Processing Nickel Free High Nitrogen Austenitic Stainless Steels through Conventional Electroslag Remelting Process

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Nickel free high nitrogen austenitic stainless steels, made through air-induction melting were processed using conventional electroslag remelting (ESR) process without application of nitrogen gas pressure over the melt. It was found possible to retain the high nitrogen contents of the original steel. The loss in nitrogen content during ESR was found to increase with increasing melt rate. Electroslag remelting was carried out on eleven steels with a base composition at around 18wt%Cr–18wt%Mn–0.1 to 0.6wt%C–0.53 to 0.9wt%N. While the air-induction melted steel had extensive porosity, the ESR ingots were all sound and free from porosity. Thus, steels made in any other process route can be successfully remelted using conventional ESR. The cast structure analysis in a typical medium carbon high nitrogen steel showed that Cr and Mn has a tendency for microsegregation. The presence of microsegregation and residual carbides affect the ductility of the cast steel.

KEY WORDS: nickel free high nitrogen austenitic steel; conventional ESR processing; microsegregation; cast steel; mechanical properties.

1. Introduction

High nitrogen steels are being increasingly sought for several applications. Though, these steels were examined three decades ago, the commercial exploitation has become possible only in the mid 80’s. The technology for reliably alloying high nitrogen contents was realised, following which commercial production was attempted. Presently, there are several viable processing routes available. This, combined with attractive properties obtained by varying the range of composition of the steel has led steel designers to exploit this material for versatile applications.

High nitrogen steels are made by induction furnaces, arc furnaces, AOD furnaces, Plasma arc furnaces and pressure ESR process. These steels made by conventional induction or arc furnace involves addition of nitrided ferro-alloys for nitrogen alloying and the addition is usually made in the final stages and casted with less holding time to minimise nitrogen loss. This eventually leads to inhomogeneity in the ingot composition. There are reports that cracking occurred in ingots processed by electric arc furnace route due to compositional inhomogeneity. The predominantly accepted production process for high nitrogen steels is the pressure ESR process. This process involves application of high nitrogen gas pressure over the molten slag pool. The equipment is complex to handle gas pressures of the order of 42 bars over the molten slag. Even in this process, double or triple melting is carried out to achieve ingot homogeneity.

Tonnage quantity steels are produced in some of the other processing routes such as ladle melting and pressure ESR process. There is no study reported as to why high nitrogen steels melted by induction or arc melting could be processed through conventional ESR route without pressure. In the present investigation, this aspect has been examined along with the characterisation of a typical cast high nitrogen steel for microstructure and mechanical properties.

2. Experimental

A series of nickel free austenitic steels were remelted using air induction furnace using nitrided ferro alloys at National Metallurgical Laboratory, Jamshedpur. The steels were received as 40 mm diameter electrode in the as-cast condition. The as-received steels were examined by radiography for their soundness and analysed for chemical composition. Electroslag remelting was carried out on eleven steels with a base composition at around 18wt%Cr–18wt%Mn–0.1 to 0.6wt%C–0.53 to 0.9wt%N. While the air-induction melted steels had extensive porosity, the ESR ingots were all sound and free from porosity. Thus, steels made in any other process route can be successfully remelted using conventional ESR. The cast structure analysis in a typical medium carbon high nitrogen steel showed that Cr and Mn has a tendency for microsegregation. The presence of microsegregation and residual carbides affect the ductility of the cast steel.

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for the as-cast tensile property evaluation after homogenisation.

3. Results and Discussion

The radiographic analysis of the as-received cast air induction melted nitrogen steel electrodes showed extensive porosity as typically shown in Fig. 2(a). While seven of the steel rods had extensive porosity, three of them were sound but with a deep pipe. All the ingots after ESR were sound ingots as shown in Fig. 2(b). Even in the case of pressure ESR process, it has been reported that ingot bulging may occur due to evolution of nitrogen during ingot solidification. However, in the present series of steels melted through conventional ESR, no bulging of the ingot or significant loss in nitrogen was observed. This could be probably due to the lower melt rates attempted in the remelting of these steels. At low melt rates, narrow metal pool with a directional solidification pattern emerges. The nucleation points for gaseous nitrogen to nucleate and evolve tends to be lower. The nitrogen gas, even if it is nucleated in the molten metal pool, escapes to the ambient atmosphere since there is no pressure applied in the present case over the slag as in a pressure ESR process. Thus, there may be loss of nitrogen content but ingot soundness would be prevailing. In addition to soundness, the ingot surfaces were smooth and free of ripples. This is due to the fact that the small volume of liquid metal generated, solidifies over a skin of solidified slag along the mould wall, the mechanism of which is well studied.

All steels investigated before electroslag remelting had
nitrogen concentration greater than their equilibrium solubility in molten condition. For 18wt%Cr–18wt%Mn steel, the equilibrium nitrogen concentrations is reported to be about 0.45%. Thus, when the steels are remelted, the decrease in nitrogen solubility as shown in Fig. 3, could result in nitrogen gas evolution from molten metal at normal atmospheric pressures. Eventually, severe losses in nitrogen contents could be expected after conventional electroslag remelting. The chemical analyses of the cast electrodes before and after ESR are shown in Table 2. It can be seen that nitrogen loss during conventional ESR process is not severe as anticipated. The nitrogen loss increases with melt rate increase as shown in Fig. 4. This could be probably due to the fact that when the melt rate is large, the molten metal pool shown in Fig. 1, is larger and there is enough chances of gas bubble nucleation taking place at the slag skin/molten metal or molten metal/slag interfaces. When the melt rate is low, the pool depth is narrow and progressive solidification could rapidly trap nitrogen on the ingot becoming solidified. In addition, the nitrogen solubility in these steels is higher in the solid state as shown in Fig. 3. This factor could lead to nitrogen partitioning more preferably in the solidifying ingot, rather than getting evolved in the molten metal pool, where solubility is low.

The usual beneficial effect of S and O removal inherent in the ESR process could be observed in Table 3. The sulphur removal is due to the highly basic nature of the slags used. The oxygen removal may be attributed to the reaction of the dissolved oxygen or stable oxide inclusions in the steel with the molten slag. Inclusions could be separated partially due to density differences between molten metal and molten slag. Both S and O are surface active elements, which are reported to play a significant role in mass transfer of nitrogen in steel melts. The presence of S and O to some extent could probably be beneficial in the nitrogen alloyed steels. It is said that S and O move to the interface, where nitrogen absorbs or evolves and they decrease the surface available for mass transfer of N at the melt/gas interfaces. Hence, it is probable in melts, where S and O contents are high, there could be a decrease in mass transfer of N from molten metal to atmosphere. Studies on such a mass transfer is reported in steels with nitrogen contents as high as 0.2 wt%. If the mechanism proposed for lower nitrogen levels are found shown in Fig. 1, is larger and there is enough chances of gas bubble nucleation taking place at the slag skin/molten metal or molten metal/slag interfaces. When the melt rate is low, the pool depth is narrow and progressive solidification could rapidly trap nitrogen on the ingot becoming solidified. In addition, the nitrogen solubility in these steels is higher in the solid state as shown in Fig. 3. This factor could lead to nitrogen partitioning more preferably in the solidifying ingot, rather than getting evolved in the molten metal pool, where solubility is low.

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valid for high nitrogen steels as well, then the presence of S and O can aid trapping N in the molten metal during remelting. In the present ESR melting, three probable reactions that could take place in the molten metal pool/slag or metal pool/slag skin interfaces are desulphurisation, deoxidation and nitrogen desorption. Since, significant decrease in O and S levels are observed as shown in Table 3, the deoxidation and desulphurisation reactions takes place more effectively at the interfaces than nitrogen desorption from the melt. Thus, the nitrogen loss is low in the conventional ESR probably due to decreased heterogenous interfaces available for nucleation and the fact that S and O may prevent N coming to the interface in preference to these elements.

The minor differences of Cr and Mn contents in the steels before and after ESR may be attributed to the local inhomogeneity in the air induction melted electrodes. This may be anticipated because the nitried ferroalloys are added to the induction melted molten metal bath during the final stages and the melt itself was not held for longer times for homogenisation. Hence, compositional inhomogeneities may be present in the as received electrodes, which may have been evened out during ESR. Even processes such as Pressure ESR are reported to give better chemical homogeneity after successive electroslag remelting.

The present study throws open the possibility of processing high nitrogen steels in conventional ESR route without pressure application. From the trends detected during the present series of experimentation, it may be even possible to do primary alloying of the steel with nitrogen using nitried ferro-alloys using the conventional ESR process. Further, electroslag castings of high nitrogen steels could be made using conventional ESR technique.

The steel 3/2 was chosen for as-cast structure evaluation. This steel was chosen because it had C and N in adequate levels for causing precipitation of carbides or nitrides during solidification. The as-cast and not heat treated microstructure of nitrogen steels showed microstructure shown in Fig. 5. The microstructure shows columnar dendritic pattern characteristic of solidification in a water cooled mould of ESR process. There was no equiaxed zone observed in the ingot mid center portion. The microstructure in Fig. 5 shows precipitates in the dendrite core as well interdendritic regions and they are more intense in the interdendritic regions. Higher magnification shows presence of lamellar precipitates in the matrix along with intragranular precipitates. The analysis of the as-cast steel by XRD, indicated presence of Cr2N type nitrides and Cr23C6 type carbides as shown in Table 4. During solidification, coring takes place segregating Cr, Mn, C and N to the interdendritic regions. The concentrations of the precipitation forming element, Cr is richer in the interdendritic region and during solidification and subsequent cooling the ingot had aged leading to carbide and nitrides precipitation. Hence the as-solidified ingot has carbides and nitrides extensively precipitated. Homogenising followed by solution treatment was carried out to dissolve these precipitates.

The microstructure of steel 3/2 after a homogenising treatment at 1 100°C for 8 hr followed by water quenching is shown in Fig. 6. The microstructure shows columnar dendrites with lesser interdendritic precipitates rich regions

| Condition                  | Phases                  | Typical planes characterised |
|---------------------------|-------------------------|------------------------------|
| As-solidified cast steel 3/2 | Austenite Cr2N          | (111) (200) (220) (311) (222) |
|                           | Cr23C6                  | (511) (420)                  |
| Cast+ homogenised at 1100°C/8 hrs/WQ | Austenite Cr2N | (111) (200) (220) (311) (222) |
|                           | Cr23C6                  | (511) (420)                  |

Fig. 5. Microstructure of the as-solidified steel 3/2 without any treatment.

Fig. 6. Microstructure of the cast steel after homogenisation at 1 100°C/8 hr followed by water quenching.

Table 4. XRD analysis of the as-cast steel.
after solution treatment. The secondary dendrite arm spacing was measured in this condition at the ingot mid centre portion which was found to be about 60 µm. The XRD analysis on the cast homogenised samples as shown in Table 4, indicated presence of Cr₂₃C₆ type carbides and the lattice parameter of the cast homogenised austenite phase in the steel was found to be 3.631 Å. Peaks for the presence of Cr₂₃C₆ was also indicated. Examination of cast structure of samples homogenised at 1100°C for 8 hr using EPMA by X-ray back scattered images shows that Cr and Mn have a tendency for microsegregation, which is not eliminated even after homogenising treatment as shown in Fig. 7. The solute rich interdendritic region appears dark. The line scan using EPMA covering one dendrite core to another in a precipitate free region shows peaks for Cr and Mn and absence of peak for C and N. Hence, it may be concluded that Cr and Mn are segregated and their effects persists even after homogenisation, while C and N are not significantly segregated in all regions and they may have been evened out during homogenising heat treatment. According to a model by Kattamis, interstitial solutes in solid solution are reported to be evened out during such homogenisation treatment. However, even after homogenisation treatment, some residual precipitates were found in the interdendritic region in the present case. The typical analysis of the constituents in the dendrite core and the interdendritic region using EPMA is shown in Table 5. The residual precipitates were identified to be chromium carbides as shown in Fig. 8. The composition of these interdendritic carbides is shown in the Table 5. The ratio of %Cr to %C+N conforms close to the composition of Cr₂₃C₆ type carbide. Hence, homogenisation at even larger time and temperature is required to give completely carbide free austenitic matrix in cast steels. It may not be a viable alternative to do very high temperature and long time homogenising treatment and as the microsegregation of substitutional solid solution may not be eliminated even then.

The mechanical properties of the as-cast steel 3/2, homogenised at 1100°C/8 hr and water quenched is compared with a typical wrought solution annealed steel reported in the literature as shown in Table 6. The comparison is made with a low carbon steel and a 0.4% C wrought steel reported in the literature of close by compositions. It is found that the as-cast steel 3/2 in the present study showed poorer ductility than the wrought hot rolled and solution treated low carbon and high carbon steels. This could be attributed to the prevalence of microsegregation and the presence of residual carbides in the cast steel which may nucleate cracks.
Usually alloy steels such as tool and die steels processed through ESR, show properties equivalent to that of wrought materials.\(^{13}\) This is because of the absence of severe microsegregation and formation of fine equiaxed grain structures in them. There are other cast steels, where ductility is adversely affected due to presence of microsegregation.\(^{19}\) The present steel 3/2 also shows poorer ductility which may be attributed to dendritic microsegregation and presence of residual carbides where brittle carbide phases could nucleate cracks. Hence, the properties of steel castings made from high nitrogen steels could have poorer ductility than wrought steels.

### 4. Conclusions

1. Once alloyed with nitrogen, it is possible to remelt nickel free high nitrogen steels by conventional ESR process without pressure. A good retention of nitrogen content is possible using this method.
2. The nitrogen loss during the conventional ESR process is dependent on the melt rate employed. The lower the melt rate, the better is the recovery of nitrogen content in the steel.
3. Sound ingots of high nitrogen steels could be produced during conventional ESR processing without nitrogen gas pressure over the melt.
4. The as-cast structure of a typical steel was characterised. The interdendritic regions were richer in carbides and nitrides. The presence of Cr\(_2\)C\(_3\) type of carbides and Cr\(_7\)N type of nitrides was observed in the interdendritic region.
5. Homogenising treatment at 1 100°C for 8 hr showed that microsegregation of Cr, Mn still persisted along with some amount of residual carbides in some interdendritic regions.
6. The mechanical properties of the cast homogenised steels show poorer ductility compared to wrought steels and is attributed to the presence of microsegregation.

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### REFERENCES

1. B. R. Nijhawan, P. K. Gupta, S. S. Bhattacharjee, B. K. Guha and S. S. Dhanjal: JISI, 205 (1967), 292.
2. B. E. Paton, B. I. Medovar, V. Yu Saenko and V. A. Tikhanov: *Proc. Spec. Electromet.*, 6, (1990), No. 3, 4.
3. D. J. Carney: Blast Furnace & Steel Plant, paper presented at Cleveland regional technical meeting of AJSI, (1955), 1377–1380.
4. V. V. P. Kutumba Rao and P. Rama Rao: *Banaras Metallurgist*, 5, (1973), No. 3, 134.
5. G. Stein, J. Menzel and H. Dorr: Proc. of Int. Conf. HNS-88, High Nitrogen Steels, HNS-88, ed. by J. Foc and A. Hendry, The Inst. of Met., Kiev, Ukraine, (1989), 32.
6. G. F. Torkhov, Yu. V. Latash, R. R. Fessler, A. H. Clauer, E. E. Fletchener and A. C. Hoffmanner: *J. Met.*, 30 (1978), 20.
7. W. Holzgruber: Proc. of Int. Conf. HNS-88, High Nitrogen Steels, ed. by J. Foc and A. Hendry, The Inst. of Met., Kiev, Ukraine, (1989), 39.
8. B. I. Medovar, A. G. Boagachenko, V. Ya. Saenko, V. A. Tikhanova, V. Ya. Maidannik, G. B. Shihupak, Yu. M. Pominar, G. I. Chernenski, S. V. Tomilenko and V. A. Ryalinin: *Adv. Spec. Electrometall.*, 4 (1990), 289.
9. V. V. P. Kutumba Rao and P. Rama Rao: *Int. Met Rev.*, 3, (1989), No. 2, 78.
10. B. E. Paton, B. I. Medovar, V. A. Tikhanov: *Adv. Spec. Electrometall.*, 6 (1990), 193.
11. G. Hoyle: Electroslag Processes—Principles and Practice, Applied Sci. Pub., London, (1983), 50, 56, 75.
12. H. K. Feichtinger: HNS-93, Proc of 3rd Int. Conf. on High Nitrogen Steels, ed. by V. G. Gavrilujik and V. M. Nadutov, Inst. of Met. Phys., Kiev, Ukraine, (1993), 45.
13. R. C. Gupta and J. Beech: *Trans. IIM*, 42 (1989), No. 6, 571.
14. O. P. Sinha and R. C. Gupta: *Tool Alloys Steels,*(1990), 45.
15. O. P. Sinha and R. C. Gupta: *ISIJ Int.*, 34 (1993), 567.
16. T. Z. Kattamis and M. C. Flemings: *Trans. AIME*, 235 (1965), 992.
17. F. C. Quigley and Del.ura: Solidification Technology, Proc. of First Army Materials Conf., ed. by J. J. Burke, M. C. Flemings and A. E. Gorum, Boise Hill Pub. Co., Mass, USA, (1992), 339.
18. C. M. Hsiao: *Trans ASM*, 52 (1960), 855.