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#### STRENGTHENING MECHANISM IN MARAGING STEEL

The strengthening mechanism in maraging steel has been investigated by Crucible Steel Company of America.<sup>(1)</sup>

A variety of iron-nickel binary, ternary, quaternary, and more complex alloys of high purity were explored for detailed fine structural and property correlations. First, the individual effect of each of the various elements in the 18-percent nickel maraging steels was clarified. This investigation was related to the effects of these elements on the matrix structures, stacking faults, and martensite morphology; the role of interaction of precipitates and substructures was also evaluated.

From their investigations of the 18Ni-Fe-based ternary and quaternary alloys, the investigators made the following conclusions.

A cobalt addition to iron-nickel binary alloy produces no solid-solution hardening, but does produce a small amount of age hardening. A molybdenum addition to the iron-nickel alloy produces significant solid-solution hardening and age hardening. Simultaneous additions of cobalt and molybdenum to the iron-nickel binary alloy produces hardening responses analogous to those obtained by adding the individual elements, and their cumulative effects are additive but not synergistic. Also, contrary to previous claims, grain-boundary precipitates do occur in molybdenum-containing alloys.

Diffraction and quantitative (corrected) electron-probe data on extraction replicas show that  $Ni_3Ti$ ,  $\alpha FeMo$ , and possibly  $NiAl$  are the age-hardening precipitates in 18 percent nickel-iron-base alloys containing single additions of aluminum, titanium, and molybdenum, and additions of molybdenum plus cobalt. The calculated stoichiometric compositions of these intermetallic compounds are  $(Ni_{0.7}Fe_{0.3})Al$ ,  $(Ni_{2.9}Fe_{0.1})Ti$ ,  $(Ni_{0.3}Fe_{0.7})Mo$ , and  $(Ni_{0.4}Fe_{0.6}Co_{0.05})Mo$  for the precipitates of these alloys in the iron-nickel-aluminum, iron-nickel-titanium, iron-nickel-molybdenum, and iron-nickel-molybdenum-columbium alloys, respectively. Electron-probe data show that cobalt does not enter the precipitated phase to any extent. Fine structures of these alloys show cobalt to decrease the precipitate growth rate. Precipitates in the iron-nickel-based alloys do not appear to coalesce to any extent,

probably because of the lower  $A_c$  temperatures of the alloys compared with most steels.

The investigators showed that the effect of cobalt on matrix strengthening was based on the lowering of the stacking fault energy (SFE) of the matrix by cobalt. The lower SFE was shown by observations of small cell size and increased twin frequency in the cobalt-containing alloys. The lower SFE discourages cross slip and retards cell growth. Thus, the average dislocation density is increased, which provides more numerous nucleation sites for precipitates. The resulting increased barrier to dislocation movement causes the observed hardness increase.

#### STRENGTHENING MECHANISMS IN WIRE PRODUCTS

In another program conducted at Crucible Steel Company of America, the strengthening of a wide variety of alloys, ranging from plain carbon steels to superalloys, in wire form was studied.<sup>(2)</sup> Emphasis was placed on eutectoid carbon steel (0.90 percent carbon) and on AFC77 intermetallic-compound-strengthened stainless steel.

In the plain carbon eutectoid steel, decreasing the isothermal transformation temperature and, thus, the interparticle spacing, resulted in the maximum attainable strength after severe cold drawing. The maximum strength obtained was 580,000 psi. Progressive drawing of wire with an initially lamellar pearlitic structure led first to the alignment of the lamellae in the longitudinal direction; in later stages, a gradual decrease in the interlamellar spacing and in the width of lamellae was observed. Studies on quenched and tempered (martensitic structure) plain-carbon steel showed that the carbide particle size and the interparticle distance (controlled by tempering temperature) had a critical effect on the maximum attainable strength and drawability of the wire. An optimum combination of strength and ductility was obtained after tempering at 800 F.

The investigators proposed a deformation mechanism described in terms of interactions among the basic variables of carbon availability, carbon mobility, and dislocation mean free path. The model involves dissolution of carbon from the initial carbide particles, migration of carbon, and interaction of carbon with dislocations. This mechanism also appears to be applicable to intermetallic-compound-strengthened steels in which diffusion of a substitutional alloying

element (rather than carbon) is needed for dislocation pinning.

Studies on AFC-77 precipitation-hardenable stainless steel showed that a remarkable strengthening effect is derived from judicious combinations of drawing and aging. Room-temperature tensile strengths up to 550,000 psi were developed; this draw-plus-aged strength is about twice the strength level attainable by heat treatment alone.

The ultrahigh strength level of AFC-77 wire was retained upon exposure at elevated temperatures. For example, at 1100 F, AFC-77 wire had a tensile strength of 307,000 psi and a 10-hour creep-rupture strength of 170,000 psi. In fact, the 10-hour creep-rupture strength at 1100 F is about the same as the tensile strength of optimally heat-treated bar material at this temperature. The AFC-77 wire, successively drawn and aged, appears to have excellent potential for elevated-temperature structural use; for example, as the high-strength heat-resistant component in advanced composite materials.

The investigators at Crucible Steel also reported that cryogenic drawing of Type 302 austenitic stainless steel resulted in a substantially higher rate of strengthening than was possible with room-temperature drawing. Although room-temperature tensile strengths of about 400,000 psi were ultimately obtained by drawing both at -320 F and at room temperature, a given strength level was obtained by considerably fewer passes by cryogenic drawing than by ambient-temperature drawing.

Cryogenic metastable austenite deformation of 3Mn-23Ni steel was also investigated. The results show that the cryogenic drawing resulted in an appreciably greater degree of strengthening than drawing at room temperature (from 50,000 to 250,000 psi versus 50,000 to 130,000 psi at 85 percent reduction in diameter). The wire drawn at room temperature remained essentially austenitic after drawing; only a very slight magnetic response was indicated after more than 80 percent reduction in diameter. On the other hand, the cryogenically drawn wire indicated magnetic response early in the deformation process.

This working at cryogenic temperatures should result in a martensitic structure finer than could be produced in any other way; consequently, a strengthening effect would be expected.

Several treatment sequences were applied to the 18 percent manganizing steel. As on AFC-77, cumulative drawing and aging treatments had a beneficial effect on strengthening this steel; 450,000 psi tensile strength was ultimately attained. Also, W-11 (HS-25 or L-605) cobalt-base superalloy was strengthened to the 430,000 psi level by cold drawing in the solution-annealed condition.

#### STRENGTHENING 9Ni-4Co STEELS BY THERMO-MECHANICAL TREATMENTS

Investigators at Manlabs are studying thermo-mechanical treatments applied to ultrahigh strength steels.<sup>(3)</sup> Emphasis is being placed on the optimization of the effects of austenite deformation and strain-tempering processes in 9Ni-4Co steels to provide strength increases with adequate toughness.

They have shown that strain tempering was not detrimental to the fracture toughness (impact energy and  $K_{Ic}$ ) of 9Ni-4Co-0.45C steel (martensitic) when evaluated on the basis of constant yield strength. In fact, the yield strength may be improved by strain tempering above the maximum value obtainable by conventional heat treatment without further decrease in  $K_{Ic}$ . Material that was ausformed 50 percent at 1300 F and then tempered at 400 F displayed a yield strength of 292,000 psi with plain strain fracture toughness,  $K_{Ic} = 65,000$  psi/inch. Also the plain strain fracture toughness ( $K_{Ic}$ ) of 9Ni-4Co-0.45 steel (martensitic) produced by ausforming was superior to that of conventionally heat treated 9Ni-4Co-0.45C steel (martensitic) of equivalent strength levels.

The effects of deformation of metastable austenite in 9Ni-4Co-0.25C steel were also studied. It was reported that the 0.25C steel displayed higher fracture toughness than the 0.45C steel at equivalent strength levels. At the 250,000 psi yield-strength level (ausformed 50 percent and tempered at 400 F), this material had  $K_{Ic} = 88,000$  psi/inch.

Ausforming and strain-tempering treatments were then combined in processing the 9Ni-4Co-25C steel. The total strengthening was found to be approximately equal to the sum of the strength increases achieved by employing these processes individually and resulted in an increase in yield strength from 206,000 to 326,000 psi. Ausforming 50 percent at 1200 F improved the yield strength from 206,000 to 249,000 psi while strain tempering 25 percent with pretempering and retempering temperatures of 400 F increased the yield strength from 206,000 to 292,000 psi (sum of the individual increases equals 129,000 psi). The effect of the combined treatments is particularly significant for this alloy since the strengthening achieved by ausforming tends to reach a limit at 50 percent deformation.

The investigators proposed a dislocation-trapping model for the mechanism of strain hardening. The creation of dislocations by deformation results in an immediate stress-induced ordering about the dislocation line of the carbon atoms existing within a critical interaction radius. These trapped carbon atoms then diffuse towards the line of the dislocation due to the elastic strain field. The carbon gradient created between the depleted region in the interaction zone and the outer unaffected region causes carbon diffusion into the interaction zone and consequently further trapping. Carbide re-solution will occur in order to build the matrix composition back up to the equilibrium value. The carbon being pumped back into solution may continue to be depleted from the matrix by being attracted toward the dislocations. The dislocation density and distribution and the pretempering and retempering temperatures all play a role in the extent of carbide re-solution that occurs.

The dislocation trapping model successfully accounts for the influence of carbon content, degree of deformation, pretempering temperature, and retempering temperature on the strength and microstructure of strained tempered martensite.

#### STRENGTHENING ULTRAHIGH STRENGTH STEELS BY DUPLEX STRESS AGING

Stress-aging treatments consist of heating alloys that are composed wholly, or in major part, of a solid-solution phase (or phases) for correct times at suitable temperatures while the material is subjected to essentially elastic stress from an external load.

As reported in the November 10, 1965, Review of Recent Developments - High Strength Steels, investigators at Watervliet Arsenal showed that single stress-aging treatments effected considerable improvements in the standard tensile properties of four ultrahigh strength steels (AISI 4340 air melted, AISI 4340 vacuum melted, AISI 4335 Si-modified, and 300M steels) without significant losses of elongation, reduction of area, or relative toughness (the energy absorbed during plastic deformation).

These investigators have continued their work and have reported the effects of duplex stress-aging treatments on three ultrahigh strength steels (AISI 4340 vacuum melted, 4335-Si modified, and 300M steel).<sup>(4)</sup> The first stress-aging treatment in the sequence developed the capacity of the materials to withstand the considerably higher stresses used in the second treatment, while still avoiding destructive creep.

The investigators concluded the followings:

- (1) While duplex stress aging develops further increases in the strength properties of vacuum-melted AISI 4340 steel, the yield strength is increased by only 15,000 psi and the relative toughness is decreased by 20 percent. On the basis of economics and mechanical-property improvement, stress aging was not considered justified for this steel. This conclusion probably applies to air-melted AISI 4340 steel also because it is somewhat inferior in relative toughness to vacuum-melted AISI 4340 steel on the basis of standard heat treatments.
- (2) Duplex stress aging usefully improves the strength properties of 4335Si-modified steel and 300M steel to a greater degree than does single stress aging. The optimum duplex stress aging treatment and resultant tensile properties of these steels are shown in Table 1.
- (3) The duplex stress aging capacities of these alloys appear to be directly related to their respective carbon and silicon contents.
- (4) On the basis of yield-strength-to-density ratios, stress aged and duplex stress aged 4335Si-modified and 300M steel become competitive with titanium alloys.

#### STRUCTURAL CHANGES ASSOCIATED WITH DELAYED FAILURE RESULTING FROM STRESS CORROSION

Investigators at Battelle Memorial Institute are studying the structural changes, associated with delayed failure, in high-strength steels due to the effect of stress and corrosive environments

on its crystal and grain structure.<sup>(5)</sup> Since the cathodic portion of the corrosion reaction will produce hydrogen, its role in the delayed failure mechanism has been of major interest to this program.

Preliminary work on the effect of applied stress on hydrogen absorption during cathodic charging of low-strength ferritic (1300 F temper) and high-strength martensitic (400 F temper) structures of AISI 4340 steel have indicated the following:

- (1) With no applied stress the ferritic structure of AISI 4340 steel absorbed about three times as much hydrogen as the martensitic structure of AISI 4340 steel during a 17-hour charging in a arsenic-saturated 2-volume-percent  $H_2SO_4$  solution at a current density of 0.5 amp/ft<sup>2</sup>.
- (2) During a fifteen-minute charging, both structures absorbed about the same amount of hydrogen with no applied stress and at stresses up to about 25 percent of their tensile strengths.
- (3) The amount of hydrogen absorbed during a 15-minute charge increased for both structures with increasing applied stress. When the applied stress exceeded 30 percent of the tensile strength of the specimens, the hydrogen absorbed in 15 minutes greatly exceeded the amount absorbed during 17 hours of charging with no applied stress.
- (4) At applied stresses above about 25 percent of their respective tensile strengths, the specimens with a martensitic structure absorbed significantly more hydrogen than the specimens with a ferritic structure.

Under the experimental conditions employed, it was not possible to study the effects of applied stresses greater than 34 percent of the tensile strength for specimens with martensitic structures because all specimens failed in less than 15 minutes of charging at these higher applied stresses.

The investigators suggest that the increased hydrogen absorption by the martensitic structures at applied stresses greater than 25 percent of the tensile strength may result from defects produced by the stress or opening of existing defects to allow easier entry of the hydrogen. Alternatively, they suggest that these applied stresses result in sufficient straining of the lattice to enlarge the interstitial hole size sufficiently to accept a hydrogen ion. An applied stress of 34 percent of the tensile strength, correcting for effect of residual compressive stresses resulting from heat treatment, would result in a lattice strain of approximately  $3 \times 10^{-3}$ . Calculations of the interstitial hole size in the iron lattice show that a strain of this magnitude would enlarge the hole size sufficiently to accept a hydrogen ion. Thus, hydrogen absorption of this steel may result from lattice strains rather than enlargement of defects.

TABLE 1. TENSILE PROPERTIES OF DUPLEX STRESS AGED 4335-81 MODIFIED AND 300M STEEL<sup>(4)</sup>

Material	Condition	Proportional Limit, psi	Yield Strength		Ultimate Tensile Strength, psi	Elongation, percent in 1 inch	Reduction of Area, percent
			0.1 % Offset, psi	0.2 % Offset, psi			
4335-81 Modified	Standard <sup>(a)</sup>	170,000	198,000	210,500	257,000	13	43
4335-81 Modified	Duplex Stress Aged <sup>(b)</sup>	270,200	274,950	274,950	274,950	9	43
300M	Standard <sup>(c)</sup>	175,000	214,000	236,000	282,500	11	37
300M	Duplex Stress Aged <sup>(d)</sup>	280,000	298,800	298,800	299,370	9	34

- (a) Heat treatment; normalized at 1600 F, 1 hour, air cooled; austenitized 1550 F for 2 hours, oil quenched; tempered at 600 F for 3 hours, air cooled.
- (b) Duplex-stress-aging treatment: 500 F for 1 hour, applied stress, 175,000 psi; 550 F for 1 hour, applied stress, 215,000 psi.
- (c) Heat treatment: normalized at 1650 F for 1 hour, air cooled; austenitized at 1650 F for 2 hours, oil quenched; tempered at 600 F for 3 hours, air cooled.
- (d) Duplex-stress-aging treatment: 600 F for 15 minutes, applied stress, 175,000 psi; 600 F for 15 minutes, applied stress, 220,000 psi.

#### REFERENCES

- (1) Banerjee, B. R., and Hauser, J. J., "Hardening Mechanisms and Delamination Studies of 18 Percent Nickel Marage Steels", Report AFML-TR-66-166, Crucible Steel Company of America, Pittsburgh, Pennsylvania, Contract AF 33(657)-10337 (March, 1966) DMIC No. 65517.
- (2) Chandok, V. K., Kasak, A., and Nechtmeister, G. C., "Strengthening Mechanisms in Wire Products", Report AFML-TR-66-63, Crucible Steel Company of America, Pittsburgh, Pennsylvania, Contract AF 33(615)-1684 (May, 1966) DMIC No. 64570
- (3) Preliminary information reported by Manlabs, Inc., Cambridge, Massachusetts, under a Navy contract.
- (4) Harrington, R. H., "Stress-Aging: A New Treatment for Alloys - Part Four: Comparison of Standard Tensile Properties for Single VS-Duplex Stress-Aging (Three-Ultra-High Strength Steels)", Report WVT-6601, Watervliet Arsenal, New York (March, 1966) DMIC No. 65137.
- (5) Preliminary information reported by Battelle Memorial Institute, Columbus, Ohio, under a Navy contract.

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