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METALLOGRAPHY OF MARAGING 350 STEEL

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ABSTRACT

A technique for etching maraging 350 steel with Glyceregia is described. Surface activation procedures are integral to this technique. Microstructural features revealed by this technique are compared with those obtained with Kalling's reagent, Fry's reagent, and 5% Nital, three etchants commonly used to reveal microstructures of maraging steels. Features which may be simultaneously revealed using Glyceregia include prior austenite grain boundaries, martensitic structure, precipitates, titanium carbo-nitrides, and reverted austenite. The other etchants examined in this investigation typically reveal only a few of the microstructural features detailed above at any one time.

INTRODUCTION

A variety of maraging steels has been commercially available for over twenty five years. One variety of these steels is a class containing 18% nickel. The high strength of this class of materials is developed due to precipitation hardening as a result of aging massive martensites. The physical metallurgy of early 18 nickel maraging steels is described in detail by Floreen(1). Strengths of these alloys range from 200 to 300 ksi. The primary alloying components are nickel, cobalt, molybdenum, and titanium. Carbon content is typically less than 0.03 percent. Heat treatment of these alloys generally consists of a solution anneal and an aging process. The solution anneal typically takes place at temperatures in excess of 1500°F for a period of one hour. It is claimed that cooling at moderate rates is sufficient to transform the solutionized austenite to 100% bcc martensite. The strength of the martensite in its solution annealed condition ranges from 140 to 150 ksi. Aging at temperatures above 900°F allows precipitation to occur. Nominal strengths can be achieved for aging times as small as one half hour. A number of investigators have attempted to identify the precipitates responsible for strengthening. Potential candidates include Ni_3Mo(2,3,4,5), FeTi(5), Fe_2Mo(4,6), and Ni_3Ti(3,6,7). Ti(C,N) is also present as a much larger precipitate. For the 200, 250, and 300 grades of maraging steels, strength increases as titanium and molybdenum content increases. Cobalt content is 8.5% for maraging 200, 7.5% for maraging 250, and 9.0% for maraging 300(8). Cobalt bearing precipitates have never been observed in any of these alloys. The role of cobalt was identified as the reduction of solubility of molybdenum in the matrix thus leading to greater numbers of molybdenum precipitates(1).

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DISCLAIMER

Vascomax 350, a maraging 350 steel, was developed in the mid-sixties by the Vanadium-Alloys Steel Company. This material was intended to be an ultra-high strength steel which retained the excellent fracture toughness properties of the 200, 250, and 300 grades. Typical mechanical properties and composition are given in Tables I and II. For a variety of reasons, the literature regarding this alloy is not as extensive as that on the 18 Ni 200, 250, and 300 grades. Heat treatment procedures are identical to those for earlier grades of maraging steels. Because the kinetics of the maraging reactions were nearly identical, it was assumed by many that the precipitation reactions were the same. A second reason is that the trade off for an increase in strength of 50 ksi over the maraging 300 grade is a reduction in fracture toughness by half from 73 to 35 ksi in(9). Such a reduction in fracture toughness makes this material suitable only for special applications in which strength cannot be sacrificed. Thirdly, fracture toughness and ductility parameters can vary over a wide range of values as result of subtle changes in heat treat parameters. As a result of the relative scarcity of literature regarding 18 Ni maraging 350 steel, many metallurgists have tended to apply the body of knowledge existing for other grades to this alloy. This extends to the metallographic techniques employed in examining the microstructure of maraging 350 steel.

PHYSICAL METALLURGY OF MARAGING 350 STEEL

Rack and Kalish have described in detail the physical metallurgy of 18 Ni maraging steel(10). Air cooling of this alloy from the austenitization temperature produces a precipitate free bcc martensite. This transformation is complete and as such, no austenite is retained. Undissolved inclusions observed in the solution annealed material are Ti(C,N) and Ti_2S. Aging at 950°F for three hours produces rod shaped orthorhombic Ni_3Mo and spherical shaped tetragonal FeTi precipitates. About 0.5 percent of the martensite also reverts to austenite with this heat treatment. With over aging further austenite reversion is observed as well as the formation of spherical Fe_2Mo precipitates.

Maraging reactions, as outlined by Rack and Kalish, proceed as follows. Initially, molybdenum atoms tend to cluster while simltaneously the cobalt atoms undergo short range ordering. Enrichment of cobalt causes rejection of nickel from iron-cobalt regions. The result is the formation of Ni_3Mo precipitates. Nickel lean regions promote the formation of the FeTi precipitate. As aging proceeds, these metastable precipitates can redissolve. Local nickel enrichment of the matrix can then promote austenite formation.

Important microstructural features which one might expect to observe metallographically in the solution annealed material are the prior austenite grain size and Ti(C,N) and TiS inclusions. Additional features which might be observed in properly aged material are the amount of reverted austenite, and precipitates which might contribute to strengthening. The remainder of this paper examines the results obtained on Vascomax 350 18 Ni maraging steel with metallographic techniques traditionally used on the 200, 250, and 300 grades and compares these results to those obtained with a technique developed at Mound Lab.

METALLOGRAPHIC PROCEDURES

Samples prepared for this study were subjected to one of two heat treatment processes. Those designated as aged only were received in the mill annealed condition and subsequently aged at 950° F. for three hours. Samples designated as solution annealed and aged were subjected to an additional solution anneal at 1500° F. for one hour prior to aging. These samples were mounted in clear lucite ring cups using 2038 Dexter Hysol mounting resin with 10% 3410 Dexter Hardner. The samples were evacuated, pressurized for a 3 hour cure at 150° F, then allowed to cool to room temperature.

Grinding was performed using 180-,320-,600- and 1000- grit silicon carbide abrasive papers on a Knuth roto grinder or a Leco-Ap 200 autopolisher using running water as a lubricant. At least three changes, at 60 second intervals, were carried out for each grade of abrasive paper. Rotation of the sample was in the clockwise direction, opposite the rotation of the grinding wheel.

Final polishing was done on a napless Metcloth or Texmet polishing cloth using Glennel 6 and 1 micrometre diamond paste with Metadi as a lubricant. Samples were polished either manually or on the Leco-ap autopolisher for a minimum of 3 minutes. Samples were rotated counter to the wheel rotation, as in grinding. Microscopic examination was used to determine the end point of polishing. All samples were cleaned with soap and water and ethyl alcohol and then cleaned ultrasonically. The samples were then placed on a Syntron vibratory polisher with 1/4 micrometre diamond slurry for 24 hours. This final polish was used to attain a flatter, more uniform sample surface. Prior to etching all samples were cleaned with soap and water followed by an ethanol rinse. They were then ultrasonically cleaned to remove any remaining contaminants.

Kalling's Reagent, Fry's Reagent, and Nital(5%) are among the etchants commonly used on maraging steel. These solutions were chosen for comparison with Glyceregia used in the technique described below. Their use was based upon ASTM(11) recommended procedures for etching of maraging steels.

The surface of maraging samples which were to be etched in Glyceregia were activated with a 10% HCL solution. Each sample was immersed in the HCL solution and swirled for 15-30 seconds. Without rinsing, the sample was immediatly placed in the Glyceregia solution, which was composed of 10ml HNO_3 , 20ml HCL, and 30ml Glycerol. Each of these samples was then electrolytically etched at 4.0 volts for 5-20 seconds. Variations in etching time produced some distinct characteristic changes in the revealed microstructure. Prior austenite grain boundaries were more evident with decreased etch time and martensitic laths were more apparent with increased etch time.

RESULTS

A typical micrograph of the microstructure of maraging 350 in the "aged only" condition, as revealed by the Glyceregia etch, is shown in Figure 1a. Careful inspection reveals some faint evidence of the prior austenite grains. Other features which are more obvious include the lathlike structure of the martensite, sub-micron precipitates, titanium carbo-nitride precipitates, and very small regions of reverted austenite. The sub-micron precipitates appear as small black dots which decorate the lath. Titanium carbo-nitride precipitates are light colored, angular, and have dimensions on the order of several microns. Reverted austenite is most easily observed in the upper left and lower right corners of Figure 1a. It appears as small elongated islands in the martensitic matrix and is shaded much lighter than the surrounding matrix.

Figures 1b, 1c, and 1d show the same specimen repolished and etched in 5% Nital, Fry's reagent, and Kalling's reagent respectively. Compared to Glyceregia, Nital is seen to have limited effectiveness as an etchant. The only microstructural features which can be discerned are a hint of the lathlike structure of the martensite and numerous small, lightly shaded regions which are assumed to be reverted austenite. Fry's reagent clearly reveals the structure of the martensite. Most sub-micron precipitates revealed by this etchant are light in shading and are difficult to distinguish from reverted austenite. When compared to the micrograph of the same specimen etched in Glyceregia, the prior austenite grains are more difficult to distinguish. The efficacy of Kalling's reagent is somewhere between Nital and Fry's reagent. The lathlike structure of the martensite is revealed somewhat better than with Nital. Some small dark precipitates can be observed with careful inspection. Reverted austenite is not evident.

The microstructure of a solution annealed and aged maraging 350 specimen, as revealed by etching in Glyceregia, is shown in Figure 2a. General features which can be observed include prior austenite grain boundaries, a lathlike martensitic structure, and reverted austenite. When compared to the aged only sample etched with Glyceregia, the reverted austenite is observed as stringers which often occur in grain boundaries, as opposed to small elongated regions. Once again, the shading of the reverted austenite is lighter than that of other features. The sub-micron precipitates are more difficult to observe than those present in the aged only specimen.

The effect of etching the same solution annealed and aged sample with a 5% Nital solution is shown in Figure 2b. Prior austenite grain boundaries and some of the sub-micron precipitates are visible. Etching with Kalling's reagent, as shown in Figure 2d, provides more contrast but tends to obscure the prior austenite grain boundaries. Sub-micron precipitates appear dark and are more easily observed than when the same sample was etched in Nital. Fry's reagent (Figure 2c), reveals some grain boundaries. Any precipitates which can be seen are shaded light. Neither Nital, Kalling's reagent, nor Fry's reagent reveal reverted austenite.

A detailed view of the titanium carbo-nitride precipitates is shown in Figure 3. These precipitates are found in all heat treatment conditions of maraging 350 and typically exhibit a cored type of structure. The outer core of the precipitate is frequently titanium carbide which can be identified by its blue to purple coloring. The inner core is titanium nitride which has a characteristic gold color.

Effects of working in maraging 350 are also revealed by Glyceregia as shown in Figure 4. This metallographic section was prepared parallel to the rolling direction. Non-uniform deformation can be seen to result in a banded structure. Reverted austenite occurs preferentially along the bands where the deformation is greatest.

Summary

Procedures for the metallographic preparation of maraging 350 have been described. An electrolytic etching technique specifically for use with maraging 350 steel has been developed. Results obtained with this technique are compared those obtained with Nital, Fry's reagent, and Kalling's reagent for two distinct heat treatments. Features revealed by the electrolytic technique include prior austenite grain boundaries, martensitic structure, precipitates, titanium carbo-nitrides, and structure resulting from non-uniform deformation.

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Figure Captions

1a) Microstructure of aged only material as revealed by Glyceregia.

1b) Microstructure of aged only material as revealed by 5% Nital.

1c) Microstructure of aged only material as revealed by Fry's reagent.

1d) Microstructure of aged only material as revealed by Kalling's reagent.

2a) Microstructure of solution annealed and aged material as revealed by Glyceregia.

2b) Microstructure of solution annealed and aged material as revealed by 5% Nital.

2c) Microstructure of solution annealed and aged material as revealed by Fry's reagent.

2d) Microstructure of solution annealed and aged material as revealed by Kalling's reagent.

3) Titanium carbo-nitride precipitate. The carbide is deep blue to purple while the nitride is gold in color.

4) Effects of working on microstructure as revealed by Glyceregia.

Table I. Mechanical Properties of Maraging Steel

BEFORE MARAGING:

Yield Strength, ksi.	140-150
Tensile Strength, ksi.	160-180
Elongation, %	16
Reduction in area, %	72
Hardness, R/C	28-32

AFTER MARAGING:

Yield Strength, ksi.	335-350
Tensile Strength, ksi.	340-350
Elongation, %	6-8
Reduction in area, %	25-45
Hardness, R/C	58-60

Table II. Chemical Composition of 350 Maraging Steel

Ni	18.50	Co	12.00	Mo	04.80
Ti	01.40	Al	0.10	Si	0.10
Mn	0.10	C	0.03	S	0.01
P	0.01	Zr	0.01	B	0.003

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