Independence of work hardening and precipitation strengthening in a nanocluster strengthened steel

S.S. Xu¹, Y. Zhao¹, X. Tong^{2,3}, H. Guo¹, L. Chen⁴, L.W. Sun⁴, M. Peng⁴, M.J. Chen¹,
D. Chen¹, Y. Cui¹, G. A. Sun⁴, S. M. Peng⁴, Z. W. Zhang^{1,*}

¹*Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, P. R. China*

²*Instrument and Source Division, Oak Ridge National Laboratory, TN, 37831, USA*

³*Department of Physics and Astronomy, University of Tennessee, Knoxville, TN, 37996, USA*

⁴*Key Laboratory of Neutron Physics and Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics (CAEP), Mianyang 621999, China*

Abstract: Work hardening and precipitation strengthening are two important strengthening methods that closely associate with dislocation density. Here, a new class of nanocluster strengthened steel with a tensile strength of ~2.02GPa and an elongation of ~7% is developed through a combination of work hardening and precipitation strengthening. The work hardening is strongly dependent on the dislocation density induced by thermomechanical treatments while there is no effect for dislocation density on precipitation strengthening. The work hardening and precipitation strengthening are independent and can be controlled separately. The strengthening effects of nanoscale precipitates are quantitatively analyzed and assessed.

Keywords: nanocluster strengthened steel; small-angle neutron scattering; work hardening; precipitation strengthening

*Corresponding author:

Email: zwzhang@hrbeu.edu.cn; Tel: +86-451-82568591 (Z. W. Zhang)

1. Introduction

Precipitation strengthening plays an important role in the design and fabrication of advanced structure materials with superior mechanical properties and strong resistance to radiation damage [1-8]. With increasing unprecedented environmental challenges, advanced ultra-high strength steels strengthened by nanoscale precipitates have been developed[9]. Precipitation strengthening requires an optimized combination of size, number density and distribution of precipitates to yield the best combination of properties, such as yield strength, hardness and ductility [10-13]. The properties of the precipitates are remarkably dependent on the thermomechanical treatments [14, 15]. At the same time, Thermomechanical treatment can also change dislocation patterns, leading to work hardening that is another strengthening mechanism [16, 17]. Thus, dislocations may play three folds of roles. The first one is work hardening similar with that in the traditional alloys without nanoscale precipitates. The second one is the effect of dislocation on the precipitation of nanoscale particles during aging. The last one is the interaction between dislocations and nanoscale precipitates during deformation.

Many studies on the effect of dislocation on the mechanical properties have been carried out. Tsuchiyama et al.[18] have investigated the behavior of deformation and dissolution of ϵ -Cu particles. They found that dislocation shearing at particle tip causes a dynamic partitioning of Cu atoms from precipitates into the matrix. The number of the particles decreases after a certain amount of cold working, and the dissolution of the dispersed particles occurs as reported in cold worked aluminum alloys[19, 20] and cold draw pearlite wires [21]. A fatigue test of 1.5 at% Cu bearing interstitial-free (IF) steel shows that maximum stress gradually decreases during the cyclic loading under a constant strain[22]. In the early stage of deformation, the precipitation strengthening is effective. However, the anomalous effect emerges after severe plastic deformation or cyclic stress loading. Thus, it is vital to understand the relationship between work hardening and precipitation strengthening, since both are associated with dislocation patterns. This understanding is the most important

prerequisite for the preparation of nanoscale precipitate-strengthened steels with a good combination of high strength and high ductility.

In this paper, nanocluster strengthened steels with different dislocation density were prepared. The nanoscale precipitates and their contributions on the mechanical properties were studied by small-angle neutron scattering (SANS) and theoretical calculations, respectively. Combining the mechanical properties and the theoretical calculation of precipitation strengthening, a thorough study of the effect of dislocation on the precipitation of nanoscale cluster and the correlation between work hardening and precipitation strengthening was conducted.

2. Experiment

A nanocluster strengthened steel with a nominal composition of Fe-1.5Mn-2.5Cu-4Ni-1Al-0.005B-1.5Mo-0.05Nb-0.1Ti-1.5W-0.08C-0.5Si (wt%) was selected for the experimental investigation. The cast ingots with a weight of ~50 kg were obtained by vacuum induction melting with magnetic stirring to ensure homogeneous distribution of alloying elements. The cast ingots were rolled to a total reduction of 80% with a starting temperature of 900°C and final temperature of 800°C through 8 passes. The final thickness of the as-rolled steel plate was 12mm. The as-rolled sample is labeled as AR. To obtain different dislocation densities, AR steel was then cold rolled to 2 mm after removing the surface oxides (labeled as ACR). One piece of ACR steel was then annealed at 900°C for 2h and then water-quenched. This treatment plays two roles. One is the solid solution treatment of the steel to make the Cu distribute in the matrix uniformly. The other role is to reduce the dislocation density. The as-annealed specimen is labeled as ACR-SS. And then all the samples, AR, ACR and ACR-SS were aged at 500°C for 5h. The aged samples are labeled as AR-AG, ACR-AG and ACR-SS-AG, respectively. In order to quantitatively evaluated dislocation density by XRD, the reference sample (RS) was prepared through recrystallizing the ACR steels at 1000°C for 1h and stress relief annealing at 750°C for 10h.

Tensile tests along the rolling direction of the samples were conducted on an Instron 5565 testing machine at a strain rate of 10^{-3}s^{-1} . The gauge length, width and

thickness of the tensile specimens were 12.5mm, 4mm and 1mm, respectively. Three specimens were tested in the same condition and the average values were reported. The yield strength is determined with the 0.2% offset plastic strain method.

Optical microscopy (OM) and transmission electron microscopy (TEM) were used to characterize the microstructure of the specimens. The TEM samples were prepared by twin-jet polishing using a solution of 5% perchloric acid and 95% ethanol at -20°C. The nanoscale precipitates were characterized using small angle neutron scattering (SANS) at the China Mianyang Research Reactor (CMRR) at China Academy of Engineering Physics. The SANS instruments equipped with a multi-blade mechanical velocity selector, a multi-beam collimation system, and a two-dimensional He-3 position sensitive neutron detector[23]. 10 mm square disks with 1mm thickness were used for the SANS characterization. High-quality SANS data over a wide momentum transfer (Q) range from 0.005 to $0.2\text{\AA}^{-1}$ were measured with two detector-to-sample distances of 1.8m and 9m, covering the Q range from 0.005 to $0.2\text{\AA}^{-1}$, respectively. The data were corrected for transmission, background, empty beam scattering, and detector efficiency and placed on an absolute scale using the direct beam method.

3. Results and discussion

Fig.1 shows the optical microstructures and the X-ray diffraction spectra of all the aged specimens. After hot rolling and aging, the microstructure of AR steel consists of the deformed lath ferrites and some recrystallized equiaxed grains embedded in the deformed matrix(Fig.1a), indicating that the predominant softening mechanism is dynamic recovery/recrystallization. Cold rolling stretched the grains, leading to longer and thinner fibrous tissues in the ACR-AG steel (Fig.1b). After annealing at 900°C for 2h followed water quenching, the deformed fibrous structure of ACR steel transformed into fine and irregular polygonal ferrite due to recrystallization, as indicated in Fig.1c. Fig.1d confirms that all specimens were consisted of a single ferrite phase, and aging causes no discernible second phase.

TEM images were taken to evaluate how dislocation density connects with various treatments. The microstructure of ACR-AG image is shown in Fig.2a, where a

high dislocation density can be clearly observed. Similar structure of dislocations can be found in AR-AG steel as shown in Fig.2b, but the number of dislocation tangles is much less than those of ACR-AG sample and dislocation networks can only be seen in ACR-AG sample. This indicates that the cold rolling causes more dislocations and dislocation tangles. The dislocation in ACR-SS-AG steel (in the Fig.2c) is tangled and the dislocation density is less than the other two samples.

The XRD peak physical broadening (β) of (110) and (211) were used to estimate the mean dislocation density (ρ_m) in ACR-AG, ACR-SS-AG and AR-AG steels. For random distribution of dislocations, the value of ρ_m is estimated by[24]:

$$\beta = b\sqrt{\rho_m}\sqrt{L}f \tan \theta_0 \quad (1)$$

Here, $b=0.25$ nm is the magnitude of the Burgers vector for iron[10] and θ_0 is the diffraction angle for the reference sample, orientation factor f is calculated according to the equation[25]:

$$f = 4(1 - 2r)/9, \quad r = (h^2k^2 + h^2l^2 + k^2l^2)/(h^2 + k^2 + l^2)^2 \quad (2)$$

The factor L is estimated according to the equation[25]:

$$L = \ln[\sqrt{\pi\alpha}C_V \ln(\sqrt{\pi\alpha}C_V)] \quad (3)$$

For the investigated steels, $\alpha = 0.11$, $C_V=7$ as for a material with body-centered cubic [25].

Based on the calculation, the dislocation density for ACR-AG, AR-AG and ACR-SS-AG steels can be evaluated as $2.96 \times 10^{15} \text{m}^{-2}$, 6.06×10^{13} and $5.33 \times 10^{12} \text{m}^{-2}$, respectively. The results are in agreement with that from TEM observation.

The engineering stress-strain curves are presented in Fig.3a and the yield strengths are summarized in Fig.3b. The yield strength of the ACR-AG steel is extraordinarily high as $\sim 2\text{GPa}$ with an elongation of $\sim 7\%$. As compared with the ACR steel, aging increases the yield strength significantly from 1428 to 2006MPa. The ACR-SS-AG and AR-AG steels have similar yield strengths, with 1.58GPa and 1.64GPa, respectively. As shown in Fig. 3b, for all the three samples, AR, ACR and ACR-SS, the increments of yield strength induced by aging are very similar as shown in Fig.3b (589MPa for ACR-SS, 588MPa for AR and 578MPa for ACR). Owing to

the different dislocation densities induced by different processing routes, work hardening contributes different yield strength. It should be noted that the processing conditions change not only the dislocation density but also the microstructure, as shown in Fig.1. Thus, the change in microstructure may contribute to the yield strength. It can be seen from Fig.1 that the ACR-SS steel has the minimum grain size. Based on the Hall-Petch equation, the minimum grain size of ACR-SS steel can provide a maximum contribution to yield strength. Thus, to identify the work hardening, the strength of ACR-SS was taken as a reference. The work hardening contributes 62 and 437MPa for hot-rolled (AR) and cold-rolled (ACR) samples, respectively. This is in agreement with the changes in dislocation density. After aging, the contribution of work hardening to both AR and ACR samples remains the similar (61 and 426MPa, respectively). These results indicate that the precipitation strengthening and work hardening are independent. The precipitation strengthening is not related to dislocation density.

The SANS data are presented in Fig.4. The detailed analysis of SANS data can be referenced in our previous paper [7]. Briefly, polydisperse log-normal size distribution of nanoscale precipitates is assumed. $I(Q)$ describes the scattering from precipitates as[26],

$$I(Q) = \Delta\rho^2 \int_0^\infty N(R)V(R)^2F(Q,R)^2dR \quad (4)$$

Where $\Delta\rho$ is the difference in scattering length density between the precipitates and the matrix. The scattering length densities of both precipitates and matrix are calculated based on the compositions measured by Atom Probe Tomography(APT) in our previous paper[27]. $F(Q,R)$ is the form factor, which can be written as $F(Q,R) = 3(\sin(QR) - QR \cos(QR))/(QR)^3$. R is the precipitate radius, and $V(R)$ is the precipitate volume. The size distribution function $N(R)$ of precipitates is treated as log-normal and is given by[28]

$$N(R) = \frac{N_0}{\sigma R \sqrt{2\pi}} \exp\left(-\frac{1}{2\sigma^2} (\ln(R) - \ln(R_0))^2\right), \quad (5)$$

where N_0 is the number density, and R_0 is the center of the distribution function. σ is the polydispersity of the precipitates. Based on the fitting, the size and number

density of precipitates are obtained and list in Table 1. It is obvious that both the size and number density for the ACR-AG, ACR-SS-AG and AR-AG steels are comparable, indicating that the nanoscale precipitation is not dependent on the dislocation density.

with the same aging processing, the size and number density of precipitates in various steels (AR-AG, ACR-AG, ACR-SS-AG steels) with different dislocation densities are comparable, indicating that the nanoscale precipitation is not dependent on the dislocation density. To identify the contributions of precipitation strengthening in this steel, the contribution from each precipitation strengthening mechanism is evaluated based on the size and number density of precipitates determined from SANS. When a dislocation cuts into an ordered nanoparticle, it creates an anti-phase boundary of specific energy. Thus, the corresponding order strengthening can be estimated by:[29]

$$\Delta\sigma_{order} = M\left(\frac{\gamma_{APB}^{3/2}}{b}\right)\left(\frac{4r_s f}{\pi T}\right)^{1/2} \quad (6)$$

Where $M=3$ is the Taylor factor, $\gamma_{APB}=0.5\text{J}\cdot\text{m}^{-2}$ is an average value of the NiAl anti-phase boundary energy[30], $b=0.25\text{nm}$ is the Burgers vector in the matrix, $\gamma_s = (2/3)^{1/2}R$ is the average precipitate radius in the glide plane, R is the average radius of the precipitates, f is the volume fraction of the precipitates, T is the line tension associated with the dislocation, approximately equals to $Gb^2/2$, and $G=80\text{GPa}$ is the shear modulus of the ferrite matrix.

The modulus strengthening has been derived by Russell and Brown as [31]

$$\Delta\sigma_{modulus} = M\frac{Gb}{L}\left[1 - \left(\frac{E_p}{E_m}\right)^2\right]^{3/4}; \sin^{-1}\left(\frac{E_p}{E_m}\right) \geq 50^\circ \quad (7)$$

Where E_p and E_m are the dislocation line energy in the precipitation and in the matrix, respectively. L is the mean particle spacing in the slip plane and can be calculated from the equation $L=0.866/(RN)^{1/2}$, where R and N are the average precipitate radius and number density of precipitates. The ratio of $\frac{E_p}{E_m}$ depends on particle radius (R) and is defined as[31]

$$\frac{E_p}{E_m} = \frac{E_p^\infty}{E_m^\infty} \frac{\log\frac{R}{r_0}}{\log\frac{r}{r_0}} + \frac{\log\frac{r}{R}}{\log\frac{r}{r_0}} \quad (8)$$

where $r=2.5b$ and $r_0=1000r$ are the inner and outer cut-off radius of the dislocation stress field, respectively, and E_p^∞ and E_m^∞ refer to the energy per unit length of a dislocation in an infinite medium. The ratio of E_p/E_m is calculated to be 0.62 for this steel.

Chemical strengthening occurs due to the production of new precipitate-matrix interfacial areas, given by[29]

$$\Delta\sigma_{\text{chemical}} = \frac{2M}{bLT^{1/2}} \cdot (\gamma_{\text{interfacial}}b)^{3/2} \quad (9)$$

where $\gamma_{\text{interfacial}} = 0.35 \text{ J} \cdot \text{m}^{-2}$ is the interfacial energy[30].

The increment in yield strength due to the coherency strain associated with the nanoscale precipitates is given by[29]

$$\Delta\sigma_{\text{coherency}} = 4.1MG\varepsilon^{3/2}f^{1/2}\left(\frac{R}{b}\right)^{1/2} \quad (10)$$

where $\varepsilon = 2/3 (\Delta a/a)$ is the constrained lattice parameter mismatch, with $\Delta a/a \approx 0.002$ [32].

The contributions from various strengthening mechanisms calculated are list in Table 2. It can be seen from Table 2 that the difference in the calculated strength from each data set of size and number density and from the average of size and density of these three alloys are less than 5% for all of the strengthening mechanisms, which is within the error range. Therefore, it is reasonable to use an average size and number density to calculate the contributions of precipitation strengthening. The contribution calculated by the average size and number density from precipitation strengthening to the yield strength increment in terms of order strengthening, modulus strengthening, chemical and coherency strengthening is 500MPa, 110MPa, 10MPa and 17MPa, respectively. The sum of the calculated strength from precipitation strengthening is 637MPa, which is very close to the experimental value of 589MPa, indicating that the calculated contributions from each precipitation strengthening are reliable.

As compared to the ACR-SS sample, the yield strength increment of AR and ACR is 62 and 437MPa, respectively. This increment is contributed from the work hardening due to the increase in dislocation density. However, the yield strength increments of all the samples (ACR-SS, AR and ACR) after aging are comparable

though all these samples have different dislocation density. These indicate that there is no effect of dislocation density on precipitation strengthening, and the precipitation strengthening and work hardening are independent. Firstly, with the same aging processing, the size and number density of precipitates in various steels (AR-AG, ACR-AG, ACR-SS-AG steels) with different dislocation densities are comparable, confirming that the nanoscale precipitation is not dependent on the dislocation density. This is also confirmed by our previous studies in similar steels[7]. Local composition fluctuation would form Cu-enriched embryos and Cu-depleted regions, which are not rely on the dislocation. The embryos become preferential sites for nucleation of nanoscale clusters when they reach a critical size. Thompson et al.[33]also found that the nanoscale precipitates were not located on dislocations in the matrix in A710-type steels.

Secondly, the precipitation strengthening is not dependent on the dislocation density. During deformation, the precipitates indeed interact with dislocation, providing the precipitation strengthening. However, the precipitation strengthening is mainly controlled by not dislocation density but the precipitate properties, specifically the size and number density of precipitates. Based on the quantitative calculation of the yield strength from various strengthening mechanisms, it can be found that three samples with different dislocation densities exhibit the similar contribution of precipitation strengthening. This is reasonable since the yield strength is responsible for a critical stress that activates the dislocation slip, regardless of the dislocation density. Actually, this phenomenon has been confirmed 40 years before. Brown et al. [29]found that the increment of critical stress, caused by the force's increment for dislocation to shear precipitates, depends on the mean radius, number density and the anti-phase domain boundary energy of precipitates, regardless of the dislocation density. Ardelle et al.[34]also found that all steels strengthened by ordered coherent precipitates have a characteristic that the precipitates are sheared by dislocation travel in groups, contributing to the precipitation strengthening. The number of dislocations in the group is determined by the number required to restore perfect order in the precipitates rather than dislocation density.

4. Conclusions

In summary, the nanocluster strengthened steel with a tensile strength of 2.02GPa and an elongation of ~7% have been successfully developed through a complex strengthening approach of work hardening (~375MPa) and precipitation strengthening (~600MPa). The work hardening is strongly dependent on the dislocation density induced by thermomechanical treatments. The nanoscale precipitates have a large number density and very fine size of ~2.63 nm, providing a significant contribution to the high strength of the steel. The number density and size of nanoscale precipitates are independent on the dislocation density. There is no effect for dislocation density on precipitation hardening. The work hardening and precipitation strengthening are independent and can be controlled separately. This paves the way to design the processing routes of high strength alloys according to different application orientations.

Acknowledgements

This work was supported by the NSFC Funding (51371062 and U1460102), NSFHLJ (ZD201411), the Scientific Research Foundation for the Returned Overseas Chinese Scholars (Heilongjiang Province), the Project for Innovative Talents of Science and Technology of Harbin (2014RFXJ006) and the High-tech Ship Research Projects Sponsored by MIIT (K24367). The neutron diffraction work at China Academy of Engineering Physics (CAEP) is greatly appreciated. The work of Tong was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, United States Department of Energy. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the US Department of Energy (DOE) under contract no. DE-AC05-00OR22725.

References

- [1] M.E. Fine, D. Isheim, Origin of copper precipitation strengthening in steel revisited, *Scr. Mater.*, 53 (2005) 115-118.
- [2] H. Guo, J. Cheng, S. Yang, X. He, Influence of combined Cu and Nb addition on the quenched microstructure and precipitation during tempering in ultra-low carbon steels, *Journal of Alloys and Compounds*, 577, Supplement 1 (2013) S619-S625.

- [3] Z.B. Jiao, J.H. Luan, Z.W. Zhang, M.K. Miller, C.T. Liu, High-strength steels hardened mainly by nanoscale NiAl precipitates, *Scr. Mater.*, 87 (2014) 45-48.
- [4] X.L. Li, C.S. Lei, X.T. Deng, Z.D. Wang, Y.G. Yu, G.D. Wang, R.D.K. Misra, Precipitation strengthening in titanium microalloyed high-strength steel plates with new generation-thermomechanical controlled processing (NG-TMCP), *Journal of Alloys and Compounds*, 689 (2016) 542-553.
- [5] D. Raabe, D. Ponge, O. Dmitrieva, B. Sander, Nanoprecipitate-hardened 1.5 GPa steels with unexpected high ductility, *Scr. Mater.*, 60 (2009) 1141-1144.
- [6] M. Hättstrand, J.-O. Nilsson, K. Stiller, P. Liu, M. Andersson, Precipitation hardening in a 12%Cr–9%Ni–4%Mo–2%Cu stainless steel, *Acta Mater.*, 52 (2004) 1023-1037.
- [7] Z.W. Zhang, C.T. Liu, X.L. Wang, K.C. Littrell, M.K. Miller, K. An, B.A. Chin, From embryos to precipitates: A study of nucleation and growth in a multicomponent ferritic steel, *Phys Rev B*, 84 (2011).
- [8] S.J. Zinkle, J.T. Busby, Structural materials for fission & fusion energy, *Materials Today*, 12 (2009) 12-19.
- [9] Z. Jiao, J. Luan, M. Miller, C. Yu, C. Liu, Group precipitation and age hardening of nanostructured Fe-based alloys with ultra-high strengths, *Sci Rep-Uk*, 6 (2016).
- [10] Z.B. Jiao, J.H. Luan, Z.W. Zhang, M.K. Miller, W.B. Ma, C.T. Liu, Synergistic effects of Cu and Ni on nanoscale precipitation and mechanical properties of high-strength steels, *Acta Materialia*, 61 (2013) 5996-6005.
- [11] T. Harry, D.J. Bacon, Computer simulation of the core structure of the $\frac{1}{2}[111]$ screw dislocation in α -iron containing copper precipitates:: I. structure in the matrix and a precipitate, *Acta Mater.*, 50 (2002) 195-208.
- [12] J.-H. Shim, Y.W. Cho, S.C. Kwon, W.W. Kim, B.D. Wirth, Screw dislocation assisted martensitic transformation of a bcc Cu precipitate in bcc Fe, *Appl Phys Lett*, 90 (2007) 021906.
- [13] A.S. Argon, *Strengthening mechanisms in crystal plasticity*, Oxford University Press Oxford, 2008.
- [14] M. Schober, C. Lerchbacher, E. Eidenberger, P. Staron, H. Clemens, H. Leitner,

Precipitation behavior of intermetallic NiAl particles in Fe-6 at.%Al-4 at.%Ni analyzed by SANS and 3DAP, *Intermetallics*, 18 (2010) 1553-1559.

[15] A.S. Murthy, J.E. Medvedeva, D. Isheim, S.L. Lekakh, V.L. Richards, D.C. Van Aken, Copper precipitation in cobalt-alloyed precipitation-hardened stainless steel, *Scr. Mater.*, 66 (2012) 943-946.

[16] D.B. Park, M.Y. Huh, J.H. Shim, J.Y. Suh, K.H. Lee, W.S. Jung, Strengthening mechanism of hot rolled Ti and Nb microalloyed HSLA steels containing Mo and W with various coiling temperature, *Materials Science & Engineering A*, 560 (2013) 528-534.

[17] H. Yi, F. Yan, N. Tao, K. Lu, Work hardening behavior of nanotwinned austenitic grains in a metastable austenitic stainless steel, *Scr. Mater.*, 114 (2016) 133-136.

[18] T. Tsuchiyama, S. Yamamoto, S. Hata, M. Murayama, S. Morooka, D. Akama, S. Takaki, Plastic deformation and dissolution of epsilon-Cu particles by cold rolling in an over-aged particle dispersion strengthening Fe-2mass%Cu alloy, *Acta Mater.*, 113 (2016) 48-55.

[19] M. Murayama, Z. Horita, K. Hono, Microstructure of two-phase Al-1.7 at% Cu alloy deformed by equal-channel angular pressing, *Acta Mater.*, 49 (2001) 21-29.

[20] C.R. Hutchinson, P.T. Loo, T.J. Bastow, A.J. Hill, J. da Costa Teixeira, Quantifying the strain-induced dissolution of precipitates in Al alloy microstructures using nuclear magnetic resonance, *Acta Mater.*, 57 (2009) 5645-5653.

[21] T. Tarui, N. Maruyama, H. Tashiro, Cementite decomposition in high carbon steel wires, *Tetsu-To-Hagane/Journal of the Iron and Steel Institute of Japan*, 91 (2005) 265-271.

[22] T. Yokoi, M. Takahashi, N. Maruyama, M. Sugiyama, Cyclic stress response and fatigue behavior of Cu added ferritic steels, *Journal of Materials Science*, 36 (2001) 5757-5765.

[23] M. Peng, L. Sun, L. Chen, G. Sun, B. Chen, C. Xie, Q. Xia, G. Yan, Q. Tian, C. Huang, A new small-angle neutron scattering spectrometer at China Mianyang research reactor, *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 810 (2016) 63-67.

- [24] R. Kuzel, Dislocation line broadening, *Zeitschrift Für Kristallographie Supplements*, 2006 (2006).
- [25] M.A. Krivoglaz, X-Ray and Neutron Diffraction in Nonideal Crystals, *Zeitschrift Für Kristallographie*, 211 (2010) 587-588.
- [26] S.R. Kline, Reduction and analysis of SANS and USANS data using IGOR Pro, *Journal of applied crystallography*, 39 (2006) 895-900.
- [27] Z.W. Zhang, C.T. Liu, X.L. Wang, M.K. Miller, D. Ma, G. Chen, J.R. Williams, B.A. Chin, Effects of proton irradiation on nanocluster precipitation in ferritic steel containing fcc alloying additions, *Acta Mater.*, 60 (2012) 3034-3046.
- [28] P. Staron, B. Jamnig, H. Leitner, R. Ebner, H. Clemens, Small-angle neutron scattering analysis of the precipitation behaviour in a maraging steel, *Journal of Applied Crystallography*, 36 (2003) 415-419.
- [29] L. Brown, R. Ham, A. Kelly, R. Nicholson, *Strengthening methods in crystals*, Applied Science, London, 9 (1971).
- [30] E. Povoden-Karadeniz, E. Kozeschnik, Simulation of Precipitation Kinetics and Precipitation Strengthening of B2-precipitates in Martensitic PH 13-8 Mo Steel, *Isij Int*, 52 (2012) 610-615.
- [31] K.C. Russell, L. Brown, A dispersion strengthening model based on differing elastic moduli applied to the iron-copper system, *Acta Metallurgica*, 20 (1972) 969-974.
- [32] R. Taillard, A. Pineau, B.J. Thomas, The precipitation of the intermetallic compound NiAl in Fe-19wt.%Cr alloys, *Materials Science and Engineering*, 54 (1982) 209-219.
- [33] S.W. Thompson, G. Krauss, Copper precipitation during continuous cooling and isothermal aging of a710-type steels, *Metallurgical Transactions A*, 27 (1996) 1573-1588.
- [34] A.J. Ardell, Precipitation hardening, *Metallurgical Transactions A*, 16 (1985) 2131-2165.

Tables:

Table 1 Size and number density of precipitates determined from SANS

	Size (nm)	Number Density (m ⁻³)
ACR-AG	2.6	2.4×10^{23}
ACR-SS-AG	2.9	1.7×10^{23}
AR-AG	2.5	3.1×10^{23}
Average	2.7	2.3×10^{23}

Table 2 The calculated yield strength from each of strengthening mechanisms

	The total strengthening (MPa)	order strengthening (MPa)	modulus strengthening (MPa)	Chemical strengthening (MPa)	Coherency strengthening (MPa)
ACR-AG	646	506	112	11	17
ACR-SS-AG	601	480	98	10	13
AR-AG	667	512	120	12	23
Average	637	500	110	10	17

Figure Captions

Fig.1 The optical microstructures of (a) AR-AG steel, (b) ACR-AG steel, (c) ACR-SS-AG steel and (d) the X ray diffraction spectra of all the aged specimens.

Fig.2 TEM micrographs of (a) ACR-AG steel, (b) AR-AG steel and (c) ACR-SS-AG steel

Fig.3 (a) The engineering stress-strain curves for AR, ACR-SS, ACR, AR-AG, ACR-SS-AG and ACR-AG samples, (b) Schematic diagram showing the effects of work hardening and precipitation strengthening on yield strength of the steel with various thermomechanical treatments.

Fig.4 The SANS-intensity distribution as a function of momentum transfer Q for ACR-AG, ACR-SS-AG and AR-AG steel.

Figure.1a

Figure.1b

Figure.1c

Figure.1d

(d)

Figure.2a

Figure.2b

Figure.2c

Figure.3a

Figure.3b

Figure.4