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Reverse ageing in hot-rolled high-carbon steel wire rod

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Abstract Effects of ageing time on area reduction of hot-rolled high-carbon steel wire rods were studied. Tensile testing and X-ray study of as-rolled wire rods were carried out. Gleeble simulation and hydrogen content determination were also conducted. The results show that the reduction of area increases with ageing time at room temperature and the UTS remain unchanged which are contrary to normal ageing or strain ageing. In normal ageing, the ductility drops and the yield strength increases. In this study, the Gleeble simulation and X-ray data support that the transformation from pearlite to austenite is normal and there is no evidence of retained austenite or martensitic transformation in the steel. The hydrogen content drops as the time passes. The drop is rapid in first few days and this drop increases the ductility in rolled high-carbon wire rod. Hydrogen reduces the cohesive strength and the pressure generated due to transformation of atomic hydrogen-to-molecular state combines with tensile stress and causes cleavage or mixed type of fracture.

Introduction

Drawn pearlitic steel wires are of common use as structure materials because of their very high strength. Some researchers added alloying elements such as silicon, vanadium to optimize the mechanical properties of pearlitic steels [1–3]. However, some authors have already presented that the higher strength was achieved during strain ageing of heavily cold drawn pearlitic steels at low temperature several years ago [4]. It is now well established that such ageing effects in steel are due to the presence of interstitial solutes, usually carbon and nitrogen, which generally diffuse to dislocations and restrict their movements [5, 6]. Moreover, due to the higher solubility of nitrogen than carbon, the former is predominantly responsible for strain ageing, although solute carbon can contribute to this phenomenon at higher temperatures [6, 7]. Thus, it is generally recognized that solute nitrogen is detrimental to the cold formability properties of steel [8, 9]. In order to prevent both static and strain ageing, one approach has been to add, a carbonitride former such as Al, B, Nb, Ti and V [10–15].

High-carbon steel wire rod, hereinafter referred to as wire rods, means semi-finished hot-rolled carbon steel products with a circular cross section of various diameters (ranging from 5 to 13 mm or higher) in the form of coiled wire, with a variable chemical composition depending upon the application of rods. The high-carbon wire rods are known for their very high strength and excellent drawability and these are used in ropes for suspension bridges, armour cables, cables for ropeways, hoisting cables in cranes, reinforcements in concrete. The “As Rolled” high-carbon wire rods show a very low ductility and thus cannot be immediately drawn into wire. They are kept for some period (normally 15–20 days) in the plant, in stocks, at room temperature during which they undergo “Reverse ageing” which leads to substantial recovery of their ductility.

Because of this intervention period between the rolling of rods and drawing of wires, the productivity rate is slowed down. This type of ageing process is different from other ageing processes. Here strain is not involved as in strain ageing and more so no precipitation occurs as the material is not heated to higher temperature followed by quenching as in quench ageing or age hardening.

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The problem with reverse ageing in high-carbon wire rod is a worldwide problem in steel industries. There is at present no theory available on this subject. When hot-rolled wire rods are tested just after rolling in wire rod mill, they show a very low ductility and hence they cannot be subjected to drawing operation. To solve this problem, steel industries all over the world typically hold the wire rods in stocks for 15 days at least where upon by natural ageing their ductility substantially improves to more than 35% reduction in area. The strength remains almost unaltered in this 'reverse ageing' phenomenon. This gives rise to a considerable inventory problem. Since the ductility improves over time in room temperature that is why it is called reverse ageing.

This investigation is aimed to unravel the mystery of the reverse ageing that occurs in high-carbon wire rod. Sometimes it is speculated that residual stress cause such problem [16] and often time, it is attributed to the rolling process itself. Since wire rods are cooled after stelmore cooling, the heat dissipation takes long time and naturally if there is any residual stress, it will relax because of the slow cooling. Similarly, if there is any rolling process to blame for such phenomenon, it should take place in other diameters wire rod or low-carbon wire rod but such problem does not exist in those conditions. One investigation has found a relationship with hydrogen with low ductility (H. Xianjun et al. private communication). Sometimes it is also speculated that martensite forms upon cooling of the wire rod and tempering and rearrangement of dislocations takes place over time [17]. It is also speculated that some retained austenite forms upon cooling which slowly transforms to bainite over time and thus it gives improved ductility. Such speculations are ruled out in this investigation through Gleeble simulation, X-ray study and mechanical property study.

Experimental procedures

Material

The wire rods of 5.5, 8 and 17 mm diameters were collected from wire rod mill just after hot rolling. The composition of the steel chosen for this study is shown in Table 1. The composition of the steel was determined using optical emission spectroscopy. The samples have hypereutectoid composition. Chromium is used for strengthening purpose. It is known that Cr, Ni, V, Mo, etc., form M_3C, M_6C, $M_{23}C_6$ compounds in ferrite lamellae and improve the strength. Ni and V, Ti, Nb are also used for strengthening purposes. Nitrogen and carbon are found to cause strain ageing. Such alloying elements reduce the effect of strain ageing by scavenging nitrogen and carbon and they form carbonitrides and carbides and eventually strengthen ferrite lamellae and improve the ductility and strength. These steels are commonly known as pre-stressed concrete (PC) steel. These are used in concrete structures for reinforcements.

Hydrogen content estimation

The hydrogen content was very accurately determined for 5, 8 and 17 mm and these sizes were chosen to see if hydrogen content varies with the sizes of wire rods. Hydrogen content was measured with the help of a DH-103 Hydrogen determinator. The DH-103 determinator includes a resistance furnace, a thermal conductivity cell to measure the hydrogen gas and a microprocessor with related electronics. The sample is weighed on a suitable balance. The weight is entered as input and the sample is placed at the mouth of reaction tube of resistance furnace. The sample is heated to 1100 °C. Hydrogen released by heating the sample is swept out the furnace by the nitrogen carrier gas to the thermal conductivity cell. The thermal conductivity cell has the ability to detect the difference in the thermal conductivity of gases. The cell consists of two pairs of matched filaments used in four legs of Wheatstone bridge. The 'reference' filaments are located in carrier gas stream at a constant pressure, flow and temperature environment. The 'measure' filaments are also maintained in a constant pressure, flow and temperature environment, but the gas composition changes as the measured gas comes through. The bridge is balanced with nitrogen flowing in both the measure and reference chamber. The introduction of hydrogen will cause the temperature of measure filament to decrease because hydrogen has a higher thermal conductivity than nitrogen. The bridge will become unbalanced and an output will be available to preamp which will result in positive reading.

Table 1 The diameter and chemical composition (wt%) of PC wire rods

PC wire rod (mm)	C	Mn	S	P	Si	Al	Ti	Cr	Ni	Mo	V	Cu	Nb	N (ppm)
5.5	0.83	0.71	0.020	0.013	0.175	0.003	<0.005	0.019	0.018	<0.005	<0.005	0.009	<0.005	80
8	0.83	0.66	0.017	0.016	0.175	0.004	<0.005	0.025	0.014	<0.001	<0.005	<0.005	<0.005	70
17	0.87	0.64	0.022	0.015	0.175	0.003	<0.005	0.031	0.014	<0.005	<0.005	0.007	<0.001	67

The amount of hydrogen will determine the magnitude of the reading. The hydrogen content was measured in ppm. The accuracy of the determinator is ±0.1 ppm.

Metallography

The wire rods of various diameters were sectioned and ground and polished using the conventional metallographic procedures and etched in nital solution. The samples were then examined in field emission gun scanning electron microscopy at an operating voltage of 20 kV. The pearlitic structure is characterized and measured for interlamellar spacing and colony size. The structure is fully pearlitic. However, the spacing and colony size have been found to vary with the size of the finished wire rod. Interlamellar spacing and colony size were determined using the linear intercept technique and such technique was used for many photographs and an average value was determined and plotted against the size of the finished wire rod. Figure 1 shows the interlamellar spacing against the wire rod size. It is evident from the graph that as the size decreases, the interlamellar spacing decreases and similarly Fig. 2 shows that as the size of wire rod decreases the colony size decreases. Although the rolling is completed at 842 °C but subsequent cooling due to stelmore causes the refinement of the microstructures. The higher reduction combined with faster cooling in wire rod refines the pearlitic nucleation and growth.

Mechanical properties

The as-received wire rods just after hot rolling and cooling were tested in universal tension testing machines. The samples were made by cutting the wire rod to one foot and gripping it in universal tensile testing machines and load was applied until the wire rods were fractured and reduction in area was measured from the change in cross-sectional area near the fractures surface. Many samples were tested for each condition and the average value was calculated and reported. The reduction in area and ultimate tensile strength (UTS) were measured at an ambient temperature and graphs were generated. The samples were also aged in 100 °C for 90 min and tested simultaneously to study the effect of temperature and ageing time on the mechanical properties of the wire rods.

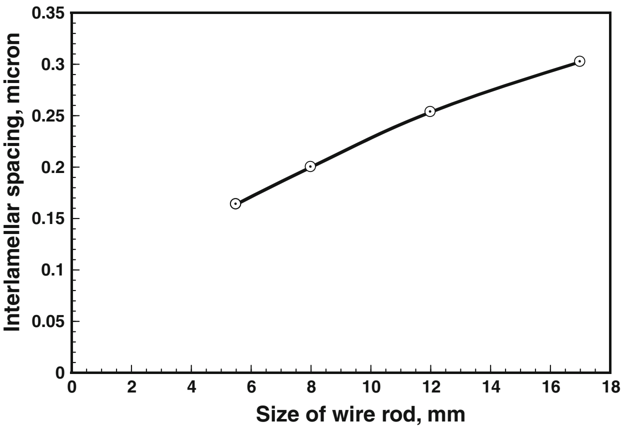

Fig. 1 Interlamellar spacing versus diameter of the rolled wire rod

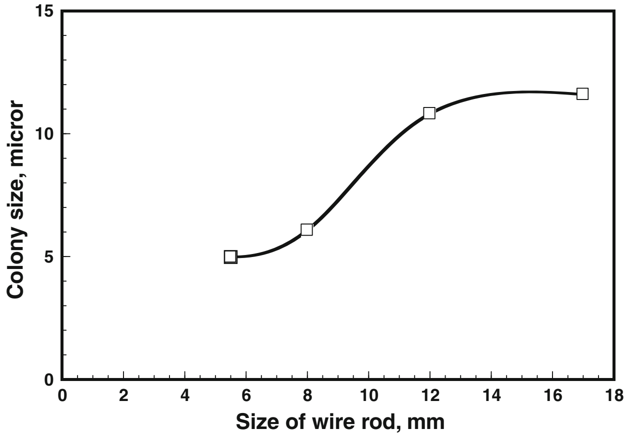

Fig. 2 Colony size versus the size of the rolled wire rod

X-ray study

The polished samples of various sizes of wire rods were exposed to X-ray generated using Cu target in a very slow scan speed. The monochromatic Cu Kα radiation was used. The fluorescence correction was also used. X'PERT Philips diffractometer was used for the X-ray study. The intensity versus 2θ was generated and plotted. Here θ is the Bragg angle for diffraction. The peaks generated by reflecting planes were identified from data tables. This data table is included with the software provided by the company. An example X-ray profile for 5.5 mm diameter was generated and presented in the "Results and discussion" section. A composite plot for the three sizes was also generated and presented in the "Results and discussion" section.

Gleeble simulation

Dilatometric analysis is a useful technique for the study of solid-state transformations in ferrous alloys [18, 19]. When a phase transformation occurs with an accompanying volume change, the dilatometric curve provides information on the change in atomic volume due to the transformation as well as on the thermal expansion characteristics. Therefore, by extracting the transformation induced volume change from the dilatometric curve and interpreting it with an analysis model, the fraction of individual phases involved in the transformation can be determined as function of time or temperature. In general, such volume change is reflected in the slope and there will be inflection from the original path and determining these inflections; one can measure the temperature at which phase transformation occurs.

To study the effect of heating and cooling rates on the phase transformation behaviour, Gleeble 1500 simulations were conducted. The simulator can also be used to loading and temperature change simultaneously. However in our case, only simple heating and cooling at a specified rate was used to study the phase transformation characteristics. The samples were 7 cm in length and the thermocouples were spot welded at the centre and the dilatometer was placed right at the centre. Transformation temperature on heating and cooling was estimated from the graphs of dilation versus temperature curves. The objective here was to study and see if there is any martensitic transformation occurring during cooling and hence the Ac1 and Ac3 and Ar1 and Ar3 were estimated. It is sometimes suspected that in wire rods some retained austenite may exist and this may transform to martensite or bainite over time and eventually this can give rise to better mechanical properties. However, such speculations were refuted which would be evident in the “Results and discussion” section.

Results and discussions

X-ray study

Figure 3 shows the profile of X-ray obtained from 5.5 mm diameter wire rod. The profile obtained does not show any martensites. In general, when martensite forms it gives rise to peak doublet but in the profile only ferrite and cementite peaks are observed. Figure 4 shows the composite profile of X-ray for all the three sizes of wire rod. In all cases, the peaks remain the same except in 17 mm diameter wire rod; the first cementite peak is not observed and the reason is that the intensity is increased and the peak is suppressed due to lower intensity. Although the intensity of the peaks is increased but martensitic peak doublets are not observed in any of the three profiles. It should be pointed out that during stelmore cooling, the cooling rate of the order of 10 °C/s is obtained but due to mass effect the larger diameter wire rod undergoes slower cooling in stelmore cooling. This absence of retained austenite or martensite is supported with Gleeble simulation experiments.

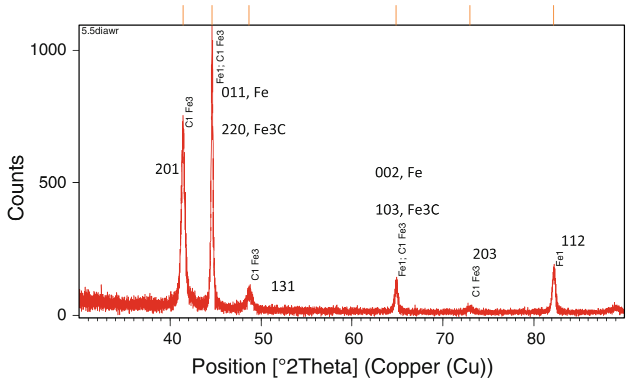

Fig. 3 X-ray diffraction patterns of the 5.5 mm wire rod taken from the cross-sectional plane

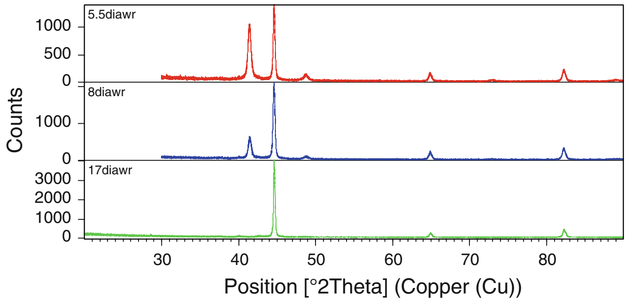

Fig. 4 The composite X-ray profile showing the peaks generated by cementite and ferrite phase of the various diameter wire rods

Gleeble simulation

Figure 5 shows the measured dilatometric curve of the 8.0 mm PC wire rod for a heating and cooling rate of 1 °C/s. Note that the curve is shifted along *y*-axis to coincide with each other in the austenite region. Similar behaviour is observed for other heating and cooling rates, but they exhibit some deviation along both the temperature and the length scales. The shift of the dilatometric curve along the length scale is ascribed to the difference in magnitude of

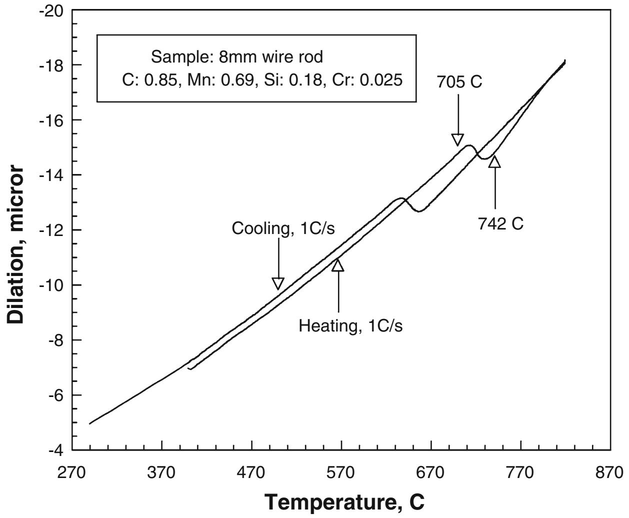

Fig. 5 The dilatometric curve for 8 mm wire rod which was subjected to 1°C/s heating and cooling cycle in Gleeble simulator

the non-isotropic effect. The transformation temperature for pearlite to austenite on heating is found to be 705 °C (Ac1) and 742 °C (Ac3) while cooling the transformation temperature is 632 °C (Ar1) and 657 °C (Ar3). The transformation on heating and cooling is different due to the effect of superheating and supercooling which is a known phenomenon. Similar curves were generated for 10 and 40 °C/s heating and cooling rates. The reason for doing so is to examine if there is any possibility of martensitic transformation upon fast cooling. Sometimes the retained austenite formation is suspected. Tables 2 and 3 show the complete list of Ac1 and Ac3 and Ar1 and Ar3 for other heating and cooling rates. The transformation is quite normal and martensitic transformation or retained austenite formation is not observed. After hot rolling of the wire rod, the wire rod undergoes stelmore cooling and the cooling rate is of the order of 10 °C/s and the lay head temperature is around 842 °C and after which the wire rod is subjected to stelmore cooling and this cooling is continued until the wire rod temperature is around 600 °C. Finally, the wire rod undergoes normal cooling in air and this makes the temperature to reach 300 °C and then goes for handling and storage. Considerable amount of time is passed during this stage and thus the residual stress if any remains get eliminated. Sometimes the residual stress generation is suspected for such anomaly in ageing behaviour that too can be ruled out since the temperature is moderately high enough and it stays in the heated state for quite some time. Hence, the residual stress is relaxed due to moderate temperature.

Table 2 Transformation temperature while heating the samples to austenite temperature 820 °C of 5.5 and 8 mm diameter wire rod

Size (mm)	Heating rate (°C/s)	Ac1 (°C)	Ac3 (°C)
5.5	1	727	748
8.0		708	727
5.5	10	722	778
8.0		725	752
5.5	40	717	774
8.0		722	770

Table 3 Transformation temperature while cooling from 820 °C (austenitizing) the samples of 5.5 and 8 mm diameter wire rod

Size (mm)	Cooling rate (°C/s)	Ar1 (°C)	Ar3 (°C)
5.5	1	654	681
8.0		632	657
5.5	10	587	668
8.0		592	642
5.5	40	579	596
8.0		565	570

Mechanical properties

Figures 6, 7 and 8 show the reduction of area change against the ageing time in days. It can be seen that the reduction of area reaches a plateau state after 4 days for 5.5 mm wire rod, whereas for 8 mm, the plateau is reached after 8 days. Similarly, the plateau is reached after 14 days of ageing in 17 mm wire rod. It is widely observed that as the diameter is increased it takes a longer time for reduction of area to recover for a stable value. The reduction of area for 5.5 mm increases from 15.5 to 32% after ageing for 4–5 days. When the wire rod is subjected to 100 °C ageing for 90 min, it reached 35% immediately after ageing and it does not change appreciably. Similarly for 8 mm wire rod, the plateau is reached after 8 days of ageing in ambient temperature but when it is aged the RA value reaches to 30% immediately. The plateau is reached after 14 days of ageing time in 17 mm diameter wire rod.

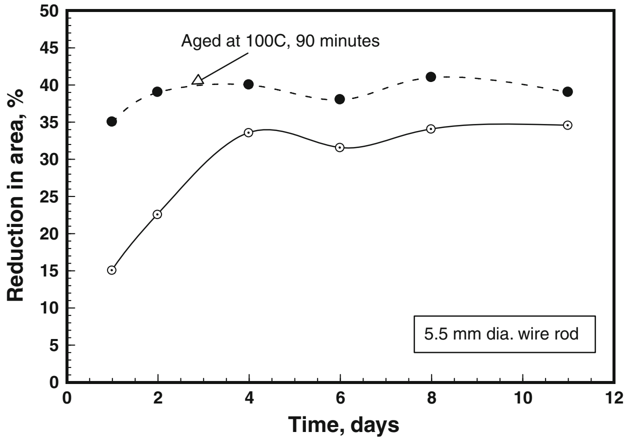

Fig. 6 The reduction of area in % is shown against the ageing time (days) for 5.5 mm diameter wire rod

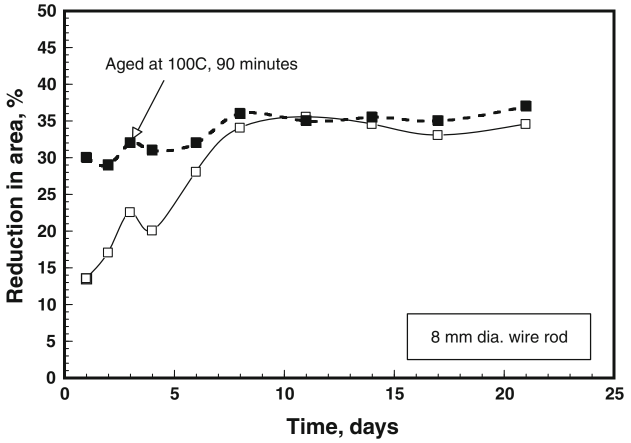

Fig. 7 The reduction of area in % is shown against the ageing time (days) for 8.0 mm diameter wire rod

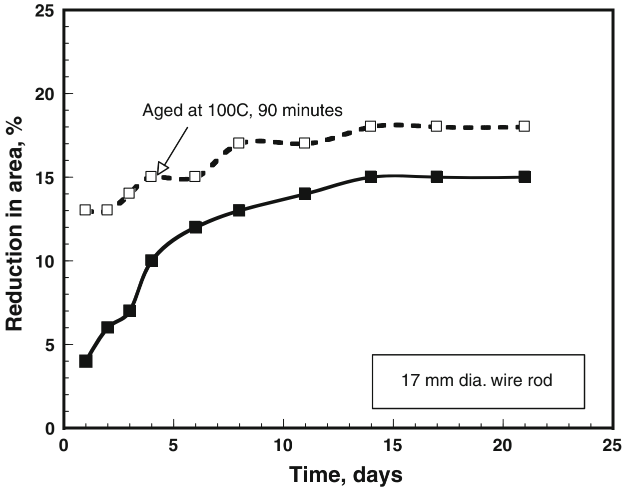

Fig. 8 The reduction of area in % is shown against the ageing time (days) for 17.0 mm diameter wire rod

One very well reason could be that the diameter of the rod is 17 mm and hence it takes longer time for hydrogen to diffuse out. When the samples are aged at 100 °C for 90 min, the RA is increased to more than 13% immediately and does not change appreciably over time. Thus, the transformation of any phase is ruled out and this increase cannot be due to any precipitation or dislocation locking or unlocking by interstitials since it happens at room temperature. Figure 9 shows the UTS as a function of ageing time. Since the UTS does not change with time appreciably hence strain ageing theory or phase transformation theory cannot be applied in this case. It was pointed out before that when strain ageing or phase transformation occurs, the change will be reflected in the UTS value and since such change is not observed and hence it can be ruled out. Thus, martensitic transformation and its tempering can be straight way ruled out. Possible cause for such effect is due to the hydrogen and this is illustrated when the hydrogen content is determined as a function of time.

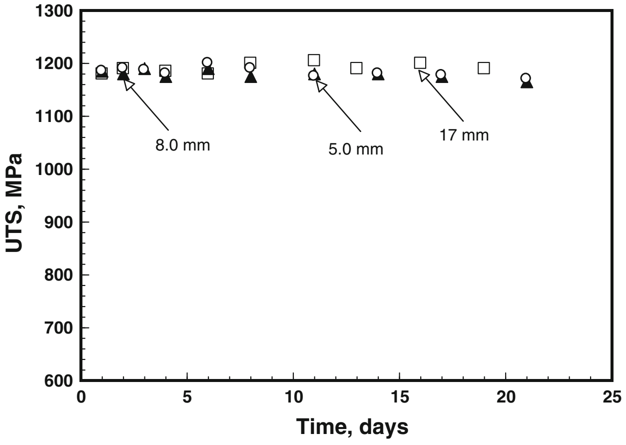

Fig. 9 The UTS is shown against the ageing time (days) for 5.5, 8, and 17 mm diameter wire rod

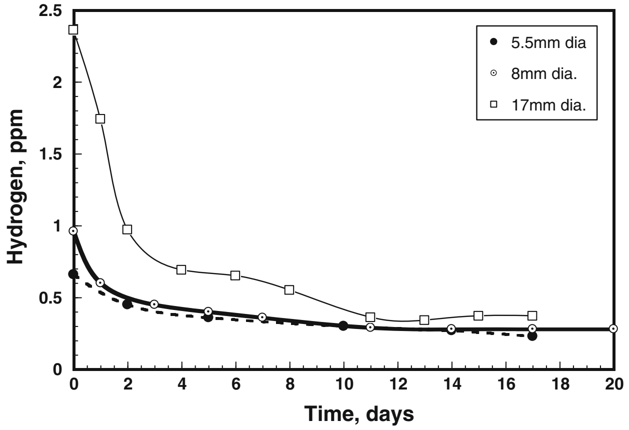

Fig. 10 The hydrogen content in ppm is shown against the ageing time (days) for 5.5, 8.0, and 17 mm diameter wire rod

Effect of hydrogen

Figure 10 shows the hydrogen content against ageing time for the three sizes of wire rod. It can be seen that the hydrogen content at zero day is the highest for 17 mm and correspondingly, it is the lowest for 5.5 mm diameter wire rod. The hydrogen content drops rapidly and it levels of after few days of ageing depending on the wire rod diameter. The hydrogen content levels of after 14 days of ageing for 17 mm wire rod, whereas for 5.5 and 8 mm, it levels of 5–6 days of ageing. Larger the diameter of the wire rod higher is the hydrogen elimination time. Thus, the problem of reverse ageing is due to the hydrogen in wire rod. Ageing the wire rod expels the hydrogen and the reduction of area is recovered immediately after ageing. The effect of hydrogen on ductility was studied by Costa and Thompson [20] and they postulated that residual hydrogen can bring down the ductility as much as 82% when the samples are charged with hydrogen. Similar observation was also made by Fang et al. (private communication) where they used hydrogen analysis and fractography to establish the fact that hydrogen causes the transformation from cleavage to ductile fracture. The hydrogen content in their study was of the order of 0.6 ppm in zero ageing time and it drops to 0.2 ppm after 10–14 days. Thus, the reverse ageing is due to hydrogen in steel. Now hydrogen can be picked up during the steel making stage due to moisture and such moisture can come from wet lime addition or any moist ferroalloy addition. It is also speculated that hydrogen is picked up during water box cooling when the rolling is conducted. It has been pointed out before that when hydrogen transforms to molecular state it generates pressure as much as 100000 atmosphere [21, 22] and this high pressure generates high hydrostatic stress and can interact with the tensile stress causing abrupt cleavage type of fracture and such fracture is seen in the first few days when wire rods were tested. It is also known that hydrogen reduces the cohesive strength of the steel. This is due to the fact that hydrogen atom is very small in size and it can diffuse to the inter-phases or even change atomic distance and thus the cohesive strength will be altered causing cleavage fracture.

Conclusions

Based on the results and discussions, the following conclusions can be drawn. It has been shown using dilatometry and X-ray results that there is no retained austenite that can transform to martensite or bainite since the data show normal transformation temperature on heating and cooling. Also no direct martensite formation is observed in the X-ray data and thus the low ductility is not due to these factors. The reverse ageing is due to the presence of excess hydrogen in steel after rolling operation. The hydrogen content changes with time and in zero ageing time, the hydrogen content is the highest and it drops drastically in the first few days and levels off after many days. Thus, this excess hydrogen causes low ductility and the ductility is recovered due to the elimination of hydrogen from the steels either at ambient temperature or at a higher temperature of ageing. The reasons for low ductility are two-fold. One is due to the fact that hydrogen reduces the cohesive strength of the steel which is envisaged in literature and the second, the transformation from atomic state-to-molecular state generates intense pressure which when coupled with tensile stress cause cleavage or mixed type of fracture of the steels depending on the ageing time.

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