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Hardening mechanism of MP159 alloy induced by aging ①

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[Abstract] The microstructural changes of both solution heat treated (ST) and cold worked (CW) MP159 alloy during aging were investigated by optical microscopy and transmission electron microscopy (TEM). The results indicate that both solution heat treated (ST) and cold worked (CW) MP159 alloy could be hardened by aging. This aging induced hardening is attributable to the precipitation of a very finely dispersed ordered cubic γ' phase particles with only several nanometres in diameter. The hexagonal close packed (HCP) ε-martensite precipitated during aging of both CW MP159 and CW MP35N, and the hexagonal ordered Co_3Mo phase of the DO_{19} structure type precipitated during aging of CW MP35N, have not been found in the present investigation.

[Key words] aging; hardening mechanism; MP159 alloy; cubic γ' phase
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1 INTRODUCTION

MP159 alloy (MP, i.e. Multiphase is a trademark of SPS Technology Inc., Newton, PA) is a new kind of cobalt base wrought superalloy, and is a later member of the family of multiphase cobalt based alloys (i.e. MP alloys). MP alloys were initially designed on the basis of the FCC (α) $\rightarrow$ HCP (ε) martensite phase transition that occurs on cooling pure cobalt below about 420 ℃[1,2]. The first member in the MP alloys was called MP35N which contains 35Co, 35Ni, 20Cr and 10Mo (in mass fraction, %), but this alloy has a maximum service temperature of only 300 ℃. In order to raise the service temperature, Slaney[3] developed MP159 alloy with a complex chemical composition (35.7Co, 25.5Ni, 19.0Cr, 9.0Fe, 7.0Mo, 3.0Ti, 0.6Nb and 0.2Al). MP159 alloy possesses the unique combination of ultra-high strength, ductility and corrosion resistance and has a maximum service temperature of 593 ℃[4]. Solution treatment (for 4 h at 1 050 ℃, AC) produces a single phase FCC structure, which has a tensile strength of about 850 MPa and a yield strength of approximately 400 MPa. Its high strength is obtained through cold working (extruding, rolling, swaging, drawing or a combination of these processes) and aging. For example, a nominal cold drawing with 48% reduction in cross-section area results in a tensile strength of about 1 585 MPa and a yield strength of about 1 415 MPa, and aging (for 4 h at 660 ℃) further increases the tensile strength to about 1 895 MPa and the yield strength to about 1 825 MPa. The alloy is being widely used for critical fasteners, jet engine components, drive components and prosthetic devices, etc.

There are many published papers investigating the strengthening mechanisms of cold working and aging for MP35N, but the conclusions are divergent[5~9], while the available literature on the strengthening mechanisms in MP159 is very limited. The cold working strengthening mechanisms in MP159 has been discussed in a separate publication[10]. In the present investigation we will study the micromechanism of the aging strengthening in MP159 alloy.

2 EXPERIMENTAL

The material is received as commercial cold drawn MP159 rods (with 48% reduction of cross-section area). The diameter of the as-drawn rod is 10 mm. A typical producing schedule for MP159 is as follows: vacuum induction melted + vacuum consumable electrode melted + hot worked + solution heat treated (ST) + cold drawn. The samples for optical metallography were etched with Kalling's reagent (100 cm^3 of absolute ethyl alcohol, 100 cm^3 of hydrochloric acid (sp gr 1.19) and 5 g of cupric chloride) heated to about 60 ℃. The samples for TEM were prepared by mechanical polishing followed by twin-jet electropolishing using a solution of 10% perchloric acid-absolute ethyl alcohol. TEM was performed using Philips-CM12 at 120 kV and JEOL-JEM-2000FXII at 200 kV.

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The solution treated (ST) MP159 is obtained by heat treating the as-received rod at 1050 ℃ for 4 h.

3 RESULTS

The Rockwell hardness of MP159 in ST and CW conditions are about HRC8 and HRC44, respectively (the values lower than HRC20 only for reference). However, the corresponding Rockwell hardness can be increased to about HRC18 and HRC52 respectively after aging heat treatment (660 ℃ for 4.15 h). The optical micrographs in ST MP159 alloy are shown in Fig. 1. The ST microstructure consists of equiaxed FCC grains with a number of annealing twins, which indicates a low coherent twin boundary energy, equivalently a low stacking fault energy. The optical micrograph and transmission electron micrograph of 48% cold drawn MP159 are shown in Fig. 2. These micrographs reveal the microstructure feature of the intersecting network of very fine platelets. These closely-spaced, intersecting network of fine platelets formed during cold drawing solution treated MP159 alloy with FCC grains have been identified to be deformation twins with high density of stacking faults[10]. The relatively high dislocation density and dislocation tangles between thin platelets can be seen in Fig. 2(b).

After aging under ST and CW conditions, no microstructual changes of samples have been detected in optical micrographs and bright field (BF) transimission electron micrographs. However, a careful diffraction study reveals the appearence of the reflections of the precipitate in both ST+ aged and CW+ aged samples. Figs. 3(a) and (b) show the selected-area electron diffraction pattern (SADP) in [001] matrix orientation and corresponding dark-field (DF) image of the reflection of the precipitate for ST+ aged sample respectively. In Fig. 3(a), we see strong spots of the FCC matrix and weak superlattice reflections which may be indexed by ordered cubic γ' phase. Fig. 3(b) indicates that the γ' precipitates are very finely dispersively distributed and precipitates are particles of only several nanometres in diameter. But BF image can not show signs of the precipitation because precipitate particles are too small. The SADP in [001] and [111] matrix direction for the CW+ aged sample are shown in Fig. 4. Fig. 4(a) demonstrates that the aged CW sample also produces the ordered solid solution, but the intensity of the superlattice spots is relative weak. Only strong spots of the FCC matrix are shown in Fig. 4(b).

Fig. 1 Optical micrograph of MP159 in ST condition

4 DISCUSSION

The physical origin of the age hardening in MP alloys is not well understood. Many researchers have investigated age hardening mechanisms in MP35N, but the conclusions, as mentioned previously, are divergent. Graham[5] pointed out that the age hardening in CW MP35N was attributed to the precipitation of Co_3Mo, an ordered hexagonal phase (DO_{19}) whose c parameter is approximately equal to that of HCP phase and whose a is approximately twice that of HCP phase, whereas the age hardening in ST MP35N was absent due to no formation of the precipitate. Graham thought that the HCP platelets formed during cold work acted as nucleation site and was necessary condition for the precipitation of Co_3Mo. In agreement with the above conclusion, Drapier et al[6]

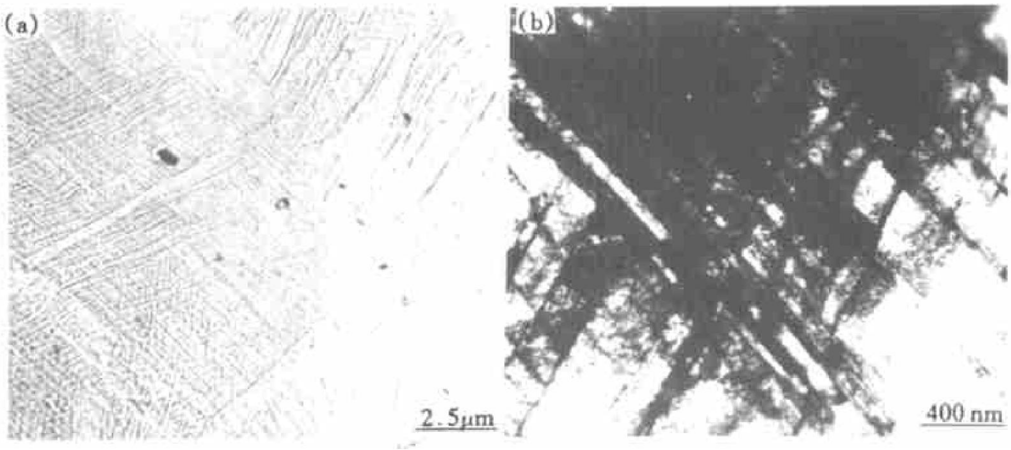

Fig. 2 Micrographs of 48% cold drawn MP159
(a) —Optical micrograph; (b) —Transmission electron micrograph

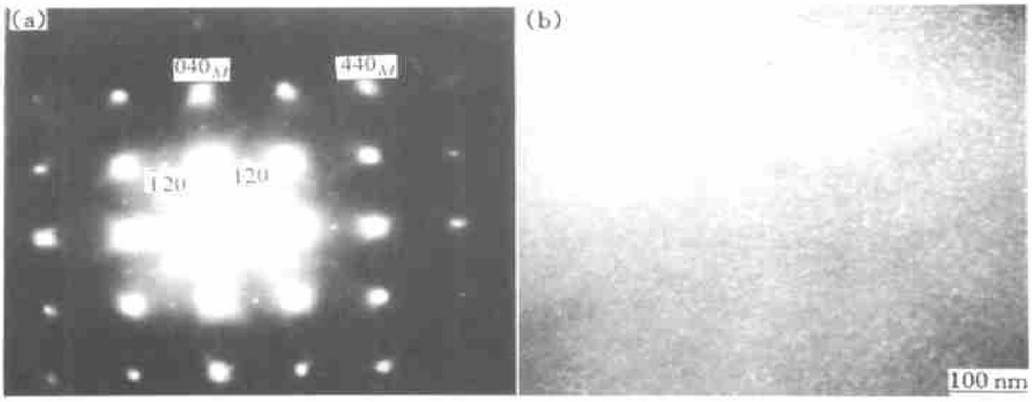

Fig. 3 ST+ aged sample
(a) —SADP of [001] matrix orientation; (b) —DF from spot 1 in [001] matrix orientation

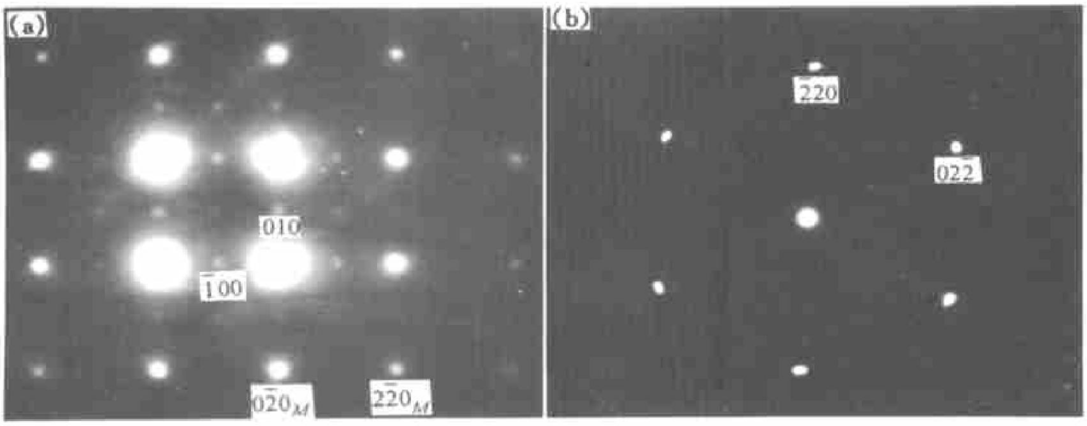

Fig. 4 CW+ aged sample
(a) —SADP of [001] matrix orientation; (b) —[111] matrix orientation

also demonstrated that the age hardening in MP35N resulted from the precipitation of Co_3Mo. However, Raghavan et al[7] and Singh et al[8] obtained different conclusions in their investigation. The investigation by Raghavan et al[7] showed that no HCP platelets were found in CW MP35N, neither did Co_3Mo in CW + aged MP35N, but the precipitation of ε-platelets, which were believed to be responsible for the age hardening, was detected in CW + aged MP35N. While the investigation by Singh et al[8] presented that no changes were seen in either hardness or microstructure in ST+ aged MP35N, but age hardening in CW+ aged MP35N was seen, however, no microstructural changes associated with this secondary hardening could be detected, although CW microstructure contained HCP-platelets which were regarded as nucleation site of Co_3Mo by Graham and Drapier et al[5,6]. Therefore, Singh et al[8] thought that age hardening of CW MP35N might arise from local solute partitioning between the matrix and HCP phase, but it is not so far clear how solute partitioning could give rise to the age hardening.

The investigation performed by the above investigators has showed that, the age treatment has no hardening effect for ST MP35N, while the same treatment has obvious age hardening effect for CW MP35N, although the physical origin of this hardening is divergent in explanation. The present investigation for MP159 indicates that the age treatment not only can result in hardening under CW condition, but also can lead to hardening under ST condition. The careful diffraction work reveals the existence of a finely disperse FCC ordered solid solution (see Fig. 3, Fig. 4(a)), i. e. Ni_3X, which has a molecular formula of $(Ni, Co, Fe, Cr, Mo)_3(Al, Ti, Nb)$[11] but could not be seen in optical microscopy and TEM (BF). No evidence of the formation of Co_3Mo has been seen in both ST + aged and CW+ aged MP159, which is in agreement with Graham's opinion[5] because of the absence of suitable nucleation site for Co_3Mo. The precipitation of ε-platelets, ever reported by Raghavan[7], is not detected either in MP159 because, if this precipitate existed, the reflections of ε-platelets should have occurred in the SADP of [111] matrix orientation according to simulating results of composite electron-diffraction patterns for MP159 alloy[12]. As shown in Fig. 4(b), only matrix reflections appeared in the SADP of [111] matrix orientation.

At present, three types of precipitates, i. e., Co_3Mo and HCP ε-platelets in the MP35N, FCC ordered solid solution γ′ phases in the MP159 alloy, were reported in aged MP alloys. Notice that: 1) HCP phase possesses the same disordered, densely packed basal plane as FCC matrix. Their difference lies in the stacking sequence (of the basal plane), being ABCABC …for FCC matrix and ABAB …for HCP phase; 2) The phase of Co_3Mo structure type possesses the same ordered, densely packed basal plane as γ′ phases. Their difference lies in the stacking sequence (of the basal plane), being ABCABC …for γ′ phase, ABAB …for Co_3Mo phase. Therefore, γ′ phase, Co_3Mo phase possess similar formation energies and any one may be precipitated depending on the alloy composition, microstructure and the precipitation temperature. For example, MP35N alloy contains 10% Mo but without Al and Ti, hence Co_3Mo precipitates were observed, while MP159 alloy contains Ti and Al elements, hence γ′ phase precipitated.

Based on the present experimental observation and the above discussion, it can be concluded that both ST and CW MP159 alloy can be hardened by aging. This is because of the precipitation of very finely disperse ordered cubic phase.

5 CONCLUSIONS

1) Both solution treated and cold worked MP159 can be hardened by aging heat treatment. The aging induced hardening is attributed to the precipitation of Ni_3Al type phase, an ordered cubic γ′ phase.

2) γ′ precipitates are very finely dispersively distributed, and present a shape of particles. Its size is only several nanometres in diameter. Optical microscopy and bright field (BF) transimission electron microscopy can not detected their existence, only a careful diffraction study can detect them.

3) Co_3Mo phase and HCP phase (ε-platelets), which were ever reported to be precipitated during aging CW MP35N alloy, are not found in ST+ aged and CW+ aged MP159 alloy.

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[REFERENCES]

[1] Nishiyama Z. Martensitic Transformation [M]. New York, NY: Academic Press, 1978.

[2] Giamei A, Burma J, Freise J. The role of the allotropic transformation in cobalt-base alloys [J]. Cobalt, 1968, 39(1): 88- 96.

[3] Slaney J S, Nebiolo R A. Development of multiphase alloy MP159 using experimental statistics [J]. Metall, 1983, 16(1): 137- 160.

[4] Kline K, Lawler M. Ultra-high strength and corrosion resistance define today' s fastener' s needs [J]. Aircr Eng, 1989(7): 2- 4.

[5] Graham A H. Strengthening of "MP alloys" during aging at elevated temperatures [J]. Trans ASM, 1969, 62 (2): 930- 935.

[6] Drapier J M, Viatour P, Coutsouradis D, et al. Hardening mechanisms in multiphase alloy MP35N [J]. Cobalt, 1970, 49(2): 171- 186.

[7] Raghavan M, Berkowitz B J, Kane R D. A transmission electron microscopic investigation of phase transformations in MP35N [J]. Metall Trans, 1980, 11A(1): 203 - 207.

[8] Singh R P, Doherty R D. Strengthening in multiphase MP35N alloy: part I. Ambient temperature deformation and recrystallization [J]. Metall Trans, 1992, 23A(1): 307- 319.

[9] Graham A H, Youngblood J L. Work strengthening by a deformation-induced phase transformation in MP alloys [J]. Metall Trans, 1970, 1(2): 423- 430.

[10] LU Shi-qiang, SHANG Bao-zhong, LUO Zi-jian, et al. Investigation on the cold deformation strengthening mechanism in MP159 alloy [J]. Metall Mater Trans, 2000, 31A(1): 5- 13.

[11] MA Shu-po, ZHANG Yun, CHANG Xin, et al. An investigation of strengthening mechanism of MP159 alloy by TEM [J]. J Mater Eng, (in Chinese), 1990(4): 35- 37.

[12] LU Shi-qiang, SHANG Bao-zhong, LUO Zi-jian, et al. Computer simulation of composite electron diffraction patterns and its application [J]. Acta Metallurgica Sinica, (in Chinese), 1999, 35(5): 554- 560.

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