

Improved Start-Up for the Ammonia Oxidation Reaction

ELECTRICAL HEATING DEVICE FOR PLATINUM-RHODIUM GAUZE CATALYSTS AND NEW PROCEDURE REDUCES EXPLOSIVE HAZARDS AND PLATINUM LOSSES AT START-UP

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The start-up operation in a nitric acid plant is one of the most important stages, from the viewpoint of safety and platinum loss, in the entire ammonia oxidation process. Usually, flame burners using hydrogen or hydrogen-containing gas preheat the platinum alloy gauze catalyst to the operating temperature. However, there are disadvantages and peculiarities in this method of initiating the start-up reaction. These are discussed here and a new electrical heating device and a new technique are described for preheating the platinum alloy gauze catalyst. The device and technique are free of these disadvantages, and together they reduce the explosive hazard and platinum losses during start-up. Results from their commercial utilisation over a 12-year period at various nitric acid plants are described.

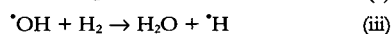
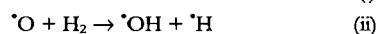
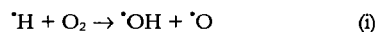
The ammonia oxidation process has been used in nitric acid production since the start of the twentieth century. As early as 1902, it was shown that the most promising catalysts for this process were platinum alloys (1) and the optimal form for the catalyst was found to be gauze, fabricated from wires of diameter 0.06–0.09 mm, and placed in stacks (2). Today, knitted or woven platinum alloy gauze is used as the catalyst for the production of nitric acid and prussic acid, and also to produce hydroxylamine sulfate.

The initial stage of the ammonia oxidation process for nitric acid production begins when an ammonia:air mixture (AAM) at a temperature of 80–200°C is input into a reactor in which platinum alloy gauzes are installed. The catalyst must be preheated to 250°C prior to the start of the ammonia oxidation in order to change this process into a high-temperature diffusional regime (3). Various techniques are used to preheat the catalyst. In commercial nitric acid plants one of the most applied techniques is to use the heat from burning hydrogen or hydrogen-containing gases. The burners used are in the form of perforated tubes mounted in the reactors near to the gauzes. These burners can either be fixed or rotating. Only 'technological air' (air pumped from a compressor) is

fed into the reactor, as it has been preheated by the combustion gases. When the temperature reaches 600°C (visible red glow) ammonia is mixed with the technological air (4). Hydrogen combustion is continued until the ammonia oxidation process is observed to start. This apparently simple start-up operation will be looked at in detail.

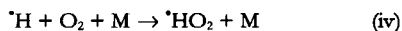
Hydrogen Oxidation by Oxygen Using Burners

The homogeneous oxidation of hydrogen using oxygen which takes place during start-up in an ammonia oxidation reactor has been studied for a long time (5) and can be described by a number of chain reactions which take place in the free space above the gauzes in the reactor, as well as on the catalyst surface. The main reactions can be described as follows:

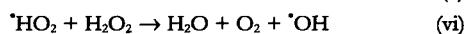
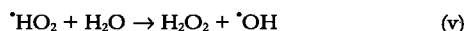


The outcome of reactions (i), (ii) and (iii) is an increase in the concentration of free hydrogen atoms which occurs as a geometric progression. The free atoms $^{\bullet}\text{H}$, $^{\bullet}\text{O}$ and the $^{\bullet}\text{OH}$ radicals are active intermediate products of the chain reactions

and easily recombine either in the volume or at the surface of the catalyst to eventually become the stable molecules: H₂O, O₂ and H₂O₂. However, for the hydrogen oxidation process the recombination reactions of ^{*}H atoms are of main interest:



where M is an arbitrary particle. It follows from Equation (iv) that chain breakage of reactions (i) and (ii) in the volume does not result in the formation of a stable molecule. A new type of peroxide radical is formed which contains excessive chemical energy and is a long-lived intermediate product. This ^{*}HO₂ radical undergoes recombination reactions:

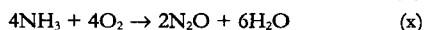
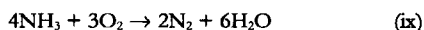
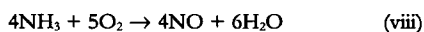


Reactions (v) and (vi) describe processes which occur at the surface of the gauze and produce considerable amounts of heat.

At the same time as the above processes are occurring, the heterogeneous oxidation of the hydrogen – which did not react according to Equations (ii) and (iii) – is taking place on the platinum alloy gauze surface:



When the temperature of the platinum alloy gauze exceeds 250°C, ammonia oxidation begins (6):



These reactions have different thermal effects which eventually define the temperature of the platinum alloy gauze catalyst.

Drawbacks of Flame Burners for Start-Up of Ammonia Conversion

Some conclusions can be drawn from the above simplified analysis. During the start-up period in a commercial ammonia oxidation reactor when the activity of the platinum alloy catalyst is not high enough, the use of flame burners masks the progress of the process towards increased

activity to the desired reaction (viii). This phenomenon bears testimony to an idea that the recombination reactions of atoms and radicals produced by the hydrogen flame on the catalyst surface (Equations (iv) – (vi)) are the dominant reactions in preheating the catalyst. However, these reactions also disable the active centres of the catalyst which are common and not dependent on the chemical character of the combustible gas (in this case hydrogen or ammonia).

Even though Equation (vii) is a promotor reaction with respect to Equation (viii) (7) and although during preheating the surface of the platinum alloy catalyst has a uniform glow, dark spots are often observed on the catalyst surface after the hydrogen to the burners is switched off. Such spots are due to side reactions (Equations (iv) – (vi)) when atoms and radicals from the hydrogen flame recombine. This well-known negative effect increases considerably if the catalyst contains impurities and poisons.

During the start-up period, which sometimes lasts for 10 or more minutes, ammonia passes through unactivated areas of the catalyst surface without being oxidised, while at the active surface areas of the catalyst it is oxidised into nitrogen oxides in the usual manner. On the downflow side of the catalyst this unreacted ammonia reacts with the nitrogen oxides to form nitrite-nitrate compounds of ammonia which tend to collect in stagnant areas of the equipment and can form a hazardous explosive situation. Such explosions have caused breakdowns in nitric acid plants resulting in prolonged downtime. Fatal accidents are also known to have occurred. Using hydrogen as the combustion gas to start-up the ammonia oxidation is also an explosive hazard and this too has caused accidents and breakdown in equipment.

Another considerable disadvantage of flame burners is the so-called 'heat wear' of the platinum alloy catalyst which can result in a burn-out of local areas of platinum alloy gauze during the start-up period. This causes additional platinum losses. Such heat wear of the platinum alloy catalyst, especially in the upper gauze, is induced mainly by local overheating to temperatures above the boiling

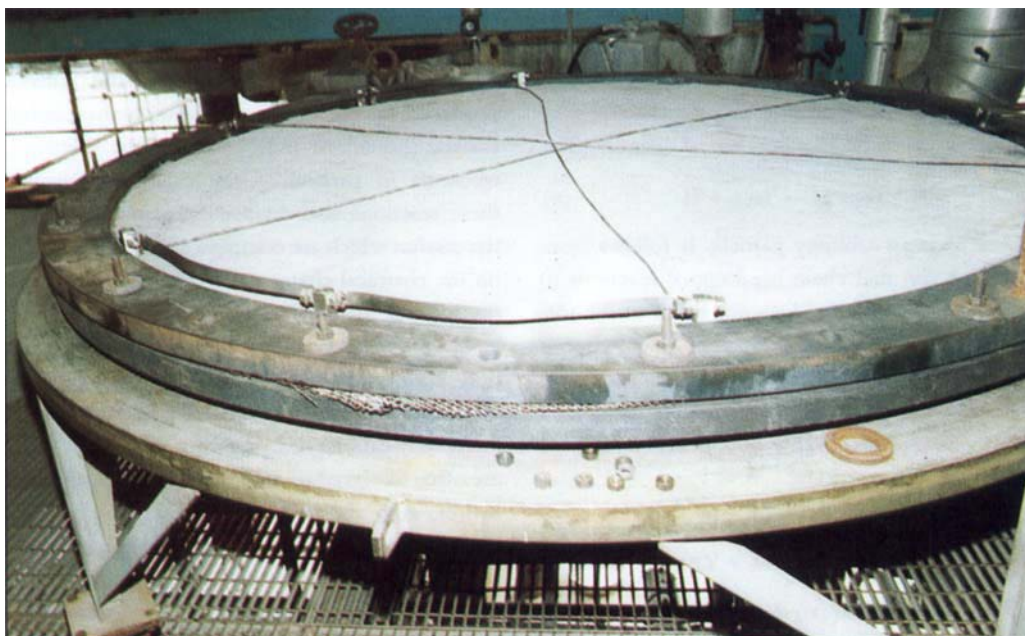


Fig. 1 An assembled pack of platinum-rhodium gauzes, 1.9 m diameter, showing the heating elements of the electrical ignition device mounted radially on the pack surface. This EID is installed in a Sumitomo concentrated nitric acid plant owned by Nitrogenmuvek Rt. in Varpalota, Hungary

points of the platinum materials, due to recombination reactions of atoms and radicals in the hydrogen flame, which have a high thermal effect (Equations (iv), (v) and (vi)). Overheating in localised areas of the platinum alloy catalyst is probably also due to the non-uniform distribution of the hydrogen flame over the gauze catalyst surface, for example, because of imperfect burners and the design of the AAM flow distributors.

An analysis of 50 Russian nitric acid plants has shown that unrecoverable platinum losses occur only during the start-up, due to using hydrogen flame burners. The platinum losses total 0.001 to 0.0015 per cent by weight or, with respect to the productivity of all the plants in Russia, 10 to 12 kg annually (the average daily expected output of each plant analysed is 355 tonnes of nitric acid).

There are other disadvantages when using flame burners for initiating the ammonia oxidation reaction. One is the possibility of ammonia pre-catalysis which can take place on the exterior surfaces of the burners, which receive additional heat as radiation from the hot platinum alloy gauzes. Last, but not least, the start-up reaction

requires a source of pressurised hydrogen, if the ammonia synthesis plant does not provide hydrogen-containing gas from one of its intermediate stages.

New Procedure and Electrical Device for Start-Up of Ammonia Conversion

All the above circumstances defined the research that was devised, directed and participated in at GIAP (8). The main aim of the research lay in finding new engineering solutions which could help towards avoiding the use of hydrogen flame burners in commercial ammonia conversion reactors. The investigations enabled us to create a unique method and devices for electrically heating isolated areas of platinum alloy gauzes, stacked in packs, to initiate the ammonia conversion reaction over the whole surface of the catalyst in the shortest possible time (9, 10).

This new electrical ignition device (EID) uses linear heating elements arranged in a unique manner on the surface of the platinum alloy catalyst which needs to be ignited. The positioning of the heating elements on the surface depends on the

Reactor Performance Data from a Reactor at the JSC Kirovo-Chepetsky Chemical Company	
AAM consumption (STP)	66,000 m ³ h ⁻¹
AAM temperature at start-up	130°C
AAM temperature during stationary periods of operation	200°C
Ammonia concentration	11 vol.%
Number of gauzes in pack	12
Total weight of gauzes in pack	24 kg
Gauze pack operating diameter	1650 mm

plant are given in the Table. The ammonia conversion reaction was started up with values for the current and voltage of 31 A and 180 V, respectively. The time taken for the spread of the reaction from the initial local areas to all the catalyst surface was about 1 minute which was somewhat longer than the calculated 25 seconds. This emphasised the point that effective work using EIDs requires very pure platinum alloy catalyst. Hence, subsequent start-up operations were preceded by special activation of the platinum alloy gauzes, using a technique devised by the authors (11). After such activation the time taken for the initiated localised reaction areas to spread over all the catalyst surface was 20 to 25 seconds. This technique was also successfully applied to activate the fouled gauzes.

Over a two year period, 15 starts-up were performed using the EID. The state of the electrical insulation of the EID and the state of the catalyst surface were inspected each time the plant was shut down. The experience gained was used as the basis for designing commercial EIDs which have two ways of inputting electrical power to the heating elements: through either the upper or lower parts of the reactor, see Figures 3 and 4, respectively.

For the UKL-7-type nitric acid plant, inputting power via the lower part of the reactor is more convenient both for assembly and operation, as there is no need to assemble and dismantle the electric power input device (assembly 2 in Figures 3 and 4) when opening the reactor to replace spent platinum alloy gauzes. This method of assembly

also achieves safe electrical insulation and prevents AAM leakage during reactor operation.

Commercial implementation of EID then began simultaneously at three UKL-7-type nitric acid plants: at JSC 'Dorogobouzh', Dorogobouzh, Smolenskaya obl., Russia; JSC 'Achema', Jonava, Lithuania and at Nitrogenmuvek Rt., Varpalota, Hungary.

During a 6-year period the Hungarian enterprise successfully used EIDs, specially designed for a Sumitomo-designed concentrated nitric acid reactor (0.8 MPa pressure), see Figure 3. The operating diameter of the gauze pack was 1.9 m. Even though the catalyst surface in this Sumitomo reactor is 40

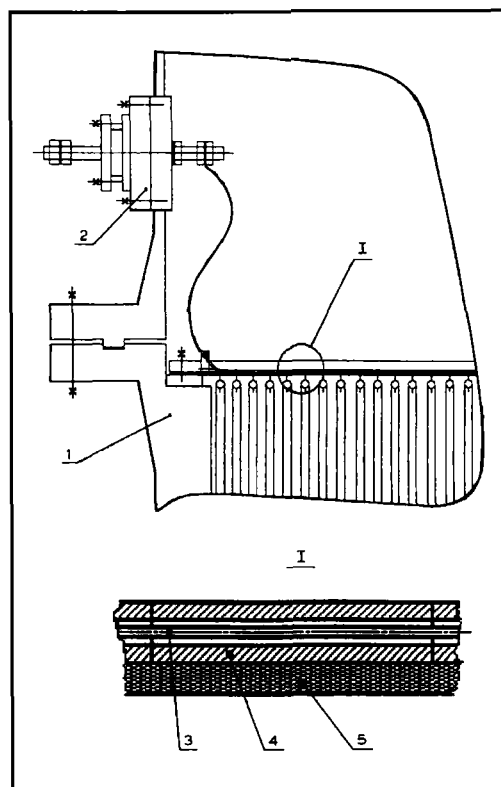


Fig. 3 Schematic of an ammonia oxidation reactor for concentrated nitric acid production. The plant is a Sumitomo design belonging to Nitrogenmuvek Rt. in Varpalota, Hungary. The electrical input is through the upper part of the shell.

- 1 - lower flange of the shell of the reactor
- 2 - electric input device
- 3 - heating wire
- 4 - insulating tubes
- 5 - Pt-Rh gauze pack



Fig. 2 A view of the four parallel heating elements of an electrical ignition device installed in a UKL-7 ammonia oxidation reactor. The elements are ~ 500 mm apart. The UKL-7 is a Russian-designed non-concentrated nitric acid plant and this particular one belongs to JSC 'Achema' in Jonava, Lithuania

performance characteristics of the reactor and on the design of the catalyst pack, see Figures 1 and 2. The heating elements are made from high electrical resistance metal alloy, in wt. %: C < 0.12, Cr = 27, Al = 5, Ti < 1, Fe remainder. They are catalytically inactive and encased in porcelain tubes for electrical insulation. The external diameter of an element is less than 5 mm.

The elements are heated electrically (for example, 220 V at 50 Hz) and monitored throughout. When in use, the EID starts up reactions (viii), (ix), and (x) only on the catalyst surface. The technique we devised for initiating the ammonia conversion reaction, incorporates the following:

- a value for the electric power which evolves per unit length of the electric heating element
- a number of EID switches in the electric circuit
- periods of time when the switches are on, and
- local areas of the catalyst surface which can be served by a single heating element of the EID.

The values of these intervals are determined by the parameters of the actual process of ammonia conversion, catalyst composition and gauze design. Using this new technique gives:

- a reduction to 10 to 60 seconds in the initiation period for the ammonia conversion reaction over the whole catalyst surface, the upper value being for large reactors using platinum alloy gauze catalysts with diameters exceeding 2.5 m, and
- a reduction in the risk of explosions – by cutting down the amount of non-reacted ammonia

passing through the gauzes. This reduction is achieved by decreasing the initiation period and preventing the undesirable recombination reactions of the 'H and 'O atoms and the 'OH and 'HO₂ radicals, as well as H₂ oxidation. These block the active centres of the catalyst which are meant to be converting ammonia to NO.

- An increase in the yield of NO, due to preventing ammonia precatalysis (precatalysis usually takes place on the exterior surfaces of the burners);
- an increase in the service life of the catalyst gauzes by preventing damage caused by heat and by preventing the gauze being fouled by oil and ferrous oxides in the hydrogen-containing gases used in the burners, and
- freedom from using hydrogen-containing gas as a method of starting up the reactor.

Results of Commercial Operations

The first test of commercial EIDs was carried out in 1987 at JSC Kirovo-Chepetsky Chemical Company's mineral fertiliser works (in Russia) using a single-pressure (0.716 MPa) nitric acid plant with a daily output of 355 tonnes of nitric acid. EIDs were installed into a reactor.

The electrical heating components included four linear heating elements arranged at intervals of 400 mm on the catalyst surface. For the first test an autotransformer was provided in the monitoring system to control the power. Data from the

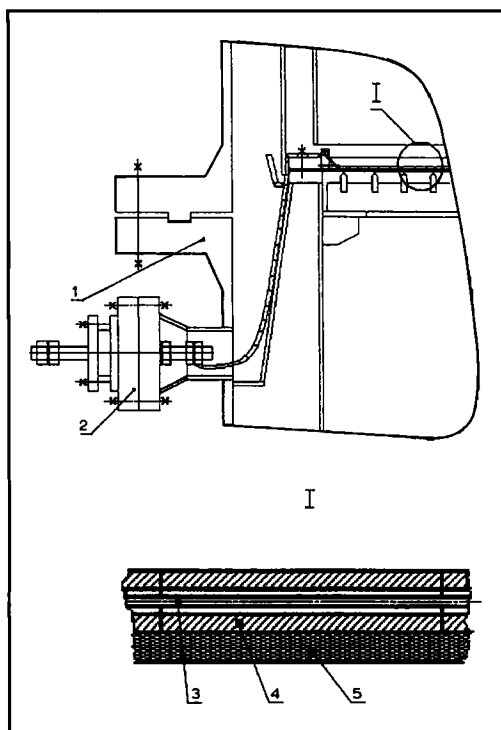


Fig. 4 Schematic of an ammonia oxidation reactor with electrical input through the lower part of its shell. The plant is a 0.716 MPa (UKL-7) single-pressure nitric acid plant being operated in Russia.

- 1 - lower flange of the shell of the reactor
- 2 - electric input device
- 3 - heating wire
- 4 - insulating tubes
- 5 - Pt-Rh gauze pack

per cent larger than the catalyst surface in the Russian UKL-7 reactor, the initiation period for both reactors is almost the same. The start-up operation for the Sumitomo plant occurs under following conditions:

- AAM consumption: 56,000 m³ h⁻¹
- AAM temperature: 200°C
- Ammonia concentration: 8 vol.%

Commercial EID implementation was found to give more advantages to woven gauze than to knitted gauze.

A new commercial EID design has been used in an ammonia conversion reactor at the Grande Paroisse nitric acid plant belonging to Chemical Industries of Northern Greece, in Thessaloniki. This single-pressure plant (0.4 MPa pressure) uses platinum alloy gauze catalyst of operating diameter

2.7 m. The EID for this reactor consisted of four linear parallel heating elements spaced 500 mm apart, as is also shown in Figure 2. Start-up was performed under the following conditions:

- AAM temperature: 170°C
- Ammonia concentration: 5 vol.%

The time for initiating the reaction did not exceed 60 seconds.

The methods and devices described here have been used successfully at nitric acid plants in Russia, Lithuania, Hungary and Greece for over 12 years. Figures 5 and 6 show some results from industrial tests performed at the Russian UKL-7

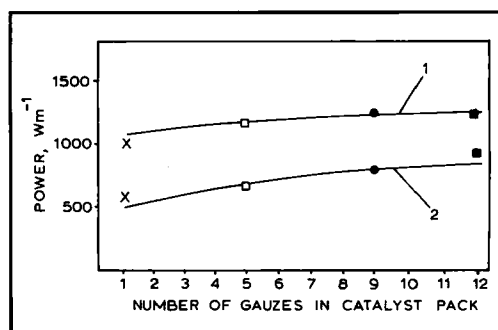


Fig. 5 The dependence of the power evolved per unit length of heating element on the number of gauzes in the catalyst pack for various reactors:

- Grande Paroisse, gauze operating diameter 2.7 m
- Sumitomo, gauze operating diameter 1.9 m
- UKL-7, gauze operating diameter 1.65 m
- x pilot unit, gauze operating diameter 0.05 m

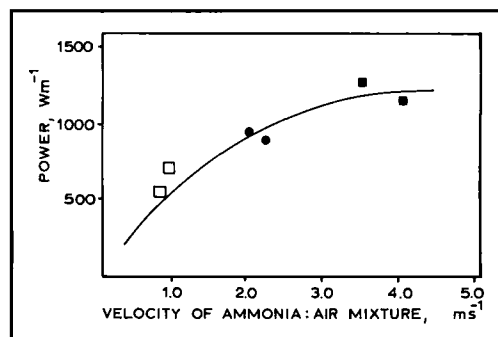


Fig. 6 The dependence of the power evolved per unit length of heating element on the ammonia:air mixture velocity, for various reactors:

- Grande Paroisse, gauze operating diameter 2.7 m
- Sumitomo, gauze operating diameter 1.9 m
- UKL-7, gauze operating diameter 1.65 m

nitric acid plant. The power evolved per unit length of heating element versus the number of gauzes in the catalyst pack is shown in Figure 5, while the power versus linear velocity of the AAM is shown in Figure 6.

Conclusions

The experience gained from implementing commercial EID has produced data which have been used for the design of devices for ammonia conversion reactors working under a wide range of technical parameters. The structure of the catalyst gauze, its size and geometric design are now taken into consideration when simulating an ammonia oxidation reaction spreading over the whole surface. Technical characteristics of the ammonia oxidation process, gauze composition and geometric characteristics of the platinum alloy gauze are also taken into account.

As a result of this research, it may be expected that this new, simple, explosion-free technique for starting-up ammonia oxidation reactors to produce nitric acid, prussic acid and hydroxylamine sulfate will find wide application in the near future.

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Ammonia Reactions on Ruthenium

Studying ammonia (NH₃) decomposition helps in understanding the kinetics of NH₃ synthesis and contributes towards cleaning up NH₃ emissions from sewage and activated sludge. For nearly a century iron catalysts have been used to synthesise NH₃ from hydrogen (H₂) and nitrogen (N₂). However, ruthenium (Ru) materials are now replacing them. The major drawback of Ru catalysts is H₂ poisoning, as H₂ retards the dissociative adsorption of N₂, which is the rate determining step in NH₃ synthesis. As cerium oxide (CeO₂) can stabilise noble metal dispersion and improve H₂ poisoning, it has been used as a catalytic support to promote N₂ activation or NH₃ synthesis.

Scientists from Osaka Municipal Technical Research Institute, Japan, have now used Ru and CeO₂ to prepare a catalyst which decomposes NH₃ with high activity (K. Hashimoto and N. Toukai, *J. Mol. Catal. A: Chem.*, 2000, 161, (1-2), 171-178). The catalyst consists of Ru-CeO₂ highly dispersed in Y-form zeolite (YZ). Ru-CeO₂/YZ works at conditions where YZ and CeO₂ are inactive.

The catalyst contained (in wt.%): 64.0 SiO₂, 19.5 Al₂O₃, 10.2 CeO₂ and 1.9 Ru. The decomposition rate was first order in NH₃. The Ru particles loaded on CeO₂/YZ reduce inhibition of the decomposition rate by H₂.

IR spectra for the catalyst showed that NH₃ decomposition at 300°C proceeded via formation of intermediate species, such as Ru-NH₃, Ru-NH₂, Ru-N₂ and Ru-H on the Ru surface.

Glass Conference in Veliky Novgorod

On 4th to 8th June 2001, the first international conference on 'Markets of Glass Fiber Materials, High-Quality Glasses, Monocrystals and Precious-Metal Equipment for Their Production' is to be held in Veliky Novgorod, Russia. Other topics likely to be discussed include the science and technology of glass and glass fibre, production and applications, manufacture of silicate products and the use of platinum metals equipment. The working languages will be Russian and English.

Further information may be obtained from NPK 'Supermetal', Ozerkovskaya nab., d. 22/24, korp. 2, Moscow, 113184, Russia; Fax: +007 (095) 5334453; E-mail: supermetal@cityline.ru.