HIGH NITROGEN STEELS

METALLURGY UNDER PRESSURE

Tsolo RASHEV

HNS

ACADEMIC PUBLISHING HOUSE
"Prof. MARIN DRINOV"

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ИЗДАТЕЛСТВО НА БЪЛГАРСКАТА АКАДЕМИЯ НА НАУКИТЕ
"ПРОФ. МАРИН ДРИНОВ"

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Translated and edited by
Stefan Semerdjiev

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The monograph considers new materials - high nitrogen steels (HNS) and High-Tech metallurgy - the metallurgy under pressure (MP), the technology of the future. As a result of thermodynamic, kinetic, physical metallurgical, technological and other investigations of the author, a number of original high nitrogen tool-making, stainless, constructional and other types of steels has been produced. Their basic mechanical and technological characteristics exceed the characteristics of conventional (nitrogen-free) analogs by 30-150%, depending on steel grade. Unique properties are observed in some cases as: lack of magnetization without Ni and C alloying; resistance of austenite against magnetic phase formation under conditions of high degree of cold plastic deformation; no intercrystallite corrosion; formation of new types of structures; several times increase of the cavitation resistance, etc.

Moreover, the monograph presents the technological, design and metal science bases of MP and of HNS in particular. The possibilities for alloying of liquid steels and alloys with cheap and effective unconventional elements (N, Ca, Mg, Zn, etc.) instead of the expensive conventional elements (Ni, W, Co, Mo, Nb, V, etc.) have been theoretically and practically proven. Thus, basically new steels and alloys have been produced. The designed and built metallurgical equipment is versatile (operation is possible under atmospheric conditions, vacuum or pressure) and highly ecological, since the processes take place in hermetically sealed spaces. The basic parameters of new industrial equipment are given together with economic data about the new processes.

The monograph comprises an analysis of the main achievements in the field of production and investigation of HNS in the developed countries, taking under consideration the specialized conferences "High Nitrogen Steels", organized in France, Bulgaria, Germany, Switzerland, Ukraine and Russia.

The monograph is of interest for scientists and engineers involved in metallurgical technology, steel-workers, founders, mechanical engineers as well as for graduate and university students attending specialty courses.

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PREFACE

Metallurgical society is recently paying more and more attention to the new type of materials, the high nitrogen steels (HNS) and to the metallurgy under pressure, (MP) considered as a new international trend. After 1988, a number of international conferences on "High Nitrogen Steels" have been held in France, Bulgaria, Germany, Switzerland, the Ukraine. "High Nitrogen Steels 95" is held in Japan, in November 1995.

During the period of 25 years [1-170] extensive work has been conducted in this field in the Institute of Metal Science of the Bulgarian Academy of Sciences (IMS-BAS) in cooperation with the NIPKITOKS Institute, the Metal Technology Corporation and the Kamet Corporation. Interesting and quite unique experience has been acquired, nonetheless, publication work was strongly suppressed until the beginning of 1989. In 1989 a national conference, "High Nitrogen Steels 89" was held in Bulgaria with very wide international participation. It was attended by participants from various countries such as: ex-USSR, France, Germany, Italy, Czechoslovakia, Hungary, and others. Among the 143 presented papers, 130 of them were devoted to steels manufactured in Bulgaria [3, 4, 172].

The author of the present monography has been both scientific advisor and co-author of the majority Bulgarian and joint international presentations. Among the recommendations of the Conference was the present monography to be published aiming to summarize the Bulgarian contribution. The survey with regard to the experience of other countries is rather incomplete, whereas the purchase of foreign literature marked a slump during the transition period after 1989. At the same time, the amount of publications started to increase rapidly, as illustrated by the hundreds of papers presented at the international conferences [171-176, 178, 179].

The characteristics of HNS proved to exceed by 30-150% as compared to the conventional steel grades. Proof was presented for the possibility of efficient and ecologically safe alloying of non-conventional and easily evaporating elements such as Ca, Pb, Zn, Mg, etc., which in combination with nitrogen form a new raw material basis for metallurgy and foundry. Metallurgy under pressure is of quite universal nature. It can be performed as a metallurgical process both at atmospheric conditions and as a vacuum metallurgy process. We consider the metallurgy under pressure as the most promising process which will become a basic (perhaps a major) trend in the progress of metallurgy in the XXI Century. However, the full and rapid progress of this trend in the science and the practice requires pluralism with respect to the theory development, technology and equipment, steel and alloy grades, etc. This is a necessity not only at the initial stages of the trend establishment, but in addition, a necessity for its further progress. There is no method, nor steel grade which can be regarded as "panacea" (a medicine for every disease and for every patient).

The immediate need for clarification of a wide range of problems resulted from the varied effect of nitrogen, its versatile role in combination with the increased pressure, on one hand, and the limited volume of the monography, on the other, does not permit sufficient attention to be paid to all issues, particularly, to the theory and the foreign experience. A separate monography is to be written with the co-authorship of Prof.Dr.A.G.Svjazin devoted to the problems of thermodynamics and kinetics of nitrogen alloying, new phase formation and growth, and the effect of the gas pressure on some metallurgical processes.

The author would appreciate any comments, proposals, and recommendations that could contribute for improvement of the monography.

The author wishes to thank the researchers of the High Nitrogen Steels Division in the Institute of Metal Science of the Bulgarian Academy of Sciences in Sofia (Ph.D. Ch.Andreev, Ph.D. N.Andreev, Ph.D. V.Manolov, Ph.D. G.Zlateva, S.Popov and al.) and the researchers from the NIPKITOKS R&D Institute for technology of high quality steels and equipment in Pernik for their assistance in the research work and their useful advices upon discussing the problems formulation. Thanks are due to the Metal Technology Corporation and Kamet Corporation in Sofia for the assistance in the production development.

The author acknowledges his gratitude to Acad. A.Balevski and Prof. I. Dimov, authors of CPCM and to IMS-BAS for their understanding and support with respect to the development of this trend in metallurgy.

The author would like to express his gratitude to his wife Dr. I.Rasheva for her devotion to long years joint research work, for writing Chapter 3.2 and for her valuable assistance in preparation of this book (monography).

INTRODUCTION

The vigorous scientific and technical progress calls for the necessity of new, high mechanical and service properties of the materials requiring lower energy, material and other expenses for an unit of product. It is well known that the conventional metallurgical technologies and equipment have practically exhausted their potential to solve these complex problems.

The analysis of the results from the theoretical and applied projects in the steel industry shows the incomplete use of the thermodynamic factors. Out of the three thermodynamic factors - chemical composition, temperature and pressure, in fact use is only made of the first two. The potential of vacuum as a negative pressure is reduced theoretically only to the maximum one negative atmosphere (-0.1 MPa), whereas the potential of the positive pressure is practically unlimited (an industrial electroslag furnace operating under 6.4 MPa pressure is working in Bulgaria since 1978). Vacuum has been thoroughly and widely studied. However, the studies on the high pressure potentials are still at initial stage, nonetheless, there is sufficient ground to think of a high technical, economic, and ecologic effect.

Namely, the new opportunity for gas alloying in equipment under gas pressure gave the new impetus toward the old idea [181-183] for nitrogen alloying. It is called old, since the first reports for the use of nitrogen as an alloying element at atmospheric conditions were published long ago - in 1938 by A.M.Samarin et al. [181] in the ex-USSR, and F.Rapatz [182], R.Scherer [183] in Germany. The work has been conducted at atmospheric pressure and the resulted nitrogen concentrations were very low, hence the effect was not great. These studies were uncapable to attract the attention of the metallurgists, therefore, had been abandoned due to the limited nitrogen solubility which has hampered its application at atmospheric conditions even today. This was also influenced by the objectively existing unfavorable effect of nitrogen in some improperly alloyed steels, in particular on their impact strength, plasticity, etc.

The second "birth" of nitrogen as an alloying element is marked by the methods and equipment for nitrogen alloying under pressure developed in some countries. This had created principally new conditions enabling to reach high nitrogen concentrations which are of great interest to the industry and the production of the so called "high nitrogen steels" (HNS). That is why it was pointed out in an editor's note to an article published in 1978 in the Soviet journal "Metal Science and Metal Heat Treatment" [186]: "The high nitrogen steels are principally new materials". And we can add to the statement above: nitrogen occurs to be a brand new alloying element.

The famous Hippocrat has once said "Dose makes the poison". In our case we may say that the dose makes the medicine, which translated to our case may sound: the dose makes the nitrogen an alloying element.

The worldwide interest to the subject is well demonstrated by the following international conferences:

HIGH NITROGEN STEELS 88, held in Lille, France [171]

HIGH NITROGEN STEELS 89, held in Varna, Bulgaria [172]
HIGH NITROGEN STEELS 90, held in Aachen, Germany [173]
NITROGEN STEELS 91, held in Zurich, Switzerland [174]
HIGH NITROGEN STEELS 93, held in Kiev, Ukraine [176]
HIGH NITROGEN STEELS 95, to be held in Kyoto, Japan

The identical title of all above referenced conferences with wide international participation and their devotion to a strictly defined problem is an acknowledgment to be big international scientific and technical event. All that could be explained with the high promising potential of the nitrogen as a strong and inexpensive alloying element for steel production (the industrially produced nitrogen is cheaper than the iron scrap). This could, also, explain the interest of the members of a number of leading companies in the USA, Germany, Japan, the ex-USSR, France, Sweden, Italy, People's Republic of Korea, the Czech Republic, India, etc., attended the conferences, as well as, of the existing associations under the same name "HIGH NITROGEN STEELS" in Germany, Austria and Switzerland.

By the term "high nitrogen steels" we mean steels, produced under gas pressure in which the nitrogen concentration is higher than its standard (normal) solubility. These steels need specific welding methods if liquid phase crystallization takes place during this process.

We have accepted the letter N designating nitrogen to be included in the symbol formula for designation of the steel grade. We have also accepted to write a whole number following the letter to designate the tenths percentage of nitrogen content in steel. The number written after the nitrogen symbol N means that the specific steel has been produced under gas pressure, and occurs to be a specific figure telling the process engineer that he has to take account of the steels specific behaviour in welding technology, heat treatment, etc.

At this stage of development it can be taken for proven that HNS have properties exceeding by 30-150% as compared to those of the nitrogen-free analogues in almost all steel classes.

Among the special merits of the Bulgarian founders is not only innovation of the metallurgy under pressure, applied for manufacturing of high nitrogen steels, but also their design of equipment and establishment of method for bulk alloying in industrial steelmaking conditions. This enables for the efficient use of a number of non-conventional easily evaporating elements such as Ca, Mn, Mg, Pb, Zn, etc., as practically new alloying materials. The alloying with nitrogen and easily evaporating elements opens a new era in the metallurgy progress. The full or partial replacement of Ni, Mo, W, V, Nb, Co and others by nitrogen, means in essence a creation of new raw material basis of metallurgy and foundry. This is not only a matter of reducing the consumption of very expensive alloying elements, but it is rather a matter of improved properties of the existing steels and production of new steels with unique properties.

Today, some of the alloying elements are reasonably considered as cancerogenous (for example Pb), whereas the strong cancerogenous effect of Mn has been proved recently. At the High Nitrogen Steels Symposium held in the

University of Czestochowa, Poland (20-22.VI.1994) Prof. Dr. S.P.Efimenko [177] had announced a new important fact about the cancerogenous nature of nickel, widely used in steels and alloys for domestic appliances and machines for the food industry, and he had mentioned that some countries started to provide dishes and domestic appliances with "nickel-free" labels as a mark for ecological safety. This had been partially observed in the study of the biological compatibility of steels on the Cr-Ni basis for implants announced in 1983 [349].

Our experience in investigation and production of HNS, shows, that the established terms "pressure" and "high pressure" have a negative psychological effect on the majority of metallurgists. It is worth mentioning here, first, that we mean not high pressures, but rather "increased" pressures of maximum 10 MPa, and second, that in other industries high pressures are long ago applied in the regular technologies. For example, the steam turbines operate today at steam pressure of 100 to 240 atm.(10 to 24 MPa), whereas in the synthetic crystals and diamonds production, as well as in the production of other high technically pure materials the gas pressure reaches 20-30 thousands of atmospheres (200 to 300 MPa) [206, 207].

Gas pressure has positive physical and the chemical influence on the process of ingot (product) formation and on the efficient control of the whole complex of technological operations during the pouring process. This has been evaluated by casting [206], and in particular, by development of method for counter-pressure casting [172] whereas a number of methods for counter-pressure casting under omnidirectional gas and hydrostatic pressure, under the influence of electromagnetic and centrifugal forces, a.o., have already been implemented.

The production of high nitrogen steels is highly effective from a technical and economic point of view, but it is also ecologically safe, because the production cannot be carried out if the plant is not closed. Grounds exist to forecast, that pressurized metallurgy (metallurgy under pressure) will be the technology of the future.

This is a principally new metallurgy. Out of the three metallurgy types - conventional, vacuum and under pressure, in fact, the metallurgy under pressure is the only one that occurs to be versatile, because the metal could be melt both at normal conditions and in vacuum.

The metallurgy under pressure is characterized by great versatility of steel grades, since it enables realization of three possible trends as stated hereunder:

- development of principally new steel grades;
- improvement of the properties and potential of the existing grades;
- revival of the old grades production having good technical and economic characteristics, however, had been abandoned because of ecological, and safety reasons. For example: the conventional wear resistant Mn13 steel (Hatfield steel) is well known for the separation of hazardous manganese vapours in the atmosphere and loss of up to 30% of the alloying manganese; a group of automatic steels based on the alloying of easily evaporating elements such as lead, a.o.

A separate monography will be devoted to the studies on the thermodynamics and kinetics of the formation and growth of the phases in HNS and the effect of the gas pressure on some metallurgical processes taking into account their importance and the huge volume of work. We would like to mention, that in the majority of cases of HNS grades alloyed with nitrogen a deviation from Sieverts law has been observed. This is supported by experiments [4, 172] demonstrating up to 110% deviation (Fig.1).

A lot of effort has been devoted to its theoretical study, because this determines both the steel casting and pouring technology, and the calculated pressure of the designed plants. At the start of the 1970s an unique equipment for melting in floating state under pressure of up to 50 (100) atm was designed for this purpose [7], providing, in our opinion, modern solutions to the problems of the thermodynamics and kinetics of saturation with nitrogen and its degassing in a wide temperature interval (1600-2000°C). We have derived a number of specific and generalized equations for obtianing the equilibrium nitrogen solubility in complex alloy liquid steels and alloys at various (and high) partial pressures of nitrogen in gaseous medium.

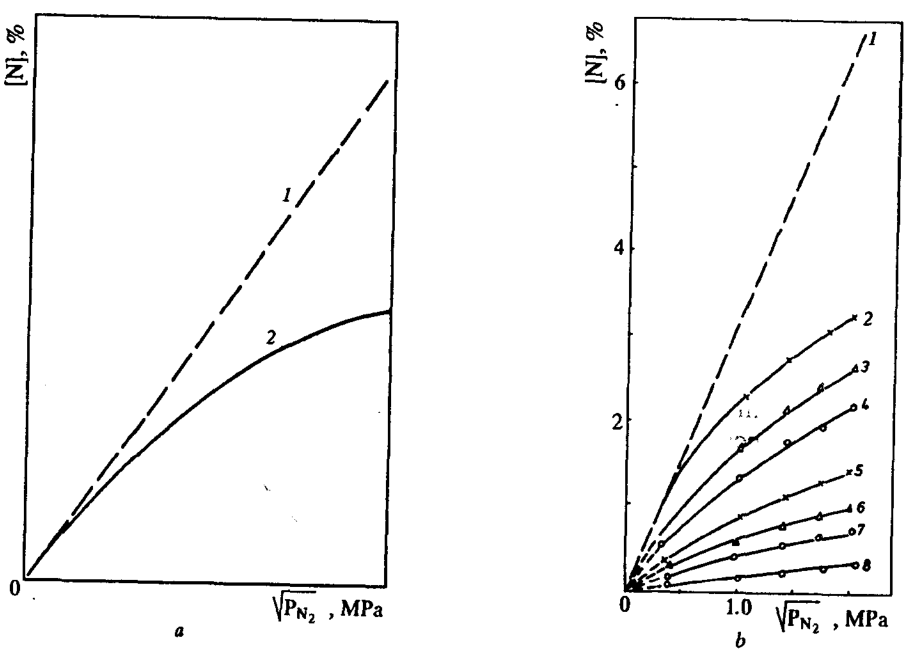

Fig.1. Dependence of nitrogen solubility in alloy steels by the partial nitrogen pressure in the gasous phase, *P*:
a - Basic dependence:
1 - Straight line - calculated by Sieverts' law; *2* - Experimental curve for alloy steels;
b - Author's studies on Fe-Cr system produced by levitation method under pressure:
1 - by Sieverts' law; *2* - 41% Cr; *3* - 35% Cr; *4* - 30% Cr; *5* - 21% Cr; *6* - 14.5% Cr; *7* - 10% Cr; *8* - 0% Cr

It occurred that in the development of HNS the fundamental science has to a great degree been in advance to the applied part which turned out to be a good situation.

According to the opinion of a number of scientists: Prof. Foct [173], Prof. Svjazin [352], Stein [180], including our views, too, the bottleneck in the development of HNS at the present stage is the lack of sufficient industrial production, which is related to the lack of clarity about the strategy in the design of industrial equipment and technologies. There is still no sufficient clarity on place of different production methods and equipment in the industry. It should be mentioned, that there is no existence of a method and equipment of the "Panacea" type, i.e., there are no technologies and equipment suited to all specific needs, because the needs and specific conditions in the worldwide practices are quite varied.

The basic difficulties in the implementation of HNS are quite obvious - these form the big trinity: the principally new steel grades, the principally new technologies, and the principally new equipment. A lot of money and sufficiently convincing economic information is needed for overcoming these difficulties, particularly in times of recession. It should be taken into account that the new equipment can fit well to the old production shops - during their reconstruction and modernization.

Regarding the implementation of new technologies and equipment, the metallurgy is well known as quite conservative and the properties of the resulting steels reach improvement very slowly with the time. This will be a strong obstacle to the implementation of the high nitrogen steels, as well. The realization of the projects would be additionally hampered by the increased complexity of the equipment (at vacuum technology level), some fears by the attending personnel because of the consequences in case of dehermetization of the equipment, as well as, the great novelty in the technology. Regardless of this fact, the "wave" of the high nitrogen steels has started. This has been confirmed by the aforementioned conferences marking a great interest by the fact that there is an already designed and produced industrial equipment and there is a regular production of high nitrogen steels in Bulgaria, Germany, and Russia. Also, the building of the first specialized shop for high nitrogen steel production has started in Bulgaria.

According to the author's data, there were 202 steels alloyed with nitrogen in 1984. The amount of the high nitrogen steels will be increased with parallel to the development of industrial casting equipment which will provide possibilities for the use of very high nitrogen concentrations without the danger of reduced plasticity, poor deformability or machinability difficulties.

The early made statements that:

-"The high nitrogen steels are principally new materials" - Metal Science and Metal Heat Treatment, ex-USSR, 1978 [186];

-"Nitrogen is and has to be considered an element of specific great importance", Pikering, USA, 1988 [171];

-"High nitrogen steels - they are the new generation of modern materials for engineering"... - Stein et al., Germany, 1988 [171],

are becoming more and more realistic today.

There are grounds to assume that high nitrogen is the brand new alloying element with a great future, and that the metallurgy of steels under gas pressure will be the metallurgy of the XXI Century.

The Governments of some countries, among which Germany, Russia, Ukraine, Poland, Bulgaria - up to 1989, have provided some financial support for the research and development of HNS. Obviously, time has come for the big companies to invest in equipment for metallurgy under pressure and in the high nitrogen steels production.

1. INDUSTRIAL EQUIPMENT FOR PRODUCTION OF HIGH NITROGEN STEELS

At the HIGH NITROGEN STEELS international conferences held in France, Bulgaria, Germany, Switzerland, Ukraine [171-176, 179] it appeared that the high nitrogen steels have proven to be a promising trend in the development of hi-tech metallurgy worldwide.

The neoclassical way for production of steels with high but in equilibrium at atmospheric conditions nitrogen concentrations reached on the account of the high consumption of nitride forming elements such as V, Nb, Cr, Mn and others [189], does not meet the economic requirements. It is suitable only for a limited range of products.

The three-dimensional alloying of solid steel (the so called "nitriding") is a process of very low productivity. The diffusion rate in solid state is well known to be several times lower than diffusion in liquid phase [194]. Furthermore, the surface saturation in solid phase is constant, whereas in liquid phase reaction it could rapidly change and increase. This process could be applied only for very thin products (foil, thin wire).

Because of the low chemical potential of the nitrogen in the gaseous phase, the low solubility of nitrogen in steels needs as a must gas pressure, and this results in considerably more complex technologies and equipment (plants, furnaces) as compared to analogous equipment operating at atmospheric conditions.

The so called alternative methods (powder metallurgy with powder alloying or mixing the steel powder with high nitrogen powder-like ferroalloys or on the basis of composite metal-metalloid reactions) are also very expensive; they are applicable in individual cases and their application is therefore limited. Because of the fact that the powder metallurgy methods have emerged earlier than the methods for HNS production, we can rather say that the HNS occur, to be some alternative to powder metallurgy for production of homogeneous steels in some specific cases in the industry.

At the present stage, the basic problem in the development of high nitrogen steels is the lack of industrial technologies and equipment for regular mass production on the market, that will provide for high and homogeneous nitrogen concentration in the volume of the solidified metal by the method of metallurgy under pressure. The high homogeneity of the ingots in terms of nitrogen, and hence of the end product, occurs to be the basic requirement to the quality of the regularly produced high nitrogen steels, naturally at the given stage of their development. Without satisfying this requirement the methods will have quite a limited application.

The available literature presents methods for alloying liquid steel with nitrogen for HNS production in induction furnace in gaseous phase under pressure, in plasma arc remelting furnaces, by the powder metallurgy methods, in electroslag remelting furnaces under pressure, by counter-pressure casting methods and in induction furnaces under pressure.

Because of the inevitable risks [171, 179] by the production of great volumes of liquid high nitrogen metal (in case of a sudden drop in gas pressure there is a danger for boiling of the metal melt which is oversaturated with nitrogen as compared to the situation in atmospheric conditions), there were no stimuls for development in industrial scale of induction or other furnaces on the basis of the principle called by us provisionally "big steelmaking bath". From this point of view, there was a suggestion that metallurgy under pressure should follow the approach of small quantity of liquid metal oversaturated with nitrogen. That is why a number of companies have undertaken the remelting processes, because in this case in the bigger ingots the volume of the liquid phase is kept not very high. Based on this the development followed the path of the pressurized electroslag remelting (PESR), electroslag arc remelting under pressure (ESARP) and plasma arc remelting under pressure (PARP).

New approaches and ways of development were reported at the HIGH NITROGEN STEELS'89 national conference with wide international participation, held in Bulgaria [172]. IMS and NIPKITOKS have presented papers on industrial equipment for production of high nitrogen steels of ingot type, electrodes for remelting and mould castings (by the counter-pressure casting method, by electroslag remelting under pressure, by pressing high nitrogen powder, a.o.). There were, also, papers on R&D work about design of industrial equipment for production of high nitrogen powders out of liquid HNS under pressure, ingots and parts - by the electroslag heating method, and developments of continuous pouring. As the development of these projects is still on-going, a brief report will be made of them in Chapter Two.

1.1. PLASMA ARC REMELTING UNDER PRESSURE - PARP

This process has been developed by a number of institutes and companies in Ukraine, Russia, Germany, etc.

The first ingot by PAR-metal was produced in the Paton Electric Welding Institute in 1963, and since then the method has found its specific application for a number of high purity alloys and steels. The investigations [184] proved the natural irregularity of the temperature field of the plasma jet, which followed with some approximation the isothermal fields in the metal bath (Fig.2), which resulted in different nitrogen concentrations.

The bulk alloying in PARP is effected on account of the dissociation of nitrogen in the plasma arc (Fig.3) under pressure up to 0.45 MPa. Because of the low saturation rate, the PARP version for saturation of the metal in the crucible is not applied in practice and the literature data [184, 202] points to some occasional application for obtaining some excessive nitrogen (as compared to this reached at atmospheric conditions).

Thus, for example, in [202] a description is made of the production of steel (25% Cr, 16% Ni, 7% Mn) in argon-nitrogen arc (75% N) at 0.4 MPa resulting in

0.6% N. The considerable inhomogeneity of the ingot in height and cross section is also noted. There is no data until now in the available literature about a regular and economically efficient production.

A PARP industrial furnace of up to 0.45 MPa is in operation in Russia for more than 10 years for production of some special tool and spring steels [401]; nonetheless publications about its technical and economic characteristics could not be found.

In summarizing the literature data, the basic reasons limiting the development of PARP at the present stage for the production of HNS will be reviewed in brief as follows:

- high total electric energy consumption (for the cycle of casting the electrode, and the ingot) - estimated higher than 2000 kWh/t steel;
- when the pressure increases following the Le Chatelier law, the reaction disintegration rate of the nitrogen molecules and saturation with nitrogen is reduced, that is why the pressure reached is limited to only 0.45 MPa;
- the conditions for handling the plasmotrons become worse (the plasma filament becomes narrower and harder);
- in the volume of the plasma torch the temperature is not uniform which results in different degrees of nitrogen dissociation and in different degrees of alloying along the steel surface sections;
- complex and expensive equipment, difficulties in production of forging and slab ingots, as well as mould castings.

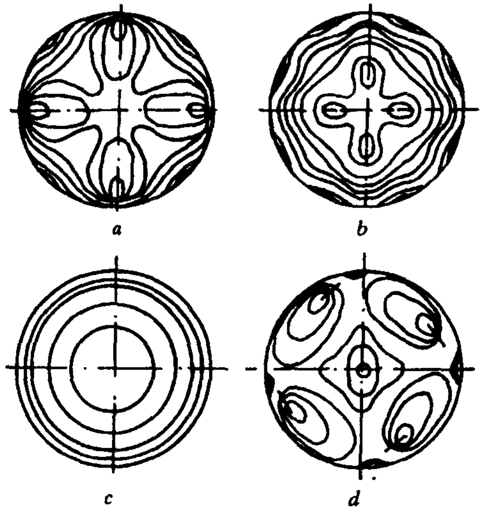

Fig.2. Isothermal fields in the metal bath of four-plasmotron furnaces for different versions of plasmotrons layout. Arrows show the locations of the plasma torches

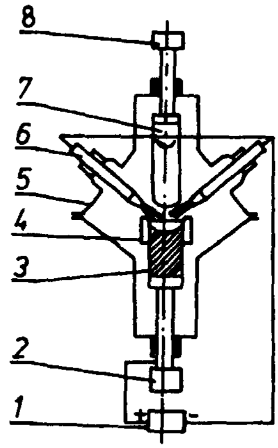

Fig.3. Schematic illustration of the plasma-arc remelting

At the HIGH NITROGEN STEELS international seminar, held at the Technical University of Czestochowa - Poland, Prof.Dr. Gammal from Aachen - Germany [351] had announced interesting results from the new process provisionally called plasma rotary atomization. The electrode which is revolved at a speed of 15000 rpm is melted and atomized by a 1000 kW plasmotron. Round drops of more than 1 mm diameter are obtained, and saturation with nitrogen up to 0.73%

of steels from the Cr18-Ni18 type containing less than 0.05%C is achieved. The porosity of the resulting product is less than 3%. A publication for the technical and economic data is expected soon.

One or two industrial installations for PARP are operating in Russia at limited gas pressure up to 0.45 MPa, and based on this some HNS are produced with some limitations only in terms of nitrogen. There are no recent publications for the operation of these plants.

1.2. POWDER METALLURGY

HNS can also be produced by the powder metallurgy methods [263]. For this purpose, use is made of different schemes of nitriding of the initial nitrogen-free powder. For example, in nitrogen atmosphere or dissociated ammonia at 550°C for 3 hours with subsequent (electric pulse) sintering at a voltage of 3-5 V and current intensity up to 1000 A; according to another scheme: the loose initial powder is sintered at 1200°C, then the resultant billets are subjected to nitriding at 600°C in nitrogen atmosphere, then the porous billets are impregnated with fillers; according to a third scheme: mixing of powder of nitrogen-free steel and nitrided ferroalloys (metal); other schemes are also created.

It is worthwhile to say that several authors in Japan, Switzerland, a.o. have achieved some scientific and practical successes. For example, Feichtinger [317] in his attempt to reduce the effect of the low mass transfer and the low coefficients of nitrogen diffusion, had developed a scheme with short diffusion distances, for example, for rolls of thin steel sheets, wire, etc. (as well as the combination of such structures with powders). In this way, better possibilities are obtained for one-dimensional surface diffusion nitriding in solid state, compared to obtaining three-dimensional structures of much bigger sizes. For example, a roll of stainless steel has been assembled in an air tight capsule, where nitrogen was fed under 0.1-0.8 MPa pressure and at 1100-1200°C the result was 0.3-1.5%N (time was not specified). After nitriding the capsule was fed to a 500-ton press and was diffusionally bonded by forging. Then followed heating at 800°C for 24 hours aimed at diffusion. Depending on the processing time, the result was either a "multigradient" or non-gradient material, both in terms of nitrogen concentration, and in terms of local strength and other properties. Quite an achievement was the resulting high plasticity (more than 300 J impact strength at minus 190°C), which solved for several industrial problems of HNS.

Unfortunately there was no data about the expenditures for processing. Consequently, it is expected high expenditures, because the technology occurs to be complex, high energy consuming, prolonged process duration, requiring high qualified operators, although the specific preparation of the initial materials is not expensive.

The processes for production of laminates, i.e., laminar materials "metalloid-metal", are limited to small sizes of the materials, so that the minimum diffusion path be less than 3 mm, and the time for alloying with nitrogen and the expenditures be reasonable. There are communications [317] for experiments carried out with high temperature materials - layers of solid and brittle nitride zones which come in sequence with nitride-free zones of increased plasticity.

In essence, these processes are based partially on the well known principles of the HIP-N process. The capsule with the powder is connected to a nitrogen conduit. In the intergranular space there is nitrogen under pressure, equal to or less than the pressure of nitrogen or argon in the furnace. It is worthwhile to notice that the resulting steels have the same strength properties as those obtained by the melting methods, and in some cases also, by remelting methods, however, the material is considerably more homogeneous. The expenditures for processing, according to our data are: for melting, atomization, drying and sorting - 2000 kWh/t; for pressing - 45 kWh/t; for sintering - 1080 kWh/t, i.e., a total for about 3100 kWh/t.

Those and the other schemes of powder metallurgy are considered by some authors [263] as "the most promising methods for production of materials with high nitrogen content". It is true that the powder metallurgy could provide for an uniform distribution of nitrogen across the whole section of the product, but unfortunately till now, the economic aspects of this process, existing for a long time, had proved its right for existence only for some individual cases, basically for small parts and parts of complex shape. There is no data in the literature about large scale production of high nitrogen powders. It is obvious, that the very low productivity, high energy consumption, process complexity, etc., have their impact. The application appears to be reasonable when the transition from liquid to solid state requires technically not feasible high pressures of nitrogen for some ferritic steels.

1.3. PRESSURIZED ELECTROSLAG REMELTING (PESR)

The technology and equipment known as PESR have been invented and experimented in Austria during a long period of time [178, 179, 185], and the last development took place in Germany [180].

Melting and not remelting is characteristic for this process. It is essentially different from the conventional remelting processes such as ESR, PAR, EBR, ESRP which are known to remelt electrodes with a chemical composition practically the same as the chemical composition of the steel grade of the required ingot, i.e., pure remelting is taking place. In the PESR process the "raw" electrode with a chemical composition different from the chemical composition of the required end ingot is alloyed (melted) with nitrogen carrying additives or with nitrogen carriers. Nitrided ferroalloys or nitrides are used as nitrogen carriers. The electrodes for this process do not contain in their volume high and homogeneous nitrogen concentrations. Thus, from the initial charge (the raw electrode and nitrogen carriers), an electroslag high nitrogen ingot is produced in the process of melting.

That is why, it would be both technologically and essentially more accurate if this process is designated as "pressurized electroslag melting (PESM)" and this would allow for a methodological differentiation of the technological features and adoption of a meaningful name. Then the term "remelting" in this work will be of