Influence of nitrogen as grain refiner in low carbon and microalloyed steels

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Abstract. Microalloyed steel is replacing using of low alloy steel in automotive industry. Microalloying elements like vanadium, niobium and titanium are used to enhance the steel property. The current work is focused on using nitrogen as a strengthening element in existing steel grade. Nitrogen in free form acts as solid solution strengthener and in combined form as precipitates acts as grain refiner for enhancing strength. The problem of grain coarsening at high temperature in case carburizing steel was avoided by increasing nitrogen level from 60ppm to 200ppm. Grain size of ASTM no 10 is obtained at carburizing temperature of 950°C by increasing nitrogen content from grain size no 6 with lower nitrogen. Mostly crankshaft is made from Cr-Mo alloyed steel. At JSW, nitrogen in the level of 130-200ppm is added to medium carbon steel to meet property requirement for crankshaft application.

1. Introduction
Microalloyed steels are group of steels which contains small addition of niobium, vanadium and titanium. The development of microalloyed steel started in sixties for flat rolled categories with niobium addition. For forging application microalloying steels was developed in 1980s [1][2]. Vanadium was the primary microalloying element and microstructure consists largely of pearlite. Currently these steel grades constitute around 12-14% of total steel production. The rising strength levels combined with excellent toughness favoured development of microalloyed steels. Microalloyed bar and forging steels are greatly used in automobile applications namely gears, crankshafts, spindle, fasteners, driveline components, connecting rods, spindle etc [3][4][5][6]. There is a high potential for this type of steel in forging application. Property of the steel is dependent on the microstructural aspects. Throughout the year’s large work have been carried out to understand the influence of these elements on microstructural aspects like effect of grain refinement, precipitate hardening and recrystallization effects during thermomechanical process. The common feature among these microalloying elements is their affinity towards nitrogen in forming nitrides and carbonitrides and these precipitates is responsible for increased properties. Generally, microalloyed steels have nitrogen content around 60-70ppm. In this work the effect of nitrogen at levels of 130-190 ppm is studied with respect to grain refinement at various temperatures is studied for case carburized steels. For increasing productivity nowadays carburizing is done at higher temperatures of 1000°C [3]. Low carbon steel grades are subjected to carburizing treatment for case hardening are prone to grain coarsening if sufficient amount of grain boundary pinning elements are not present at these high temperatures. Moreover, the development of crankshaft material with increased nitrogen content is discussed in this paper.
2. Strengthening mechanisms

The micro-alloyed steels are developed by means of a suitable combination of chemical composition and thermo-mechanical treatment parameters to achieve good strength without compromising toughness, ductility and formability. Properties of a material depend on the metallurgical features. The yield strength of steel can be increased by one or more of several strengthening mechanisms. [7][8][9]

a) Dislocation strengthening: the resistance to dislocation movement due to the obstacles presented to other dislocations. b) Grain-boundary strengthening: grain-boundary hindering of dislocation movement. With fine grains very high strength may be achieved. c) Solid-solution strengthening: the resistance to dislocation movement due to the presence of interstitial or substitutional solute atoms in a crystal lattice. The limitation of this mechanism is imposed by the solubility limit in each alloying system. d) Precipitation strengthening: the resistance to dislocation movement due to the effect of second-phase particles. Second-phase particles like precipitates formed from a supersaturated solid solution which is more present in practice. The limitation of this mechanism is governed by the influence of the size and shape on toughness, not on the strengthening. The dominant mechanism is grain-boundary strengthening, because the influence on the grain size can be accomplished by a modification of chemical composition and process parameters. The stability of austenite grains depends on the number of precipitates rather than their type. Any development in metallurgical aspect is focussed on grain refinement. Grain refinement has played a greater role in achieving higher mechanical properties. The combined effect of grain refinement and precipitation hardening in microalloyed steel replaced conventional C-Mn and Cr-Mo steels. Fine grain size is essential for high strength steels. Figure 1 shows with lower grain size better properties can be achieved. Small amount of titanium helps in maintaining the grain size at higher temperature. Figure 2 shows role of microalloying elements in grain refinement, recrystallization and precipitation hardening.

![Figure 1. Strength variation with grain size](image)

| Microalloying Elements | Precipitation strengthening after hot rolling | Precipitation strengthening after normalizing | Influences recrystallization during hot rolling | Refines grain size on normalizing | Refines grain size during high temperature austenizing |
|-----------------------|---------------------------------------------|---------------------------------------------|-----------------------------------------------|---------------------------------|-----------------------------------------------|
| V                     | VN,VC                                       | VC                                         | -                                             | VN                              | -                                             |
| Nb                    | NbCN                                        | -                                          | Nb,NbCN                                       | NbCN                            | -                                             |
| Ti                    | TiC                                         | -                                          | -                                             | TiC                             | TiN                                           |

Table 1. Role of microalloying elements [2]
3. Nitrogen in steel
Nitrogen acts as both beneficial and detrimental element in steel based on the product application. Nitrogen causes yield-point phenomena and results in stretcher-strain formation in deep drawing operation. Formation of AlN causes intergranular fracture in continuously cast steels [10]. The blessing effect of nitrogen is it helps in grain refinement forming precipitates with Al, Ti, V and Nb. In general steel nitrogen with Al in steel is used for grain refinement. AlN precipitate along grain boundary and retards grain growth at high temperature. The size of these particles influence effect of grain refinement. AlN precipitates helps in grain refinement up to 900°C. Nitrogen is also beneficial in stabilizing the austenitic phase. Free nitrogen in steel helps in strengthening by solid solution strengthening mechanism as they are interstitial atoms. The behaviour of nitrogen in solid steel has to be understood for its use in steel.

4. Case Carburizing application
4.1 Experimental procedure:
JSW steel limited Salem works, India produces long product special steels for automotive applications namely crankshaft, gears, bearings and many through Energy optimizing Furnace-Ladle Furnace-Vacuum Degassing-Caster route. The billets produced from billet caster is hot rolled to get the final product of different sizes. In the current work 30mm dia bars was taken for study. Table 1 shows typical chemistry for conventional and modified case carburizing grade taken for understanding the grain coarsening behaviour at high temperature for different nitrogen levels.

| Type         | C   | Si  | Mn  | P   | S   | Ni  | Cr  | Mo  | Al  | N   |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1 unmodified | 0.20| 0.27| 0.80| 0.016| 0.004| 0.03| 1.09| 0.20| 0.029| 90ppm|
| 2 Modified   | 0.20| 0.25| 0.88| 0.010| 0.023| 0.20| 1.05| 0.2  | 0.028| 190ppm|

5 Samples from both the material are subjected to McQuaid- Ehn test as per ASTM E-112 for understanding grain coarsening at different temperatures of 850°C, 875°C, 900°C, 925°C, 950°C, 975°C, 1000°C, 1025°C and 1050°C.

4.2 Results
The samples after the test is polished, etched and grain size is measured under optical microscope. Table 3 shows ASTM grain size no for type 1 steel with carburizing temperature. It can be seen that till 900°C fine grain size of ASTM no 9 to 10 is achieved. With further increase in temperature grain coarsening has started and worsened with increasing temperatures.

| Temp°C | 850 | 875 | 900 | 925 | 950 | 975 | 1000 | 1025 | 1050 |
|--------|-----|-----|-----|-----|-----|-----|------|------|------|
| Sample 1 | 10.6 | 10.3 | 9.3 | Mix 8.2/4 | Mix 6.2/4 | 5.6/4 | 4.7/3 | 4.3/3 | 4.3/3 |
| Sample 2 | 10.5 | 9.9 | 9.3 | Mix 8.2/4 | Mix 5.8/3 | 5.7/4 | 4.8/3 | 5.3/3 | 4.5/3 |
| Sample 3 | 10.7 | 10.6 | 9.2 | Mix 6.0/3 | Mix 6.2/4 | 5.6/4 | 4.5 | 5.2/2 | 3.9/1 |
| Sample 4 | 10.7 | 10.5 | 10.1 | Mix 6.8/4 | Mix 5.8/4 | 5.5/3.5 | 5.5/3 | 3.6 | 4.4 |
| Sample 5 | 10.7 | 10.1 | 10.2 | Mix 9.7/1 | Mix 4.2/2 | 5.3/4 | 3.5 | 3.7/2 | 3.8 |
Figure 2 shows coarsened grain microstructure of samples subjected to carburizing temperature of 950°C and 1000°C.

![Microstructure images](a) AGC No. 0-2 50 μm  (b) AGC No. 0-1 50 μm

**Figure 2.** Microstructure at a)950 °C b)1000°C

**Table 4.** Grain Size at different temperatures for N=190ppm

| Temp°C | 850 | 875 | 900 | 925 | 950 | 975 | 1000 | 1025 | 1050 |
|--------|-----|-----|-----|-----|-----|-----|------|------|------|
| Sample 1 | 10.6 | 10.6 | 10.5 | 10.6 | 10.6 | 10.4 | Mix10.3/2.0 | Mix3.4/1.0 | Mix4.9/2.0 |
| Sample 2 | 10.8 | 10.8 | 10.7 | 10.7 | 10.8 | 10.7 | Mix10.1/2.0 | Mix 2.9/1.0 | Mix2.9/1.0 |
| Sample 3 | 10.8 | 10.9 | 10.7 | 10.7 | 10.8 | 10.6 | Mix5.3/1.0 | Mix2.8/1.0 | Mix 3.0/1.0 |
| Sample 4 | 10.8 | 10.8 | 10.8 | 10.7 | 10.7 | 10.5 | Mix2.5/0.0 | Mix2.2/0.0 | Mix3.7/-1.0 |
| Sample 5 | 10.9 | 10.7 | 10.5 | 10.6 | 10.5 | 10.3 | Mix1.3/0.5 | Mix 2.5/1.0 | Mix 1.7/0.5 |

From table 4 it can be seen that fine grain size of ASTM no 10 are obtained till 975°C. Beyond 975°C grain coarsening have started. The reason is due to formation of more AlN precipitates due to increased nitrogen content.

5. Crankshaft application

In this development the strength of a medium carbon steel is obtained by increasing nitrogen content and adding titanium to existing medium carbon steel. Table 5 gives the chemical composition of existing and modified grade. Medium carbon steels without chromium and molybdenum is not used for crankshaft application. The modified steel grade has lower carbon and manganese compared to existing grade. In this development solid solution strengthening effect of nitrogen and precipitation hardening by formation of TiN is used for strength improvement.

**Table 5.** Chemical composition of crankshaft grade

|          | C     | Si    | Mn    | Al   | Nppm | Ti   |
|----------|-------|-------|-------|------|------|------|
| Existing | 0.45  | 0.20  | 0.70  | 0.02 | 75   | Trace|
| Modified | 0.40  | 0.20  | 0.58  | 0.002| 160  | 0.01 |

Table 6 show properties of the modified grade which is comparable to existing grade with reduced carbon and manganese content.
Table 6. Properties for modified grade

| Condition   | Ultimate tensile strength (Kg/mm²) | Yield strength (Kg/mm²) | Elongation % | Reduction in area % | Charpy Joules | Hardness BHN | Grain Size ASTM No |
|-------------|------------------------------------|-------------------------|--------------|---------------------|---------------|--------------|-------------------|
| Rolled      | 62.5                               | 47.3                    | 32           | 36                  | 44            | 179          | 7                 |
| Normalized  | 63                                 | 46.7                    | 32.5         | 35.5                | 45            | 183          | 7                 |

Figure 3 shows microstructure after heating at different temperature. Even at 1100°C grain size no of 5 is achievable in the modified grade. At forging temperature of 1100°C the modified grade meets industry requirement of grain size no 5. Formation of AlN and TiN precipitates have reduced grain coarsening at high temperatures.

Figure 3. Microstructure at different temperature and corresponding grain size

6. Conclusion
The effect of high nitrogen content in two different application of steel grades is studied. Grain coarsening started at 950°C in case carburizing steel grade with nitrogen levels of 90 ppm, whereas fine grains are obtained even at 950°C in these grades of steel having 190 ppm nitrogen. Formation of more AlN precipitates have contributed to grain refinement at higher temperatures. Increased nitrogen content helped in processing the material at higher temperatures. AlN is effective till 900°C and for higher temperatures vanadium and niobium is added which adds to increased cost of production. Here to reduce cost, nitrogen a cheaply available element is used to prevent grain coarsening at higher temperatures.

For crankshaft application nitrogen is used to get the same property of medium carbon steel with reduced manganese and carbon content. So the above work uses nitrogen effectively for grain refinement strengthening and solid solution strengthening.

7. References
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