

Pressurized metallurgy for high performance special steels and alloys

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Abstract. The pressure is one of the basic parameters which greatly influences the metallurgical reaction process and solidification of steels and alloys. In this paper the history and present situation of research and application of pressurized metallurgy, especially pressurized metallurgy for special steels and alloys have been briefly reviewed. In the following part the physical chemistry of pressurized metallurgy is summarized. It is shown that pressurizing may change the conditions of chemical reaction in thermodynamics and kinetics due to the pressure effect on gas volume, solubility of gas and volatile element in metal melt, activity or activity coefficient of components, and change the physical and chemical properties of metal melt, heat transfer coefficient between mould and ingot, thus greatly influencing phase transformation during the solidification process and the solidification structure, such as increasing the solidification nucleation rate, reducing the critical nucleation radius, accelerating the solidification speed and significant macro/micro-structure refinement, and eliminating shrinkage, porosity and segregation and other casting defects. In the third part the research works of pressured metallurgy performed by the Northeastern University including establishment of pressurized induction melting (PIM) and pressurized electroslag remelting (PESR) equipments and development of high nitrogen steels under pressure are described in detail. Finally, it is considered in the paper that application of pressurized metallurgy in manufacture of high performance special steels and alloys is a relatively new research area, and its application prospects will be very broad and bright.

1. Introduction

There are three thermodynamic parameters in the metallurgical reaction and the metal solidification process, namely chemical composition, temperature and pressure of the system. The metallurgical reaction and solidification process, especially in the metallurgical reaction and solidification process with gas phase is greatly influenced by pressure.

The metallurgical process at present, especially ferrous metallurgy process is carried out mostly at atmospheric pressure or under the pressure of less than 0.1MPa (vacuum). High pressure hydrometallurgy-leaching has been applied in non-ferrous metallurgical industry [1-5]. The earliest research work-“Pressure NaOH leaching aluminum mineral” was done by a chemist, K. J. Bayer since 1887. Since the 1940s, high pressure hydrometallurgy had been used in production of heavy non-

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ferrous metals including Ni, Cu and Co etc.. In the 1970s, the greatest advances were made in acid leaching in zinc concentrate treatment under pressure. In the 1980s, the most important progress in the pressure leaching was the use of pressure pre oxidation of refractory gold ore to replace the roasting. Application of pressure technology in ferrous metallurgy process is mainly concerning two aspects. One is for the process with gas in the reaction, using pressure to increase reaction speed, shorten the reaction time, such as bath smelting reduction, BOF, etc. [6-7]. However, up to now there is not a real application in industry. The other is to increase the solubility of gases and volatile elements in liquid steel in the steelmaking temperature under the pressure, such as “dephosphorization by Ca reduction”, “high nitrogen steels” etc.. Bulgarian people developed pressurized metallurgy method of pilot and industrial IMS-BAS method in the 70's of last century, with large molten pool melting method which can produce ingot from 500Kg, 1300Kg, 2500Kg [8-9]. Since 1980's, a series of methods for manufacture of high nitrogen steels have been developed, such as hot isostatic pressing melting(HIP), pressurized induction furnace melting(PIM), pressurized electroslag remelting (PESR), pressurized ladle nitrogen purge(PLBN), pressurized plasma arc melting(PARP), pressurized arc slag remelting (PASR) etc. [10-11].

There are two ways that pressure affects casting solidification and structure formation: mechanical effects related to the physical phenomena at macro level (elastic and/or plastic deformation, intensification of heat exchange between casting and mould, variation of cooling rate, control of mould filling, etc.) and thermodynamic and transport phenomena at micro level (changes in phase diagrams, physical properties, Gibbs free energy, chemical potentials, specific heat, surface tension, diffusion coefficients, etc) [12]. The former is effective at the pressure of several MPa, while the latter is valid at the pressure of more than 10MPa or even more than 0.1GPa. The earliest work concerning the effect of pressure on the structure and properties of the material was done by Nobel Prize winner P. W. Bridgman in 20-30s of the last century. He developed techniques to achieve high pressures (~10 GPa) and investigated pressure effects on thermal and electrical conductivities, melting, reaction kinetics, viscosity, compressibility, tensile strength and a variety of other properties and phenomena.[13] Bridgman's work demonstrated the importance of pressure for studying continuous and discontinuous changes in the structure and properties of matter. His scientific results and engineering solutions have found a very large number of practical applications.

There are many research works regarding casting technology under high pressure for the light metals and alloys [14-19]. G. Zhang studied 515GPa high pressure on the microstructure of Al2Si alloy [14]. R. Li performed the microstructure and properties of ZnAl alloy under the action of high pressure [15-16]. The results show that the microstructure of ZA43 alloy was obviously refined without the formation of coarse dendrite, replaced by a small, granular structure on the cross section with random distribution, and the hardness of ZA27 alloy solidified at high pressure of 2.5 GPa was 55.8% higher than atmospheric pressure. A few works on casting of iron and steel under high pressure were made because it is relatively difficult to apply a high pressure at high temperature due to high melting points of such materials [12, 20].

The aim of this work is to understand the physical chemistry during melting and solidification of special steels and alloys at pressurized condition in order to improve the existed pressurized processes or to find new methods of pressurized metallurgy for manufacture of high performance special steels and alloys.

2. Physical chemistry of pressurized metallurgy

2.1. Gas equation

Ideal gas equation can be expressed by the relation

$$PV = nRT \quad (1)$$

where P , V , T are the pressure, volume and temperature of ideal gas, respectively; R is gas constant, n the number of mole. For a real gas, Van der Waals equation can be used.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (2)$$

Where a and b are constants. Pressure is a basic thermodynamic parameter. The change of P makes the change of T and V .

2.2. Gas solubility in liquid and solid steel

Gas solubility in liquid steel can be expressed by Sievert's law.

$$[G\%] = K\sqrt{P_G} \quad (3)$$

It is shown that the solubility of gas in molten steel of $[G\%]$ is proportional to the square root of gas partial pressure. However, the solubility will deviate from the Sievert's law with the increase of pressure. Therefore, a modified equation at pressure above 0.1MPa is applied as follows:

$$[G\%] = K(\sqrt{P_G})^{1-\delta} \quad (0 \leq \delta < 1) \quad (4)$$

Where δ is the correction factor of pressure. A new model for calculation of nitrogen solubility in molten stainless steel in a wide range of the alloy concentrations, temperatures, and pressures has been successfully established by introducing a new term of pressure-effect on nitrogen activity coefficient which is 0.06 [21].

$$\begin{aligned} \lg[\%N] = & \frac{1}{2} \lg(p_{N_2}/p^\theta) - \frac{188}{T} - 1.17 - \left(\frac{3280}{T} - 0.75 \right) (0.13[\%N] + 1.118[\%C] + 0.043[\%Si] \\ & + 0.011[\%Ni] + 3.5 \times 10^{-5}[\%Ni]^2 - 0.024[\%Mn] + 3.2 \times 10^{-5}[\%Mn]^2 \\ & - 0.01[\%Mo] + 7.9 \times 10^{-5}[\%Mo]^2 - 0.048[\%Cr] + 3.5 \times 10^{-4}[\%Cr]^2 + \delta_N^p \log \sqrt{p_{N_2}/p^\theta}) \end{aligned} \quad (5)$$

where $\delta_N^p = 0.06$, when $p_{N_2}/p^\theta > 1.0$; $\delta_N^p = 0$, when $p_{N_2}/p^\theta \leq 1.0$.

Figure 1 gives the nitrogen solubility of the austenitic stainless steels at different nitrogen partial pressure, which means that the high nitrogen austenitic stainless steels can be produced under the high pressure condition. As shown in figure 2, the nitrogen solubility of Fe-18Cr-18Mn alloy increases 0.3% when the temperature decreases from 2000K to 1750K, which means that low temperature is favorable to increase the nitrogen solubility of stainless steel.

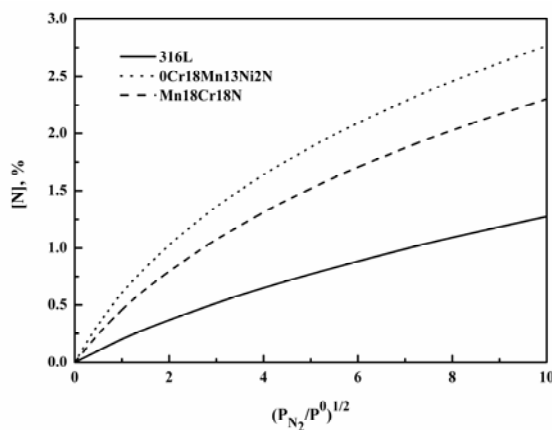


Figure 1. Effect of nitrogen partial pressure on nitrogen solubility of austenitic stainless steels at 1873K.

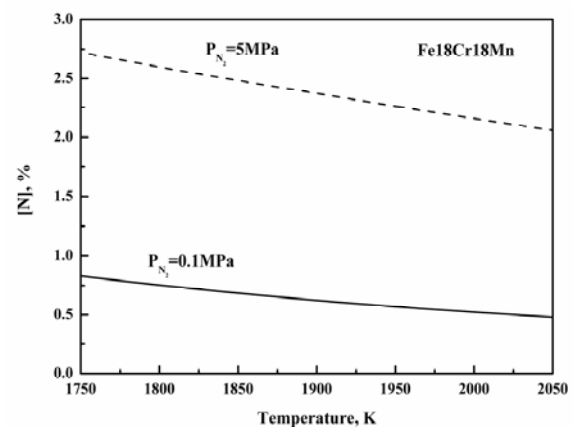


Figure 2. Effect of temperature on nitrogen solubility in liquid Fe-18Cr-18Mn alloy at 0.1MPa and 5MPa.

We also developed a model for calculation of nitrogen solubility in δ and γ phase of stainless steel [22]. As shown in figure 3, with the increase of nitrogen partial pressure, δ phase region gradually decreased, when nitrogen pressure up to 0.6MPa, δ phase completely disappeared. The solidification process directly entering from the liquid phase into the γ phase austenite region, which effectively suppressed the precipitation of nitrogen in solidification process

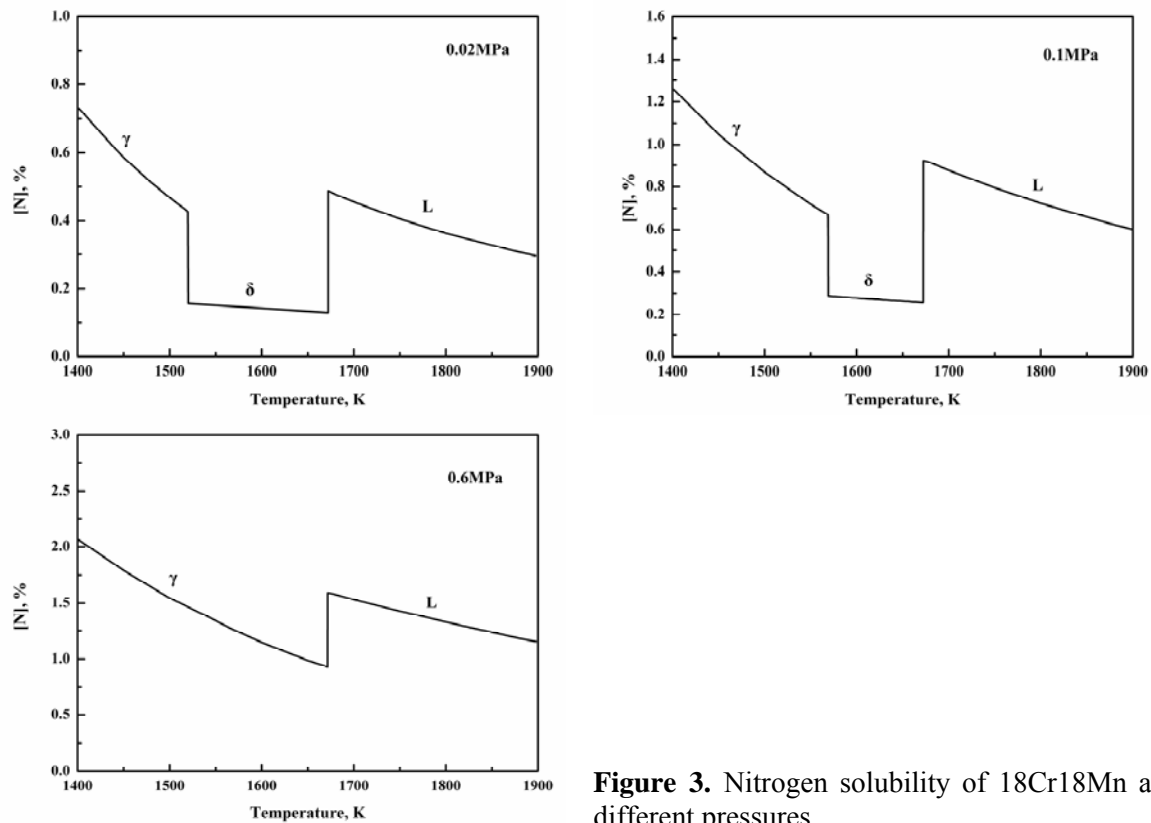


Figure 3. Nitrogen solubility of 18Cr18Mn at different pressures.

In fact, in addition to N, H, O, many of the elements in the steelmaking temperature (for example temperature of 1873 K) exist in gaseous state, such as Ca, Mg, K, Na, Pb, Sn, Zn, Li, Bi, which has very high vapor pressure and are easily volatilized under normal pressure. The increase in pressure can significantly improve the solubility of these elements in molten steel, and thus play a role in that cannot be achieved under normal pressure. For example, increasing the pressure of Ca, Mg can significantly improve the treatment effect of liquid steel, greatly increase the utilization rate.

2.3. Chemical reactions with gas

The chemical reaction will take place in the direction in which gas generates or the volume increases with the decrease of pressure. Vacuum (by reducing pressure) will promote the reaction: $[C] + [O] = \{CO\}$, for example. The chemical reaction will take place in the direction in which the volume decreases with the increase of pressure (by pressurization), for example, $N_2 = 2[N]$.

2.4. Effect of pressure on activity and activity coefficient

$$\left(\frac{\partial \ln a_i}{\partial P} \right)_{T, C_j} = \frac{\bar{V}_i - \bar{V}_i^0}{RT} \quad (6)$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T, C_j} = \left(\frac{\partial \ln f_i}{\partial P}\right)_{T, C_j} = \frac{\bar{V}_i - \bar{V}_i^0}{RT} \quad (7)$$

Where a_i , γ_i , f_i - activity, activity coefficients of component i in the standard state of pure substance and Henry's law, respectively; \bar{V}_i , \bar{V}_i^0 partial molal volumes of component i at present pressure and at standard pressure, respectively.

2.5. Effect of pressure on melting point or phase transformations

The Clausius–Clapeyron relation can be expressed

$$\frac{dT}{dP} = \frac{T\Delta v}{\Delta H} \quad (8)$$

The equation relates the slope of the temperature–pressure boundary for coexisting phases at some point (T , P) to the specific enthalpy of phase transformation ΔH and the specific volume change Δv . Equation (8) is very useful because it permits quantitative estimates to be obtained from the thermodynamic parameters for phase transformation. Using the Clausius–Clapeyron equation, changes in phase transformation temperature with pressure can be calculated with following formula.

$$T_{eq}(P_0 + \Delta P) = T_{eq}(P_0) + \Delta P \frac{dT_{eq}}{dP} = T_{eq,0} + \Delta P \frac{T_{eq,0}\Delta v}{\Delta H} \quad (9)$$

Where T_{eq} , $T_{eq,0}$ are the equilibrium temperatures for phase transformation, ΔP pressure increment, Pa. Figure 4 shows the correlations between melting point and pressure for aluminium and the eutectic temperature and pressure for the Al-Si system [12]. However, the pressure effecting on melting point or phase transformations becomes obvious when the order of magnitude of pressure is more than 0.1 GPa.

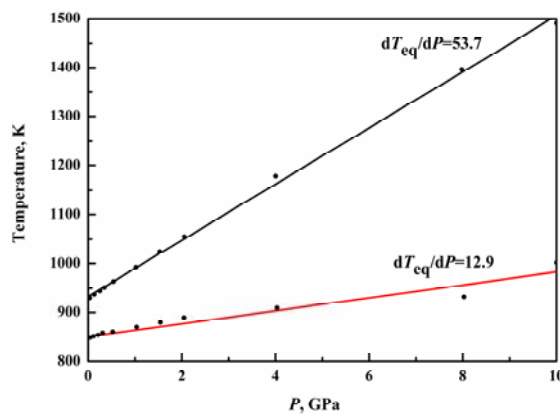


Figure 4. Melting point of aluminium T_m and eutectic temperature of Al-Si system T_{cut} as function of pressure.

2.6. Pressure effect on interfacial free energy

$$\left(\frac{\partial \sigma}{\partial P}\right)_T = \Delta P \left(\frac{\partial V_A}{\partial P}\right)_T \quad (10)$$

As the volume of every closed system with constant phase composition decreases with pressure, i.e. $(\partial V_A / \partial P)_T < 0$, an increase in pressure will decrease the interfacial free energy. The interfacial free energy determines the critical radius for solid phase nucleation. Since an increase in pressure decreases the interfacial free energy (surface tension) of the crystal/melt interface, the critical radius for nucleation will decrease proportionally. This in turn will increase the number of nucleation sites and consequently refine the solidified structure.

2.7. Effect of pressure on nucleation

Pressure effects on critical radius for nucleation can be expressed.

$$r = \frac{2\sigma dT}{[\Delta T(V_2 - V_1)dP]} \quad (11)$$

where σ is the surface tension, J m^{-2} .

Pressure effects on nucleation rate I can be determined by equation

$$\ln I = \ln a - \frac{b}{(d + P)^2} - cP \quad (12)$$

Where a , b , c , d are constants. The increase of pressure will decrease the critical radius for nucleation, and will increase nucleation rate, and then refine the solid's structure. Figure 5 presents the simulation results of nucleation in Fe-0.6%C alloy at various solidification times under atmospheric pressure and pressure of 10 MPa [23].

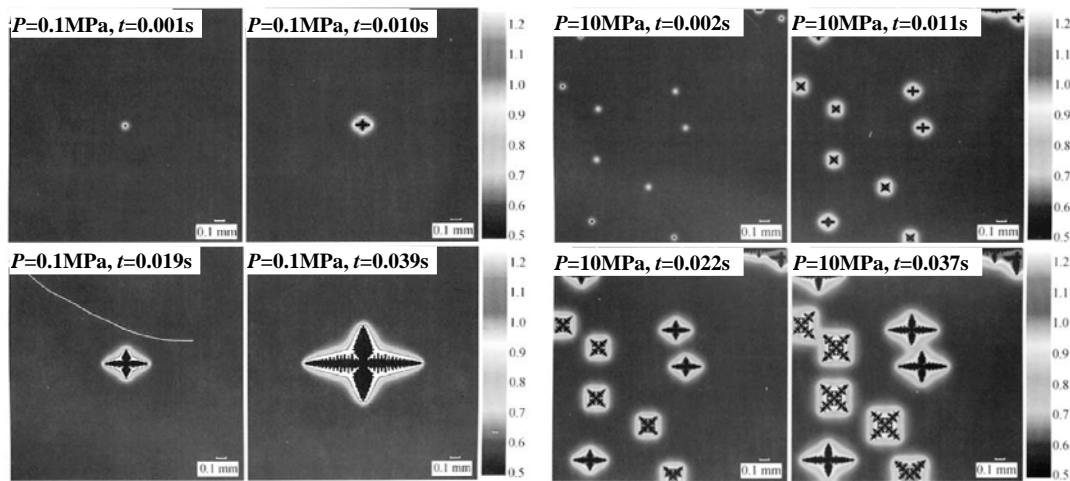


Figure 5. Dendrite morphologies of Fe-0.6%C alloy at various solidification time under atmospheric pressure and pressure of 10 MPa (simulation).

2.8. Effect of pressure on heat transfer between casting and mould

External pressure during solidification increases the metal/mould contact and raises the heat transfer coefficient. Theoretical and experimental research on the solidification of Al-Si eutectic alloy against steel dies have shown that a pressure of 196 MPa increases the heat transfer coefficient h by a factor of 15 from about 3.4×10^3 to $5.25 \times 10^4 \text{ W m}^{-2} \text{ K}^{-1}$. The structures as shown in figure 6 [24] are formed in high nitrogen steel ingots solidified in a metal mould under various gas pressures: $P_1=0.1 \text{ MPa}$, $P_2=1.7 \text{ MPa}$ and $P_3=3.6 \text{ MPa}$. Owing to the plasticity of semisolid and solid regions of solidifying ingot, the heat exchange between mould and casting is forced by an external pressure, which results in a reduction in total solidification time, decrease in local solidification time (LST), the increase in cooling rate V_{cool} and, finally, the refinement of the dendritic structure. These results indicated that refinement of casting structure can be realized even at relatively small increases of pressure. Figure 7 shows that the heat transfer coefficient between casting and mould is greatly influenced by pressure [25].

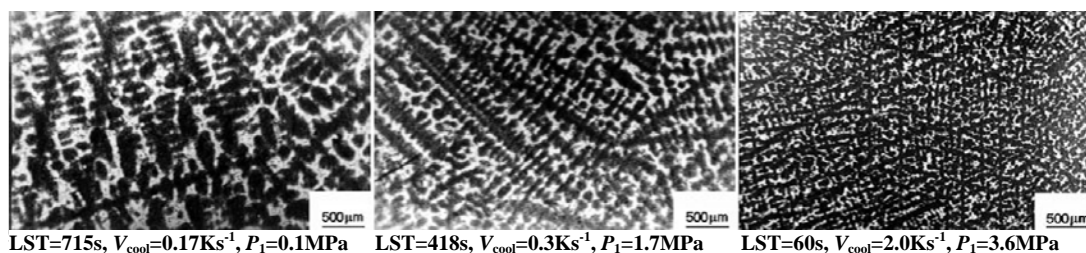


Figure 6. Structure of high nitrogen steel solidified in metal mould under different gas pressures: all structures are observed in very same region of ingots.

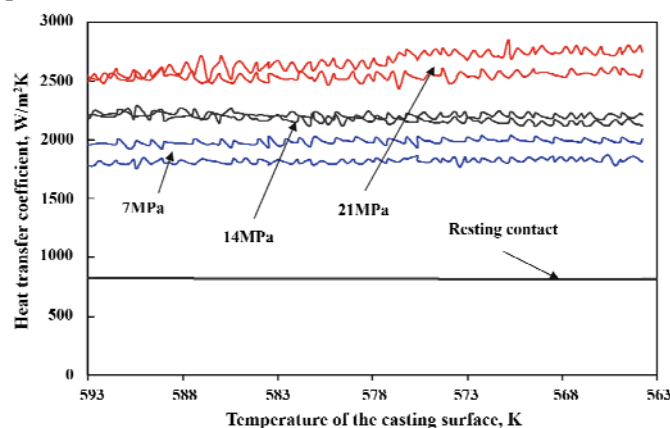


Figure 7. Effect of pressure on heat transfer coefficient between casting and mould.

3. Manufacture and application of special steels and alloys by pressurized metallurgy

According to the above fundamental consideration, there are two useful effects of pressure on special steels and alloys in manufacture process. One is to increase the solubility of gases or volatile elements in steel or alloy by pressurization, for example, to obtain high nitrogen steels that have been made by many research works. To increase the solubility of volatile elements (Ca, Mg ...) in steel or alloy will be the future works. The other is to refine the solidification structure of steel or alloy by improvement of heat transfer between casting and mould at relatively small increases of pressure (≤ 10 MPa). However, more high pressure (10-100MPa, even more) will be difficult to be realized in steel industry.

3.1. Manufacture of high nitrogen steels (HNS) by pressurized metallurgy

There are different approaches to manufacture of high nitrogen steels, as shown in figure 8. Except for EAF and AOD process, other methods including gas purging, induction furnace, plasma arc melting, arc slag remelting (ASR) and PESR can work either in normal pressure or increased pressure. Of course, the pressurized method is more effective to obtain high nitrogen content for steel or alloy.

In our laboratory a 25kg pressurized induction furnace with max pressure of 6MPa and a 50kg pressurized ESR furnace with max pressure of 7MPa have been established a few years ago, as shown in figure 9. Several types of high nitrogen steels including austenitic stainless steels and martensitic stainless steels have been manufactured by PIM, as shown in table 1. The working pressure during the melting and casting can be controlled separately. The pressures are normally controlled at 0.2-0.5MPa at melting stage and at 1.0-1.5MPa at casting stage. Nitrogen alloying in steel was realized by adding chromium nitride and nitrogen gas absorption. The percentage of gas alloying could be from 20%-100% which depends on the nitrogen pressure and aimed nitrogen content in steel. The rate of nitrogen absorption from gas into liquid steel is quite fast due to strong magnetic stirring of liquid steel and slag-free on top of bath. For example, Cronidur30 with 0.55% nitrogen in table 1 was prepared by gas alloying without addition of chromium nitride. Figure 10 shows the macrostructure and photo by γ -ray detection of HNS-A ingot, and nitrogen and oxygen distribution in ingot. It can be seen from the figure that except significant shrinkage in the upper part of ingot, the rest of the macrostructure is very

uniform, and compact without holes. Table 2 gives the N, O distribution at different positions of ingot HNS-A made by PIM. The results indicate that there is not macrosegregation of nitrogen in ingot. Non-metallic inclusions in the HNS-A ingot mainly are Al_2O_3 , MnS and $\text{Al}_2\text{O}_3\text{-TiN}$ with the sizes of less than $5\mu\text{m}$. After homogeneous solid solution treatment of ingot at 1100°C for 1 hour and water cooling, the microstructure with uniform austenite is shown in figure 11.

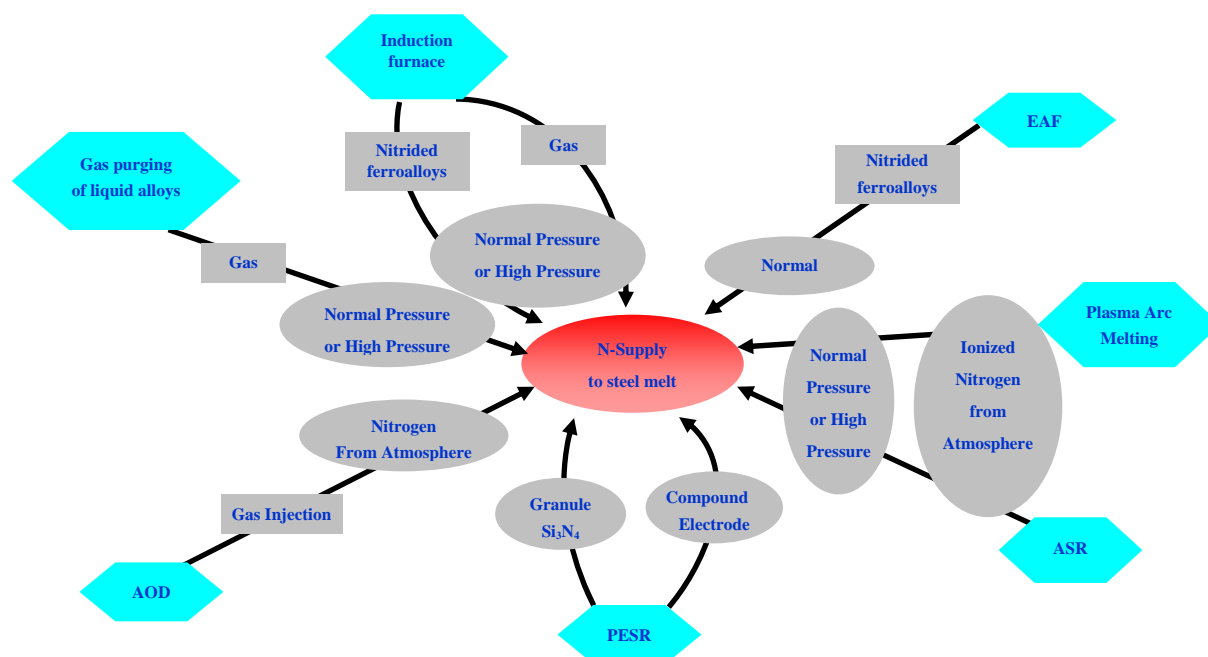


Figure 8. Manufacture of high nitrogen steels (HNS) by different methods.

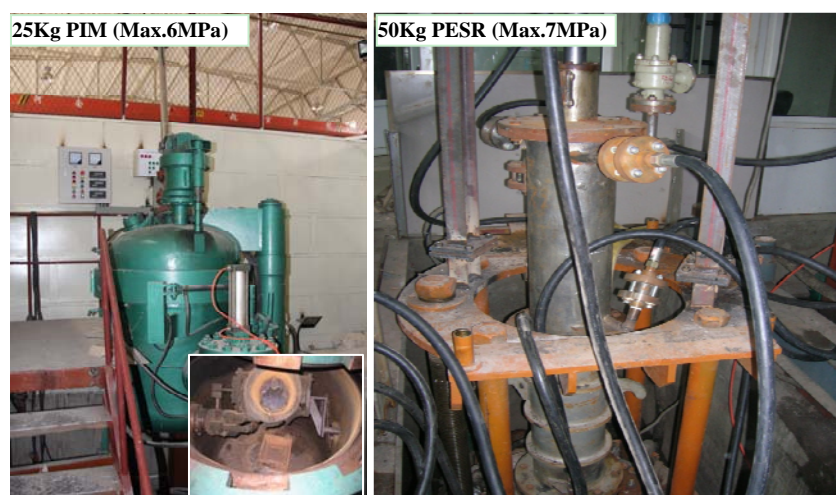
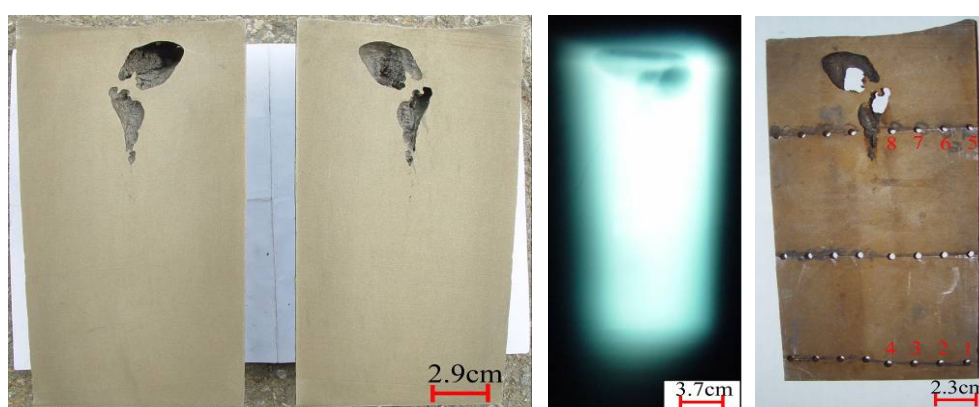


Figure 9. The lab-scale PIM and PESR equipments.

Table 1. Chemical composition of high nitrogen steels made by PIM, wt%.

No.	Steel grade	Cr	Mn	Mo	C	N	O	Al	P	S
HNS-A	18.0Cr16.5Mn2.0Mo0.8N	18.02	16.10	1.96	0.046	1.08	0.0033	0.01	0.014	0.0080
HNS-B	18.0Cr16.5Mn2.0Mo1.0N	18.56	15.29	1.98	0.051	1.20	0.0130	0.01	0.013	0.0080
P900N	18Cr18MnN	18.27	18.47	--	0.100	1.20	0.0023	0.02	0.010	0.0029
P900NMo	18Cr18Mn2MoN	18.26	17.87	2.02	0.110	1.23	0.0054	0.03	0.011	0.0028
P2000	18Cr14Mn3MoN	17.88	14.17	2.97	0.110	1.15	0.0026	0.02	0.012	0.0029
Cronidur30	15Cr1MoN	15.33	0.52	0.99	0.310	0.40	0.0026	0.03	0.013	0.0026

**Figure 10.** Macrostructure of HNS ingot prepared by PIM.**Table 2.** N, O distribution at different positions of ingot HNS-A made by PIM, wt%.

	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8
N	1.10	1.10	1.10	1.10	1.08	1.08	1.08	1.08
O	0.0033	0.0041	0.0035	0.0051	0.0055	0.0034	0.0061	0.0030

**Figure 11.** The microstructure of HNS-A after solid solution treatment.

The high nitrogen austenitic stainless steels with very uniform and compact macrostructure have been made by 50kg pressurized electros slag remelting furnace with the pressure from 2.0-3.2MPa by using composite electrode with mixture of nitrides and deoxidizers, as shown in figure 12. Table 3

gives the chemical composition of HNS manufactured by PESR. The precipitation behaviour, mechanical properties, corrosion resistance properties and biological properties of high nitrogen austenitic stainless steels have been systematically investigated associated with the nitrogen concentration and the other influence factors [26-32]. The results show that HNS manufactured by PESR exhibits good mechanical properties, excellent corrosion resistance properties and the excellent blood compatibility.



Figure 12. Composite electrode and Macrostructure of P2000 ingot made by PESR.

Table 3. Chemical composition of HNS manufactured by PESR, wt%.

Grades	MPa	Cr	Mn	C	Si	P	Mo	Ni	N
A	2.1	21.22	15.92	0.120	0.49	0.023	--	--	1.21
P900N	2.0	20.13	16.51	0.100	0.54	0.020	--	--	1.00
P900NMo	2.1~3.0	18.34	18.36	0.068	0.50	0.024	2.13	--	0.93
P2000	3.0	17.06	13.18	0.042	0.75	0.021	3.37	--	0.79
B	3.2	21.33	--	0.026	0.72	0.019	2.05	4.00	0.88

3.2. Application of special steels and alloys by pressurized metallurgy

The family of high nitrogen steels consists of not only austenitic, martensitic stainless steel, and also ferritic stainless steel, high speed tool steel and die steel. As shown in table 4, there are many performance characteristics for future applications in industry. For example, nitrides uniformly distributed in tempered high nitrogen martensitic stainless steel can improve the strength and hardness of steel. The excellent resistance against wear as well as pitting corrosion of CRONIDUR 30 (15% Cr, 1% Mo, 0.4% N), promotes this steel for application in aviation. Typical applications are bearings in aviation turbines and ball screw gearing shafts, also used for rams in water cooled turbo drills and screws, fasteners for the chemical, car, and construction industry [33]. Figure 13 gives examples of application of high nitrogen austenitic stainless steels in manufacture of human medical materials, precision thin wall tube and retaining ring forging for large thermal power unit (P900N) by Chinese companies based on our research results.

With the progress of manufacturing technology, the cost of manufacturing will continue to be reduced together with further improvement of the performance; the scope of application of high nitrogen stainless steel will continue to expand. The highest tensile strength of high nitrogen stainless steel is currently 3600MPa, may be more than 4000MPa in the future, which still maintain a good ductility and high corrosion resistance. Therefore, it can be expected that high nitrogen stainless steels will be widely used in transportation (car, train, and ship), construction (such as ultra-high strength rebar), aerospace industry, atomic energy, ocean engineering and military industry in the future.



Figure 13. Examples of application of high nitrogen austenitic stainless steels.

Table 4. Performance characteristics of different high nitrogen steels.

Type	N, wt%	Grades	Performance characteristics
Austenitic Stainless Steel	$\leq 1.20-2.80$	Cr18Mn18N Cr18MnN) 16Cr14Mn3MoN Cr25Mn11Si3N	The strength is increased, the low temperature impact toughness improved obviously; Excellent corrosion resistance and resistance to stress corrosion; Stabilization of austenite and non-magnetic stability
Ferritic Stainless	0.08-0.60	Cr12Ni2Mo2VN 1Cr12Ni3Mo2VN	Nitride dispersion distribution The high temperature creep properties Improved
Martensitic stainless	0.08-1.60	4Cr13MoN X30CrMoN15-1	The strength and wear resistance is increased greatly, the low temperature impact toughness improved obviously
High speed tool steel	0.08-0.60	W6Cr5V2N W2Cr6V2N	The refinement of solidification structure Nitride dispersion distribution
Die steel	0.10-0.60	55NiCrMoV7N 55CrVMoN	The refinement of solidification structure The strength and toughness improved obviously

4. Summary and outlook

Pressurization may change the conditions of chemical reaction in thermodynamics and kinetics, and make the volatile element increase solubility in molten metals, not only to raise the utilization rate of the elements, but also to improve the roles of these elements in metal melt, such as purifying and alloying.

Pressurization can also enhance heat transfer and the cooling effect between casting and mould, reduce the local solidification time, promote the refinement of solidification structure and eliminate shrinkage, porosity and segregation and other casting defects. This phenomenon can appear even at relatively small increases of pressure (at several MPa), which means that this technology could be easily realized in industry in the near future.

The high pressure may change the physical and chemical properties of metal melt, thus greatly influencing phase transformation during the solidification process and the solidification structure, such as increasing the solidification nucleation rate, reducing the critical nucleation radius, accelerating the solidification speed and significant microstructure refinement. The pressure has effect on solute distribution coefficient and diffusion coefficient of elements during solidification, and affects the segregation behavior of elements during solidification process.

The pressurized technology used in ferrous metallurgy mainly concerns the high nitrogen steels, especially high nitrogen stainless steels. The behaviours of Ca, Mg, K, Na, Pb, Sn, Zn, Li, Bi and other volatile elements in pressurized steelmaking process is still in the embryonic stage of research. Application of pressurized metallurgy in manufacture of special steel and alloy is a relatively new research direction, so its application prospects will be very broad and bright.

Acknowledgements

This project supported by the National Nature Science Foundation of China (No.51434004, U1435205, 51304041) and the National High Technology Research and Development Program of China (863 Program) (No. 2012AA03A502). In addition, the work is supported by Program for Liaoning Innovative Research Team in University with the grant No. LT20120008.

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