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An Internal Friction Study of a Vanadium Microalloyed Steel by a Dynamic Mechanical Thermal Analyser

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Abstract

The internal friction of a C-Mn-Al-V-N steel was investigated using a dynamic mechanical thermal analyser (DMTA) under different austenitisation time, cooling and tempering conditions. Internal friction measurements using a DMTA instrument showed energy loss peaks at different temperatures for a frequency of 1 Hz. For example, as well as the normal nitrogen peak, other broader loss peaks were observed centred on 100°C in the case of air-cooled samples austenitised at 900°C for 1 h. This is most probably due to carbon or nitrogen atom jumps associated with Fe-N-V sites, since the energy barrier which must be overcome for a carbon or nitrogen atom to break away from the foreign atom such as vanadium will be larger than that in a normal interstice. In addition, this abnormal damping peak disappeared after tempering at 450°C for 72 h. This indicates the precipitation of carbon and/or nitrogen.

Key words: Interstitial atoms, Internal friction measurement

Introduction

Interactions between interstitial and substitutional atoms have been observed by several investigators (Fast and Dijkstra, 1951; Dijkstra and Sladek, 1953) and have been extensively studied, particularly for iron containing manganese in substitutional and nitrogen in interstitial solution. These studies originated from the desire to know more about the underlying mechanisms of phenomena noted in the study of the quench ageing of binary Fe-C and Fe-N alloys as well as of ternary Fe-Mn-C and Fe-Mn-N alloys (Fast, 1951).

According to a theory expounded by Snoek (1947) and Polder (1945) the height of the peak is, at low carbon concentration, proportional to the concentration and inversely proportional to the absolute temperature. It applies not only to the case of carbon or nitrogen in α-iron, but also to solutions of carbon nitrogen or oxygen in other bcc metals such as vanadium and niobium. In a binary Fe-N or Fe-C alloy low temperature peaks occur at 25 and 40°C respectively for a frequency of 1 Hz (Fast and Dijkstra, 1951). It must undoubtedly be ascribed to jumps of nitrogen or carbon atoms between normal interstices (Fe-Fe). The situation is more complex in ternary Fe-Mn-N or Fe-Mn-C alloy. For instance, the measurement of internal friction showed that replacing 0.5% of the metal atoms in iron containing about 0.02 wt % N by manganese atom caused a broadening of the Snoek peak. Apart from a shoulder on its low temperature side, the damping graph could be resolved into the ordinary Fe-N-Fe peak and an unexpected peak with its maximum at a temperature about 10°C higher. This peak indicated that a nitrogen atom was more strongly bound in an interstice where it neighbours a manganese atom (Mn site) than in an interstice where it is surrounded by iron atoms only (Fe site). Similary, peaks have been identified corresponding to Mn-N-Mn sites.

In principle it could be expected that the height of the low temperature peak reaches its maximum with increasing nitrogen content, eventually to drop to zero when all favourable sites around Mn pairs are occupied by nitrogen atoms. The possibility of resolving the damping internal friction spectra of many Fe-Mn-N alloys into three single relaxation peaks has been confirmed by several investigators (Couper and Kennedy, 1967; Enrietto, 1962). It is, however, far from easy to derive three peak temperatures and their corresponding activation enthalpies from the experimental graphs without making use of computer curve fitting routines making an assumption that the individual damping spectra are Gaussian.

The analysing of damping peaks in the C-Mn-Al-V-N steel which was used for the measurement of damping peaks between 7-450°C is much more complex compared to binary or ternary alloys. For example, there is evidence that manganese, aluminium and vanadium affect the diffusivity of carbon atoms. For example, Laxar et al. (1961) studied strain ageing and internal friction in low carbon steel containing from 0.04 to 2.36 weight percentage aluminium. The internal friction indicated that carbon and aluminium atoms interact. This is evidenced by three abnormal peaks in the internal friction curves of these steels. The interaction of carbon with aluminium atoms lowers the mean diffusivity of carbon and inhibits precipitation as iron-carbide. Hence, abnormal peaks Fe-C-Al were observed at higher temperatures and in the higher aluminium steels enough carbon is retained in solid solution to cause strain ageing.

Dynamic strain ageing behaviour in microalloyed steels was examined by this author (Gündüz, 2000) using a C-Mn-Al-V-N steel which occasionally shows low toughness in the sub-critical heat affected zone. The cause was attributed to dynamic strain ageing, where materials show lower ductility and higher yield strength due to the interaction between mobile dislocations and diffusing solute atoms. In the present work, dynamic mechanical thermal analysis (DMTA) testing was carried out to investigate the anelastic behaviour of C-Mn-Al-V-N steel due to the presence of interstitial carbon and nitrogen. If there is carbon and/or nitrogen in solid solution, energy loss is associated with the migration of carbon and/or nitrogen atoms between adjacent random octahedral interstices. The aim of this work was to examine the behaviour of carbon and nitrogen, which are the two major elements causing strain ageing to occur, at 7 to 450°C. DMTA results, obtained from the vanadium steel, were also compared with a vanadium steel containing no aluminium and pure iron.

Experimental Procedure

A series of DMTA experiments were carried out for a temperature range of 7-450°C. The anelastic effect leads to a decay in the amplitude of vibration in materials under cyclic loading and therefore a dissipation of energy by internal friction. In DMTA the material is strained cyclically at different frequencies and temperatures. This allows, at least in principle, the identification of the loss process in operation. In this technique a sinusoidal load is applied to the material. In the presence of anelastic behaviour the strain will lag behind the applied stress, the more so the higher the anelastic contribution in the material. This phase lag is usually represented as tangent of the lag angle, tan δ, and is referred to as the loss tangent.

Samples for DMTA experiments were obtained from vanadium steel, vanadium steel containing no aluminium and pure iron. Table 1 shows the chemical compositions of the steels studied. Samples from vanadium steel or vanadium steel containing no aluminium were austenitised at 900°C for 1 or 26 h and then air cooled (2.5°C/s) or tempered at 450°C for 72 h after air cooling. However, samples from pure iron were heat treated at 650°C for 1 h to allow carbon and nitrogen resolution and then either air cooled or furnace cooled.

Table 1. Chemical compositions of steels (wt %).

C	Si	Mn	P	S	Cr	Mo	Ni	Sol. Al	N	Ti	V
Vanadium Steel											
0.14	0.40	1.41	0.02	0.03	0.03	0.005	0.05	0.035	0.017	< 0.005	0.10
Vanadium steel containing no aluminium											
0.11	0.27	10.16	< 0.005	0.005	-	-	-	-	0.012	-	0.09
Pure iron											
0.003	< 0.001	< 0.001	0.0003	0.0011	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	-	< 0.001

All samples were cut to dimensions of 1 × 5.5 × 55 mm. Afterwards, they were wet ground to a dimension of 0.51 × 5.1 × 50.1 mm. Finally, all samples were chemically polished in a bath containing 30 ml distilled water, 30 ml hydrogen peroxide, 3 ml sulphuric acid and 2.25 g oxalic acid to a dimension of 0.5 × 5 × 50 mm. Air-cooled pieces were stored in a refrigerator at subzero temperatures until the test was carried out in order to prevent movement of carbon and/or nitrogen. However, tempered samples were stored at room temperature in a dessicator.

Samples were carefully fixed into the machine and they were tested in single cantilever mode, in which the sample was inserted symmetrically and horizontally beneath the clamp bars. The sample should only pass through the left-hand clamp frame clamp and the drive clamp, it should not impinge upon the right-hand side of the frame. Following the obligatory calibration procedure three runs were made for each sample over the temperature range 7-450°C to observe energy loss peaks which result from the migration of free carbon and nitrogen to octahedral interstices expanded along the strain direction. These were made at a frequency of 1 Hz. The bending deflection was set to 64 μm, which gives the best results for this apparatus. This deflection corresponds to a maximum strain of 5×10^{-4} s^{-1}, which involves purely elastic deformation.

A heating rate of 1°C/min was used for all runs. The first run was carried out from 7 to 200°C. However, the second and third run were made from 7 to 450°C after the first run. The specimens were allowed to cool to room temperature in the furnace using water as a coolant. Further cooling below room temperature, i.e. 7°C, which is the minimum temperature obtained under present laboratory conditions, was carried out using antifreeze. Values of the loss tangent at different temperatures were collected by a PC interfaced with the thermal analyser for each run.

In order to isolate the solute atoms contribution to tan δ, the values obtained for pure iron were subtracted from those obtained for the vanadium steel austenitised at 900°C for 1 or 26 h. In this way, the contribution of other loss mechanisms such as dislocation climb are removed.

Results and Discussion

Pure iron

Internal friction measurement by a dynamic mechanical thermal analyser showed energy loss peaks at different temperatures for a frequency of 1 Hz. Figure 1 shows DMTA results of the air-cooled and furnace-cooled pure iron. It is noted that the air-cooled samples showed a nitrogen peak at 25°C due to jumps of nitrogen atoms between normal Fe-Fe interstices. However, the nitrogen peak decreased but another small peak appeared at 40°C after furnace cooling. In a binary Fe-N or Fe-C alloy low temperature peaks occur at 25 and 40°C respectively for a frequency of 1 Hz (Fast and Dijkstra, 1951).

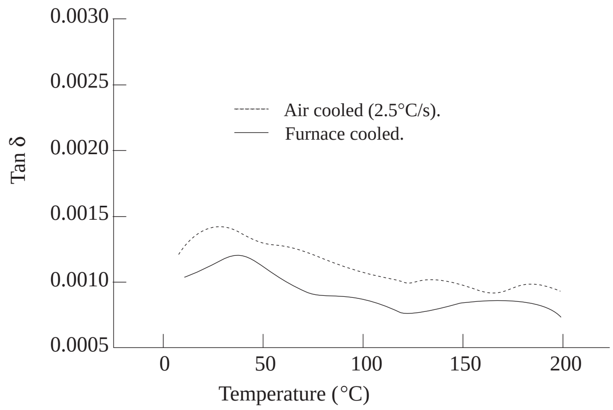

Figure 1. DMTA results for pure iron austenitised at 650°C for 1 h and then either air cooled or furnace cooled.

Vanadium steel

Figure 2 shows DMTA results for the air-cooled samples austenitised at 900°C for 1 h. Figure 2 also includes DMTA results of the air-cooled samples tempered at 450°C for 72 h. As is seen, samples in the air-cooled condition contain a larger amount of nitrogen in solid solution compared to that of the tempered sample. Tempering at 450°C may have removed the nitrogen from solid solution as a vanadium nitride. Samples which were austenitised at 900°C for 1 h and then air-cooled showed a strong peak which is a nitrogen peak at around 7°C which is lower compared to the jumps occurring at 25°C in binary Fe-N alloy at 1 Hz.

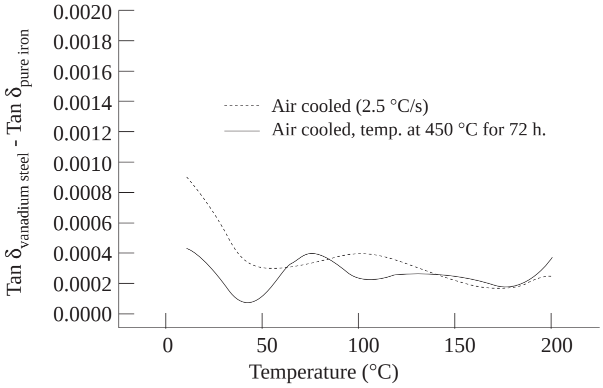

Figure 2. DMTA results of vanadium steel samples austenitised at 900°C for 1 h.

However, Couper and Kennedy (1967) with the aid of a digital computer, resolved the nitrogen-induced damping graphs for three Fe-Mn-N alloys containing 0.12%, 0.7% and 1.6% Mn, respectively for a frequency of 1 Hz. The damping graphs for the 0.12% Mn alloy could be analysed in terms of two peaks, the normal peak at 23°C and a peak at 34.5°C believed to correspond to jumps of nitrogen atoms from Mn sites to Fe sites. They also observed that the spectra for the 0.7% and 1.6% Mn alloys could be resolved into three peaks third having its maximum at 7°C. Couper and Kennedy (1967) suggest that the latter peak is the hybrid of two peaks with almost identical parameters, one due to jumps of nitrogen atoms associated with pairs of manganese atoms, and another due to nitrogen atoms jumping from Fe sites to Mn sites (Fe-N-Mn sites). Therefore, the damping peak, which is observed at around 7°C in the present experiment, is the nitrogen peak resulting from nitrogen atom jumps between Fe-Fe sites and Fe-Mn or Mn-Mn sites.

Besides the nitrogen peaks, other broader loss peaks were observed centred on 100°C for the air-cooled samples, see Figure 2. This could be due to nitrogen and carbon atoms jumps associated with Fe-V sites. Jamieson and Kennedy (1966) observed an abnormal internal friction peak occurring in the range 81-91°C at 1 Hz in the iron specimen containing 0.62% V. Dijkstra and Sladek (1953) also observed a normal nitrogen peak at 22°C and an abnormal peak at 87°C in iron containing 0.5% V and N at 1 Hz. They estimated that the abnormal peak in the internal friction always appeared at the high temperature side of the normal peak, since the energy barrier which must be overcome for a nitrogen atom to break away from the foreign atom will be larger than that in a normal interstice. In the case of manganese and vanadium, it is apparent that the larger the relative height of the abnormal peak, the further the latter is shifted toward a higher temperature. Also this abnormal damping peak which was observed at 100°C in the air-cooled samples disappeared after tempering at 450°C for 72 h. This indicates the precipitation of carbon and/or nitrogen.

Figure 3 also shows the DMTA results for the air-cooled vanadium samples austenitised at 900°C for 26 h and also it shows the results of the tempered samples at 450°C for 72 h after air-cooling. It is noted that the air-cooled samples austenitised at 900°C for 26 h contained a higher nitrogen content compared to the tempered sample. However, the air-cooled samples austenitised at 900°C for 26 h showed a smaller nitrogen peak at around 7°C compared to the samples austenitised for 1 h. Austenitisation at 900°C for 26 h removes nitrogen from solid solution as AlN; for instance Gladman (1997) showed that AlN gradually replaces VN during austenitisation. The solubility of AlN is also lower compared to VN and VC at 900°C (Narita, 1975); therefore AlN should be present at the austenitising temperature. These imply that samples austenitised for 26 h should contain lower nitrogen content in austenite as expected.

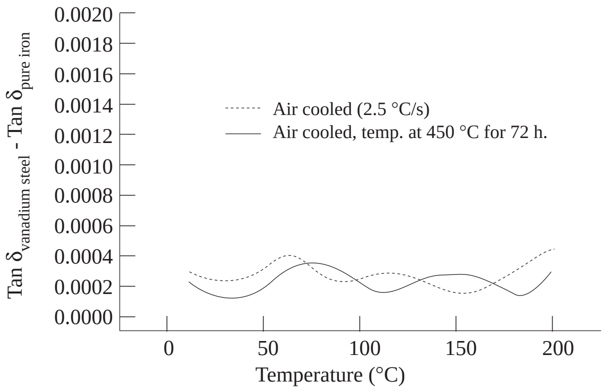

Figure 3. DMTA results of the vanadium steel samples austenitised at 900°C for 26 h.

The internal friction measurements confirm that the amount of nitrogen is lower in the samples austenitised for 26 h. Moreover, samples austenitised for 26 h showed loss peaks at 60 and 120°C at 1 Hz after air-cooling. From the theory expounded by Snoek (1947) and Polder (1945) a reasonable explanation for the existence of those peaks can be made by considering the possible stress-induced diffusion jumps which might occur. They are:

Carbon jumps from Fe-Fe to Fe-Mn interstices or vice versa

Carbon jumps from Fe-Fe to Fe-V interstices or vice versa

Carbon jumps from Fe-Fe to V-V interstices or vice versa

Vanadium steel containing no aluminium

Figure 4 shows DMTA results for vanadium samples containing no aluminium. The steel samples presented in Figure 4 were heat treated at 900°C for 1 h and then air-cooled or tempered at 450°C for 72 h after air-cooling. Figure 4 indicates that vanadium steel samples containing no aluminium showed a stronger nitrogen peak at 25°C compared to pure iron or vanadium steel in the air-cooled condition. This is as expected due to the larger amount of nitrogen in the vanadium sample containing no aluminium after air-cooling. In addition, a shoulder at around 88°C was observed since the energy barrier which must be overcome for a nitrogen atom to break away from the foreign atom such as Mn or V will be larger than in a normal interstice as proposed by Dijkstra and Sladek (1953).

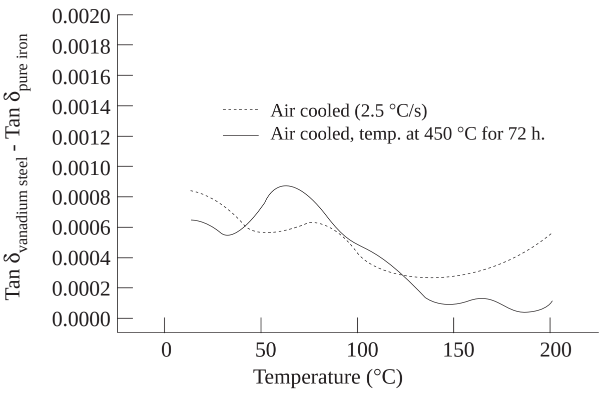

Figure 4. DMTA results of the vanadium samples containing no aluminium, austenitised at 900°C for 1 h.

Steel samples from vanadium steel, pure iron and vanadium steel containing no aluminium which showed additional internal friction peaks and also some of the damping peaks which were observed in the air-cooled condition were eliminated after furnace cooling or tempering at 450°C for 72 h. For instance, the amount of nitrogen decreased in vanadium steel samples austenitised for 1 h after tempering at 450°C for 72 h, Figure 2 indicating that tempering removes nitrogen from solution as VN.

A loss peak which was observed at 100°C in the air-cooled samples austenitised for 1 h disappeared after tempering. However, samples austenitised for 1 h showed an abnormal peak at 75°C after tempering at 450°C for 72 h. Vanadium steel samples austenitised for 26 h showed a drop in the nitrogen peak and an increase in the abnormal peak at 75 and 150°C after tempering at 450°C for 72 h. These peaks were initially present at 60 and 120°C after air-cooling before tempering. Vanadium steel containing no aluminium also showed a decrease in the nitrogen peak and an increase in a loss peak at around 60°C after tempering at 450°C for 72 h.

The rapid drop in the nitrogen peak and the concurrent rise in the abnormal peaks at various temperatures in either the 1 or 26 h austenitised and tempered vanadium steel or vanadium steel containing no aluminium after air-cooling may indicate a preference of carbon or nitrogen for the Fe-Mn, Mn-Mn, Fe-V or V-V interstices. In other words, the free energy is lowered by moving carbon or nitrogen atoms from Fe-Fe to Fe-Mn, Fe-V or V-V interstices. The preference of carbon for vanadium atoms and the resultant higher activation energy required for it to leave an Fe-V interstice would be expected to lower its diffusivity. The precipitation of carbides during tempering require carbon diffusion over a relatively long distance compared to those involved in the migration of carbon to dislocations in the strain ageing process (Laxar *et al.*, 1961). Intuitively, therefore, in this case the carbon diffusion distance would be proportional to dislocation density. Therefore, vanadium may decrease the diffusivity of carbon or nitrogen at lower temperatures but at higher temperatures carbon and/or nitrogen can diffuse more freely and cause damping peaks. Both the vanadium steel and vanadium steel containing no aluminium showed abnormal peak adjacent to the high temperature side of the normal peak after air-cooling or tempered conditions.

Glen (1957) also studied the effect of vanadium on the high temperature tensile strength of normalised low carbon steel and he found that the addition of sufficient vanadium suppressed strain age hardening at about 200°C because all the interstitial solute is fixed at interstices adjacent to the vanadium atom. However, at higher temperatures some of the interstitials are free. In these steels a maximum in flow stress was obtained at about 400-500°C. This also gives an indication that vanadium atoms decrease the diffusivity of interstitials at lower temperatures.

Figures 5 and 6 show the DMTA results after the second and third run of the air-cooled samples austenitised at 900°C for 1 h or tempered at 450°C for 72 h. It should be noted that the height of the carbon and nitrogen peaks and also other abnormal peaks present on the high temperature side of the normal peak observed after testing at low temperature ranges from 7 to 200°C (first run) decreased rapidly with testing at higher temperature ranges from 7 to 450°C (second or third run) which indicates the precipitation of carbon or nitrogen in α-iron.

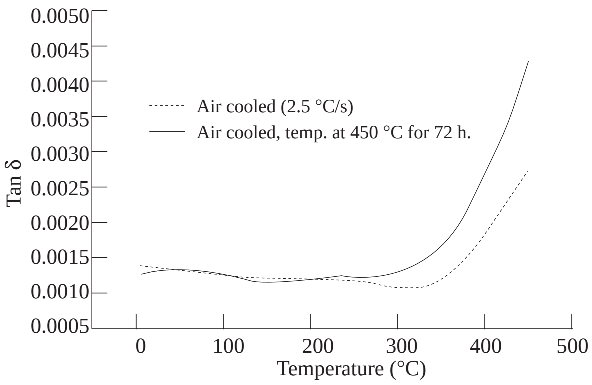

Figure 5. DMTA results of vanadium samples austenitised at 900°C for 1 h and either air-cooled or tempered at 450°C for 72 h (second run).

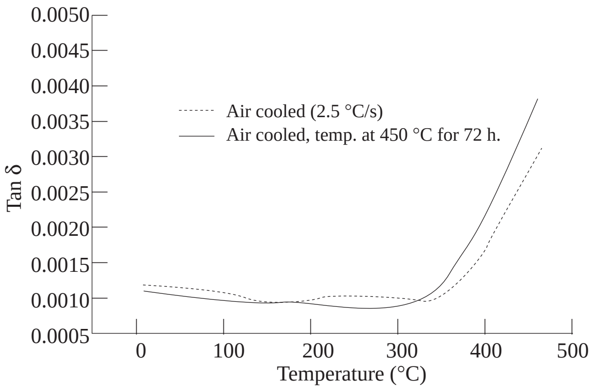

Figure 6. DMTA results of vanadium samples austenitised at 900°C for 1 h and either air-cooled or tempered at 450°C for 72 h (third run).

Conclusions

Internal friction measurements using a DMTA instrument have indicated that the air-cooled samples (austenitised at 900°C for 1 or 26 h) showed abnormal peaks at the high temperature side of the normal peak. For instance, as well as the normal nitrogen peak, other broader loss peaks were observed centred on 100°C in the case of air-cooled samples austenitised at 900°C for 1 h. This is most probably due to carbon or nitrogen atom jumps associated with Fe-N-V sites, since the energy barrier which must be overcome for a carbon or nitrogen atom to break away from the foreign atom such as vanadium will be larger than that in a normal interstice. In addition, this abnormal damping peak has disappeared after tempering at 450°C for 72 h. This indicates the precipitation of carbon and/or nitrogen.

Dynamic mechanical thermal analysis methods throw some light upon the hight of the carbon and nitrogen peak which is directly proportional to the amount of dissolved atoms and thus decreases with increasing precipitation. Damping peaks at different temperatures also indicated the diffusion of free carbon and nitrogen in C-Mn-Al-V-N steel. These at least explain dynamic strain ageing phenomena in C-Mn-Al-V-N steel which showed lower toughness in the subcritical heat affected zone due to interaction between mobile dislocation and free interstitial solutes (carbon and nitrogen).

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