Martensitic Transformation during the Sintering of High Strength P/M Silicon-Manganese Steels

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Introduction: In the past, variety of steels with wide range of mechanical properties satisfying the structural requirements necessary for engineering applications have been developed by selecting a suitable amount and combination of alloying elements. The application of these steels mainly depends on the cost for processing them into the product form which includes the cost of alloying elements also. For many years powder metallurgical research and development has been aimed at introducing the costly elements like nickel , copper, tungsten, molybdenum and vanadium into their alloying techniques. Now it is of interest and need to develop new alloying systems on the basis of more economic elements like silicon and manganese. Recent developments in powder making and consolidation techniques have made it possible to incorporate high oxygen affinity alloying elements, such as, silicon and manganese, to result in high strength steels. They have already proved their importance as deoxidisers and desulphurisers in conventional metallurgy. Silicon raises A3 point, lowers A4 point and stabilises the α region in the Fe-Si phase diagram and thus wedge out γ -region as shown in Fig 1. Silicon readily forms the intermetallic compounds, such as, Fe_3Si, Fe_2Si, $FeSi_2$, Fe_2Si_5 etc. From the phase diagram, the silicon forms a transient liquid phase at 1180°C causing an excessive swelling during heating and shrinkage and soaking period, respectively, leading to the strong dimensional changes, limiting its application for structural components. Recently an idea of compensating these dimensional changes by addition of suitable alloying element such as manganese has been forwarded. Manganese raises A4 point and lowers A3 point by which it widens the γ-region and thus stabilizes the austenite as shown in Fig 2. Manganese when added to plain

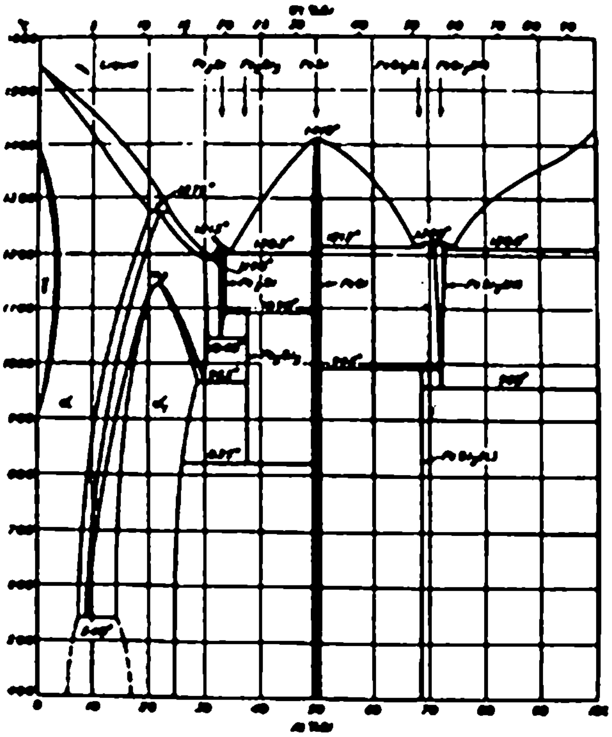

FIG. 1- Binary phase diagram of Fe-Si System

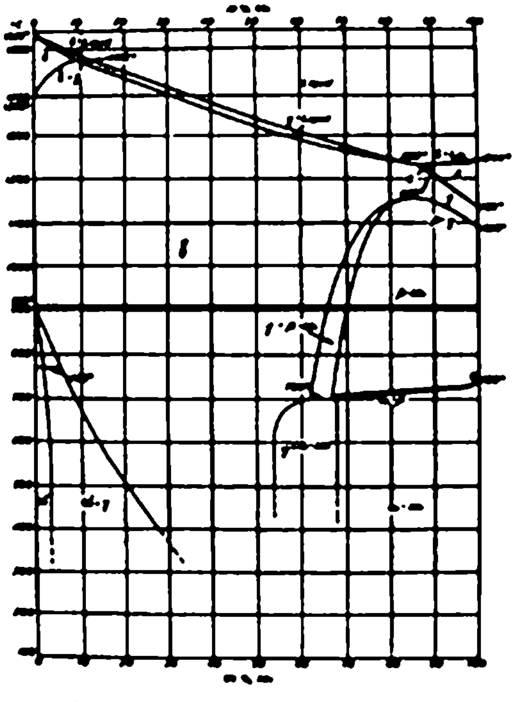

FIG.2- Binary phase diagram of Fe-Mn System

carbon steels, combines with carbon to form stable compounds like Mn_3C_4 and Mn_3C whereas with silicon it forms stable silicides, such as Mn_2Si, MnSi, etc. The combination of silicon and manganese has already proved to be a better substitute for other expensive alloying elements in conventional steel technology , whereas their use in powder metallurgy was hindered due to the high oxygen affinity when they are in powder form. But this barrier was compensated with use of silicon manganese in the compound form as ferrosilicon and ferromanganese[1]. The dialatometric curves shown in Fig 3 clearly depict the zero growth characteristics within soaking period with an excessive swelling peak just below the transformation temperature due to the formation of new phases. The excessive swelling peak is due to the melting of ferro silicon which has shifted to the lower temperatures. The ternary phase diagram shown in Fig 1 indicates the bound of crystallization surfaces as well as the liquid phase field represented by the shadowed area at the sintering temperature of 1180°C. Thus , theoretically steel may be developed with a combination of silicon and manganese in iron which may substitute the conventional expensive copper and nickel alloyed P/M steels, used for expensive copper and nickel alloyed P/M steels used for manufacturing structural components.

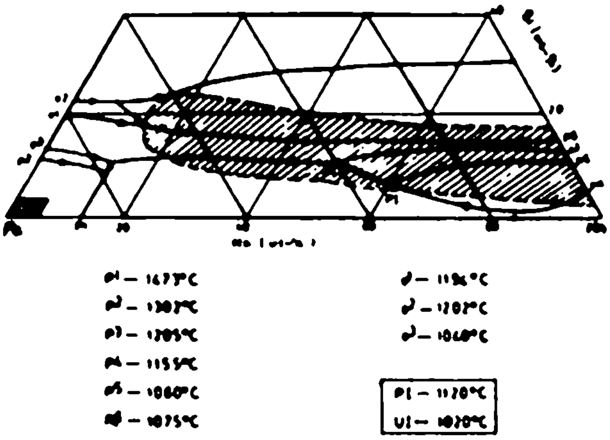

Fig.3: Section of Ternary Phase Diagram of Fe-Si-Mn System showing Liquid-Solid Relations

Experimental: In the present investigation electrolytic iron, ferrosilicon and ferromanganese powders were used as raw materials. Initially the individual powders were milled to a suitable particle size distribution. These powders were then characterized physically and chemically in terms of apparent density, tap density, flow rate and composition.

All the powders have been analysed for shape morphology and size distribution by scanning electron microscopy technique typical photographs of iron, ferromanganese and ferrosilicon powder particles have been shown in Fig 4. The diffusion couples were formed for iron-ferrosilicon and iron ferromanganese and sintered them at different temperatures ranging from 1000-1200°C for 60 minutes in hydrogen atmosphere. The microstructure photographs taken at the respective edges have been shown in Fig 5 and 6, respectively. The suitable amounts of ferrosilicon and ferromanganese powders were mixed with iron powder and subjected to the homogenization treatment for 30 minutes in a stainless steel ball mill of

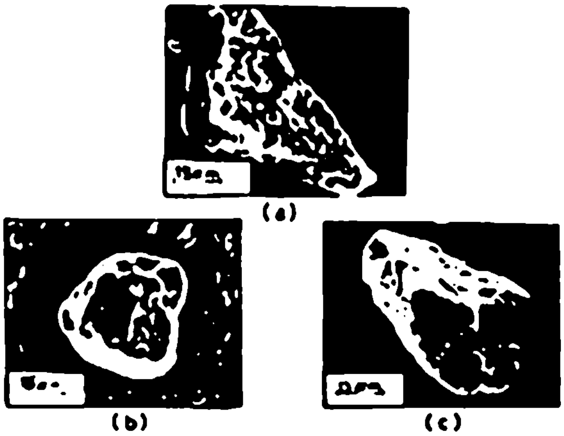

Fig.4: SEM Micrograph of a) Electrolytic iron, b) Ferromanganese, c) Ferro-silicon powders

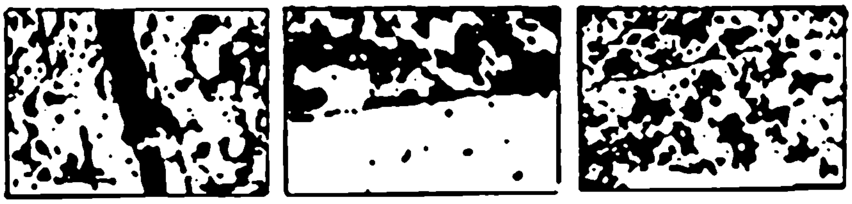

Fig.5 : Microstructures of Fe-FeSi Diffusion Couples formed at a) 1000°C, b) 1100°C, c) 1200°C

Fig.6. Microstructures of Fe-FeMn Diffusion Couples formed at a) 1000°C, b) 1100°C, c) 1200°C

capacity 1.5 litres and with ball to charge ratio 1:10. The stainless steel balls of diameter 9.5mm were used during the milling operation. The uniformly/regular mixed powders were shaped into geometries at different pressures ranging from 100-800 MPa in rigid cylindrical die cavities. During the compaction, Zinc stearate was used as lubricant for powders and also for die material. Based on the results of preliminary experiments, a compacting pressure of 500MPa was selected throughout the experimental investigation. The effect of compacting pressure on the green density of samples has been studied and plotted in Fig 8. These samples were sintered at different temperatures and for various soaking periods in a hydrogen atmosphere with a dew point of -57°C and flow rate of 26.5 ml/min. The effect of sintering temperature on the density has been shown in Fig 9. The sintered samples were analysed for their mechanical and microstructural behaviour. The effect of sintering variables on the mechanical properties has been studied and the corresponding results have been plotted in Figs 10, 11 and 12. The microstructural analysis has been carried out to arrive at some structure-property relationship. Typical unetched and etched microphotographs of samplels have been shown in Figs 13, 14, 15 and 16, respectively.

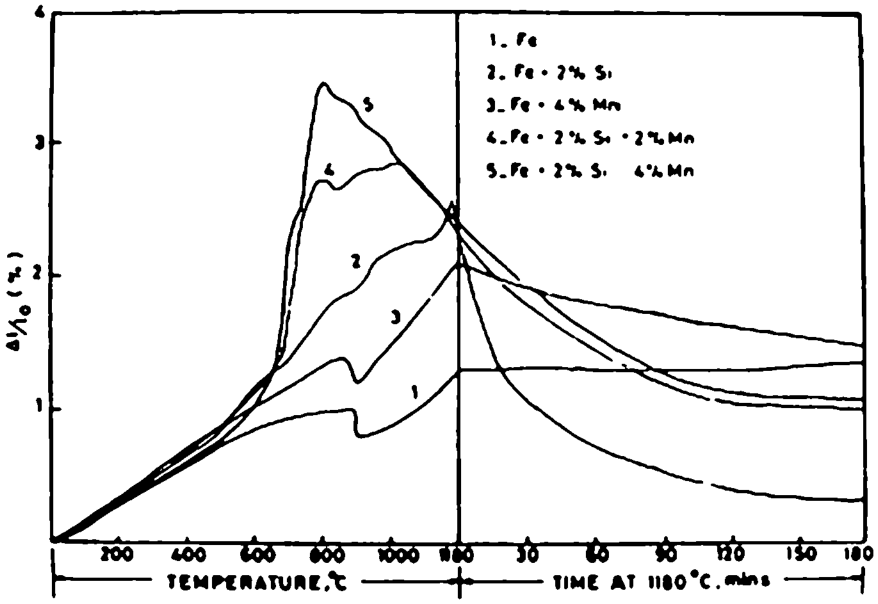

Fig.7: Dimensional Change $\Delta l/l_0$ during Sintering of Compacts from Fe-Mn, Fe-Si, Fe-Si-Mn Powder and of pure Fe

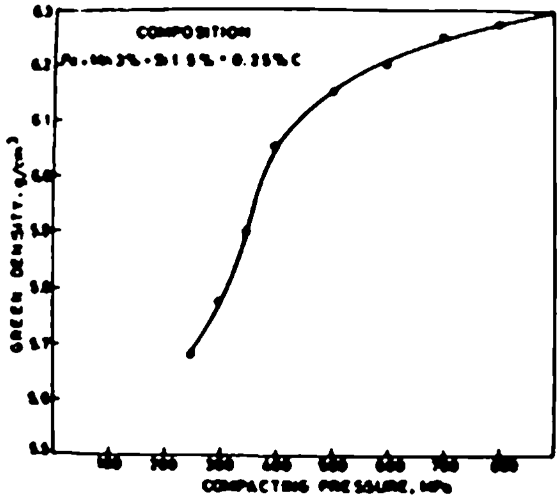

Fig.8: Effect of Compacting Pressure on Green Density of Blended Powders

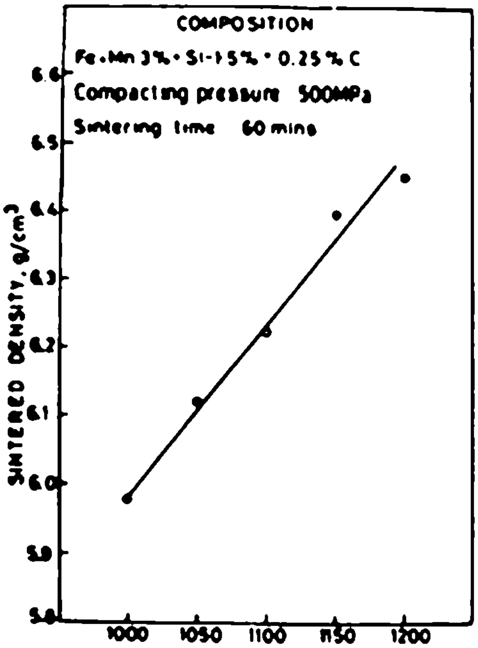

Fig.9: Effect of Sintering Temperature on Sintered Density of Steel Samples

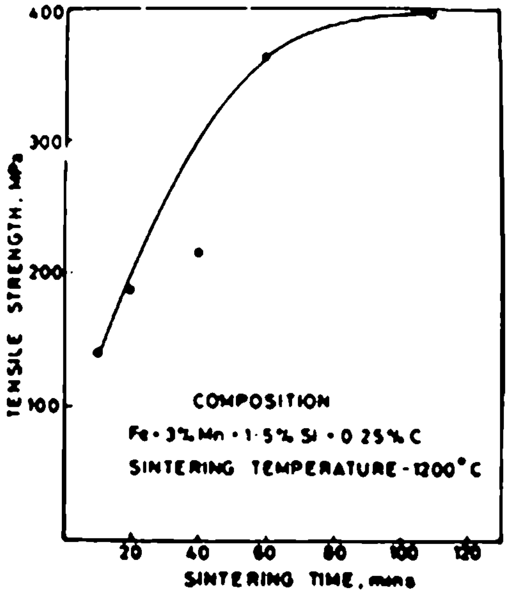

Fig. 10: Effect of Sintering Time on Tensile Strength of Steel Samples

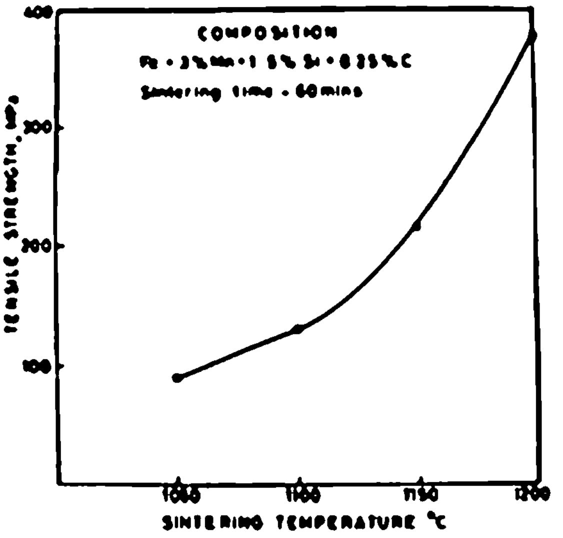

Fig.11: Variation of Tensile Strength with Sintering Temperature of Steel Samples

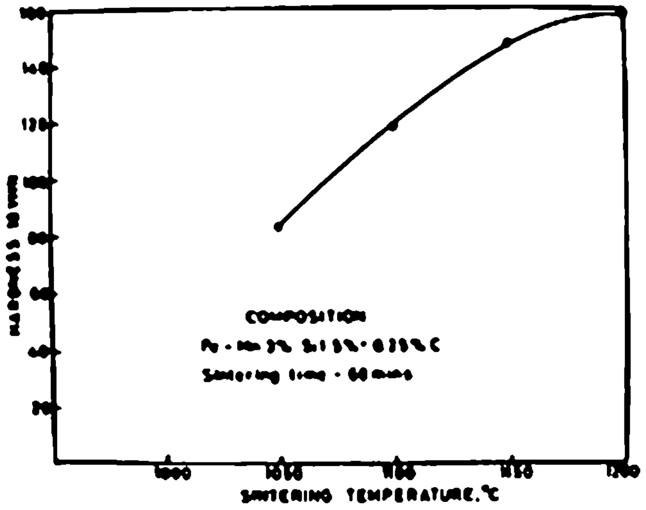

Fig.12: Effect of Sintering Temperature on Hardness of Steel Samples

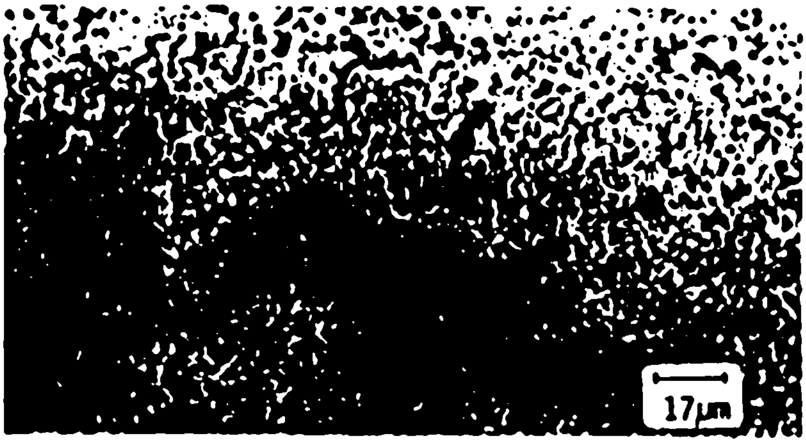

Fig.13: Unetched Microstructure of a typical Silicomanganese Steel showing the Inhomogeneity

Fig.14: Unetched Microstructure of a typical Silicomanganese Steel showing the Inhomogeneity (at higher magnification)

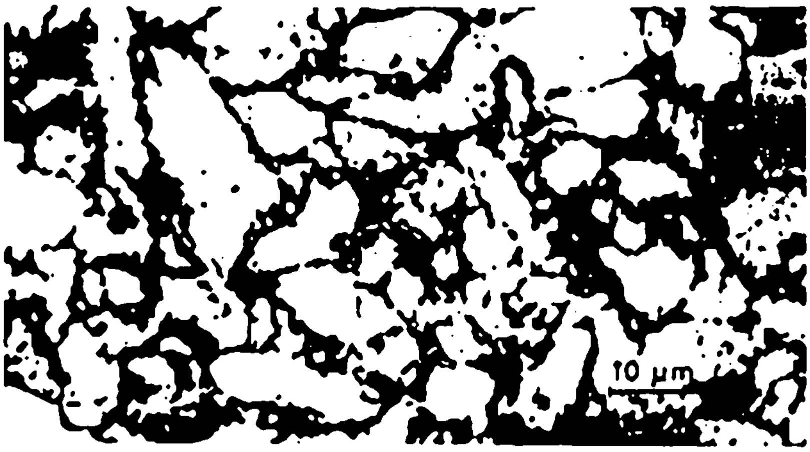

Fig.15: Etched Microstructure of a typical Silicomanganese Steel

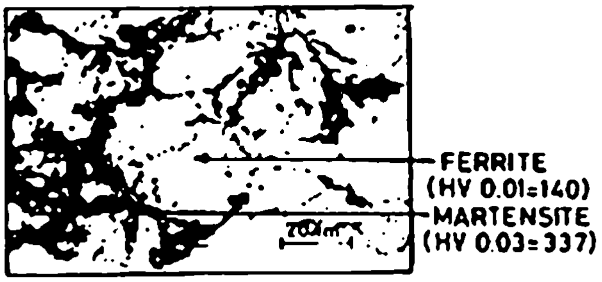

Fig.16: Typical Microstructure of Steel containing 1.5% Si and 2% Mn, sintered at 1200°C for 60 min.

Results & Discussion: The physical and chemical characteristics of ferrosilicon, ferromanganese, iron powders and mixed powders shows that with the increase of ferrosilicon content the apparent and tap densities increase whereas with that of ferromanganese additions a minor change is observed in the above densities. This is due to the fact that the density of ferromanganese is comparable to iron whereas ferrosilicon is lighter than iron. The variation in flow rate is of random nature but it is comparable to the flow rates used in powder metallurgy industry. The scanning electron micrograph of these powder particles shown in Fig 4 clearly depicts the shape of iron powder particles as triangular which is the characteristic of the electrolytic technique of producing powders. The shapes of the ferromanganese and ferrosilicon are irregular and the texture of the surface seems to be rough which may be due to the impact during mechanical milling. The photomicrographs in Figs 5 & 6 indicate that the suitable sintering temperature would be 1200°C. The microstructure of Fe-FeSi diffusion couple sintered at 1100°C shows a homogeneous structure. Similarly for the iron ferromanganese diffusion couple a demarcation line is clearly visible for the samples sintered at 1000°C and 1100°C, whereas for the sample sintered at 1200°C, it shows a homogeneous structure. The comparison of the diffusion couples of iron-ferrosilicon and iron-ferromanganese at temperatures 1000°C, 1100°C and 1200°C, it can be noted that the diffusion welding is rapid in case of iron ferromanganese diffusion couple than that for iron-ferrosilicon diffusion couple. This may be attributed to the fact that manganese diffusion in iron is faster than that of silicon. In addition to this, the melting of ferrosilicon gives rise to the appreciable amount of expansion/swelling which can be confirmed from Fig 7. The effect of compacting pressure on the green density of the sample as shown in Fig 8 indicate that as the compacting pressure increases from 200 to 800 MPa the green density increase from 5.68 g/cm^3 to 6.26 g/cm^3. The preliminary sintering experiments carried out for the samples compacted at different pressures indicate that the sintered densities of the samples compacted at the pressures above 500 MPa. This may be attributed to the fact that, at higher pressures the gas gets entrapped which, while sintering expands and comes out of the sample leaving behind the appreciable amount of porosity which in turn causes reduction in sintered density[3]. From Fig 9 it may be noted that as the sintering temperature increase from 1000°C to 1200°C, the sintered density goes on decreasing from 5.98 $gm/cm^3$to 6.45 g/cm^3. Above 1300°C of sintering temperature, the samples undergo excessive swelling. From Figs 10 & 11 it is observed that as the sintering temperature and time increase, the tensile strength increases. An increase of sintering temp. of the order of 150°C (from 1050°C to 1200°C) has resulted in a quantum jump in tensile strength from 96 MPa to 386 MPa. The samples sintered at 1200°C for various sintering times ranging from 20 to 120 minutes have shown tensile strengths ranging from 135 MPa to 397 MPa, respectively. In industries, large sintering periods are uneconomical,hence a sintering time of 60 minutes giving a tensile strength of the order of 375 MPa has been selected. Fig 12 indicates that as the temperature increases from 1050°C to 1200°C, the hardness level increases from 80 VHN to 158 VHN. The unetched microstructures in Figs 13 and 14 depict clearly the inhomogeneity in a circular shape. The etched microstructure in Figs 15 and 16 shows the liquid phase at the grain boundaries, different phases such as ferrite and martensite. The better mechanical properties along with the consistent microstructure may be attributed to the martensitic transformation taking place during the sintering itself. Thus eliminating additional heat treatment. In case of Fe-Mn binary systems, the martensitic transformation takes place at the level of 6% of manganese whereas in these steels it has been observed at 3% of the manganese. This is because of appropriate amount of silicon of the order of 1.5 percent and the inhomogeneties created due to interdiffusion of alloying elements from their ferro compounds[4]. The high rate of densification above 1050°C is due to the appearance of liquid phase during sintering. The formation of liquid phase is due to the melting of intermetallic compounds between the iron-silicon manganese which have lower melting point than the sintering temperature.

<u>Conclusions</u>: A non-conventional martensitic transformation has been observed in these steels which is taking place without quenching and at lower manganese content. The silicomanganese steels thus developed in the present investigation show superior properties to those expensive powder metallurgical steels with copper and nickel as alloying elements. The mechanical properties of these steels can be, further improved by additional heat treatment or cold working, to suit the specific requirements of structural components.

References

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