$$

The hydrolysis reaction occurred according to the equation

$$2((CH_3)_2CHO)_3Al + (3 + n)H_2O = Al_2O_3\cdot nH_2O + 6(CH_3)_2CHOH \tag{4}$$

With alumina sols, it was also the proportion of water that contributed to their storage lives and gelation rates. However, the gelation rate was less important in that particular case because the AlO(OH) sol was directly used to produce the desired forms of powdered aluminium oxides, γ-Al_2O_3 and boehmite. As a matter of fact, boehmite was found to act much better as a filling material for the washcoats. During annealing, together with SiO_2, boehmite formed coatings firmly attached to the metallic substrate.

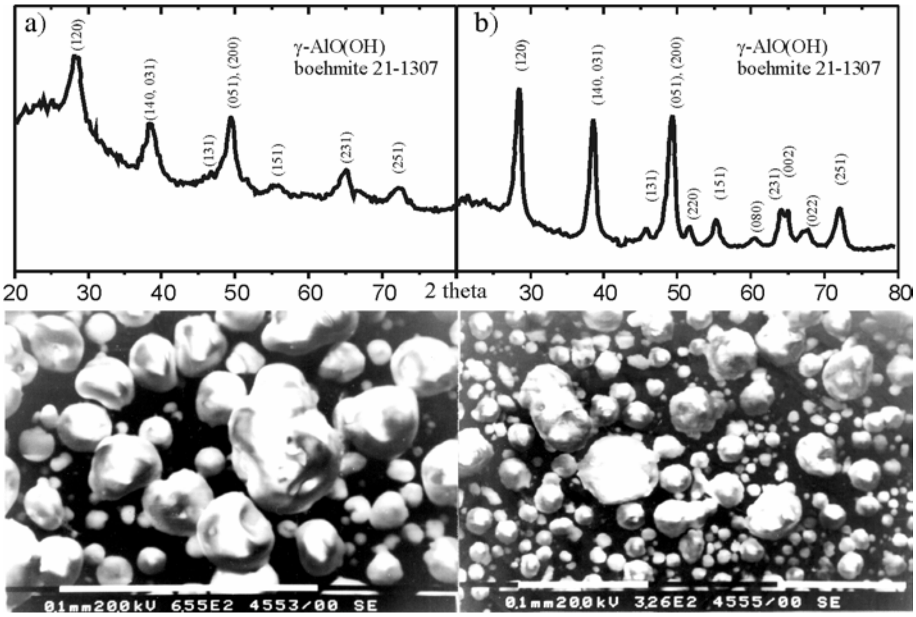

Fig. 1. XRD spectra and micrographs of boehmite powders: a) < 100 μm, b) < 25 μm

The boehmite form of aluminium oxide, AlOOH·H_2O, was obtained by alternating drying at 120–200 °C and ball-grinding of the gelified aluminum sol. Figure 1 shows the diffraction patterns identifying the type of the boehmite: Boehm25 (fraction < 25 μm) and Boehm100 (<100 μm). The Boehm25 peaks are more distinct, which indicates that the particles of Boehm25 are more homogeneous than those of Boehm100. The bottom part of the figure shows the microscopic images of both fractions. Boehm25 was used as a filling agent to improve the tightness of the contact between the SiO_2-based coatings and the metallic substrate.

2.3. Catalytic performance of the powders

Aluminium powders were impregnated with catalytic compounds in the course of diesel soot oxidation. The activities of the metal oxides tested in this work can be arranged in the following sequence:

$$CeO_2 \text{ (from nitrate)} > PbO > La_2O_3 > CeO_2 > V_2O_5 > CuO > Co_3O_4$$

$$> Bi_2O_3 > Mo_2O_3 > NiO > Fe_2O_3 > MnO_2 > Cr_2O_3 > ZnO > MgO > ZrO_2 > WO_3$$

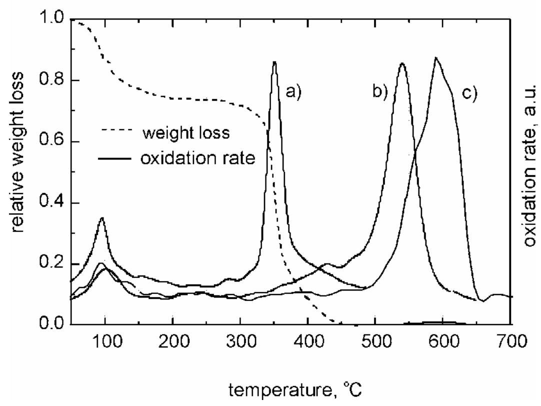

Fig. 2. Curves of oxidation and oxidation rate for diesel soot mixed with CeO_2/Al_2O_3 powder (a), mixed with Al_2O_3 only (b), and for synthetic soot mixed with Al_2O_3 (c)

Figure 2 shows the DTA/DTG plots of diesel soot oxidation over CeO_2/Al_2O_3, where the relative soot mass decrement and the soot combustion rate are related to the temperature-programmed reactor (2 °/min increment). These results were compared with those for diesel soot combustion over pure Al_2O_3 and for synthetic soot, the temperature of the maximum soot combustion rate (mass decrement) being adopted as the temperature of soot ignition. With CeO_2 from cerium nitrate, the ignition temperature amounted to 350 °C. Such a decrease in the soot ignition temperature substantiates the need of incorporating CeO_2 into ceramic catalytic coatings. There are noticeable differences between the diesel soot and synthetic soot. The combustion temperature with synthetic soot approaches 600 °C, whereas that with diesel soot is approximately equal to 540 °C. Apart from water desorption, the curve depicting the combustion of the flame soot is a plane one up to about 520 °C. At the same time, the diesel soot sample has already 'lost' half of its mass, which should be attributed to the presence of soluble organic fractions (SOF) burning at lower temperatures and initiating the ignition of the solid soot fraction. In the majority of instances, an active catalyst influences SOF (which resorb from the surface of the soot particulates at elevated temperatures) and decreases their ignition temperature [7].

Selected powders with an active phase – after thorough mixing with the silica sol of appropriate physicochemical parameters in a homogenizer – were deposited onto a suitably prepared support surface. The support was a heat-resisting steel foil, containing FeCr (23%) Al (5%) with admixed lanthanides.

2.4. Preparation of metallic surfaces

The preparation of the metallic surfaces prior to the deposition of the oxide layers plays an important role. In our study it included the following procedures: degreasing, development of the external surface (in order to increase the adhesion of the layer) and rinsing. The development of the surface was carried out with two methods, by selective etching or roughening. In the first method, the samples underwent thermal etching with mineral acid solutions until a mass decrement of 3 to 7% was achieved. With a 10%H_2SO_4+10g/l HCl mixture at 70 °C, this took about 3 minutes. The homogeneous etching requires an appropriate degreasing as a prior step. Using the etching method together with the developed geometrical surface yielded a selective enrichment with aluminium in oxide form. This supported the adhesion of the deposited oxide layer to the substrate. The samples were then rinsed many times. However, he surface analysis by the Auger electron method revealed the presence of sulfur, which must have penetrated there as a result of the etching operation. Sulfur is a highly undesirable element, as it becomes a high-temperature corrosion centre. For this reason, the pneumatic roughening method seemed to be far more advantageous. Thus, the 100 μm corundum ejected at a pressure of 1.8 atm from a distance of approximately 20 cm was adopted as the optimum procedure. The homogeneous surfaces obtained in this way were cleaned pneumatically to remove the abrasive material, and then rinsed in an ultrasonic washer.

2.5. Catalytic coatings and their resistance to high-temperature corrosion

Metallic surfaces were coated in single or multiple operations by immersion or via a pneumatic shower. All samples were dried at 20 to 90 °C for 48h and then calcined in a temperature-programmed oven up to 750 °C. High-temperature corrosion resistance was tested according to a procedure described elsewhere [6].

3. Results and discussion

In Figure 3, the dependence of the relative mass increment of the optimum catalysts, (57%) Ce–(3%) Mn/(18%) SiO_2 + (22%) Al_2O_3 on the number of thermal shock cycles for various thicknesses of the ceramic coatings is shown. The silica sols prepared were found to be good binders which provided an appropriately tight contact not only with the metallic substrate but also with the catalytic oxides added. These oxides accounted for up to 90% of the total ceramic layer mass. We obtained durable ‘thick’ layers constituting up to 30% of the catalyst mass. These large amounts of active substances are of a great importance in that particular case, because the external geometrical surface alone can be in contact with the soot particulates. In all of the investigated samples, the corrosion was lower than in the reference. According to expectations, thick coatings are best suited for the protection of metallic surfaces. With a 31 wt.% layer, the increment in the catalyst mass (due to the oxidation of the metallic surface) amounted only to 0.2% and was the lowest one determined in the samples under study.

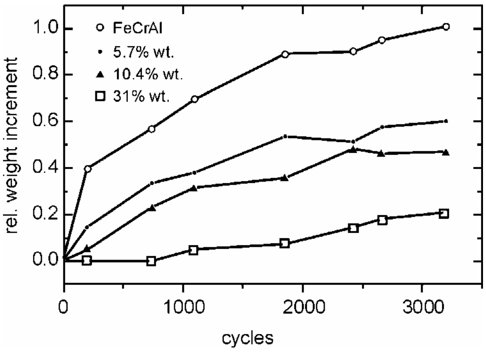

Fig. 3. High-temperature corrosion (oxidation) in thermal shock cycles for various thicknesses of the CeMn/AlSiO optimal ceramic coatings and FeCrAl foil as a reference sample[*]

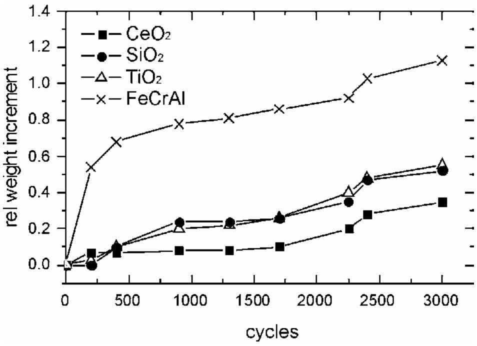

Fig. 4. High-temperature corrosion (oxidation) in thermal shock cycles for various ceramic coatings

Figure 4 characterizes the Al_2O_3 coatings with TiO_2, SiO_2 or CeO_2 admixtures. They were obtained by the shower method, using an AlO(OH) sol solution with the addition of the SiO_2 sol or the TiO_2 sol (or TiO_2 anatase), with the aim to impregnate them with active substances. Each of the three coatings seems to protect the metallic surface sufficiently well against high-temperature corrosion. After 3000 cycles, there was no visible indication of destruction. This finding holds for coatings whose mass did not exceed 3 wt. % of the total catalyst mass. Thicker coatings were comparatively prone to abrasion and cracks already after the initial cycles of thermal shocks.

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[*] Percentage concentration of ceramic coating in the total weight of a catalyst was regarded as a measure of thickness.

The samples displayed a slight mass increment, which fell below 0.6 wt. %. The coating with the CeO_2 additive (20 wt. %) was only moderately better, showing a mass increment of 0.4% compared to the 1.2% increment in the sample with no ceramic layer.

3.1. Electron scanning of the surface

The ceramic layer 15–20 μm thick showed no cracks either before or after a thermal shock (Fig. 5). The micrographs of Fig. 6 display the cross-sections of the CeO_2-Mn/$SiO_2Al_2O_3$ coating. The micrograph 4446 reveals a tight contact between the coating and the substrate (uniform area on the right-hand side).

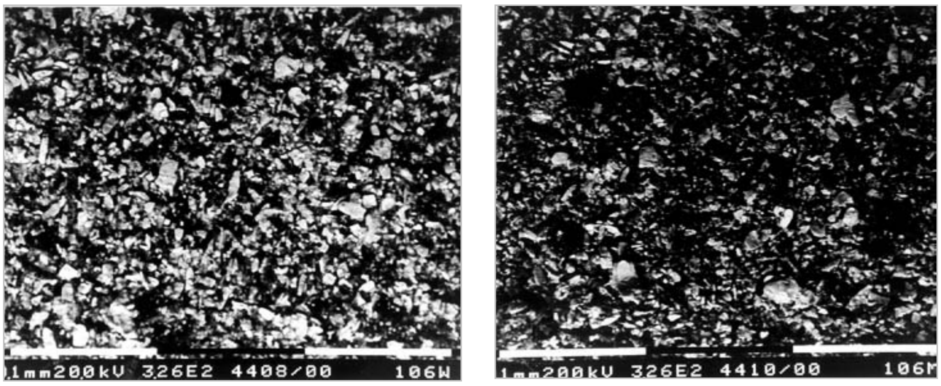


Fig. 5. SEM micrographs of the ceramic layers before (left) and after (right) thermal shocks

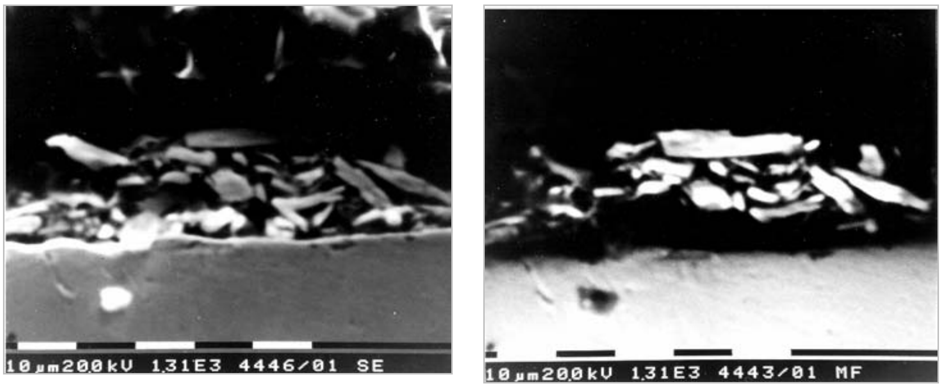
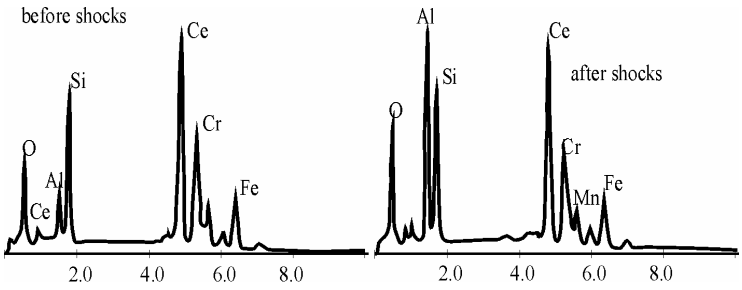


Fig. 6. SEM micrographs of the cross-sections of the CeO_2-Mn/$SiO_2Al_2O_3$ coating

The bright crystallites visible in the micrograph 4443 taken with the material contrast are active cerium oxides uniformly distributed in the top part of the layer. No segregation of Cr or Fe from substrate bulk to surface was evidenced, but – advantageously – it was Al that segregated (surface concentration rose from 14 to 24 wt. %), forming a protective layer on the metal surface and a bond with SiO_2/Al_2O_3 (coated by



Composition	O	Al	Si	Ce	Cr	Mn	Fe
Before shocks	17.9	13.8	10.7	48.5	2.2	1.1	5.8
After shocks	23.3	24.1	9.3	36.1	1.7	0.9	4.6

Fig. 7. XRD spectrum of the CeMn/$SiO_2Al_2O_3$/FeCrAl catalyst surface. Composition (wt. %) of the catalyst surface before and after exposure to high temperature

the sol-gel method). These findings are all evidenced by the spectra (Fig. 7) from XRD analysis.

3.2. Verification of the catalytic protective layer

Making use of the DTA and DTG techniques, the catalytic activity of the coating in the diesel soot oxidation reaction was determined. Soot was spread onto the trap-catalyst directly from the exhaust pipe of an SW 400 ANDORIA diesel engine and was combusted in a temperature-programmed reactor. Two peaks (at 350 °C and 470 °C) corresponding to the maxima of the soot oxidation rate were distinguished (Fig. 8).

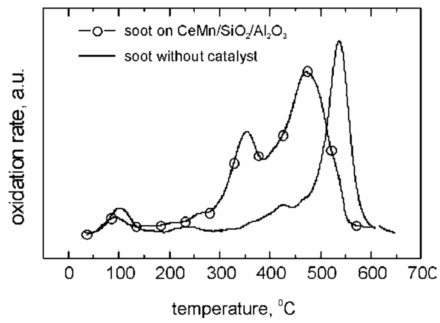


Fig. 8. Curves of oxidation rate for diesel soot spread on the CeMn/$SiO_2Al_2O_3$/FeCrAl catalyst and for diesel soot without any catalyst

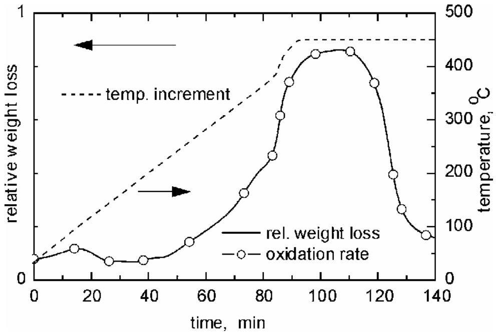


Fig. 9. Curves of oxidation and oxidation rate for diesel soot spread on the CeMn/$SiO_2Al_2O_3$/FeCrAl catalyst at a surface density of 6.5 g/m^2 in a temperature programmed reactor (increment 4 °/min up to 450 °C; flashed line)

This indicates that the soot combustion proceeded first in the tight contact mode and then in the loose contact mode [8]. It should be noted that real exhaust gas temperature to which the trap-catalyst will be exposed hardly ever surpasses 400 °C. To provide a complete oxidation of the soot collected in the filter, it is necessary for the catalyst to act as an igniter so as to initiate the reaction at 350 °C. The heat released in the course of the reaction raises the temperature of the catalyst, thus enabling combustion of the remaining soot portion. With a programmed temperature increment of 4 degrees per minute up to 450 °C and a soot surface density of 6.5 g/m^2_{filter}, soot conversion amounted to 96% (Fig. 9).

4. Conclusions

Considering the promising results of the laboratory tests, prototypes of trap-catalysts (made of FeCrAl foams varying in pore size) were constructed and coated with a catalytic protective layer, Ce-Mn/SiO_2-Al_2O_3 (Fig. 10). They are now tested on the buses of municipal transport.

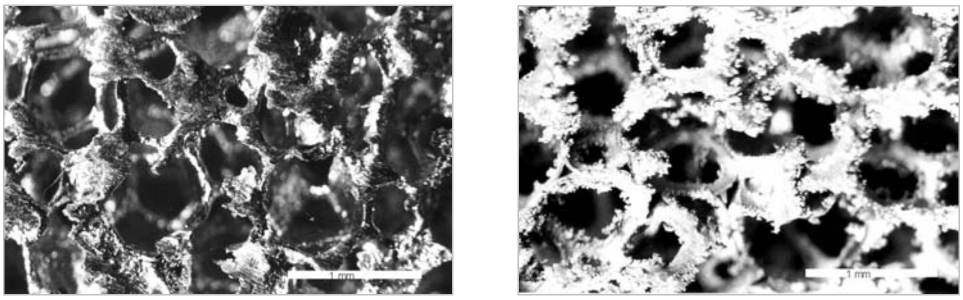


Fig. 10. FeCrAl foam support uncoated (left) and coated with CeMn/$SiO_2Al_2O_3$ layer (right)

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