APPLICATION OF HIGH ENERGY PLASMA FOR SMART THERMAL PROCESSING

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Nano-science & technology is one of the most important 4 scientific fields regarding the technological policy in Japan. Material processing is now progressing towards more precise and controllable smart stage. Regarding thermal processing, an important key should be the applied heat source. And plasma is fundamentally the most superior heat source, because of high temperature, high energy density, easy controllable, etc. Therefore more precious plasma system has been expected for smart thermal processing. The gas tunnel type plasma system developed by the author has high energy density and also high efficiency. The concept and the feature of this plasma system are explained and the applications to the various thermal processing are described in this paper. One typical application is plasma spraying of ceramics such as Al_2O_3 and ZrO_2. The characteristics of these ceramic coatings were superior to the conventional ones. The ZrO_2 composite coating has the possibility of the development of high functionally graded TBC (thermal barrier coating). Another application of gas tunnel type plasma is surface modification of metals. For example the TiN films were formed in a very short time of 5 s. Finally the development of new type of smart plasma system and application of high-energy plasma to the environmental problems are also discussed.
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1. INTRODUCTION

In order to apply Nano-science & technology to Material Science, the material processing should be developed towards more precise and controllable smart stage. Regarding an applicable heat source, plasma is one of the most superior heat sources, because of high temperature, high energy density, easy controllable, etc. Therefore more precious plasma system has been expected in order to establish a smart thermal processing.

The gas tunnel type plasma system developed by the author has high energy density and also high efficiency [1-3]. The outline of this plasma system and the applications to the various thermal processing are described briefly in the following chapters. One of typical applications is plasma spraying of ceramics such as Al_2O_3 and ZrO_2 [4]. The characteristics of these ceramic coatings by the gas tunnel type plasma spraying were superior to that by the conventional plasma jet.

The ceramic coatings produced by the plasma spraying are effective as thermal barrier coatings (TBC) for high temperature protection of metallic structures because of having high temperature resistance. For example, the zirconia (ZrO_2) coating is used as TBC in hot sections of gas turbine engines and/or diesel engine and in high temperature parts of detonation furnace. It allows the high temperature operation and results to increasing the efficiency of the engine and the durability of the critical components.

While the large porosity and the high melting point is advantage of ZrO_2 coating, the porosity has disadvantage for the adoption under the critical conditions such as high temperature and high corrosion environment. The resistance for thermal shock and high temperature corrosion are important properties in the high performance TBC. New type plasma spray methods are expected for using the excellent characteristics of ceramics such as corrosion resistance, thermal resistance, and wear resistance [5] by reducing the porosity and increasing the coating density.

Now, a high hardness ceramic coating could be obtained by means of the gas tunnel type plasma spraying, which were investigated in the previous study in detail [6,7,8,9]. The Vickers hardness of the zirconia (ZrO_2) coating was increased with decreasing spraying distance, and a higher Vickers hardness could be obtained at a shorter spraying distance. At L=30 mm, when P=33 kW, the Vickers hardness of ZrO_2 coating was about Hv=1200 [10]. This corresponds to the hardness of sintered ZrO_2. Usually, the Vickers hardness of this sprayed coating became 20-30% higher than that of conventional plasma spraying.

ZrO_2 coating formed has a high hardness layer at the surface side, which shows the graded functionality of hardness [11,12]. With the increase in the traverse number of plasma spraying, the hardness distribution was much smoother, corresponding to the result that the coating became denser. For TBC, the spalling of the coating is also very important problem as well as the coating quality.

Another application of gas tunnel type plasma is surface modification of titanium. As the results, TiN films of 10µm thickness were formed in a very short time of several seconds.

In this paper, the performance of high hardness ZrO_2 composite coating was investigated and the merit as TBC (thermal barrier coating) was clarified. The effect of alumina mixing on the Vickers hardness of the ZrO_2 composite coating was also clarified in order to develop high functionally graded TBC. Moreover the adhesive characteristics of such high hardness zirconia-alumina (ZrO_2-Al_2O_3) composite coatings were investigated as well as its mechanical properties. Especially, the influence on the thickness of the zirconia composite coating was discussed.

Finally, other application of high-energy plasma to thermal processing and the environmental problems etc, and. the development of new type of smart plasma system are also discussed.

2. GAS TUNNEL TYPE PLASMA SYSTEM

The schematic of gas tunnel type plasma torch developed by the author is shown in *Fig. 1*. The working gas makes a strong vortex flow in the chamber, and forms low pressure gas tunnel along the torch center axis. This makes plasma production easier, and the strong vortex constricts and stabilizes the plasma jet. The feature of gas tunnel type plasma is shown in Table 1 as compared to the conventional ones. The gas tunnel type plasma system has high energy density and also high efficiency. [1,2,3]

One example of application of the gas tunnel type plasma is the thermal spraying. *Figure 1* shows the gas tunnel type plasma spraying torch. The experimental method to produce the high hardness ceramic coatings by means of the gas tunnel type plasma spraying have been described in the previous papers [4,6,7,8,9].

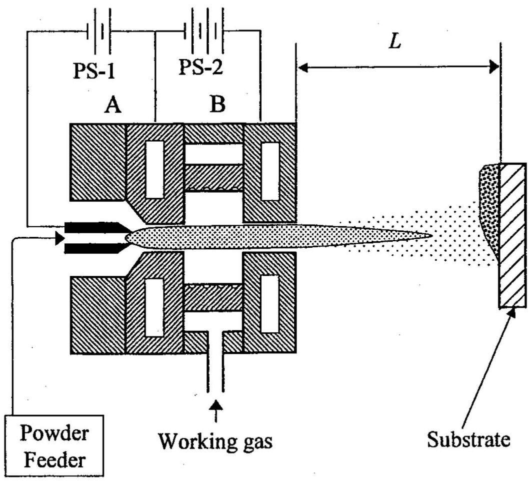

Fig.1. Schematic of the gas tunnel type plasma spraying torch

Table 1. Comparison between gas tunnel type plasma jet and conventional ones

	Gas tunnel type plasma jet	***Conventional ones***
Temperature	15000 K	10000 K
Energy density	10^5 W/cm^2	10^4 W/cm^2
Heat efficiency	80%	50%

The spraying powder is fed inside plasma flame in axial direction from center electrode of plasma gun. So, the spraying powder was molten enough in the plasma, and the plasma spraying for high melting point ceramics is available. The coating is formed on the substrate traversed at the spraying distance: *L*. In this case, the gas divertor nozzle diameter was *d*=20 mm.

This plasma system has many possibilities for the industrial applications to the various thermal processing, such as plasma spraying, surface modification. The typical applications are:

1) Plasma spraying of ceramics (Al_2O_3 and ZrO_2 etc.)
2) Surface modification of Ti materials (Nitridation)
3) Other Applications such as nano-science, functional materials processing technology
4) Application to environmental problems, others.

Moreover, the development of new type of smart plasma system is planned in order to apply to thermal processing of materials and the environmental problems and so on.

3. GAS TUNNEL TYPE PLASMA SPRAYING

3.1. CHARACTERISTICS of GAS TUNNEL TYPE PLASMA SPRAYING

The gas tunnel type plasma spraying can make high quality ceramic coating compared to other plasma spraying method. *Table 2* shows the quality (hardness, porosity, etc.) of the Al_2O_3 coating by gas tunnel type plasma spraying [6,7]. The hardness was like sintered alumina: *Hv*=1,200 and high density, porosity was half of the value of the conventional ones. Even when the working gas is argon and low input of 20 kW, we can obtain enough high Vickers hardness of *Hv*=800.

Table 2. Comparison between gas tunnel type plasma spraying and conventional type for Al_2O_3 coating.

(Input =45kW, Distance = 65-100mm)

	Gas tunnel type plasma spraying	***Conventional ones***
Vickers hardness	1200	800
Porosity	10%	20%

Thus it can be easy to produce the high hardness ceramic coatings by means of the gas tunnel type plasma spraying.

3.2. EXPERIMENTAL PROCEDURE

The gas tunnel type plasma spraying torch used was shown in *Fig. 1*. The experimental method to produce the ceramic coatings by means of the gas tunnel type plasma spraying is as follows. After igniting plasma gun, the main vortex plasma jet is produced in the low pressure gas tunnel. The spraying powder is fed from center inlet of plasma gun. The coating was formed on the substrate traversed at the spraying distance of *L*.

The experimental conditions for the plasma spraying are shown in *Table 3*. The power input to the plasma torch was about *P*=25 kW, and the power input to the pilot plasma torch, which was supplied by the power supply PS-1, was turned off after starting of the gas tunnel type plasma jet. The spraying distance was short distance of *L*= 40 mm.

Table 3. Experimental conditions

Powder:	ZrO2 + Al2O3 Mixture
Traverse number: N	1~30
Power input, *P* (kW):	25~28
Working gas flow rate, *Q* (l/min): 180	
Powder feed gas, *Q feed* (l/min):	10
Spraying distance, *L* (mm):	40
Traverse speed, *v* (cm/min):	25~1000
Powder feed rate: *w* (g/min):	20~35
Gas divertor nozzle dia., d (mm)	20

The working gas was Ar gas, and the flow rate for gas tunnel type plasma spraying torch was *Q*=180 l/min, and gas flow rate of carrier gas was 10 l/min. The powder feed rate of zirconia/alumina mixed powder was *w*=20~35g /min. The traverse speed of the substrate was changed the value from *v*=25 to 1000 cm/min. Also the traverse number was changed 1-30 times. The thickness of the coating was 50~250μm. Also, high speed traverse of *v*=1000cm/min, 30 times.

The chemical composition and the particle size of Zirconia (ZrO_2) and/or alumina (Al_2O_3)powder used in this study was respectively shown in *Table 4*. This ZrO_2 powder was commercially prepared type of K-90 (PSZ of

8% Y_2O_3), and Al_2O_3 powder was the type of K-16T. The substrate was SUS304 stainless steel (3x50x50), which was sand-blasted before using.

The Vickers hardness Hv_{50}, Hv_{100} of the sprayed coatings was measured at the non-pore region in those cross sections under the condition that the load weight was 50g, 100 g and its load time was 15sec 25 s. The Vickers hardness: Hv_{100} was calculated as a mean value of 10 point measurements. The distribution of the Vickers hardness in the cross section of the coating was measured at each distance from the coating surface in the thickness direction. The microstructure of the cross section of zirconia composite coating was observed by an optical microscope.

Table 4. Chemical composition and size of zirconia and alumina powder used (20~80% Al_2O_3 Mixture)

	Composition (wt%)	Size (μm)
ZrO_2	ZrO_2 Y_2O_3 Al_2O_3 SiO_2 Fe_2O_3	
	90.78 8.15 0.38 0.20 0.11	10-44
Al_2O_3	Al_2O_3 Na_2O SiO_2 Fe_2O_3	
	99.8 0.146 0.01 0.01 10-35	

The adhesive strength between the ZrO_2 composite coating and the substrate was measured by using the tension tester original designed. The test piece for adhesive strength was 10mm square and the coating surface side and substrate side was respectively attached to each holder by polymer type glue. The load for the tester could be changed 0~200kg. The kgf/cm^2 was used as a unit for the adhesive strength of the composite coating. The adhesive strength of the ZrO_2 composite coatings was mainly measured in the case of different coating thickness.

4. RESULTS AND DISCUSSION

4.1 EFFECT of ALUMINA MIXING RATIO on THE VICKERS HARDNESS of ZIRCONIA COMPOSITE COATING

Regarding the Vickers hardness on the cross section of ZrO_2 composite coating produced by the gas tunnel type plasma spraying at the same spraying time, the coating thickness was the same and the maximum Vickers hardness of ZrO_2 composite coating was also same. But the graded functionality became much better with increase in the traverse number.

Figure 2 shows the dependence of Vickers hardness of ZrO_2 composite coatings, on the Al_2O_3 mixing ratio R([illegible]). In this case, the coating thickness was approximately 200 μm at P=25 kW, L=40 mm, when the traverse number was two times.

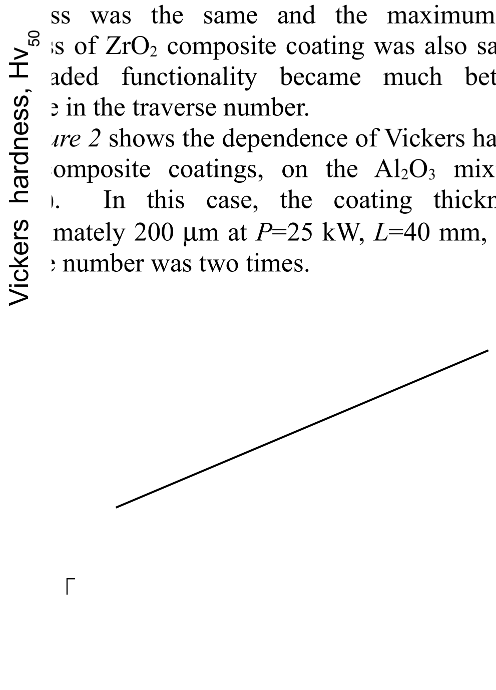

Fig.2. Dependence of Vickers hardness of zirconia composite coating on the alumina mixing rate. 2 times traverse at L=40mm when P=25kW

The Vickers hardness of ZrO_2 composite coating was increased as the increase in the Al_2O_3-mixing ratio. The coating hardness corresponds to the high hardness of Al_2O_3 particles. Namely, the Vickers hardness of Al_2O_3 coating was Hv_{50}=1440.

The hardness distribution of the ZrO_2composite coating has remarkable graded functionality in the case of large Al_2O_3 mixing ratio. Because, the part near the substrate did not change so much, but the Vickers hardness near the coating surface became much higher. This leads to the development of a high functionally TBC.

4.2 EFFECT of HIGH SPEED TRAVERSE on COATING QUALITY

For an increase in the traverse number, the surface temperature of the coating during spraying became higher. Therefore it would be expected that coating density would be increased when the traverse number increases.

Figure 3 is the cross section of composite coating produced by high speed traverse at P = 25 kW, L = 40 mm. Traverse times was 30 times. This speed: 1000cm/min was 10 times higher than normal speed traverse like Fig.2. The thickness was about 150μm. It consisted of 2 different layers, white and gray layers were deposited alternatively. The analysis by EPMA revealed that white is zirconia (ZrO_2) and gray is alumina (Al_2O_3).

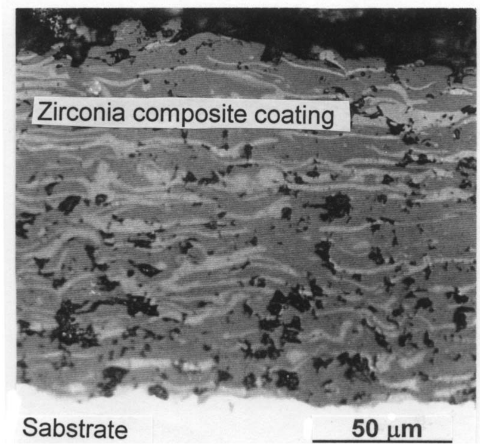

Fig. 3. Microhotograph of cross section of zirconia composite coating. The traverse number was 30 time traverse. Sprayed at L=40mm when P=25 kW

White ZrO_2 layer was a flat sprat of uniform thickness, and embedded parallel in the Al_2O_3 matrix of low melting temperature. The black parts in the coating are pores, and are distributed in the whole coating. The surface side has fewer pores compared to the coating near the substrate. The structure is denser towards the surface of the coating.

Figure 4 shows the distribution of Vickers hardness: Hv_{50} of the zirconia/alumina composite coating shown in Fig.3 (coating thickness: about 150μm). Here, the left side axis is the surface of the coating. The distribution of this composite coating has a highest value in the coating at the surface side: The maximum hardness was near to Hv_{50} =

1300 at the distance from the coating surface of l=40 μm, and decreased linearly like towards the substrate side.

Regarding the effect of traverse number, the uniformity of pores was improved and the deviation of hardness distribution was decreased. Therefore, the high speed and high number traverse improved the grade functionality of coating hardness. It shows the possibility of high performance TBC by the high speed traverse processing.

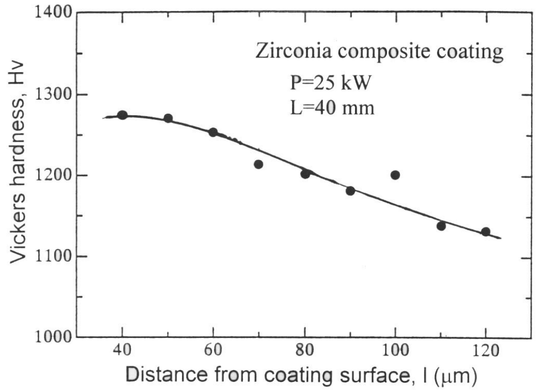

Fig.4. Distribution of Vickers hardness of zirconia composite coating sprayed by 30 times traverse at P=25kW, L=40 mm

4.3 INFLUENCE of PLASMA THERMAL PROCESS on THE COATING

The maximum Vickers hardness of ZrO_2 composite coating was almost the same when the coating thickness was the same. But the graded functionality became much better, and the distribution of Vickers hardness was much smoother as the traverse number was increased. This means that the structure at the surface of the coating was denser by the thermal process of the high energy plasma.

Regarding the microphotograph of ZrO_2/Al_2O_3 coating produced by the gas tunnel spraying on the fixed substrate for 3s spraying time, the coating thickness was about 250 μm, and white and gray layers were deposited alternatively as the same as Fig.3.

The graded functionality of the structure is remarkable, and small pores are distributed disparately in the whole coating while large pores existed near the substrate. The surface side has fewer pores and dense, compared to the coating near the substrate. This was caused by the thermal process of the high energy plasma from the surface side of the coating.

In this case, the Vickers hardness was linearly decreased in the thickness direction towards the substrate side. The dense microstructure led to the suppression of the deviation of the hardness distribution.

4.4 ADHESIVE STRENGTH of ZrO_2 COMPOSITE COATING

The adhesive strength of the ZrO_2 composite coatings was decreased when the thickness was large. In the case of small coating thickness (100μm), the adhesive strength was large: more than 140 kgf/cm^2 for the coating thickness below 100μm. While, the value was F = 100~ 120 kgf/cm^2 when the thickness was more than 200μm. Therefore the thick coating was much easier to break than thin coating, but the adherence was improved when the traverse number was large.

5. OTHER APPLICATION OF SMART PRAZMA SYSTEM

Other application of gas tunnel type plasma is surface modification of metals such as nitridation, carbonization, etc. For example the TiN films were formed in a very short time of 5 s by the irradiation of N_2 plasma jet as shown in *Fig.5.* The thickness of TiN film was 10 μm and the film is high quality (homogeneous and high density). The Vickers hardness was about 1700 on the cross section of the film.

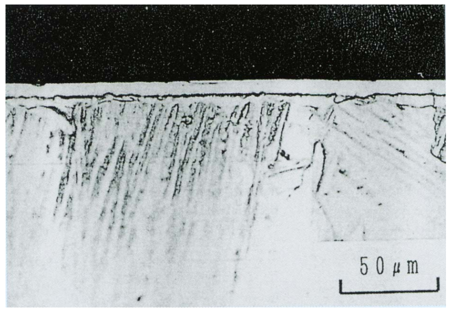

Fig.5. Microhotograph of cross section of TiN film. Ti substrate irradiated at L=70mm when P=20 kW

Now, the temperature increase of weather is global problem for the environmental reservation. Especially CO_2 is one of the resource gases of worse effect. By using the high energy plasma, the recombination and transformation to resources was a good solution for the problem. *Fig. 6* shows the system for CO_2 treatment (recombination and transformation to resources).

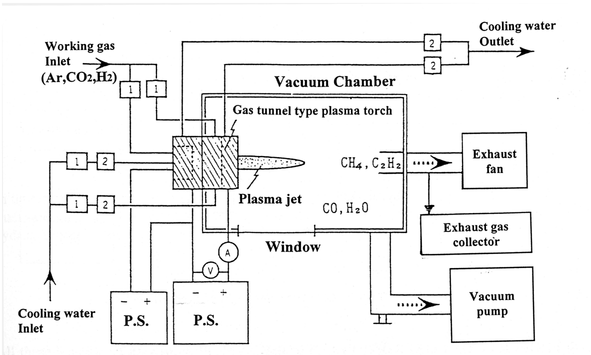

Fig.6. High energy plasma system for the recombination of carbon dioxide

The working gas containing CO_2 is resolved by the plasma and transformed to CO, C, CH_4, C_2H_2, CH_3OH, etc. and produced to the resources as carbon materials and fuels. This method has a great advantage for the treatment of CO_2 gas and also has a possibility for producing new materials such as nano carbon, nano tube, etc.

For the further wide application of plasma system, the development of new type of smart plasma system: confront electrode type plasma jet are conducting in my lab.

CONCLUSIONS

The following results were obtained during the application of the gas tunnel type plasma system developed.

1) The gas tunnel type plasma system has high energy density and also high efficiency as compared to the conventional ones, and can be applied to the various thermal processing.
2) One typical application is plasma spraying of ceramics such as Al_2O_3 and ZrO_2. And the characteristics of these ceramic coatings were superior to the conventional ones
3) The ZrO_2 composite coating has graded functionality on the hardness and the porosity, and has a possibility of the development of high functionally graded TBC (thermal barrier coating).
4) Another application of gas tunnel type plasma is surface modification of metals. TiN films were formed in a very short time of 5 s.
5) The development of new type of smart plasma system, and application of high-energy plasma to the environmental problems are now undergoing.

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ПРИМЕНЕНИЕ ВЫСОКОЭНЕРГЕТИЧЕСКОЙ ПЛАЗМЫ ДЛЯ ВЫСОКОКАЧЕСТВЕННОЙ ТЕРМИЧЕСКОЙ ОБРАБОТКИ

А. Кобаяши

Нано- наука и технология являются одним из четырёх наиболее важных направлений технологической политики в Японии. Сейчас технология обработки материалов выходит на стадию использования более точных и контролируемых высококачественных методов. С точки зрения термической обработки, ключевым элементом должен быть источник тепла. Плазма изначально является наиболее удобным таким источником благодаря своей высокой температуре, высокой плотности энергии, лёгкой управляемости и т. п. Поэтому предполагается использование более совершенных плазменных систем для высококачественной термической обработки. Разработанное автором плазменное устройство на основе газового разряда туннельного типа характеризуется большой плотностью энергии и высокой эффективностью. В представленной работе описаны концепция этого устройства, его особенности и применение для разных видов термической обработки. Типичным применением является плазменное распыление таких керамических материалов, как Al_2O_3 и ZrO_2. По своим свойствам эти керамические покрытия обладают большими преимуществами по сравнению с обычными покрытиями. На основе композитного покрытия с ZrO_2 можно создать многофункциональное высококачественное покрытие, создающее термический барьер. Ещё одним применением плазменного устройства на основе газового разряда туннельного типа является модификация поверхности металлов. Например, плёнки TiN формировались за очень короткое время - 5 с. В заключение обсуждаются также разработки новых типов высокоточных плазменных устройств и использование высокоэнергетической плазмы в задачах, связанных с охраной окружающей среды.

ЗАСТОСУВАННЯ ВИСОКОЕНЕРГЕТИЧНОЇ ПЛАЗМИ ДЛЯ ВИСОКОЯКІСНОЇ ТЕРМІЧНОЇ ОБРОБКИ

А. Кобаяши

Нано- наука і технологія є одним з чотирьох найбільш важливих напрямків технологічної політики в Японії. Зараз технологія обробки матеріалів виходить на стадію використання більш точних і контрольованих високоякісних методів. З погляду термічної обробки, ключовим елементом повинне бути джерело тепла. Плазма споконвічно є найбільш зручним таким джерелом завдяки своїй високій температурі, високій щільності енергії, легкої керованості і т.п. Тому передбачається

використання більш досконалих плазмових систем для високоякісної термічної обробки. Розроблений автором плазмовий пристрій на основі газового розряду тунельного типу характеризується великою щільністю енергії і високою ефективністю. У представленій роботі описана концепція цього пристрою, його особливості і застосування для різних видів термічної обробки. Типовим застосуванням є плазмове розпилення таких керамічних матеріалів, як Al_2O_3 і Zr_2. Завдяки своїм властивостям ці керамічні покриття мають великі переваги в порівнянні зі звичайними покриттями. На основі композитного покриття з Zr_2 можна створити багатофункціональне високоякісне покриття, що створює термічний бар'єр. Ще одним застосуванням плазмового пристрою на основі газового розряду тунельного типу є модифікація поверхні металів. Наприклад, плівки TiN формувалися за дуже короткий час - 5 с. На закінчення обговорюються також розробки нових типів високоточних плазмових пристроїв і використання высокоэнергетичної плазми в задачах, зв'язаних з охороною навколишнього середовища.