

Nitrogen alloying of AISI 310S in an induction furnace

by Y.N. Turan* and A. Koursaris†

SYNOPSIS

A series of experiments was carried out in a vacuum-induction furnace to investigate the solubility of nitrogen in stainless steel type 310S. Melts were made under constant and variable partial pressures of nitrogen so that the absorption of nitrogen from the atmosphere could be examined. Additions of nitrogenized ferrochromium were made to give high nitrogen contents in the steel.

Nitrogen contents of up to 0,16 wt per cent were obtained under gaseous atmospheres. With additions of nitrogenized ferrochromium, nitrogen contents of up to 0,525 wt per cent were obtained. Comparisons of the latter value with existing data indicate that the equilibrium concentration of nitrogen was reached for the experimental conditions used.

SAMEVATTING

Daar is 'n reeks eksperimente in 'n vakuuminduksieoond uitgevoer om die oplosbaarheid van stikstof in vlekvrystaal, tipe 310S, te ondersoek. Smeltings is onder konstante en veranderlike stikstofdeeldrukke uitgevoer sodat die absorpsie van stikstof uit die atmosfeer ondersoek kon word. Ferrochroom waarby stikstof gevoeg is, is bygevoeg om 'n hoë stikstofinhoud aan die staal te gee.

'n Stikstofinhoud van tot 0,16 massapersent is onder gasatmosfeer verkry. Met die byvoeging van ferrochroom waarby stikstof gevoeg is, is 'n stikstofinhoud van tot 0,525 massapersent verkry. Vergelykings van die laasgenoemde waarde met bestaande data dui daarop dat die ewewigskonsentrasie van stikstof bereik is vir die eksperimentele toestande wat gebruik is.

INTRODUCTION

Since the 1920s there has been enormous interest in the effect of nitrogen on austenitic stainless steels¹. The main reasons for this are that nitrogen is a strong austenite-stabilizing element, and can be used as a partial replacement for nickel, which is a very costly metal. Nitrogen also increases the strength of stainless steels without adversely affecting their ductility. In addition, the formation of chromium nitride in stainless steel is not as detrimental as the formation of carbide, which results in sensitization of the steel. For these reasons, new types of austenitic stainless steels have been developed, such as the 2XX series, 304N, 316N, nitronic types, and many other nitrogen-containing commercial austenitic stainless steels. However, it is well known, that gases in metals can have detrimental effects such as the formation of pores, which reduce ingot yield and may result in difficulties during hot-working of the material. The processing of liquid alloys containing high concentrations of nitrogen may also present problems owing to a probable reduction of gas solubility with decreasing temperature and the possible evolution of considerable quantities of gas during solidification. In order to obtain high concentrations of nitrogen in stainless steels, it may therefore be necessary to develop advanced melting and casting techniques like plasma-arc melting and slag remelting, in which very high nitrogen pressures can be attained.

* Previously of the Department of Metallurgy and Materials Engineering, University of the Witwatersrand, Johannesburg. Now at American Iron and Brass Foundry, P.O. Box 3709, Alrode, 1451 Transvaal.

† Department of Metallurgy and Materials Engineering, University of the Witwatersrand, P.O. Wits, 2050 Transvaal.

© The South African Institute of Mining and Metallurgy, 1992. SA ISSN 0038-223X/3.00+0.00. Paper received 25th January, 1991; modified paper received August 1991.

Table I

Development of process technologies for the production of high-nitrogen stainless steels

Year	Process	Ingot size kg
1960	Pressure-induction furnace, basic investigations	25
1965	Laboratory-scale pressure electro-slag remelting	20
	Pressure plasma furnace	1 000
1970	Pressure electro-slag remelting	1 000
1980	First production-scale pressure electro-slag remelting	8 000
1985	Pressure electro-slag remelting	2 000

The solubility limit of nitrogen in austenite can be varied through changes in the processing conditions. Holzgruber² recently reviewed the development of processes for the production of high-nitrogen steels. His survey is presented in Table I.

Each process has its own constraints, which are related to the production capacity, the rate of production, and the compositional homogeneity of the ingots. However, plasma-arc melting and electro-slag remelting are the most efficient processes for the production of high-nitrogen steels. A nitrogen concentration of 1 wt per cent can be achieved by these methods.

However, the amount of nitrogen in nitrogen-containing austenitic stainless steels is generally limited to a maximum of 0,15 wt per cent. This higher nitrogen content has been achieved in austenitic stainless steels through an increase in the manganese content, which increases the solubility of

nitrogen, or through melting and casting by the use of advanced techniques like plasma-arc melting¹.

The present paper deals with the alloying of AISI 310S with nitrogen up to the solubility limit in a vacuum-induction furnace.

EXPERIMENTAL PROCEDURES

The solubility of nitrogen in 310S was determined on ingots cast under different partial pressures of nitrogen in a laboratory vacuum-induction furnace. The casting temperature was nearly constant, varying between 1450 and 1460°C. The furnace is rated at 52 kW, with a nominal frequency of 3000 Hz. The furnace was equipped with the following facilities:

- a gas-inlet valve, which permits melting and casting under different gas atmospheres,
- a multiple power lead-through for thermocouples and a dip thermocouple to measure temperatures,
- a charging device with an effective volume of approximately 0,5 litre,
- a Divac vacuum gauge with a measuring range of 1 to 0,001 atm., and
- a sintered-magnesia crucible with magnesite pouring spouts.

The molten metal was poured into flake-graphite cast-iron moulds of 64 mm square section and 250 mm depth. The capacity of the moulds was about 6 kg of steel.

Castings were produced with the following aims:

- (1) to obtain a range of nitrogen contents up to the solubility limit in steel 310S by additions of nitrogenized ferrochromium in an atmosphere of 0,6 atm. of nitrogen, and
- (2) to investigate the pick up of nitrogen by nitrogen-free 310S under nitrogen partial pressures of up to 0,8 atm., the object being to determine the amount of nitrogenized ferrochromium required for a specific nitrogen content in the steel since some of the nitrogen would be introduced from the furnace atmosphere.

Small pieces of 310S were charged into the crucible, and the vacuum chamber was closed and evacuated. The charge was preheated for 20 to 30 minutes at a power input of 20 kW. Nitrogen gas was allowed into the chamber via the gas inlet until the required pressure was reached. The power input was then increased to 40 kW. Once the metal had melted, the nitrogenized ferrochromium was added, the temperature was measured and, about 5 minutes later, the metal was poured into the ingot mould. The ingots were allowed to cool in the furnace.

RESULTS

The as-cast ingots, when examined visually, were found to be sound in regard to gas porosity. The maximum nitrogen concentration attained in the alloy was 0,121 wt per cent under a nitrogen partial pressure of 0,79 atm. Figure 1 shows the dependence of the nitrogen content of the steel on the partial pressure of nitrogen in the vacuum-induction furnace. This reveals that the nitrogen content was approximately proportional to the square root of the nitrogen partial pressure, i.e. the relationship followed Sievert's law.

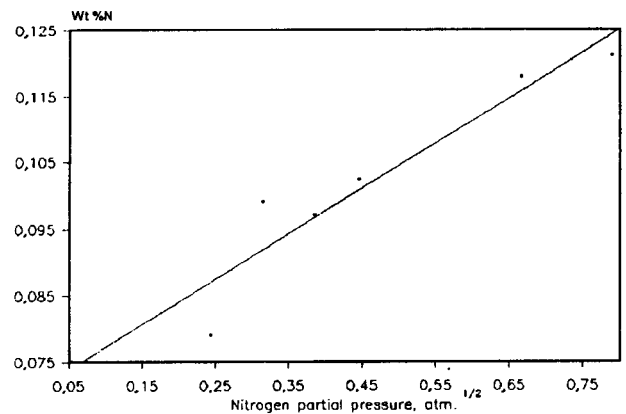


Figure 1—The effect of the nitrogen partial pressure on the solubility of nitrogen in 310S steel

Statistical analysis of the results gave rise to the following equation, which had a correlation coefficient of 0,94:

$$\%N = 0,13 P_N^{0,15}$$

The exponent of the above equation (0,15) is lower than that of Sievert's equation, which is 0,5 because equilibrium conditions had not been attained.

The nitrogen content of the castings was examined as a function of the additions and is presented in Figure 2. The horizontal line shows the amount of nitrogen that was picked up from the nitrogen atmosphere. The sloping line represents the amount of nitrogen gained from the nitrogenized Fe-Cr. Both lines were obtained from calculations of material balance and from chemical analyses. A typical material balance is shown in Table II.

First, the amount of nitrogen in the steel was calculated from the amount of nitrogenized Fe-Cr added. The calculated nitrogen content was then compared with that found by chemical analysis. The concentration of nitrogen obtained by chemical analysis was 0,12 to 0,13 wt per cent higher than the calculated value (Table II). It is therefore clear that some nitrogen was picked up from the nitrogen atmosphere. In order to check these results, four additional castings were made without the addition of nitrogenized Fe-Cr under a nitrogen atmosphere of 0,6 atm. Ingots

Table II
A typical material-balance calculation

Item	Mass g	Cr		Ni		C		N	
		%	g	%	g	%	g	%	g
310S	6000	24,48	1468	19,24	1154	0,047	2,82	0,017	1,062
Fe-Cr-N	250	65,4	163,5	0	0	0,026	0,065	9,25	23,12
Calculated analysis	6250	26,11	1632	18,47	1154	0,046	2,885	0,386	24,18
Chemical analysis		26,36		18,47		0,044		0,525	
Loss or gain		0,243		0,00		0,00		0,138	
Casting temperature	1450								

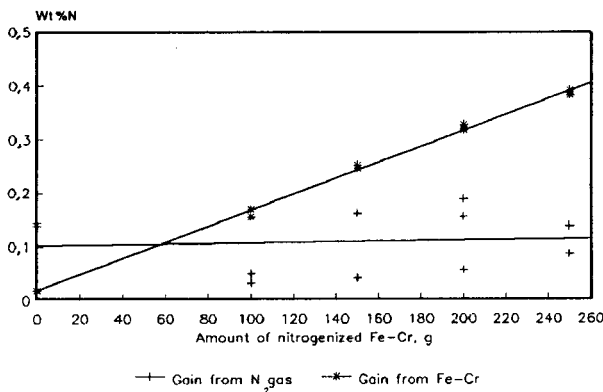


Figure 2—The recovery of nitrogen from nitrogenized Fe-Cr and from the furnace atmosphere

produced in this manner were found to contain between 0,13 and 0,15 wt per cent nitrogen, proving that some nitrogen had been picked up from the furnace atmosphere. The recovery of nitrogen from the added Fe-Cr was also determined, and was found to be 100 per cent in all cases (Table II).

DISCUSSION

In general, the solubility of a gas in an alloy is much greater in the liquid state than in the solid state. Gas solubility usually increases with increasing temperature, and reaches a maximum under equilibrium conditions. The concentration of a gas in a metal at equilibrium depends on the partial pressure of that gas over the liquid metal. This effect is described by Sievert's law, which can be stated as follows:

$$1/2N_2 (gas) \rightarrow N$$

$$[\%N] = k \cdot \sqrt{p}$$

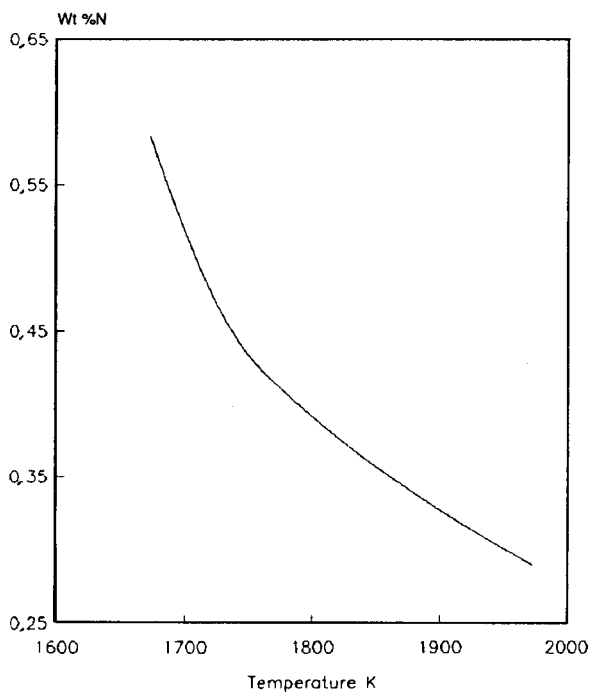


Figure 3—The calculated solubility of nitrogen in 310S steel at 0,6 atm. partial pressure of nitrogen

where p is the partial pressure of the gas over the alloy, and k is the solubility constant, which depends on the nature of the gas and temperature.

Vapa and Pehlke³, in their study of the solubility of nitrogen in liquid Fe-Cr-Ni, Fe-Cr, and Ni-Cr alloys, found that the solubility of nitrogen in austenitic stainless steels conforms to Sievert's law, and that chromium markedly increases the solubility of nitrogen in these alloys. In Fe-Cr-Ni alloys, it was found that the solubility of nitrogen in the liquid alloy decreased with increasing temperature. From the data in the Addendum, the solubility of nitrogen in liquid 310S was calculated as a function of temperature (Figure 3). This shows that higher concentrations of nitrogen in such alloys would be obtained if the partial pressure of nitrogen over the alloy were increased and the lowest possible casting temperature were used.

Figure 1 demonstrates that the solubility of nitrogen increased linearly with the square root of the nitrogen partial pressure, as might have been expected. Since the rate of nitrogen absorption from the atmosphere in the liquid metal is low, it was not possible to reach the saturation content of nitrogen in a relatively short time. Therefore, to obtain higher nitrogen contents in 310S, it was necessary to add nitrogenized ferrochromium, which resulted in a rapid increase in the nitrogen content of the alloy. It is apparent from Figure 2 that 0,12 to 0,13 wt per cent nitrogen was introduced from the atmosphere, while the remaining nitrogen originated from the nitrogenized ferrochromium.

A maximum nitrogen content of 0,54 wt per cent was obtained in 25 Cr-20 Ni alloy produced by thermochemical methods⁴. Thus, 0,525 wt per cent nitrogen is close to the equilibrium nitrogen content that can be attained in 310S under the conditions used in this study. The actual casting temperature was in the region of 1450°C (about 1720 K). As can be seen from Figure 3, the actual nitrogen content (0,525 per cent) was very close to the calculated value (0,50 per cent).

The effects of alloying elements on the solubility of nitrogen in a liquid Fe-18 Cr-8 Ni alloy at a pressure of 0,1 MPa and a temperature of 1600°C are summarized in Figure 4. It can be seen that chromium increases the solubility of nitrogen, but nickel, which is the second most important element in austenitic stainless steels, decreases it.

Unlike liquid Fe-Cr-Ni ternary alloys, little research has been conducted on the solubility of nitrogen in austenite. Recently, the solubility of gaseous nitrogen in austenite was reported by Kikuchi *et al.*⁴. Their results, which are summarized in Figure 5 for different types of alloys, show that the solubility of nitrogen in Fe-25 Cr-20 Ni alloy increases with decreasing temperature in the region of the liquid and in the austenite. Their results agree with those of Vapa and Pehlke³.

The maximum concentration of nitrogen obtained in the present study (0,525 wt per cent) was also compared with that predicted from thermodynamic calculations. This value is 0,025 per cent higher than the calculated equilibrium value. It was therefore assumed from these results that the nitrogen concentration (0,525 wt per cent) was the

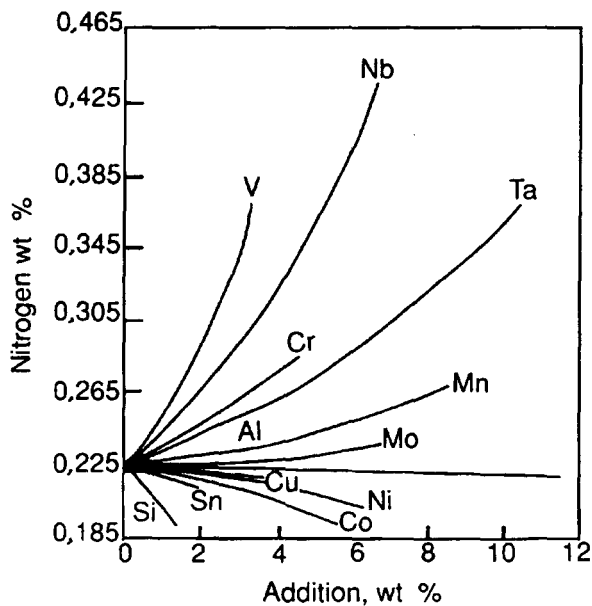


Figure 4—The effect¹ of alloying on the solubility of nitrogen in a liquid Fe-18Cr-8Ni alloy at 0,1 MPa partial pressure of nitrogen and 1600°C

equilibrium concentration at the temperature used.

Figure 5 demonstrates that the solubility of nitrogen in austenite is higher than in the liquid 25Cr-20Ni alloy. Therefore, there will be no tendency for the evolution of gas during the transformation from liquid to austenite or during the reheating of ingots, as is the case with most steels. This is the reason why no gas pores were observed in the ingots that were made.

The maximum nitrogen content attained in this study was compared with data from the literature. As indicated in Table III, the maximum nitrogen concentration (0,525 per

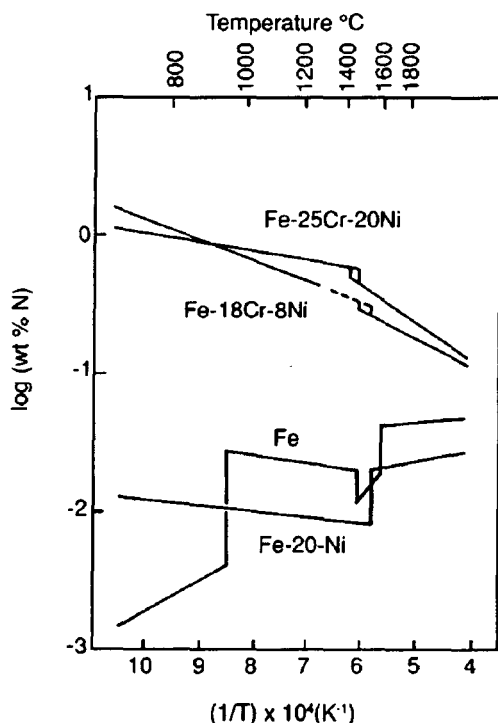


Figure 5—Temperature dependence of nitrogen solubility at 1 atm. pressure of nitrogen in three austenitic stainless steels³

Table III

The nitrogen content attained in austenitic stainless steels with different production techniques

Base alloy	Production technique	Nitrogen wt %	Reference
25 Cr-20 Ni	Induction furnace, 0,6 atm. of nitrogen	0,525	This study
25 Cr-20 Ni	Thermochemical production (0,66 atm. for 10 h)	0,54	5
25 Cr-16 Ni-7 Mn	Plasma-arc remelting	0,6-0,7	6
20 Cr-3 Ni-5 Mn	Pressurized electro-slag remelting	0,85	7

cent) obtained in this study compares well with the values obtained by other researchers, who used a variety of techniques to prepare alloys.

CONCLUSIONS

- (1) By induction melting and casting, a range of nitrogen contents with a maximum of 0,525 wt. per cent was obtained in alloy 310S.
- (2) The solubility of nitrogen in liquid 310S increased with decreasing casting temperature.
- (3) Nitrogen concentrations of 0,12 to 0,13 wt per cent were introduced in the metal from a nitrogen atmosphere with a partial pressure of 0,6 atm. Higher nitrogen contents were obtained by the addition of nitrogenized ferrochromium shortly before the alloy was cast.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to Middelburg Steel & Alloys for financial support and for the test material provided.

REFERENCES

1. REED, R.P. Nitrogen in austenitic stainless steels, *J. Miner. Met. Soc.*, vol. 41, no. 3. Mar. 1989. pp. 16-21.
2. HOLZGRUBER, W. Process technology for high nitrogen steels. *HNS-88*. Foct, J., and Hendry, A. (eds.). London, Institute of Metals, 1989. pp. 39-48.
3. VAPA, H., and PEHLKE, R.D. Nitrogen solution and titanium nitride precipitation in liquid Fe-Cr-Ni alloys. *Metall. Trans. B*, vol. 8B. Sep. 1977 pp. 443-450.
4. KIKUCHI, M., KAJIHARA, M., and FRISK, K. Solubility of nitrogen in austenitic stainless steel. *HNS-88*. Foct, J., and Hendry, A. (eds.). London, Institute of Metals, 1989. pp. 63-74.
5. KAJIHARA, M., KIKUCHI, M., and CHOI, S.K. Cellular precipitation of Cr₂N in chromium-nickel austenitic steels. *Phase Transformations '87 Conference Proceedings*. Lorimer, G.W. (ed.). London, Institute of Metals, 1988. pp. 265-268.
6. TORIKHOV *et al.* Thermomechanical processing parameters for a high-nitrogen stainless steel prepared by plasma-arc remelting. *J. Metals*, Dec. 1978. pp. 20-27.
7. STEIN, G., MENZEL, J., and DÖRR, H. Industrial manufacture of massively nitrogen alloy steels. *HNS-88*. Foct, J., and Hendry, A. (eds.). London, Institute of Metals, 1989. pp. 32-38.

ADDENDUM: CALCULATION OF SOLUBILITY

The solubility of nitrogen in 310S liquid was calculated from data given by Vapa and Pehlke³.

$$\log (\%N) = \log (\%N)_{Fe} - \log f_N$$

$$\Delta G_N^\circ \int (4720 \pm 1050) + (23,40 \pm 0,59) =$$

$$-RT \ln \frac{\%N}{\sqrt{P_{N2}}}$$

$$\therefore \log (\%N)_{Fe} = -247/T - 1,22$$

$$\log f_N = \sum e_N^i \cdot (\%i) + 1/2 \cdot \sum e_N^{\ddot{i}} \cdot (\%i)^2 +$$

$$\sum e_N^{\ddot{ij}} \cdot (\%ij)$$

The first- and second-order parameters are as follows:

$$e_N^{Cr} = -164/T + 0,0415$$

$$e_N^{Ni} = 8,33/T + 0,0019$$

$$e_N^{Mn} = -133,8/T + 0,035$$

$$e_N^{CrCr} = 3,35/T - 0,0012$$

$$e_N^{NiNi} = -3,67/T + 0,0021$$

$$e_N^{CrNi} = 1,60/T - 0,0009$$

$$e_N^{MnMn} = 17,63/T - 0,011$$

$$e_N^{CrMn} = 2,16/T - 0,0005$$

$$e_N^{NiMn} = 0,09/T - 0,0007.$$

At 1873K,

$$e_N^C = 0,103$$

$$e_N^{CC} = 0,014.$$

The chemical composition of 310S is taken as follows:

%Cr 25, %Ni 20, %Mn 1,5, %C 0,04.

Engineering symposium

The Engineering Institution of Zambia (EIZ) is to hold a symposium in Chingola (Zambia) from 9th to 11th November, 1992.

THEME

Advances in Scientific Research and Engineering in the Southern African Region.

OBJECTIVES

To promote business by communicating recent scientific and engineering developments and innovations, and to exchange ideas about the future in the light of liberalization in the region.

CALL FOR PAPERS

Broad topics:

- Advances (Innovations) in:
 - Telecommunications
 - Transport (Road/Railway)
 - Manufacturing Industries
 - Non-destructive Test Techniques
- Chemical Industry and the Environment
- Food Processing Technology Appropriate for the Consumer in the Region

- Water Engineering:
 - Irrigation
 - Reclamation of Water
 - Domestic Water Supply.
- Mining and Mineral Processing
- Energy:
 - Hydro
 - Solar
 - Nuclear
 - Organic
- Pollution Control and Sewage Treatment.

CLOSING DATES

Abstracts: 30/04/92

Papers: 31/07/92

All correspondence to

Dr G. M. Beene CEng. MICHEME MEIZ
Chairman
Organizing Committee
P.O. Box 10761
Chingola
Zambia.

Zinc conference

The Australasian Institute of Mining and Metallurgy (AusIMM) and the Canadian Institute of Mining, Metallurgy and Petroleum will jointly sponsor Zinc '93, The International Symposium on Zinc held every eight years. The Symposium will be held in Hobart, Australia, from 10th to 13th October, 1993, celebrating the centenary of The AusIMM. The Institution of Mining and Metallurgy, The Mining and Materials Processing Institute of Japan, and The Minerals, Metals and Materials Society are supporting organizations.

VENUE AND TOURS

Hobart, situated on the island of Tasmania, is an appropriate venue for the Symposium, since the area supports significant base-metal mines at Hellyer and Rosebery. There will be a post-Conference tour covering the geology, exploration, mine, and concentrator at both locations. Downstream processing to metal products occurs at the Pasminco Metals-EZ electrolytic zinc refinery, situated close to the Conference venue. This company will celebrate its 75th year of zinc production following an extensive modernization programme.

A pre-Conference tour is planned to study the geology and exploration of the Mt Isa area and its mines, concentrators, and smelters. There will be an alternative tour to the ISF near Newcastle and a galvanizing plant.

The Conference will cover all aspects of zinc production, from exploration to downstream processing and end-use of the metal and its alloys. The proceedings of Zinc '93 will be published for distribution at the Conference. Dr I G Matthew has been appointed Editor.

PAPERS

Papers, including poster presentations, are invited worldwide on the following topics:

- Geology and exploration
- Mining
- Mineral processing
- Extractive hydrometallurgy
- Extractive pyrometallurgy, including ISF technology
- Recycling and residue treatment
- Alloys and end-uses.

TIMETABLE FOR PAPERS

Receipt of abstracts	31 July 1992
Notification of acceptance	30 September 1992
Deadline for receipt of final paper (5 000 words) as camera ready document	1 February 1993

FURTHER INFORMATION

Enquiries should be addressed to

Charmayne Perera
The Australasian Institute of Mining and Metallurgy
P.O. Box 122
Parkville
Victoria 3052
Australia.

Tel: (03) 347 3166; Fax: (03) 347 8525.

Centenary conference

The 1993 AusIMM Annual Conference celebrates the centenary of The Australasian Institute of Mining and Metallurgy, whose inaugural meeting was held in Adelaide on 4th April, 1893. While recognizing 100 years of development in the mining industry, the Conference provides an opportunity to consider current exploration, mining, and metallurgical practices, and trends for the future.

Venue: Adelaide Conference Centre
Keynote: Lectures will be given by eminent speakers from Australia and overseas

Field trips: Olympic Dam and historical copper towns in South Australia

Deadlines:

Receipt of Abstracts	1 May 1992
Notification of acceptance of abstracts	12 June 1992
Papers to Editorial Committee for final review	1 October 1992
Final copies of papers	1 December 1992

Papers: Papers are invited in the following categories:

- Mining
- Metallurgy
- Geology
- Mining heritage/historical
- Mineral economics/finance
- Environment
- Legislation.

Schedule: Those wishing to present papers are invited to submit a 200 word abstract to

R.K. Johns
c/o Department of Mines and Energy
191 Greenhill Road
Parkside 5063
South Australia.
Tel: (08) 274 7500
Fax: (08) 272 7597.