

Effects of alloying elements on low-temperature tempering behaviors of high carbon martensite

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The effects of alloying elements on low-temperature tempering behaviors, including the kinetics and microstructure change especially in the 0th and 1st stages of tempering, are investigated in this study. Fe-3.6 at% C (0.8 mass%) and Fe-3.6 at% C-2 at% M (M = Al, Si, Mn, Cr) were used for comparison. As-quenched specimens were tempered after subzero cooling in liquid nitrogen by either continuous heating to 873 K at various rates of 5-20 K/min, or isothermal holding at various temperatures between 333 and 453 K. The tetragonality of martensite in the as-quenched specimens is confirmed by in-situ neutron diffraction analysis, which is gradually decreased during continuous heating, especially in the temperature range of metastable carbide precipitation, i.e., in the 1st stage of tempering. Its decreasing rate is strongly retarded by Al addition, whereas the effects of the other alloying elements are relatively small. As for the specimens isothermally held at 363 K, it was found that the reduction in solute carbon content and the degree of heterogeneous carbon distribution in the form of carbon clustering and carbide precipitation are relatively smaller in the Al added alloy than in the other alloys by 3-dimensional atom probe analysis, which is consistent with the retarded tempering kinetics by Al addition during continuous heating. It is considered that these alloying effects on the low-temperature tempering reactions such as carbon clustering and carbide precipitation is mainly attributed to the variation in diffusivity of carbon.

Keywords: martensite, tempering, microstructure, precipitation, tetragonality

1. Introduction

As-quenched martensite has high strength but suffers from low ductility and toughness, which needs to be tempered for practical applications. During tempering of martensite, microstructure change can be divided into several stages, i.e., 0th stage - carbon clustering and segregation, 1st stage - metastable ϵ/η -carbide precipitation, 2nd stage - retained γ decomposition and 3rd stage - θ -carbide (cementite) precipitation. In order to increase the hardenability of steel to obtain martensite and suppress its softening during tempering, substitutional alloying elements are generally added. Compared with the widely investigated alloying effects on high-temperature tempering of martensite, the studies on alloying effects in low-temperature tempering, which is important to obtain desirable fatigue property and wear resistance, are quite limited. Therefore, the objective of this study is to clarify microstructure evolution during low-temperature tempering of high carbon martensite with addition of various third alloying elements, by particularly focusing the reactions of the 0th and 1st stages.

2. Experiment

Fe-3.6 at% C (denoted as Base alloy) and Fe-3.6 at% C - 2 at% M (M = Al, Si, Mn, Cr, denoted as M alloy) were used. After austenitization at 1123-1273 K for 0.6 ks, these alloys were quenched into iced water and immediately subzero treated in liquid nitrogen to prepare as-quenched martensite for subsequent tempering treatments. The as-quenched specimens were either continuously heated to 873 K at various rates of 5-20 K/min, or isothermally held at various temperatures of 333-453 K, whose kinetics were evaluated

by calorimetric, dilatometric and resistometric analyses, respectively. Furthermore, in-situ neutron diffraction experiment and microstructure observation using transmission electron microscope (TEM) and 3-dimensional atom probe (3DAP) were conducted.

3. Results and Discussion

Fig. 1 shows the in-situ neutron diffraction profiles of the Base alloy continuously heated at a rate of 10 K/min. The tetragonality of martensite (e.g., see peak splitting of $002_{\alpha'}$) and the existence of retained γ are confirmed in the as-quenched (AsQ) specimen. During continuous heating, tetragonality of martensite gradually decreases, and the peaks of retained γ become disappeared at around 573 K. Similar results can also be observed in the other alloys with alloying addition.

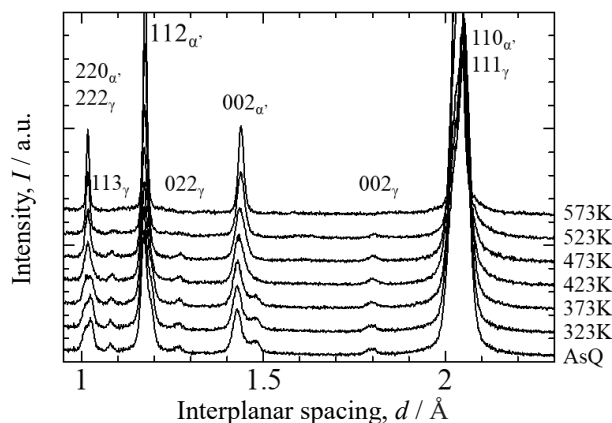


Fig. 1 Neutron diffraction profiles of the Base alloy continuously heated at a rate of 10 K/min.

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Fig. 2 shows the change of martensite tetragonality during continuous heating measured by in-situ neutron diffraction. The tetragonality of martensite is gradually decreased during heating, especially in the temperature range of the 1st stage of tempering, as was determined based on the results of preliminary calorimetric and dilatometric measurements. Its decreasing rate is strongly retarded by Al addition, whereas the effects of other alloying elements are found to be relatively small. Such alloying effects are also recognized by the kinetics analysis during continuous heating.

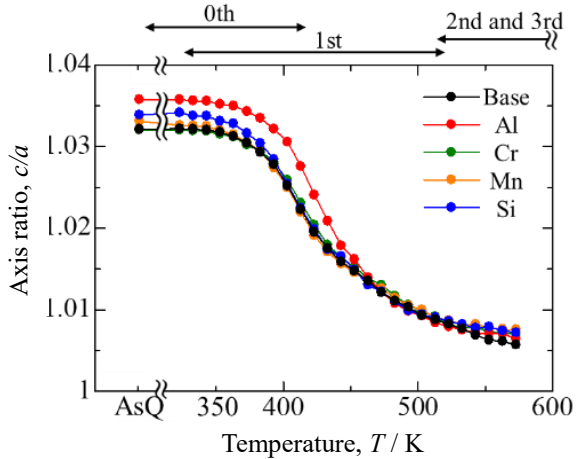


Fig. 2 Change in tetragonality of various alloys continuously heated at a rate of 10 K/min.

To explain these alloying effects, microstructure analysis using 3DAP was conducted. Fig. 3 shows 3D carbon atom maps of the Base and Al alloys after isothermal holding at 363 K for 10.8 ks as an example, which corresponds to the 1st stage of tempering by considering the tempering parameter correlating continuous heating with isothermal holding. In these specimens, carbon enriched regions (> 6 at.%) represent the precipitation of metastable iron carbide, whose amount seems to be smaller in the Al alloy than that in the Base alloy.

For quantification of the degree of the heterogeneity in carbon distribution induced by carbide precipitation, μ parameter, which represent the deviation from random distribution of carbon as a person function, and reduction amount in solute carbon content of the alloys are analyzed and shown in Fig. 4. In Fig. 4(a), a lower value in the Al alloy than the Base alloy indicates the retardation effect on carbide precipitation kinetics by Al addition. This is also consistent with the relatively smaller reduction in solute carbon content in the Al alloy in Fig. 4(b). Considering the linear relationship between tetragonality and solute carbon content, this result corresponds well to the retardation effect on decreasing rate of tetragonality in Fig. 2. The values of μ parameter and reduction in solute carbon content in the Mn and Si alloys are roughly same as those in the Base alloy, whereas some retardation effect on tempering kinetics is recognized by Cr addition. Considering the kinetics analysis and microstructure observation made in this study, the magnitude relationship of retardation effects on the 0th and 1st stages of tempering by alloying addition is in the order of Al > Cr > Si = Mn (= Base). Such magnitude relationship of retardation effects by alloying addition is well consistent

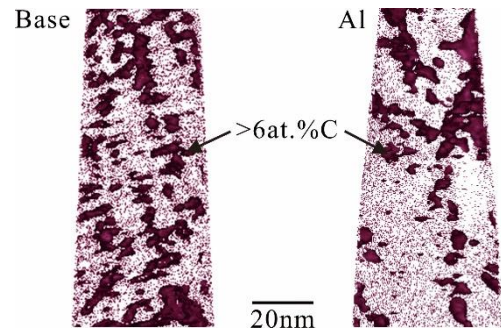


Fig. 3 Carbon atom maps of the Base and Al alloys isothermally held at 363 K for 10.8 ks.

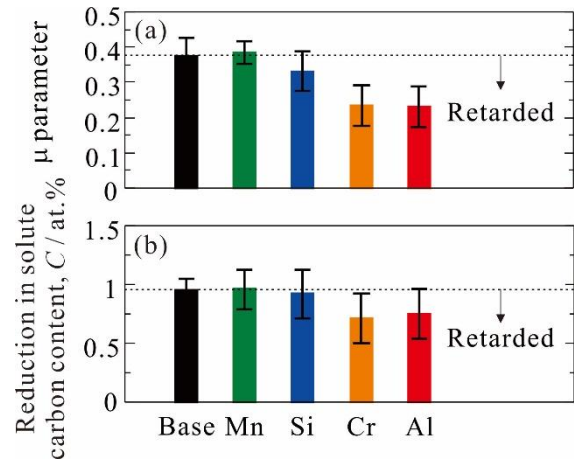


Fig. 4 (a) μ parameter and (b) the reduction amount of the solute carbon content in various alloys isothermally held at 363 K for 10.8 ks.

with the tendency of reduced carbon diffusivity obtained from first-principles calculation, which is attributed to the trapping effect of carbon diffusion in the vicinity of alloying element¹⁻³.

5. Conclusions

The alloying effects on low-temperature tempering behaviors, especially in the 0th and 1st stages of tempering, are investigated by kinetics analysis and microstructure observation. The following results were obtained.

1. In the Base alloy, tetragonality of martensite gradually decreases during continuous heating, especially in the temperature range of the 1st stage of tempering.
2. Decreasing of tetragonality and heterogeneity in the carbon clustering/precipitation with reduction of solute carbon content during tempering are strongly retarded with Al addition.
3. The degree of retardation on low-temperature tempering kinetics by alloying observed is well consistent with the tendency of reduction in carbon diffusivity.

References

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