Characterisation of long term aging behaviour of 9Cr–1Mo ferritic steel using ultrasonic velocity

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Anish Kumar
Indira Gandhi Centre for Atomic Research

B.K. Choudhary
Indira Gandhi Centre for Atomic Research, Kalpakkam - 603102, India

Kota bhanu sankara rao
University of Hyderabad

Baldev Raj
Indira Gandhi Centre for Atomic Research

Characterisation of long term aging behaviour of 9Cr – 1Mo ferritic steel using ultrasonic velocity

Anish Kumar, B. K. Choudhary, T. Jayakumar, K. Bhanu Sankara Rao and Baldev Raj

The measurement of ultrasonic velocity of 9Cr – 1Mo ferritic steel thermally aged at 793 and 873 K exhibited four distinct regimes in the variation of ultrasonic velocity with aging time. These different regimes have been correlated with the progressive evolution and coarsening of precipitate microstructure studied using TEM and microhardness measurements. The study revealed that ultrasonic velocity can be used to examine the secondary precipitation in the steel and the use of this technique as such can be extended to the health assessment of a component during service. **MST/5420**

The authors are in the Metallurgy and Materials Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India (anish@igcar.ernet.in). *Manuscript received 4 February 2002; accepted 16 April 2002.*

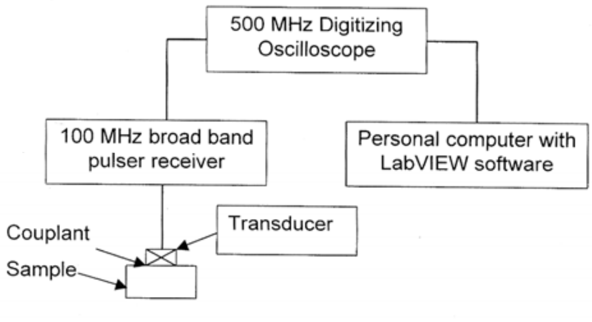
Introduction

Ultrasonic technique finds favour in the characterisation of microstructures, evaluation of materials properties, and assessment of defects during heat treatment, fabrication and in service inspection of the components.[1,2] Ultrasonic parameters such as velocity and attenuation are used for the characterisation of grain size and volume fraction of secondary phases and for the assessment of hardness, yield strength, fracture toughness and creep and fatigue damage.[2–9] In Nimonic alloy PE 16, Jayakumar *et al.*[7] correlated the ultrasonic shear and longitudinal velocities with the variations in density and elastic modulus owing to the occurrence of secondary phases. The velocity increased linearly with increases in the volume fraction of γ' precipitates in this alloy. In nickel base superalloy Inconel 625, ultrasonic velocity measurements have been correlated with precipitation of various intermetallic phases such as γ'', $Ni_2(Cr,Mo)$ and δ.[10] Ultrasonic velocity has been found to increase with the precipitation of these intermetallic phases and the dissolution of γ'' and $Ni_2(Cr,Mo)$ results in a decrease in the velocity. While explaining the effect of coherent precipitates, Fouquet *et al.*[3] have pointed out that in the presence of precipitates, the material can be considered as a composite of three components, i.e. matrix, matrix/precipitate interface and precipitate. Since ultrasonic velocity depends on the Young modulus and density of the material,[2] it is dependent upon the Young modulus and density of these three components.[3] In the case of an incoherent matrix/precipitate interface, the loss of coherency leads to a decrease in the Young modulus of the interface and hence reduces the effective ultrasonic velocity in the material. The formation of coherent precipitates results in an increase in ultrasonic velocity and the coarsening and dissolution of these precipitates decrease the velocity.[3]

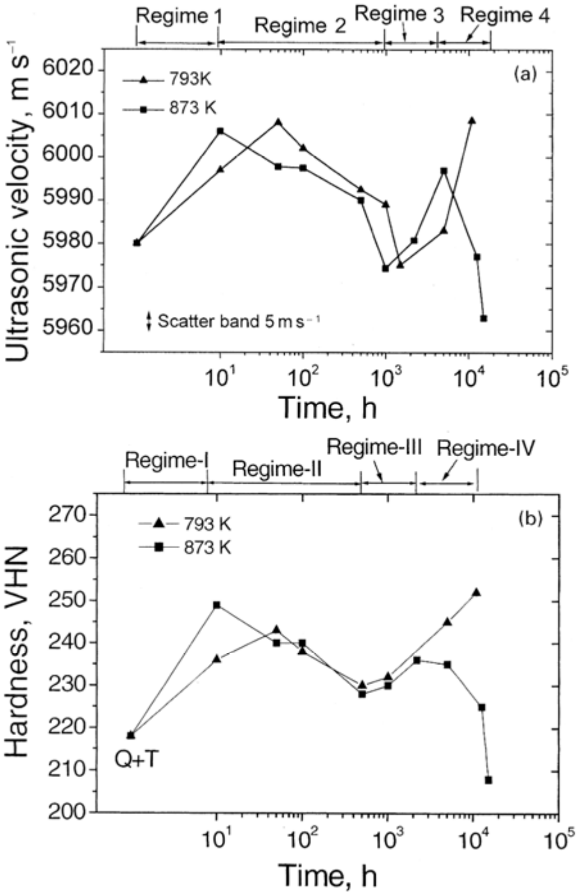
Ferritic 9Cr – 1Mo steel is an important material for steam generator applications operating at high temperatures for long durations. Materials operating at elevated temperatures undergo thermal aging resulting in microstructural degradation, which in turn influences the mechanical properties. In view of this, an attempt has been made to characterise the long term aging behaviour of 9Cr – 1Mo steel using ultrasonic velocity measurements. The ultrasonic velocity has been measured in specimens quenched and tempered (Q+T) and thermally aged at 793 and 873 K for durations ranging from 10 to 15 175 h. The variation in ultrasonic velocity with exposure time has been correlated with the microhardness and the precipitation behaviour of the steel examined using TEM.

Experimental

The chemical composition (wt-%) of 9Cr – 1Mo ferritic steel tube plate forging (1000 mm dia. and 300 mm thick) used in this investigation was Fe – 0·10C – 0·75Si – 0·63Mn – 0·02P – 0·001S – 9·27Cr – 1·05Mo – (190 ppm)N. The alloy was supplied in the Q+T condition: 1223 K for 5 h, water quenched, followed by 1023 K for 8 h, air cooled. Blanks of the Q+T alloy (12 mm dia. and 60 mm long) machined in the thickness direction from the outer annulus of 300 mm of the forging, were thermally aged at 793 and 873 K for durations ranging from 10 to 5000 h. For long aging times up to 15175 h, the specimens were taken from the unstressed shoulder regions of the creep specimens tested at 793 and 873 K. The details of creep testing and microstructures examined by optical microscopy have been described, elsewhere.[11] For ultrasonic measurements, surface grinding of these specimens was carried out to obtain a constant thickness of 5 mm and plane parallelism to an accuracy of ±2 μm. The experimental set up used for the ultrasonic measurements is shown in Fig. 1. Ultrasonic velocity was measured at room temperature using a 15 MHz longitudinal beam probe. A 100 MHz broad band pulser/receiver (M/s Accutron, USA) and a 500 MHz digitising oscilloscope (Tektronix TDS524) were used for carrying out the ultrasonic measurements. Cross-correlation technique has been used for precise velocity measurements.[12]



1 Experimental setup for ultrasonic velocity measurement



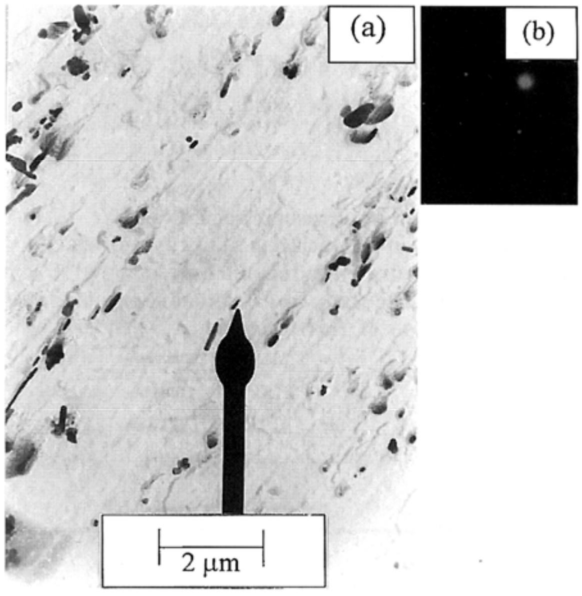
a ultrasonic velocity; *b* hardness

2 Variation in ultrasonic velocity and hardness (0·490 N load) with aging time at 793 and 873 K: various regimes shown for aging at 873 K

The ultrasonic velocity measurements were made at 500 MHz digitising frequency and the gated backwall echoes from the oscilloscope were transferred to the personal computer with the help of GPIB interfacing and LabVIEW software. The accuracy in time of flight measurement was better than 1 ns and the maximum scatter in the ultrasonic velocity was $\pm 2{\cdot}5$ m s^{-1}. The Vickers microhardness measurements were carried out at 0·490 N load on all the specimens. An average hardness value from five measurements taken in each condition is reported. The maximum scatter was ± 5 HV. Studies via TEM were carried out on the carbon replica extracted from Q+T and thermally aged specimens using analytical TEM, Philips CM 200. The energy dispersive X-ray (EDX) analysis spectra and selected area diffraction (SAD) patterns were taken for the identification of various precipitates.

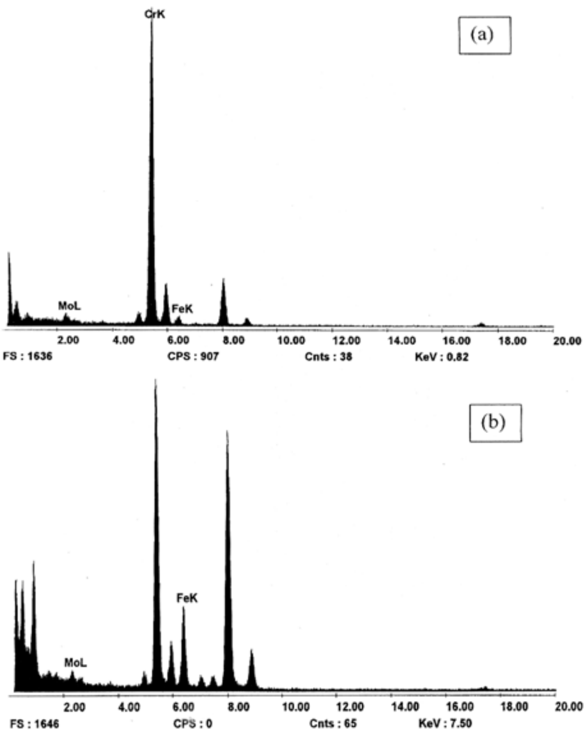
Results

The variation in ultrasonic velocity with aging time at 793 and 873 K is shown in Fig. 2*a*. For better clarity in the discussion, the observed variation in the velocity is divided into four regimes. In regime (1), ultrasonic velocity increases with aging time at short durations. With increasing aging time at intermediate durations, ultrasonic velocity decreases in regime (2) followed by a reversal in trend i.e., an increase in ultrasonic velocity in regime (3). Following an increase in velocity to a peak in regime (3), a sharp reduction in ultrasonic velocity is noticed in regime (4) in specimens aged at 873 K. The influence of aging temperature is reflected in a decrease in the times to onset of regimes (2) and (3) and the presence of regime (4) in specimens aged at 873 K. The regime (4) is not observed in the specimens aged at 793 K. The variation in microhardness with aging time also exhibited four different regimes similar to that observed for ultrasonic velocity (Fig. 2*b*). Like ultrasonic velocity, hardness increases in regime (1), exhibited a decrease in regime (2) and an increase in regime (3) followed by a sharp reduction in regime (4).



3 *a* TEM of 9Cr–1Mo steel in quenched and tempered condition and *b* selected area diffraction pattern of precipitate shown by needle

Studies via TEM on carbon replica extracted from Q+T specimen exhibited presence of precipitates at prior austenite grain and lath boundaries and in the intralath matrix regions. Figure 3*a* shows globular precipitates in the interlath and acicular precipitates in the intralath regions. The analysis of SAD pattern (Fig. 3*b*) and EDX spectrum (Fig. 4*a*) revealed that the intralath precipitates (shown by a needle in Fig. 3*a*) are mainly of Cr_2X type with hexagonal close packed structure. This chromium rich precipitate has been identified as Cr_2N.[13–15] The globular precipitates at the grain and lath boundaries are mainly of $M_{23}C_6$ [$(Cr\ Fe)_{23}C_6$] type with face centred cubic structure. Figure 4*b* shows an EDX spectrum obtained for this precipitate. Thermal aging for short duration resulted in further precipitation of Cr_2N precipitates. This can be seen in Fig. 5*a* for specimen aged for 10 h at 873 K. Further aging causes the coarsening of both $(Cr\ Fe)_{23}C_6$ and Cr_2N precipitates. Figure 5*b* shows an example for specimen aged for 1000 h at 873 K. The presence of a few thread like precipitates, which nucleate and grow at Cr_2N/matrix interface in the matrix (shown by a needle in Fig. 5*b*) and adjacent to $(Cr\ Fe)_{23}C_6$ at the boundaries, is also observed in this specimen. The analysis of SAD pattern (Fig. 6*a*) revealed close packed hexagonal structure and EDX spectrum (Fig. 6*b*) showed enhanced Mo and Si levels in the precipitate, which is consistent with Laves phase (nominally Fe_2Mo). It has been reported that the nucleation and growth of Fe and Mo rich Laves phase at Cr_2N/matrix interface is promoted by the depletion of Cr in the regions adjacent to Cr_2N.[16] With further aging, enhanced precipitation of Fe_2Mo can be seen in the specimen aged for 10 850 h at 793 K (Fig. 7*a*). Thermal aging for the longest duration of 15 175 h



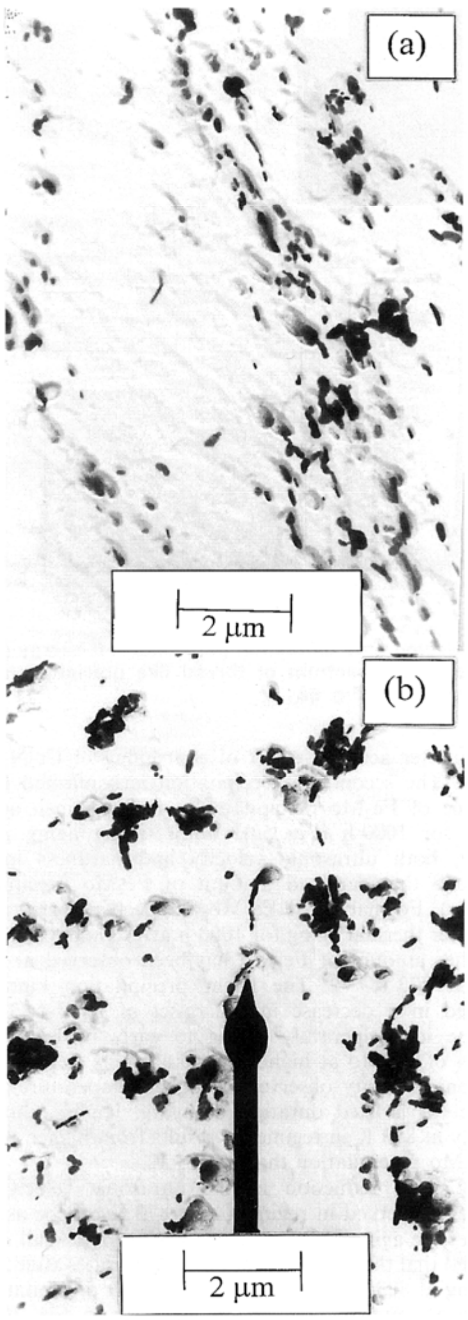
a precipitate in Fig. 3*a*; *b* interlath precipitate

4 Energy dispersive X-ray spectrum of precipitate shown by needle in Fig. 3*a* and of an interlath precipitate of $M_{23}C_6$ type

at 873 K results in the absence of fine thread like Fe_2Mo precipitates in the matrix region with an overall reduction in matrix and boundary precipitates (Fig. 7*b*). In addition to some lenticular precipitates (resulting from coarsening of acicular Cr_2N and thread like Fe_2Mo precipitates) in the matrix, coarse globular precipitates are seen in the matrix and at the boundaries in this micrograph. These observations are consistent with those reported for 9Cr–1Mo steel.[13–17]

Discussion

The observed similar trend in the variations in ultrasonic velocity and microhardness with aging time (Fig. 2) suggests that the changes in the microstructure of the steel owing to thermal aging have similar influence on both the parameters. The initial increase in the ultrasonic velocity in regime (1) can be ascribed to the formation of fine Cr_2N precipitates in the intralath regions at short duration of aging (Fig. 3*a*). This increased precipitation at short duration of aging results from the aging of specimens at lower temperatures of 793 and 873 K than the 1023 K used for tempering treatment.[14] The formation of fine precipitates in specimen aged at 873 K saturates early compared with that in specimen aged at 793 K resulting in lower duration of regime (1) at 873 K. Following detailed analysis of the precipitates present after thermal aging at 823 K for durations 1000 and 5000 h, Senior *et al.*[17] pointed out that the relative frequency of Cr_2N decreases rapidly with increasing aging time and the relative frequency of $M_{23}C_6$ remains nearly constant. The constancy in the relative frequency of $M_{23}C_6$ results from a gradual increase in the relative frequency of $M_{23}C_6$ at the grain and lath boundaries and a decrease in $M_{23}C_6$ in the matrix region. This is consistent with that observed after thermal aging

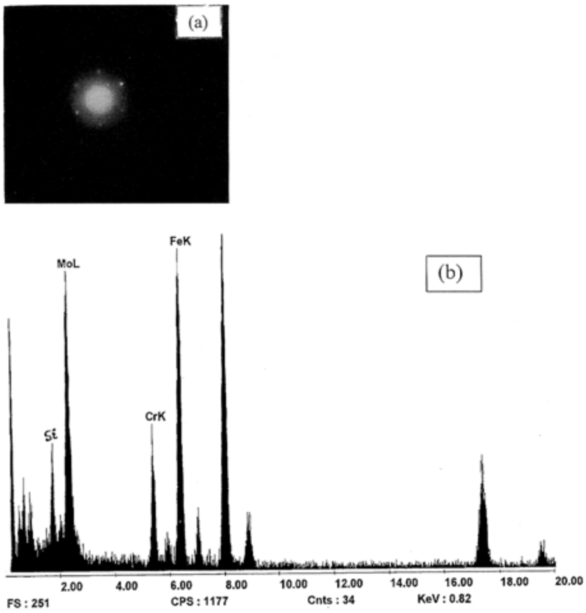


a 10 h; *b* 1000 h

5 Micrograph (TEM) of 9Cr–1Mo steel thermally aged at 873 K for different times

for 1000 h at 873 K (Fig. 5*b*) and is reflected in a decrease in hardness in regime (2) with increasing aging time owing to reduced contribution from precipitation hardening. The gradual decrease in ultrasonic velocity in regime (2) is attributed to the coarsening and consequent decrease in number density of Cr_2N precipitates. The influence of aging temperature is reflected in lower ultrasonic velocity at 873 K compared with that observed at 793 K (Fig. 2*a*). This results from the faster coarsening of Cr_2N at higher temperature for a fixed duration of aging in this regime.

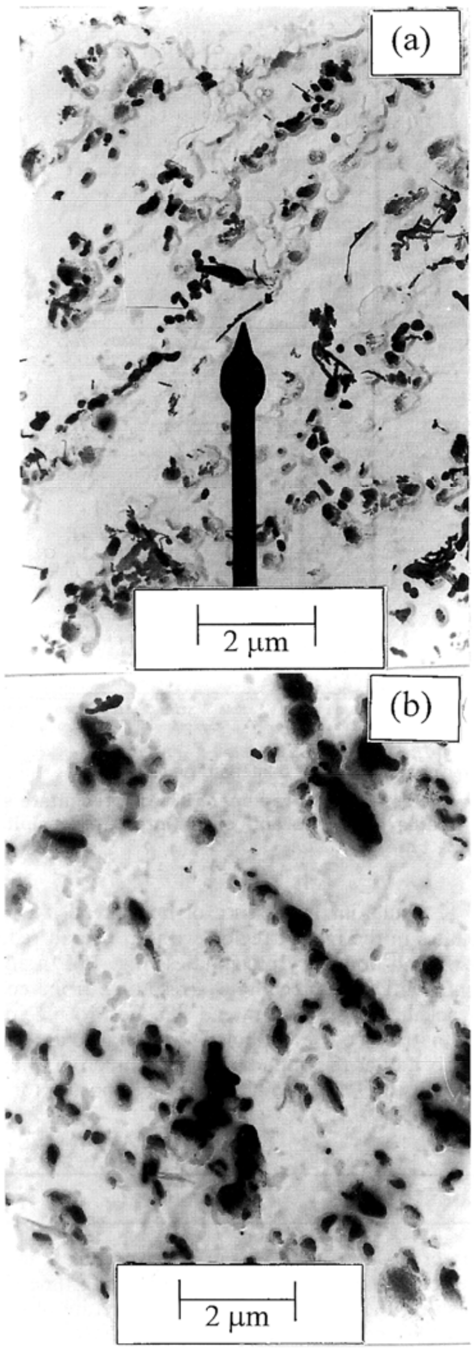
Following a decrease in the ultrasonic velocity in regime (2), a rapid increase in the velocity is observed in regime (3). This reversal in trend in the velocity is attributed to the occurrence of secondary precipitation in the steel, which



6 ***a*** **selected area diffraction pattern and** ***b*** **energy dispersive X-ray spectrum of thread like precipitate shown by needle in Fig. 5*b***

also counter acts the effect of coarsening of Cr_2N precipitates. The secondary precipitation is confirmed by the presence of Fe_2Mo precipitates in the specimen aged at 873 K for 1000 h (Fig. 5*b*). With further aging in this regime, both ultrasonic velocity and hardness increase owing to the increased amount of Fe_2Mo precipitation (Fig. 7*a*). Formation of Fe_2Mo has been reported in this steel after thermal aging for 1000 h at 773 and 823 K.[14–17] A higher amount of Fe_2Mo has been observed at 823 K than at 773 K.[14,16] The faster precipitation kinetics is reflected in a decrease in the onset of regime (3) with increase in temperature owing to early nucleation and growth of Fe_2Mo at higher temperature as well as higher ultrasonic velocity observed at higher temperature in this regime for a fixed duration of aging. Higher ultrasonic velocity at 873 K in regime (3) results from higher amount of Fe_2Mo precipitation than at 793 K.

The sharp reduction in the ultrasonic velocity and hardness observed in regime (4) at 873 K can be ascribed to excessive aging at long durations (Fig. 7*b*). Wall *et al.*[14] reported that the formation of Fe_2Mo saturates after 5000 h of aging at 823 K. In the absence of fresh precipitation of Fe_2Mo at long aging durations (as seen in Fig. 7*b*), the dominant coarsening and dissolution processes result in a rapid decrease in the number density of precipitates with increase in aging time and thereby decreases the ultrasonic velocity. Regime (4) is not observed in specimen aged at the lower temperature of 793 K. This can arise from the fact that this regime may appear at much longer times than the aging durations used in this investigation. The study clearly demonstrated that the ultrasonic velocity is sensitive to microstructure of the steel and the use of this technique can be extended to assess the microstructural degradation and its influence on the state of health of a component during service, by judicious selection of time periods between any two consecutive inspections.



a 793 K for 10 850 h; *b* 873 K for 15 175 h

7 Micrographs (TEM) of thermally aged 9Cr–1Mo steel

Conclusions

In 9Cr–1Mo steel, the variation in ultrasonic velocity observed as four distinct regimes is correlated with the progressive evolution of precipitate microstructure and variation in hardness with aging time. The study revealed that the ultrasonic velocity is sensitive to microstructure in terms of detecting the fresh formation of Cr_2N precipitates at short durations and the onset of secondary precipitation such as the formation of Fe_2Mo precipitates at intermediate durations and its coarsening at long durations. The influence of temperature is reflected in the faster kinetics in terms of nucleation and growth of precipitates at higher temperature. These observations suggest that the ultrasonic technique can be used for quality control during heat treatment and for the assessment of health of a component during service.

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