Age Hardening in Martensitic/Bainitic Matrices in a Copper-Bearing Steel

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In order to understand the influence of matrix microstructures on age-hardening behavior in a copper-bearing steel, NAK 80, the phase transformation of austenite (during a variety of continuous cooling treatments) and the consequent precipitation of copper particles (during isothermal aging) were investigated by dilatometry, optical metallography, hardness measurement, transmission electron microscopy, and field-emission-gun transmission electron microscopy (FEG-TEM). It was found that at a wide range of cooling rates (about from 30 to 0.3°C/s) after austenitization at 900°C for 15 min, the steel produces a mixture of martensite and bainite. Three different pre-treated specimens, which had been continuously cooled at 120, 5 and 1°C/s, respectively, were studied in order to determine their response to copper age-hardening. The results show that the general level of peak hardness for the fully martensitic specimen is the lowest when compared with those of the other two specimens, which contained a mixture of nearly equal volume fractions of martensite and bainite. The findings in this work show that tempering martensite during aging drastically hinders the hardening of copper precipitates.

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1. Introduction

The use of low carbon, copper bearing, high strength, low alloy steels for applications in heavy engineering has drawn considerable interest in the last two decades because the steels can provide excellent combinations of good toughness, strength, weldability, and resistance to corrosion.¹⁾ Hardenability-enhancing elements such as manganese, nickel, chromium, and molybdenum are added to the steels in order to obtain relatively uniform microstructures throughout the heavy sections after they have been quenched from the austenite phase field. As a result, variations in the levels of bainite and/or martensite can be produced depending on the alloying and cooling rates employed. In addition, strength is further achieved by the precipitation of copper-rich particles during aging, instead of by the precipitation of carbide particles.²⁻⁴⁾ Researchers⁵⁻¹⁰⁾ have reported copper precipitation in related steels during continuous cooling and isothermal aging. Little detail is known yet about the microstructural characterization of these steels, and it has not yet been established whether the copper precipitates in both bainite and martensite matrices. A great deal of early research has focused on Fe-Cu alloys¹¹⁻¹⁸⁾ and ultra-low carbon ferrite steels,^{19,20)} and the results have provided valuable information. However, both the precipitation behavior of copper particles in the bainitic and martensitic matrices and the crystallography of precipitation in commercial steel still need to be investigated.

In most age-hardened Cu-bearing steels^{6,7,21)} (e.g. A710-type and HSLA 80 steels), the carbon content is not higher than 0.05 mass%; the carbide precipitation would hence have very little effect on copper age hardening. However, tempering definitely interferes with copper age hardening as the carbon concentration in steel increases. For comparison with the work by Banadkouki *et al.*,²¹⁾ who studied age harden-

ing in a HSLA 80 with bainitic and martensitic matrices, the aims of this study are first, to understand the phase transformation during continuous cooling in a copper-bearing steel with 0.13 mass% carbon, and second, to investigate the effects of its various matrix microstructures on age hardening. The precipitation of copper particles in this steel has also been observed by using a field-emission-gun transmission electron microscope.

2. Experimental Procedures

NAK 80 steel was developed by Daido Steel Co., LTD, and applied as the plastic synthetic mold material. The steel studied was prepared through vacuum refining, homogeneous forging and age hardening. The chemical composition of the steel studied is listed in Table 1. One reason why NAK 80 was chosen as the experimental material is that it is a copper-bearing steel with a higher level of carbon than the general age-hardened steels. Another reason is that the hardenability of the steel makes the production of bainitic microstructure easy. In this work, all the continuous cooling treatments were carried out on a Dilatronic III RDP deformation dilatometer produced by Theta Industries, Inc. Before the preparation of the dilatometric specimens, the pieces of steel were homogenized at 1200°C for 3 days while sealed in a quartz tube containing pure argon, subsequently being quenched in water. After decarburization layer had been removed, the specimens were then machined to cylinder 3 mm in diameter and 6 mm in length. The dilatometer was interfaced with a computer workstation (PDP 11/55 central processor) in order to analyze the resulting data. The software package (provided by Theta Industries, Inc.) allows flexible and complete control to execute continuous cooling transformation experiments. The length, time and temperature information was recorded in microsecond intervals, and the level of vacuum was maintained at 10^{-5} Torr (10^{-3} Pa) to protect the specimens from oxidation.

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Table 1 Chemical composition of the steel (mass%).

C	Si	Mn	P	S	Ni	Cr	Mo	Al	Cu	Fe	O
0.13	0.58	1.56	0.023	0.003	3.09	0.33	0.26	0.83	1.08	Bal.	0.0004

In order to investigate the effect of different cooling rates on the microstructure of NAK 80 after austenitization at 900°C for 15 min, the specimens were cooled to room temperature at cooling rates ranging from 0.05 to 120°C/s. The Ac_1 and Ac_3 were determined to be 725°C and 875°C, respectively, by analyzing the dilatometry at the heating rate of 25°C/s. After the continuous cooling treatment, the specimens were held in a heat treatment furnace at temperatures of 400, 500 and 600°C for 0.5 to 100 h for aging treatments, followed by the removal of the decarburization layer.

The corresponding microstructures were examined by using optical microscopy and transmission electron microscopy. Both specimens were slit from the dilatometric specimens. A hardness measurement of the specimens to be examined optically was taken using a Vickers hardness tester with a load of 30 g. Based on these data, the transformation regions during continuous cooling were defined. Thin-foil specimens were prepared for TEM from 0.25 mm thick discs slit from the specimens used in the dilatometric experiments. The discs were thinned to 0.05 mm by abrasion on silicon carbide paper and then electropolished in a twin-jet electropolisher using a solution of 5% perchloric acid, 25% glycerol, and 70% ethanol⁽²²⁾ at ambient temperature and 30 V potential. They were examined using a JEOL JEM-100CX TEM operating at 100 kV, JEOL JEM-2010F FEG-TEM operating at 200 kV, and Philips CM200 FEG-TEM operating at 200 kV, respectively. An energy-dispersive X-ray spectrometer (EDS), installed on the Philips CM 200 FEG-TEM, was used for the microanalytical measurements, with the specimens held in a beryllium holder tilted from the normal by 25°, which is the take-off angle. The X-ray count rate was optimized to about 1000 counts per second, a lifetime of about 50 s. The electron probe size was approximately 1 nm.

3. Results and Discussion

3.1 Overview of continuous cooling transformations

3.1.1 Hardness, optical microscopy and dilatometric curve

Figure 1 shows hardness as a function of cooling rate. The data reported represents the average of at least eight tests for each set of experimental condition; the corresponding error bar for standard deviation is also indicated in Fig. 1. The fastest cooling rates (120 ~ 60°C/s) produce microstructures with hardness consistent with those of martensite microstructures, and a plateau at about 425 Hv is evident. With a decreasing cooling rate, hardness drops rapidly, eventually reaching another plateau at about 320 Hv. The rapid hardness decrement corresponds with mixtures of martensitic and bainitic structures, and the lower plateau is associated with microstructures consisting mainly of bainitic ferrite.

Representative optical metallographs of dilatometer specimens cooled at rates from 120°C to 0.05°C/s are shown in

Fig. 1 Hardness of specimens cooled at various rates.

Fig. 2. Fully martensitic structures, which are associated with the higher hardness plateau in Fig. 1, are presented in Figs. 2(a) and (b); the mixtures of martensitic and bainitic structures are displayed in Figs. 2(c)–(f); fully bainitic structures which are related to the lower hardness plateau in Fig. 1 are shown in Figs. 2(g) and (h). For the alloy studied, the hardenability with respect to bainitic transformation was so good that a nearly complete bainitic structure could be produced even after continuous cooling at the rate of 0.05°C/s.

Figure 3 shows the complete dilatometric curves obtained from the specimens which were continuously heated at the rate of 25°C/s to 900°C, then held at 900°C for 15 min, and finally cooled at a wide range of cooling rates (120 ~ 0.05°C/s). From the profiles for relative length change versus temperature, the transformation start temperatures during various continuous cooling conditions were determined. The most notable feature is that at higher and lower cooling rates, the transformation start temperature tended to be constant, 375°C and 525°C respectively; these two temperatures would be very near the M_s (martensite start temperature) and B_s (bainite start temperature) in the TTT curve of the steel studied.

The optical metallographs (Fig. 2.) show that austenite in the steel studied transformed into martensitic and bainitic structures over a wide range of continuous cooling rates. However, the microstructural details for martensite and bainite cannot be differentiated in the optical metallographs of the samples cooled at the intermediate cooling rates (30 ~ 0.3°C/s), and the volume fractions of martensite and bainite can not be measured. However, by analyzing the dilatometric curves, the volume fractions of bainite and martensite can be approximated. The graphical method is illustrated in Fig. 4.⁽²³⁾ For a given cooling rate, the volume fraction of bainite (f_b) present in the microstructure at the M_s temperature is mea-

Fig. 2 Optical metallographs obtained from dilatometer specimens cooled at rates: (a) 120, (b) 60, (c) 30, (d) 10, (e) 5, (f) 1, (g) 0.3, and (h) 0.05°C/s.

sured from the dilatometric curve by comparing the dimension of the sample relative to the limiting dimensions when the sample is fully austenitic or fully ferritic. The latter cases are represented at the M_s temperature by extrapolating the high and low temperature ends of the dilatometric curve, respectively. Figure 4 shows that at the M_s temperature, the volume fraction of bainite $f_b = d/D$. If it is reasonable to assume that after martensite transformation, the amount of austenite that is retained at ambient temperature can be neglected, then the fraction of martensite (f_m) is identical to that of austenite at the M_s temperature; i.e., $f_m = 1 - d/D$. As the results of the transmission electron microscopy show, the amount of austenite retained in the specimens treated with a variety of continuous cooling rates is very small. According to the above graphic method, the volume fractions of bainite obtained in the samples cooled at various cooling rates were measured. The volume fraction of bainite versus the cooling rate is plotted in Fig. 5. This result is in good agreement with the hardness data (shown in Fig. 1.).

3.1.2 Transmission electron microscopy

(1) Specimens cooled at 60°C/s

The microstructure of the specimen cooled at 60°C/s is shown in Fig. 2(b), and this cooling rate is associated with a hardness of 420 Hv. Figures 6(a) and (b) present the bright field (BF) and centered dark field (CDF) TEM images obtained from a specimen cooled at 60°C/s for the correspond-

Fig. 3 Dilatometric curves obtained from specimens austenitized at 900°C for 15 min and then continuously cooled at a wide range of cooling rates (120–0.05°C/s).

Fig. 4 Illustration of the graphical method of determining the volume fraction of bainite f_b obtained at the M_s temperature from analysis of dilatometric data.

ing metallograph shown in Fig. 2(b); lath martensite and film-like retained austenite can be clearly identified. The orientation relationship between the martensite and retained austenite were analyzed by using the selected area diffraction patterns (SADP) (Fig. 6(c)). The martensite appears to have a zone axis of $[111]_{\text{bcc}}$, and the retained austenite a zone axis of $[110]_{\text{fcc}}$. The $(1\bar{1}\bar{1})$ plane in the retained austenite was parallel to the $(0\bar{1}1)$ plane in the martensite as well, which in-

Fig. 5 Plot of the volume fraction of bainite versus the cooling rate.

indicates a Kurdjumov-Sachs orientation relationship between the retained austenite and martensite. It is worth noting in Figs. 6(a) and (b) that several lathes of martensite coalesced into a thick plate. A few coarse plates can even be observed on an optical scale, for example, the bimodal structures (as shown with arrows) in Figs. 2(a) and (b). In the optical metallograph, the strongly bimodal-shaped plates appear as light-etching matrix structures, with lower hardness values, when compared to the gray-etching matrix structures, as tested by a Vickers hardness tester with a load of 10 g. This striking feature of the bimodal characteristic in lath martensite microstructures is sometimes observed, but rarely highlighted or reported. The possible mechanism for coalescence has been proposed by Bhadeshia *et al.*^{24,25} who attributed this phenomenon to significant undercooling and a lack of impingement at the early stages of growth.

(2) Specimens cooled at 5°C/s

Specimens cooled at 5°C/s showed a hardness of 360 Hv. The bimodal features in the optical metallograph of the specimen cooled at 5°C/s (Fig. 2(e)) are similar to those in the optical metallographs of the specimens cooled at 30 and 10°C/s. (Figs. 2(c) and (d)). Montages of TEM BF micrographs obtained from the specimens cooled at 5°C/s are shown in Figs. 7 and 8. In the upper left-hand region of Fig. 7, a part of the coalesced thick plate of lower bainite (with a single variant of intraplate carbides) can be identified. The other structures in Fig. 7 are uncoalesced lower bainite, with a more uniform distribution of plate thickness and a few intra-plate carbide particles can be found within the uncoalesced plates (indicated by the arrow). In the middle and lower regions in Fig. 8, auto-tempered martensite is characterized by bimodal-shaped coarse plates (with several variants of sheet-like intra-plate carbides); the other structures in Fig. 8 are the subunits of lower bainite. These observations suggest that both coalescence and carbide precipitation could have occurred in the specimens cooled at 30, 10 and 5°C/s; the results could explain the bimodal features (as pointed by arrow marks) in the optical metallographs in Figs. 2(c)–(f).

(3) Specimens cooled at 1°C/s

The microstructures of the specimens cooled at 1°C/s, iden-

Fig. 6 Transmission electron micrographs for illustrating the lath martensite and retained austenite obtained from the specimen cooled at 60°C/s: (a) bright field image; (b) dark field images; (c) corresponding diffraction patterns.

tified by a hardness of 345 Hv, as related by optical microscopy, consisted of dispersed bimodal-shaped plates (*i.e.*, coalesced thick plates of lower bainite and auto-tempered martensite) in gray etching structure matrices shown in Fig. 2(f). Figure 9 shows a TEM micrograph of upper bainite obtained from the specimen cooled at 1°C/s. Parallel lathes, with a thickness of about 0.2 μm , grow from the prior austenite grain boundary; these fine sub-structures in the matrix cannot be distinguished under the optical microscope and appear to be gray-etched. It should be emphasized that in this investigation, the effects of coalescence were frequently observed in the microstructures of lath martensite and lower bainite. Similar effects could not be found for upper bainite, presum-

ably because of the lower chemical driving force available at higher transformation temperatures and because of a greater degree of plastic accommodation of the shape deformation

(due to reduced yield strength). At elevated temperatures, the carbon would tend to partition rapidly from upper bainite platelets into the residual austenite. Consequently, the distribution of plates of upper bainite was observed to be much more uniform, and the plates were separated by rather thicker films of retained austenite. On the other hand, the distribution of plates of lath martensite was not uniform (Fig. 6(a)) due to the effects of coalescence, and the corresponding retained austenite films between the plate were much thinner.

(4) Specimens cooled at 0.05°C/s

The TEM micrograph of Fig. 10(a) shows the copper pre-

Fig. 7 Transmission electron micrograph shown the bainite structures obtained from the specimen cooled at 5°C/s.

Fig. 8 Transmission electron micrograph shown the auto-tempered martensite structure obtained from the 5°C/s cooled specimen.

Fig. 9 Transmission electron micrograph shown the upper bainite structure obtained from the specimen cooled at 1°C/s.

Fig. 10 Transmission electron micrograph (a) bright field image and (b) centered dark field image showing the copper precipitates in matrix obtained from the 0.1°C/s cooled specimen.

precipitates obtained from the specimen cooled at 0.1°C/s. The CDF image (Fig. 10(b)) shows randomly-distributed copper precipitates. In order to obtain the information about the elemental compositions of the copper precipitates, a EDS study was performed on a FEG-TEM. It shows that copper precipitates are Fe-based, with a high content of Cu (about 40 mass%) and a low level of Ni. The surrounding matrix

could have interfered with efforts to determine the chemical composition of the copper precipitates (because the precipitates were extremely fine and embedded in the matrix), even though the diameter of the electron beam was reduced to 1 nm during chemical microanalysis.

3.2 Isothermal precipitation hardening behavior

3.2.1 Aging hardening curve

The volume fractions of martensite and bainite in the specimens cooled at 120, 5 and 1°C/s were measured by analyzing the dilatometric curves, as shown in Fig. 5; they are 100% martensite, 42% bainite with 58% martensite, and 58% bainite with 42% martensite, respectively.

Figures 11 to 13 are plots of hardness versus aging time for the three pre-treated specimens continuously cooled at 120, 5, and 1°C/s to ambient temperature and then aged at 400, 500, and 600°C, respectively, for different time intervals up to 100 h. Among the three different aging temperatures, the lowest temperature (400°C) produced the hardening peak after a comparatively long time. Softening is most pronounced at the highest temperature (600°C), where the tempering had an extremely strong effect. It is clear from Figs. 11–13 that the age-hardening behavior is greatly dependent on the corresponding matrix structure.

It is obvious that both tempering of martensite/bainite matrices and age-hardening of copper precipitation occur competitively during the aging process. In order to further illustrate the influence of the matrix structure on age-hardening, the hardness versus aging time and hardness increments versus aging time at specific aging temperatures are plotted in Figs. 14–17. The two pre-treated specimens cooled at 5 and 1°C/s (containing 58% martensite with 42% bainite, and 42% martensite with 58% bainite) exhibit nearly the same hardness when aged at 400 and 500°C, as shown in Figs. 14 and 16; for these two samples, the peak hardness occurs at 400°C after 50 h, and at 500°C after 5 h. As to the specimens cooled at 120°C/s (containing 100% martensite), the peak hardness occurs at 400°C after 25 h, and at 500°C after 5 h. The level of peak hardness for the fully martensitic matrix is lowest when compared with those of the other two matrices (Figs. 14 and 16). This result is in disagreement with that reported by Banadkouki *et al.*,⁽²¹⁾ who claimed that the marten-

Fig. 11 Effect of aging time and temperature on the hardness of the specimen cooled at 120°C/s.

Fig. 12 Effect of aging time and temperature on the hardness of the specimen cooled at 5°C/s.

Fig. 13 Effect of aging time and temperature on the hardness of the specimen cooled at 1°C/s.

Fig. 14 Effect of aging time on hardness of various pre-treated matrices for aging at 400°C.

Fig. 15 Hardness increment as a function of aging time at 400°C.

Fig. 16 Effect of aging time on hardness of various pre-treated matrices for aging at 500°C.

Fig. 17 Hardness increment as a function of aging time at 500°C.

site matrix had the advantages in age-hardening over the bainite matrix. As a matter of fact, the carbon content of the steel studied in their research work (0.05C–0.25Si–1.4Mn–0.85Ni–1.10Cu, mass%) was relatively lower than that in the present work (0.13C mass%). The degree of carbon supersaturation in the martensitic matrix definitely has a profound effect on the tempering. The higher the degree of carbon supersaturation, the more rapid the reaction rate of tempering is. In this work, tempering of a fully martensitic matrix during aging at 400 and 500°C drastically brings about a significant loss of strength and also leads to a state in which it cannot achieve the full age-hardening potential of the steel (Figs. 15 and 17). It is clear that tempering phenomena and copper age hardening took place competitively during the aging process. Although the fully martensitic matrix at the initial stage provided plenty of defects for the nucleation sites of copper particle precipitation, the isothermal aging at 400 and 500°C could not achieve a higher peak hardness when compared to the martensite/bainite mixed matrix. Figures 15 and 17 also clearly indicate that the absolute value of the peak hardness is lower in martensite than in bainite. This result is presumably because the martensite matrix had degenerated much more than the martensite/bainite mixed matrix, and therefore, a full age-hardening potential was much more difficult to reach.

The data for hardness increments during aging at 400 and 500°C reflects the fact that during aging treatment, the tempering response is more sensitive in martensite than in bainite.

Carbon has a very potent solid solution strengthening effect. Thus the strength of martensite drops rapidly as the carbide particles precipitate during the initial stage of aging. For the bainitic structure, most of the carbon is not in solid solution, and the existing carbide particles become coarse carbides that have little influence on strength. The effect of tempering is therefore always milder in bainite than in martensite. Therefore, for the initial structures with higher volume fractions of bainite, the isothermal holding during aging treatment can highly contribute to the strength due to the precipitation hardening of copper-rich particles. This important finding is emphasized by Figs. 15 and 17.

3.2.2 Transmission electron microscopy

(1) Peak aging condition

Figure 18 shows the TEM micrograph taken from the specimen cooled at 5°C/s and then aged at 500°C for 5 h (*i.e.*, the peak aging condition, as shown in Fig. 16). It illustrates that the aging treatment caused the tips of the upper bainitic ferrite platelets to round-off. However, the broad faces of the platelets were less affected and retained their slab-like shape. This retention of the shape of the broad faces is primarily due to pinning by carbide particles that precipitated from an austenite film trapped between the bainite sub-units. Within the bainite ferrite sub-units, large amounts of extremely fine precipitates were located on the networks of dislocations. A FEG-TEM lattice image with electron diffraction patterns obtained from the specimen cooled at 5°C/s and then aged at 500°C for 5 h is presented in Fig. 19; it illustrates the lattice image for a copper precipitate well embedded in a matrix. A lattice image experiment was conducted in which the specimen foil was tilted to a [111] zone with respect to the matrix, and as a result, lattice fringes from the matrix {110} planes were obtained. The copper precipitate was in the form of an elliptical shape with a short axis of about 16 nm and a long axis of about 26 nm. The banded structure with a thickness of approximately 2 nm was found within the precipitate. The bands were seen to be parallel to this set of matrices {110}. The fringes within the parallel bands formed a zigzag pattern (as indicated by a square mark); this feature was very similar to that of the twinned 9R structure reported in the study by Othen *et al.*¹⁵⁾ However, the diffraction pattern for the precipitate (as shown in Fig. 19(b)) was not clear enough to identify

Fig. 18 Transmission electron micrograph showing the upper bainite structure obtained from the specimen cooled at 5°C/s and then aged at 500°C for 5 h.

Fig. 20 Transmission electron micrograph obtained from the specimen cooled at 5°C/s and then aged at 600°C for 5 h.

Fig. 21 Transmission electron micrograph obtained from the specimen cooled at 5°C/s and then aged at 600°C for 5 h.

Fig. 19 FEG-TEM lattice image and coresponding diffraction patterns for copper precipitate obtained from the specimen cooled at 5°C/s and then aged at 500°C for 5 h: (a) image; (b) and (c) corresponding diffraction patterns of the copper precipitate and matrix.

the corresponding crystal structure. Further research on this is still needed.

(2) Overaging condition

Figures 20 and 21 show the TEM micrographs taken from the specimen continuously cooled at 5°C/s to room temperature and then aged at 600°C for 5 h. Figure 20 shows that the copper particles were distributed within the bainitic ferrite platelets and that some coarse carbide particles were located at the boundaries of bainitic ferrite plates. Figure 21 illustrates that the copper particles and several irregular-shaped coarse carbide particles were dispersed within the degenerated auto-tempered martensite matrix; the variants of sheet-like intra-plate carbides have become lump-shaped. It is suggested that the bainitic structure is more stable than auto-tempered martensite during aging. At higher aging temperatures, the degeneration of martensite and the coarsening of copper particles cause a loss of strength. Figure 22 shows the TEM micrograph taken from the specimen continuously cooled at 5°C/s to room temperature and then aged at 600°C for 25 h; there is some evidence of bainitic ferrite subunit coalescence, and several variants of the rod-shaped copper particles can be seen clearly.

Figures 23 and 24 show the FEG-TEM lattice images of fine copper precipitates taken from the specimens cooled at 5°C/s to room temperature and then aged at 600°C for 5 and 25 h respectively. The former had an elliptical shape with a thickness of 10 nm and a length of 23 nm, and the latter had a rod-like morphology with a thickness of 12 nm and a length of 22 nm. The EDS data shows that ϵ -copper precipitates are Cu-based, with a high content of Fe and a high level of Ni

Fig. 22 Transmission electron micrograph shown the upper bainite structure obtained from the specimen cooled at 5°C/s and then aged at 600°C for 25 h.

Fig. 23 FEG-TEM lattice image for copper precipitate obtained from the specimen cooled at 5°C/s and then aged at 600°C for 5 h.

in the ratio (mass%) of 45.3 : 34.5 : 15.8 for Cu, Fe and Ni, respectively, taken from a copper precipitate in the specimen aged at 600°C for 5 h. Figure 24(b) illustrates that the fcc copper precipitate had a Kurdjumov-Sachs orientation relationship with the bcc matrix. This crystallographic orienta-

Fig. 24 FEG-TEM lattice image and cooresponding diffraction patterns for copper precipitate obtained from the specimen cooled at 5°C/s and then aged at 600°C for 25 h: (a) image; (b) the corresponding diffraction patterns of the copper precipitate and matrix.

tion is expected simply because the copper crystal can replace the austenite crystal, based on their same fcc lattice with unit cells of extremely similar size.

It was assumed that copper formed in spherical clusters (with a bcc structure) in the early stage of aging. The clusters grew until they reached a critical size, at which point an in-situ transformation to fcc precipitates occurred. The precipitates were observed to grow further, with an elliptical shape and finally with a rod-like shape. Recent high resolution electron microscopic studies have revealed that a complex fcc-like intermediate structure, a twinned 9R structure,^{8,15} forms during the transition between bcc and fcc structures. In the present study, the precipitate with a twinned 9R structure has not been identified as yet. More research on high resolution

TEM is needed.

4. Conclusions

An investigation has been made of the copper aging hardening response in a NAK 80 steel. Based on hardness measurement, dilatometry, optical metallography, transmission electron microscopy and field-emission-gun transmission electron microscopy, the important conclusions of this work are summarized as follows.

(1) The results from dilatometry, optical metallography, and hardness measurement indicate that the hardenability with respect to bainite transformation is so good that the steel can virtually fully transform to bainite at a very slow cooling rate (0.05°C/s). At cooling rates ranging from 30 to 0.3°C/s , it gives a mixture of martensite and bainite.

(2) Three various pre-treated matrices (obtained from continuous cooling at 120, 5 and 1°C/s , respectively, after austenitization at 900°C for 15 min) consist of 100% martensite (by volume fraction), 58% martensite with 42% bainite, and 42% martensite with 58% bainite separately. It is found that the general level of peak hardness for the fully martensitic matrix is lowest when compared to those for the other two matrices.

(3) The two pre-treated matrices containing 58% martensite with 42% bainite and 42% martensite with 58% bainite possess nearly the same aging hardness when aged at 400 and 500°C . However, the latter matrix has a significantly higher value of hardness than the former matrix when aged at 600°C . The results reflect the fact that during aging, the tempering response is more sensitive in martensite than in bainite. The evidence from the transmission electron microscopy also reveals that bainite ferrite morphology is less affected, and retained its slab-like shape even when aged at 600°C for a long period of time.

(4) Tempering by carbide formation and the resultant coarsening and modification of the substructure hinders copper precipitation hardening. Tempering of fully martensitic matrix during aging leads to a significant loss of strength and also brings about a state in which it cannot achieve the full age-hardening potential of the steel. A mixture with nearly equal volume fractions of martensite and bainite is demon-

strated to exhibit superior age-hardening over a microstructure containing mainly martensite.

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