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AGE HARDENING IN BINARY MARTENSITIC Fe-Ni ALLOYS

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Introduction

Despite the expenditure of much effort, we still do not have a concensus regarding the form of the Fe-Ni phase diagram at temperatures below 500°C. In a paper published in 1963, Heumann and Karsten (1) concluded that the fcc Fe-Ni solid solution decomposed eutectoidally at 345°C and 52 at.% Ni to a mixture of $FeNi_3$ and α-Fe and that the maximum solubility of Ni in α-Fe was 6.5% at 345°C. In a later paper, Goldstein and Ogilvie (2) also concluded that the solubility of Ni in α-Fe reached a maximum, but they placed the temperature of the maximum between 400 and 500°C. They did not mention a possible eutectoidal reaction nor refer to the earlier work of Heumann and Karsten. Shunk's compilation of 1969 (3) presents the Heumann and Karsten diagram, but the later ASM review (4) does not.

The work reported herein was begun in an attempt to confirm the eutectoidal transformation reported by Heumann and Karsten, to determine what changes in mechanical properties might result from it, and to reveal the structure of the transformation products. The study is incomplete, but because of the long periods required to obtain data we concluded that an interim report was warranted.

Materials and Procedures

The study was begun with four alloys with nominal Ni contents of 5, 9, 21 and 30 weight percent. The compositions and dimensions of these alloys are listed in Table I.

TABLE I

Composition (wt %) and Thickness of Specimens

Alloy	Ni	C	Thickness, mm
5 Ni	5.05	0.009	17.8
9 Ni	8.9	0.002	17.7
21 Ni	20.9	0.022	17.8
30 Ni	30.0	0.045	16.5

Specimens from the four alloys listed in Table I were treated in the following manner:

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1. Sealed in quartz capsules, back-filled with a partial pressure of argon.
2. Heated to 1150°C, held 7 days, air-cooled.
3. Removed from capsules, reheated to 1000°C, quenched in brine, refrigerated to -195°C.
4. Reheated to 1000°C, quenched in brine, refrigerated to -195°C.
5. Cold-rolled to 50% reduction in thickness.
6. Heated to 300, 335, 400 and 450°C, held for 2000 hr (7.2×10^6 s).

It was intended to repeat Steps 5 and 6 through several cycles, but because of pronounced hardening, this plan could not be followed for all alloys. Aging was done in air furnaces, with the specimens wrapped in stainless-steel foil.

Two additional alloys were held for 500 hours at the same four temperatures, without prior cold work. Their compositions were 31.5% Ni, 0.02% C and 34.8% Ni, 0.04% C. Both alloys were austenitized at 1000°C, quenched in brine, then twice cooled to -196°C. Specimens of each of these alloys were aged 500 hours (1.8×10^6 s) at 300, 335, 400 and 450°C.

After we noted that the greatest amount of hardening occurred in alloys containing about 30% Ni, six alloys containing, nominally, 24, 26, 28, 30, 32 and 34 wt % Ni were vacuum-melted from Plast-Iron Type 104A and high-purity nickel, cast as 7-kg ingots and hot-rolled to plates 25 mm thick. Specimens cut from these plates were homogenized 5 days at 1205°C in quartz capsules, air-cooled to room temperature, then cooled to -196°C. Then they were austenitized at 900°C, brine-quenched and twice cooled to -196°C to transform most of the austenite to martensite. Specimens were then aged without prior cold work in molten lead baths at selected temperatures between 300 and 460°C.

Diamond pyramid hardness (DPH) was obtained with a 10-kg load. Retained austenite was determined by a standard X-ray diffraction technique (5).

Results and Discussion

Specimens of the four original alloys (Table I), each aged 2000 hours at 300, 335, 400 and 450°C after 50% cold reduction by rolling, were removed from the furnaces, cooled to room temperature and cold-rolled again, with the results shown in Table II.

After this second cold reduction, the specimens were again aged for 2000 hr at the same temperatures as before and cooled to room temperature. Because of the problem encountered in the previous cold-rolling step (Table II), the hardness was measured in all the specimens before rolling was attempted. This time, all the alloys were cold-reduced 50% without difficulty with the exception of the 30% Ni alloy aged at 400, 335 and 300°C. All specimens were returned to the furnaces for a third 2000-hr aging period. Following this aging treatment, the hardness was again determined, the specimens were cold-rolled an additional 50% (with the same exceptions previously noted) and returned to the furnaces for an additional 2000-hr aging for a total of 8000 hours. The effects of these treatments on hardness are summarized in Table III.

Table II

Second Cold Reduction of Fe-Ni Alloys, After Aging 2000 Hours

Prior Aging Temperature, °C	Alloy	Final Thickness, mm	% Reduction	Remarks
450	5	4.45	50	normal
	9	8.31	5	end split, rolling halted
	20	4.45	50	normal
	30	4.45	50	normal
400	5	4.45	50	normal
	9	6.05	30	end split, rolling halted
	20	4.45	50	normal
	30	7.42	15	too hard to continue
335	5	4.45	50	normal
	9	4.45	50	normal
	20	4.45	50	normal
	30	7.72	10	too hard to continue
300	5	4.45	50	normal
	9	4.45	50	normal
	20	4.45	50	normal
	30	7.52	15	too hard to continue

Table III

Effects of Cold Work and Aging on the Hardness of Fe-Ni Alloys

Alloy	Aging Temperature, °C	Hardness (DPH) After Successive Steps of Cold Rolling 50%, Then Aging 2000 Hours			
		Step 1	Step 2	Step 3	Step 4
5 Ni	300	Hardness not measured	245	264	284
	335		225	246	248
	400		159	185	117
	450		122	116	101
9 Ni	300		255	275	276
	335		241	253	251
	400		200 (30% CR)	210 (60% CR)	186
	450		153 (5% CR)	162	153
20 Ni	300		320	348	382
	335		302	348	374
	400		302	317	303
	450		251	251	234
30 Ni	300		536 (15% CR)	538 (no CR)	557 (no CR)
	335		527 (10% CR)	528 (no CR)	532 (no CR)
	400		416 (15% CR)	408 (no CR)	400 (no CR)
	450		261	263	237

The microstructure of the 5% Ni alloy aged at 400 or 450°C consisted of recrystallized α-iron, in accordance with both proposed phase diagrams (1-4). The microstructure of the 9% Ni alloy, aged at 400 or 450°C, included pools of γ in a matrix of α, also in accordance with both diagrams. The more complicated, unrecrystallized structures remaining after aging these two alloys at 400 and 450°C were not investigated further. Their hardness was no more than would be expected from the cold work.

The 20% Ni alloy aged at 300 or 335°C hardened considerably; the 30% Ni alloy aged at these temperatures demonstrated remarkable hardening, achieved, for the most part, during the first 2000 hours of aging. The structures of these hardened specimens consisted of retained γ plus martensite, with a high density of precipitate particles in the martensite plates. Typical electron transmission micrographs of the 30% Ni alloy aged at 400°C are shown in Figure 1. Identification and structure of the precipitate and its crystallographic relationship with the parent α′ will be reported when this phase of the study is completed.

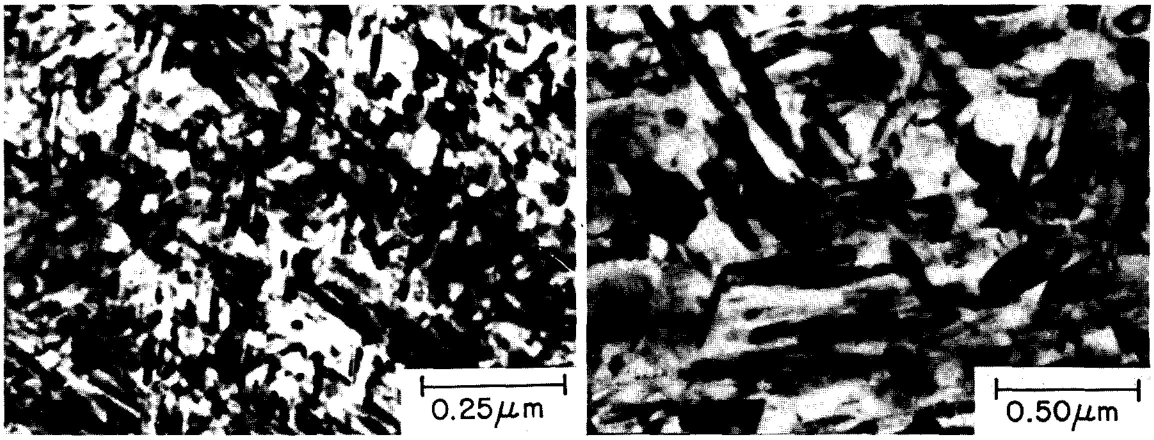

FIG. 1. Transmission electron micrographs of Fe-30%Ni, quenched to form martensite, cold-worked and aged 1000 hours at 400°C.

Precipitates have been observed in Fe-Ni meteorites. Lin, et al., (6) found a precipitate which they concluded was γ formed by the reaction path γ → α′ → α + γ, and Knudsen, et al., (7) detected the presence of an ordered FCT phase FeNi. To the best of our knowledge, no one has previously observed a precipitate in binary Fe-Ni alloys in controlled laboratory heat treatments.

Prior cold work is not required for hardening of Fe-Ni alloys, as shown in Fig. 2-5. Figure 2 indicates that a 31.5Ni-0.02C alloy, quenched to develop a structure of martensite and retained austenite, increased in hardness from 228 to 438 DPH after aging at 335°C for 500 hours. Its companion alloy, containing 34.8% Ni and 0.04% C, showed no hardening at all during aging at 400°C.

In the usual manner, the rate of hardening is a function of both composition and aging temperature (Fig. 3 and 4). We are not certain that we have attained the maximum hardening in this system. The greatest extent of hardening occurred in the 32% Ni alloy, which increased from 204 to 424 DPH. Longer aging of the 30% Ni alloy may produce even greater hardening.

Figure 5 shows the hardening in Fe-30Ni is accompanied by an increasing content of γ, at least at aging temperatures above 335°C. The as-quenched structure of this alloy consists of martensite + 15% retained austenite, with a hardness of 248 DPH. When the microstructures converted to 100% γ by aging at 460°C, the hardness is 183 DPH. When the specimen is aged so that a fine precipitate forms in the martensite, the hardness is 360.

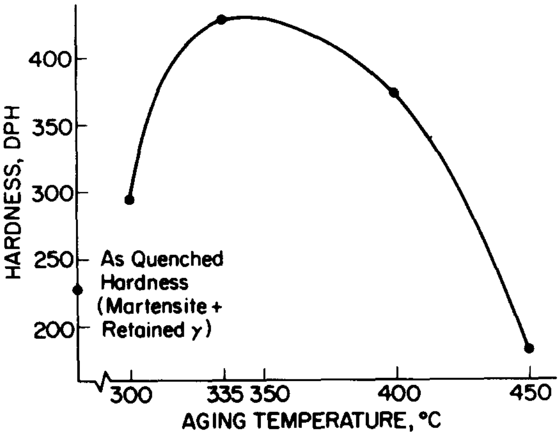

FIG. 2. Hardening of Fe-31.5% Ni alloy during isothermal aging (500 hours at temperature).

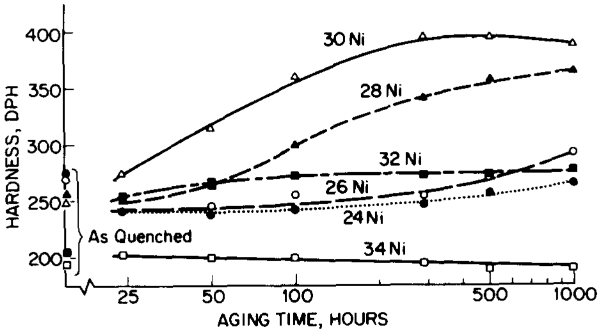

FIG. 3. Hardness change in Fe-Ni alloys aged at 400°C.

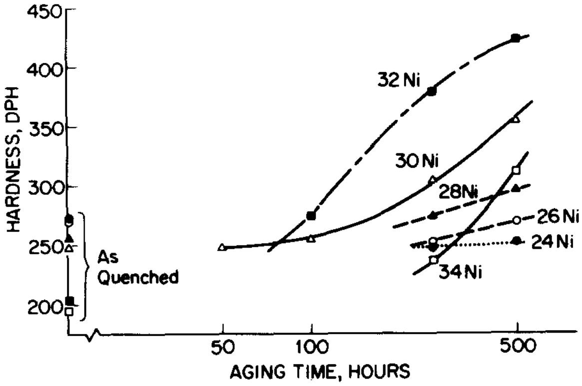

FIG. 4. Hardness change in Fe-Ni alloys aged at 335°C.

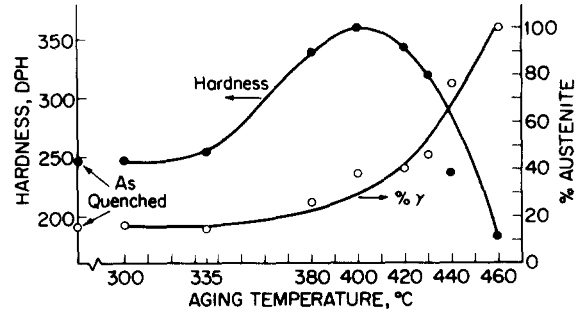

FIG. 5. Hardness and formation of austenite during isochronal aging of Fe-30Ni alloy (100 hours at temperature).

Conclusions

1. Fe-Ni alloys containing about 28 to 34% Ni, quenched and refrigerated to produce the maximum amount of martensite, can be hardened considerably by subsequent aging in the temperature range 300 to 430°C.

2. The rate of hardening can be increased by cold working the martensite before aging.

3. The hardening is accomplished by formation of a fine precipitate in the martensite.

4. The identity of the precipitate has not been established.

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