OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
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U. S. ATOMIC ENERGY COMMISSION

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16

STUDIES OF BRITISH NIOBIUM-STABILIZED STAINLESS STEELS

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H. E. McCoy

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ABSTRACT

The thermal stabilities of three stainless steels have been studied: niobium-stabilized steels (18 Cr–8 Ni), (25 Cr–20 Ni), and (20 Cr–25 Ni). It was found that the tendency to form sigma while annealing in the 650 to 850°C temperature range increased in order with the 20 Cr–25 Ni, 18 Cr–8 Ni, and 25 Cr–20 Ni steels. It was found that cold working increased the amount of sigma phase formed. It was also found that the 18 Cr–8 Ni steel formed a martensitic phase during either cold working or subcooling. This phase was not brittle but did cause an increase in the strain hardening of the steel.

INTRODUCTION

A joint British-United States program has been estabilished to study the in-pile stress-rupture behavior of several British stainless steels. The alloys chosen for study were niobium-stabilized steels (18 Cr–8 Ni), (20 Cr–25 Ni), and (25 Cr–20 Ni). Since test specimens were to be exposed to temperatures of 650 to 850°C for times up to 2600 hr, control specimens were annealed for comparable times to determine whether these steels are metallurgically stable. The results of the tests are summarized in this report.

EXPERIMENTAL DETAILS

The steels investigated were obtained as tubing with measurements of 0.4-in. OD × 0.010-in. wall thickness. The compositions are given in Table 1. To prepare specimens that could be cold worked easily, the tubing was split and flattened to obtain small 0.010-in.-thick strips. All of the specimens were sealed in quartz for annealing.

Table 1. Chemical Analyses of Stainless Steels

Alloy Designation	Element (%)									
	Cr	Ni	Mn	Si	S	P	Nb	C	O	N
Cast R119	18.00	8.15	0.62	0.46	0.003	0.0066	0.55	0.065	0.012	0.011
Cast C-61	Not analyzed, nominal niobium-stabilized steel (25 Cr–20 Ni)									
Cast L16	19.97	25.56	0.82	0.44	0.005	0.0044	0.61	0.031	0.042	0.016
Cast R121	18.94	24.47	0.82	0.42	0.014	0.0055	0.68	0.088	0.065	0.020

Magnetic susceptibility measurements were made on several of the specimens using a small magnet attached to an analytical balance. The force required to separate the magnet and specimen was determined.

RESULTS

Niobium-Stabilized Steel (18 Cr–8 Ni), Cast R119

The microstructure of this steel was quite sensitive to polishing procedure. The structure obtained by standard metallographic procedures, followed by etching in aqua regia, is shown in Fig. 1. The same specimen electrolytically polished and etched with 5% chromic acid is shown in Fig. 2a. The structure in Fig. 2 is as expected for an annealed austenitic material. By cooling the same specimen in liquid nitrogen, an acicular product resulted (Fig. 2b). Further studies showed that this product was martensite and that its formation was induced by both cold working and cooling. Since mechanical polishing promotes the formation of the martensite, it is quite easy to obtain "false" microstructures. Although several of the microstructures that will be presented fall into this category, they are presented to illustrate the kinetics of sigma formation in this alloy.

The microstructure of the niobium-stabilized steel (18 Cr–8 Ni) after annealing at 1050°C and aging for 500 hr at 650 and 850°C is shown in Figs. 3 and 4, respectively. The quantity of second phase formed at 650°C is quite small, but relatively large amounts were formed at 850°C. After aging at 650°C for 1300 hr (Fig. 5), the grain boundaries etch out quite quickly, indicating the segregation of impurities in these areas. After 1300 hr at 750°C (Fig. 6), the amount of second phase present is quite large. It is also apparent that cold working promotes the formation of this phase. Some of the specimens were etched in aqua regia and others in 5% chromic acid; a comparison of the structures produced by the two etchants is shown in Fig. 7. The martensite needles are revealed more sharply by the aqua regia, and the chromic acid seems to more readily attack an intergranular precipitate. On the basis of the etching

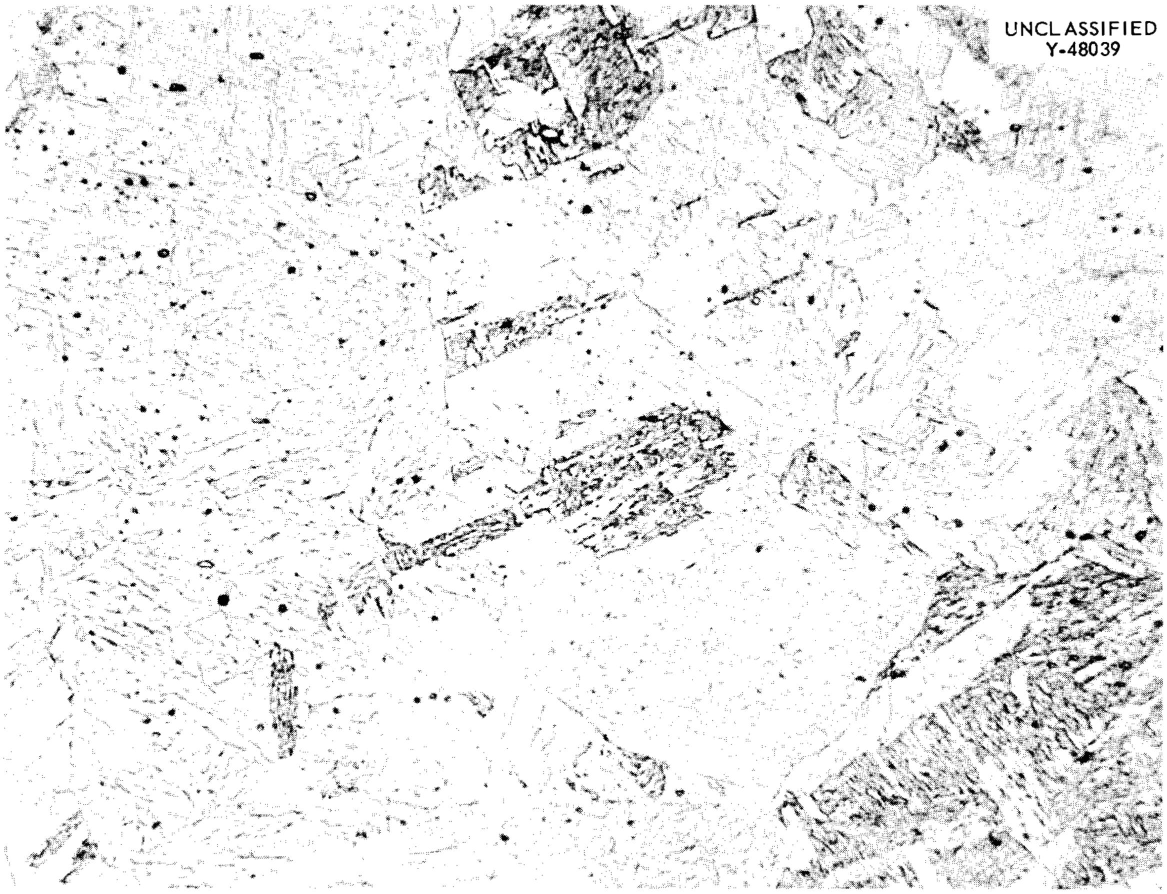


Fig. 1. Photomicrograph of Niobium-Stabilized Steel (18 Cr–8 Ni) After Annealing 1 hr at 1050°C in Argon. Etched in aqua regia. 500×

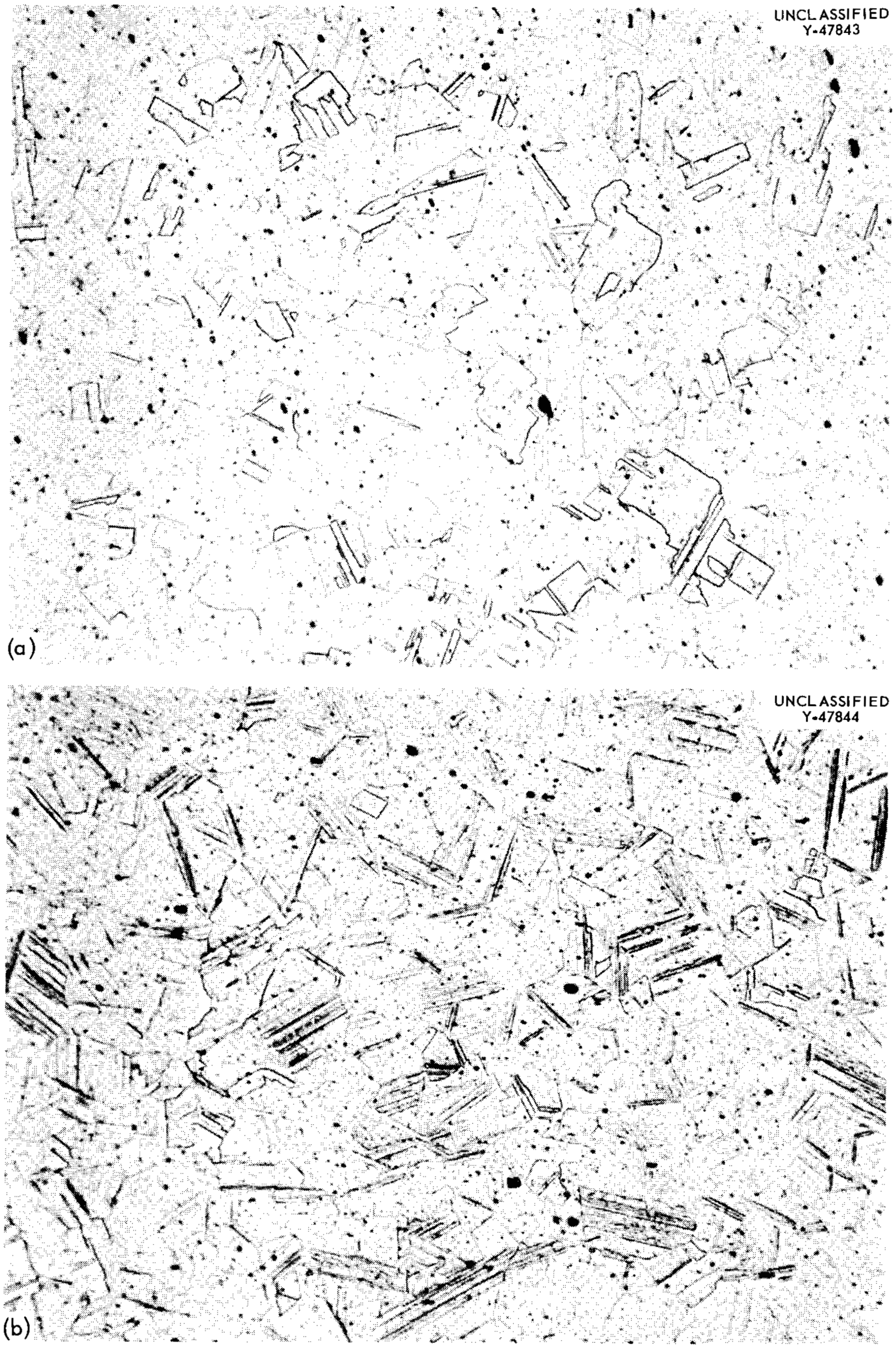


Fig. 2. Photomicrograph of Niobium-Stabilized Steel (18 Cr–8 Ni) After Annealing 1 hr at 1050°C in Argon. Electropolished and etched in 5% chromic acid for 15 sec at 6 v. (a) As etched; (b) etched and quenched in liquid nitrogen. 500×. Reduced 23%.

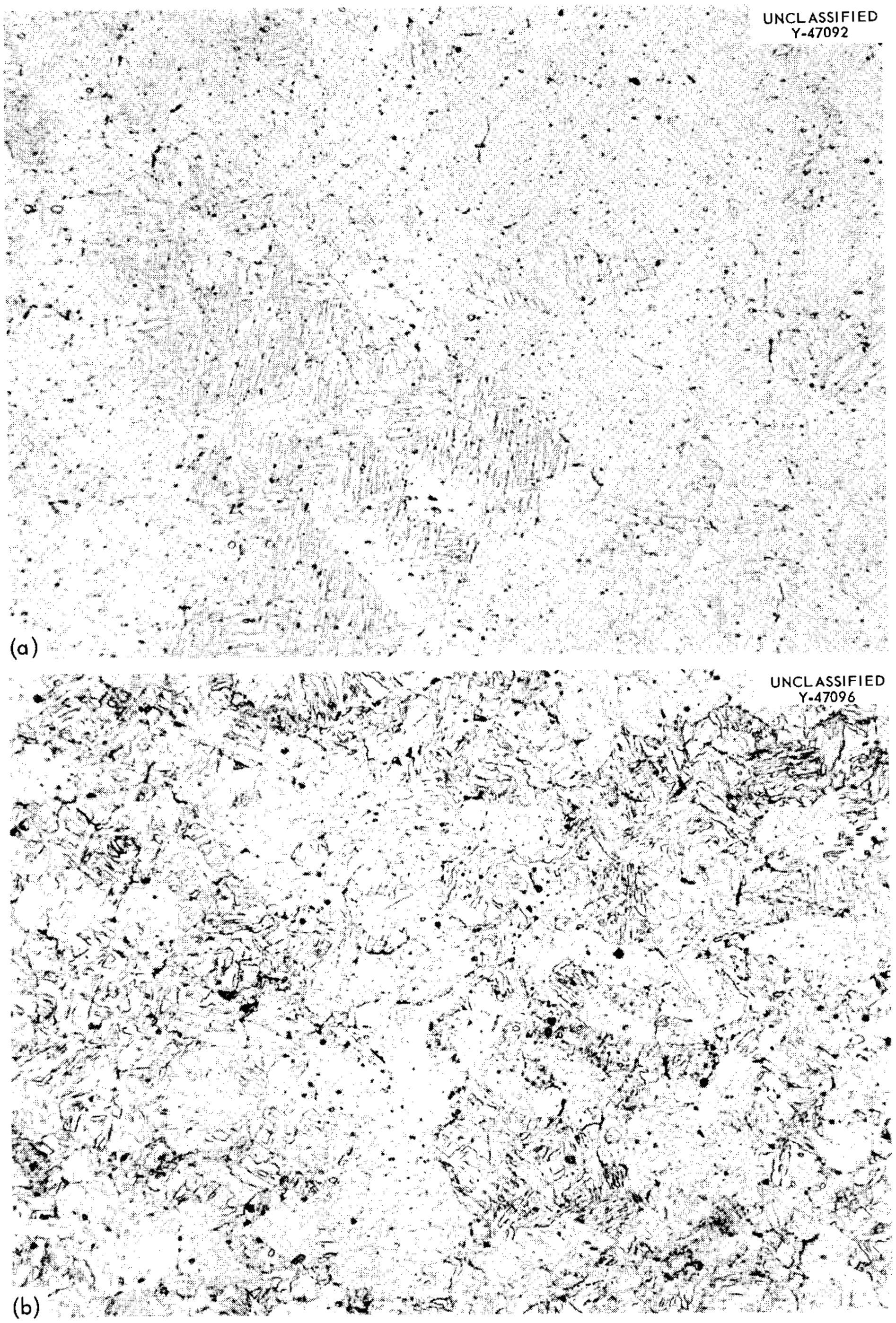
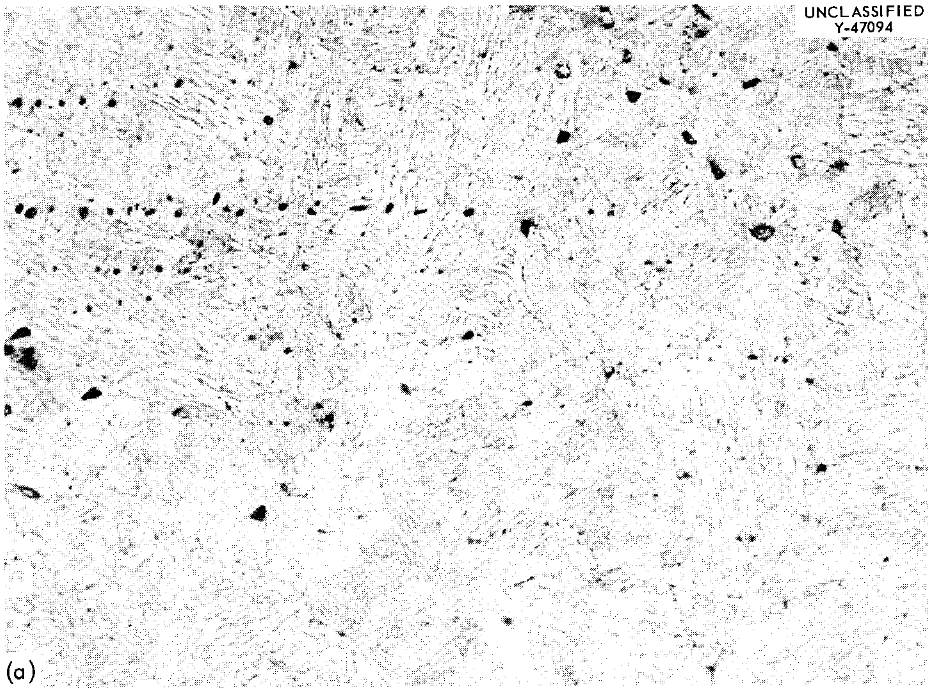


Fig. 3. Photomicrograph of Niobium-Stabilized Steel (18 Cr–8 Ni) After Aging 500 hr at 650°C. (a) Annealed 1 hr at 1050°C prior to holding at 650°C (b) Annealed 1 hr at 1050°C and cold rolled 10% prior to holding at 650°C. Etched in aqua regia. 500×. Reduced 21%.



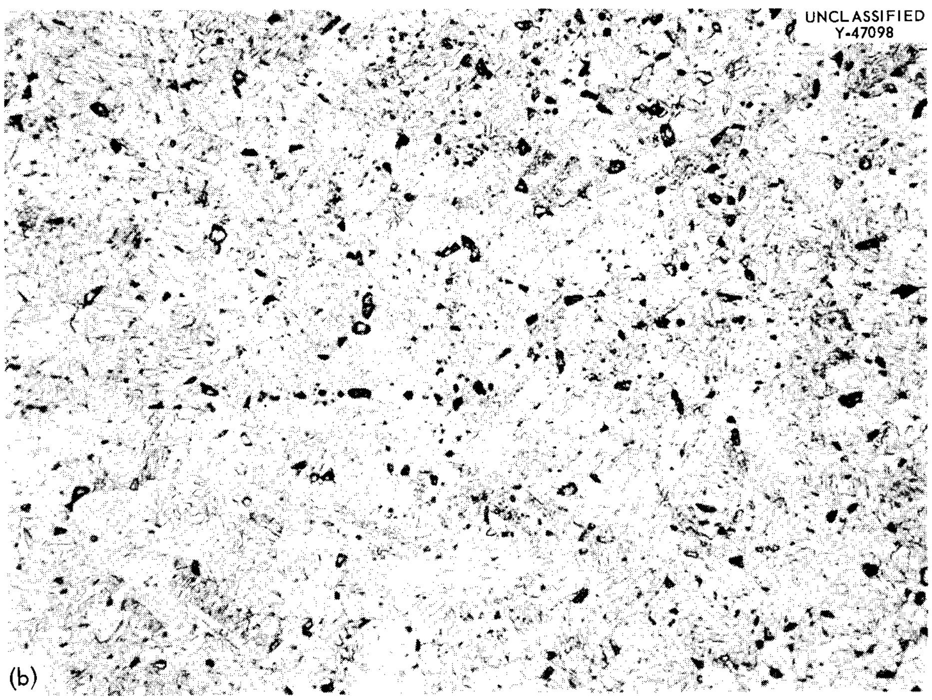


Fig. 4. Photomicrographs of Niobium-Stabilized Steel (18 Cr–8 Ni) After Aging 500 hr at 850°C. (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in aqua regia. 500X. Reduced 21%.

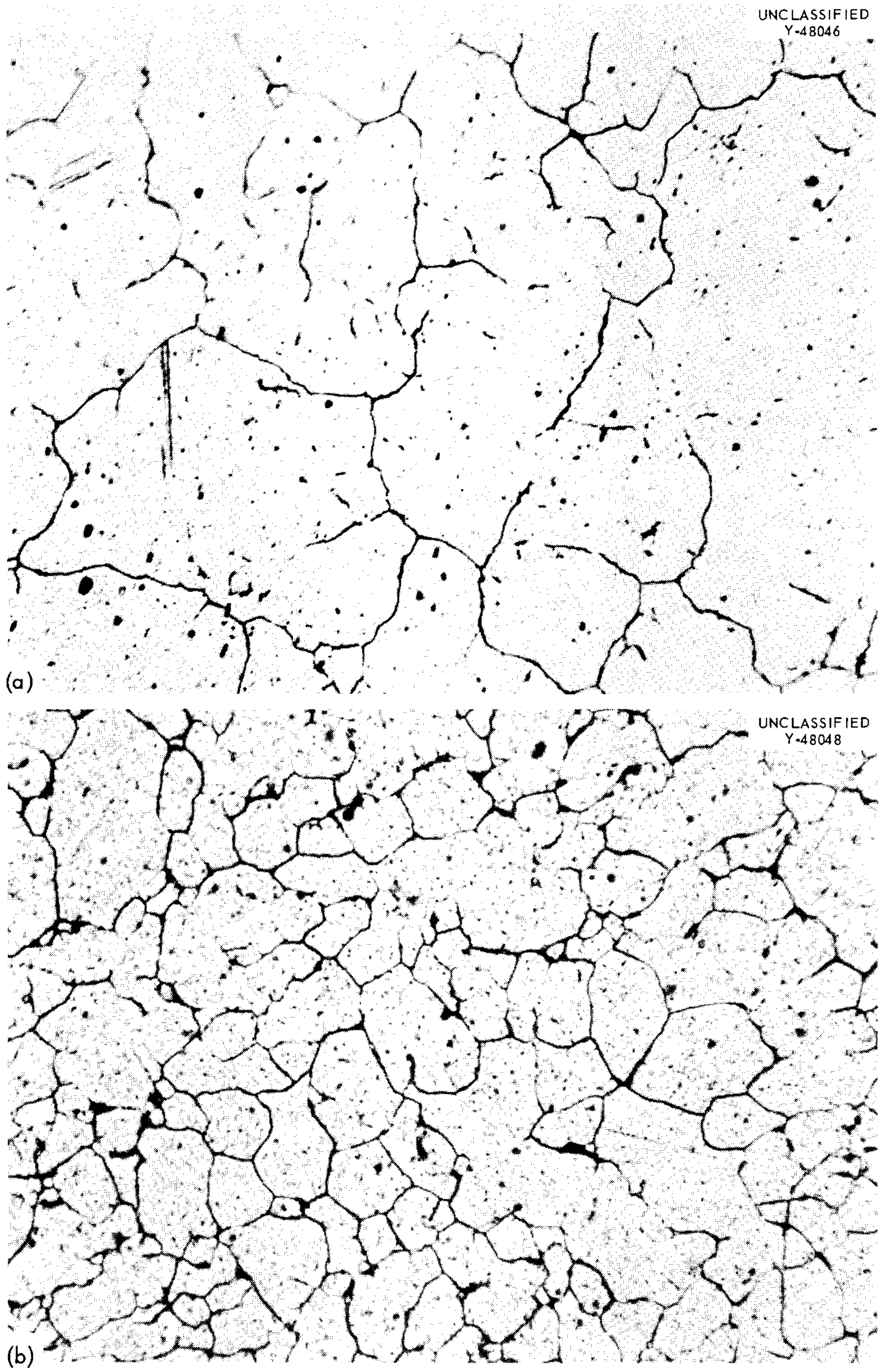
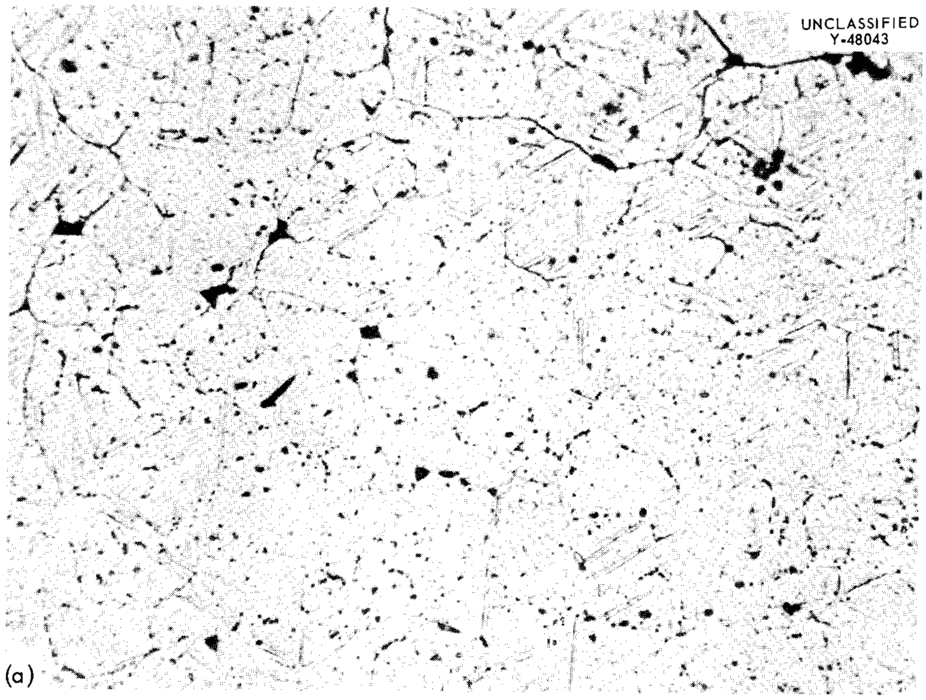


Fig. 5. Photomicrographs of Niobium-Stabilized Steel (18 Cr–8 Ni) After Aging 1300 hr at 650°C. (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in 5% chromic acid. 500X. Reduced 23%.



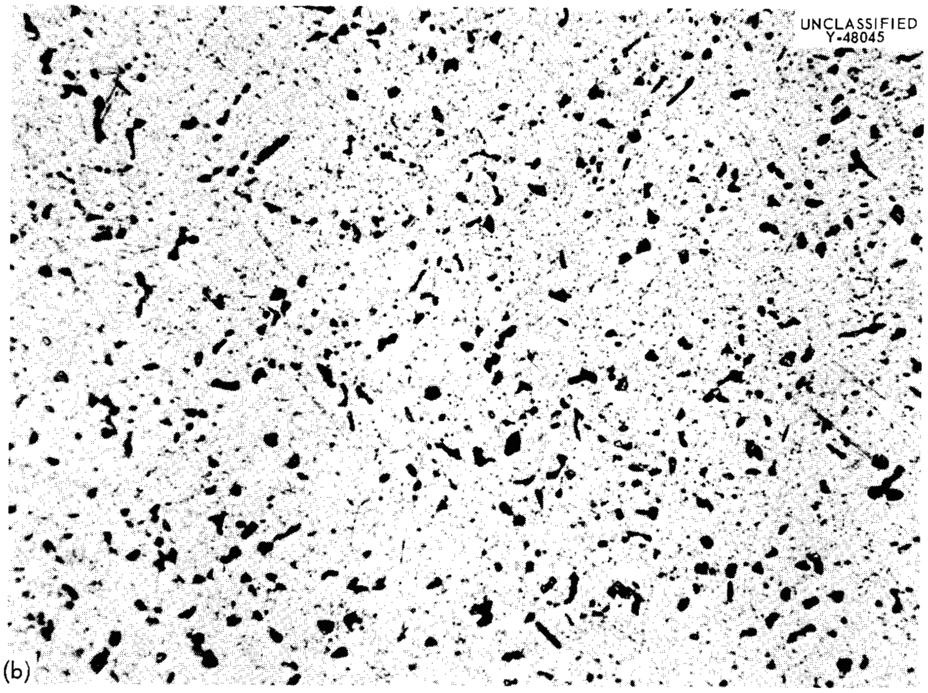


Fig. 6. Photomicrographs of Niobium-Stabilized Steel (18 Cr–8 Ni) After Aging 1300 hr at 750°C. (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in 5% chromic acid. 500X. Reduced 22%.

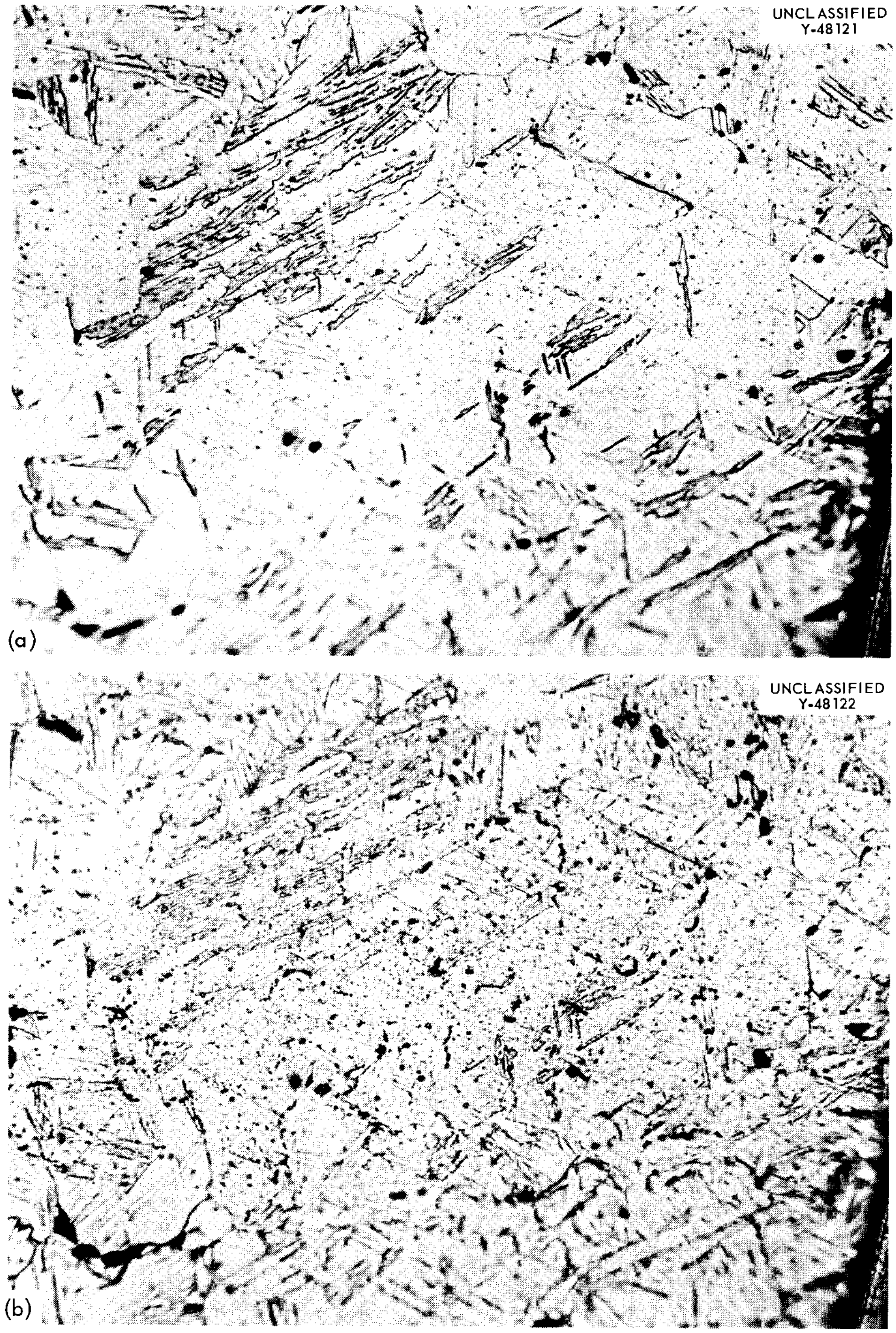


Fig. 7. Photomicrographs of Niobium-Stabilized Steel (18 Cr–8 Ni) Aged 1300 hr at 750°C. (a) Electrolytic polish with glyceria regia etch; (b) electrolytic polish with electrolytic etch in 5% chromic acid. 500X. Reduced 20%.

characteristics of steels, as summarized by Dulis and Smith,[1] it is quite probable that the phase being attacked selectively by the chromic acid is sigma phase. It is also important to note that martensite is present even in the electropolished specimen. Hence, it appears that holding at 750°C for an extended period has increased the temperature at which martensite begins to form to above room temperature.

Figure 8 shows that aging at 850°C for 1300 hr results in very little sigma formation. Martensite needles and another phase, which is probably ferrite, are also present.

Aging at 650°C for 2600 hr resulted in the formation of considerable quantities of sigma phase (Fig. 9). The quantity of sigma formed under these conditions is greatly increased by cold working. Aging at 750°C also produces large amounts of sigma with the quantity being enhanced by cold working (Fig. 10). At 850°C the large precipitate particles in the annealed material are probably ferrite (Fig. 11). In the cold-worked material, most of these particles were attacked by the etchant and are probably sigma.

Several tests were run to confirm the metallographic indication that a martensitic transformation occurred in this steel. Specimens were given various treatments and were then subjected to x-ray studies to determine the phases present. Specimens air cooled from 1050°C were found to exhibit lines only for austenitic steel and niobium carbide. Quenching in liquid nitrogen introduced a set of weak lines for a body-centered cubic structure having a parameter close to that of alpha-iron. Cold working at room temperature produced strong lines for the same body-centered cubic phase. Cold working near −196°C produced the same phases.

A relatively crude experiment was run to determine the temperature at which the martensitic transformation began to occur. A specimen which was initially water quenched from 1050°C was cooled to successively lower

[1]E. J. Dulis and G. V. Smith, Symposium on the Nature, Occurrence, and Effects of Sigma Phase, ASTM Spec. Tech. Pub. No. 110, p. 3 (1951).

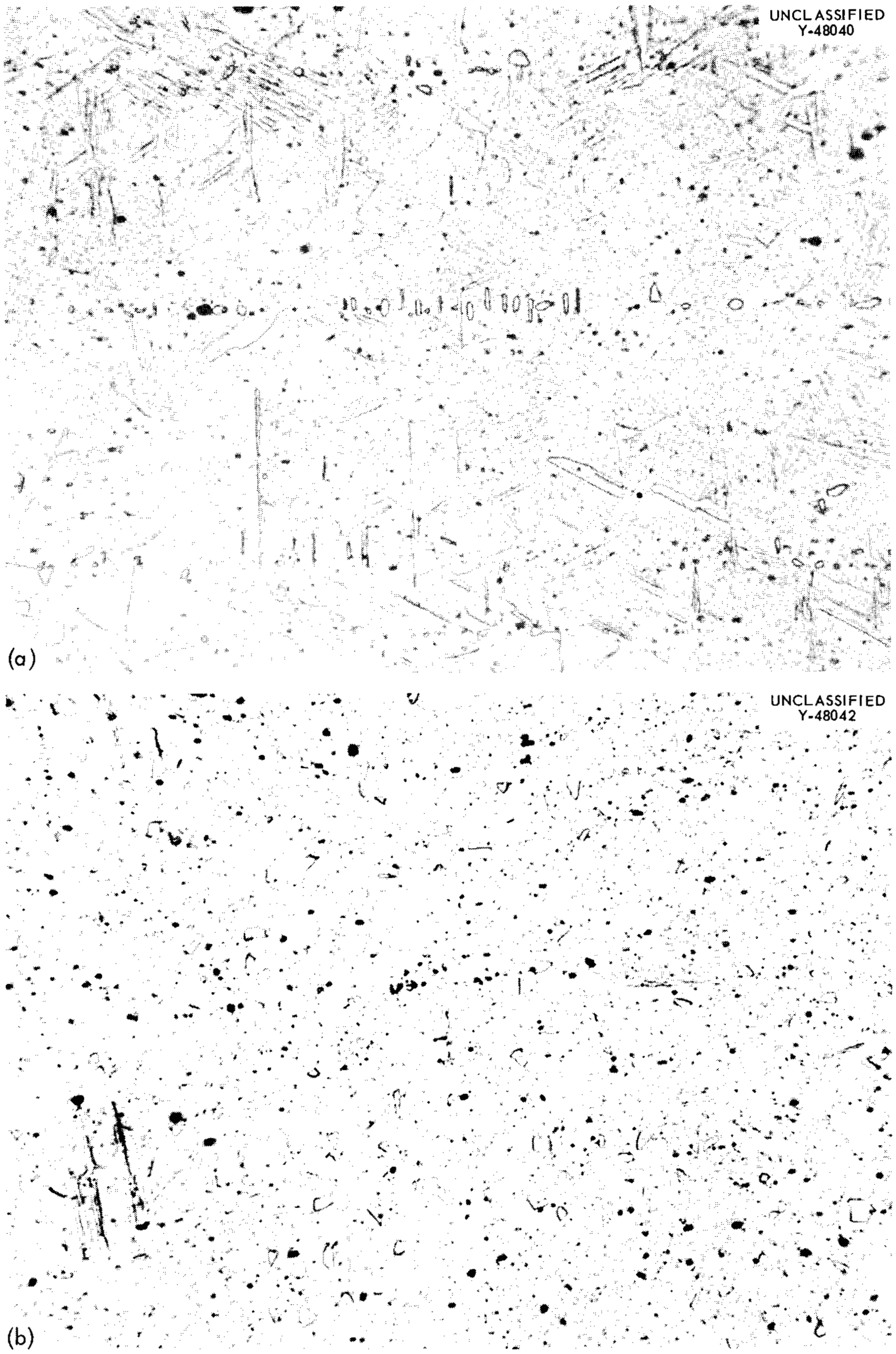


Fig. 8. Photomicrographs of Niobium-Stabilized Steel (18 Cr–8 Ni) Aged 1300 hr at 850°C. (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in 5% chromic acid. 500×. Reduced 23%.

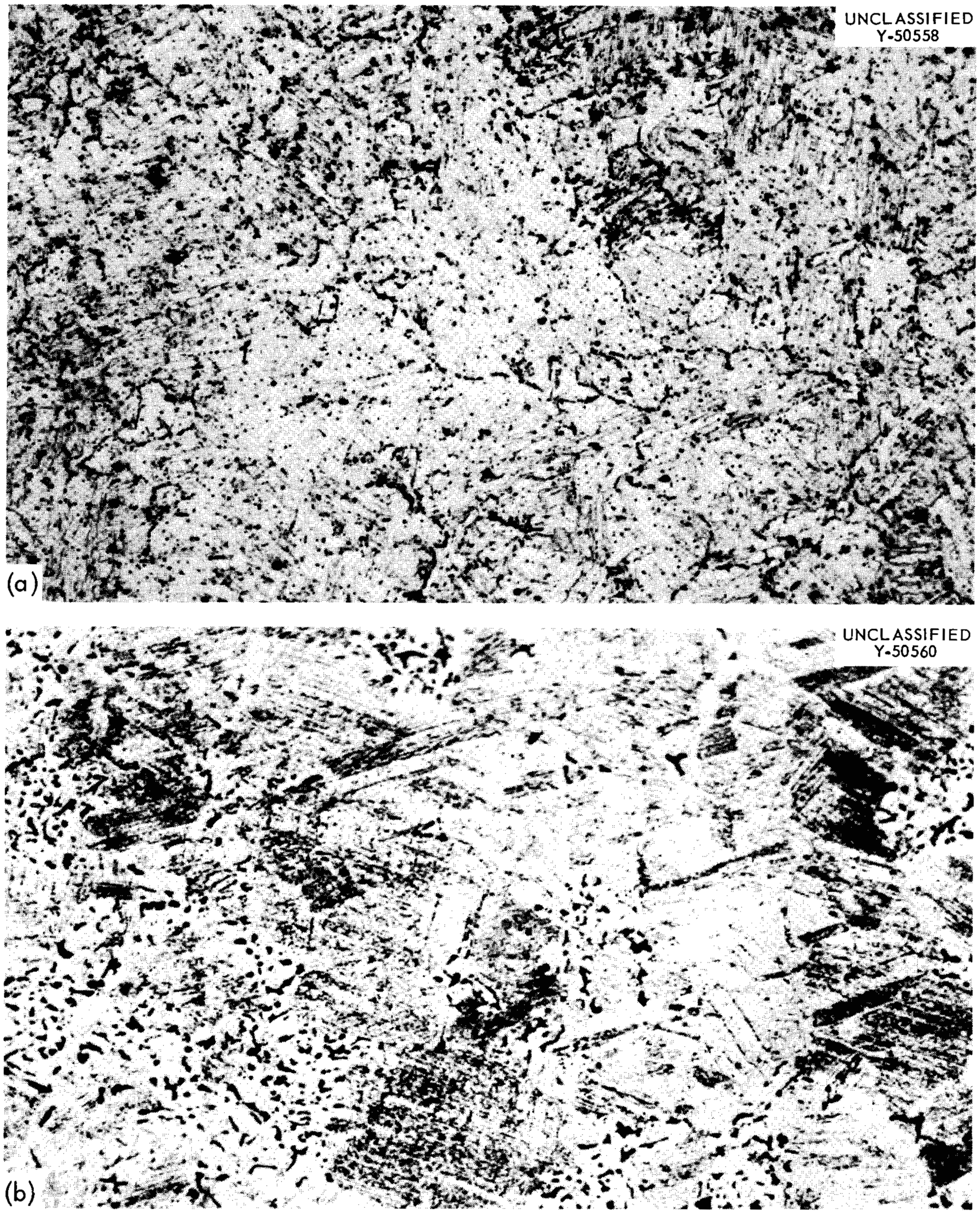


Fig. 9. Photomicrographs of Niobium-Stabilized Steel (18 Cr–8 Ni) Aged 2600 hr at 650°C. (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in glyceria regia. 500×.

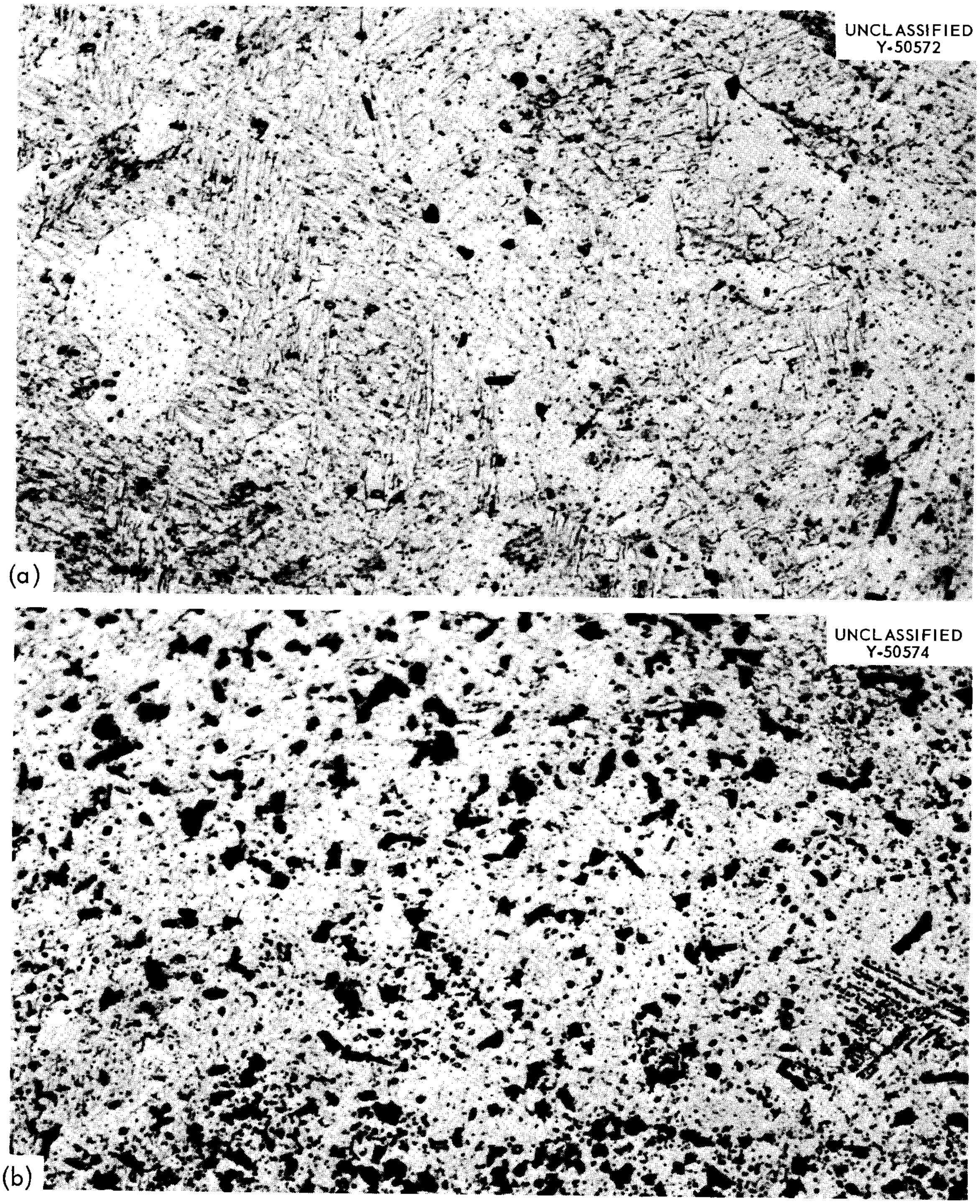


Fig. 10. Photomicrographs of Niobium-Stabilized Steel (18 Cr–8 Ni) Aged 2600 hr at 750°C. (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in glyceria regia. 500×.

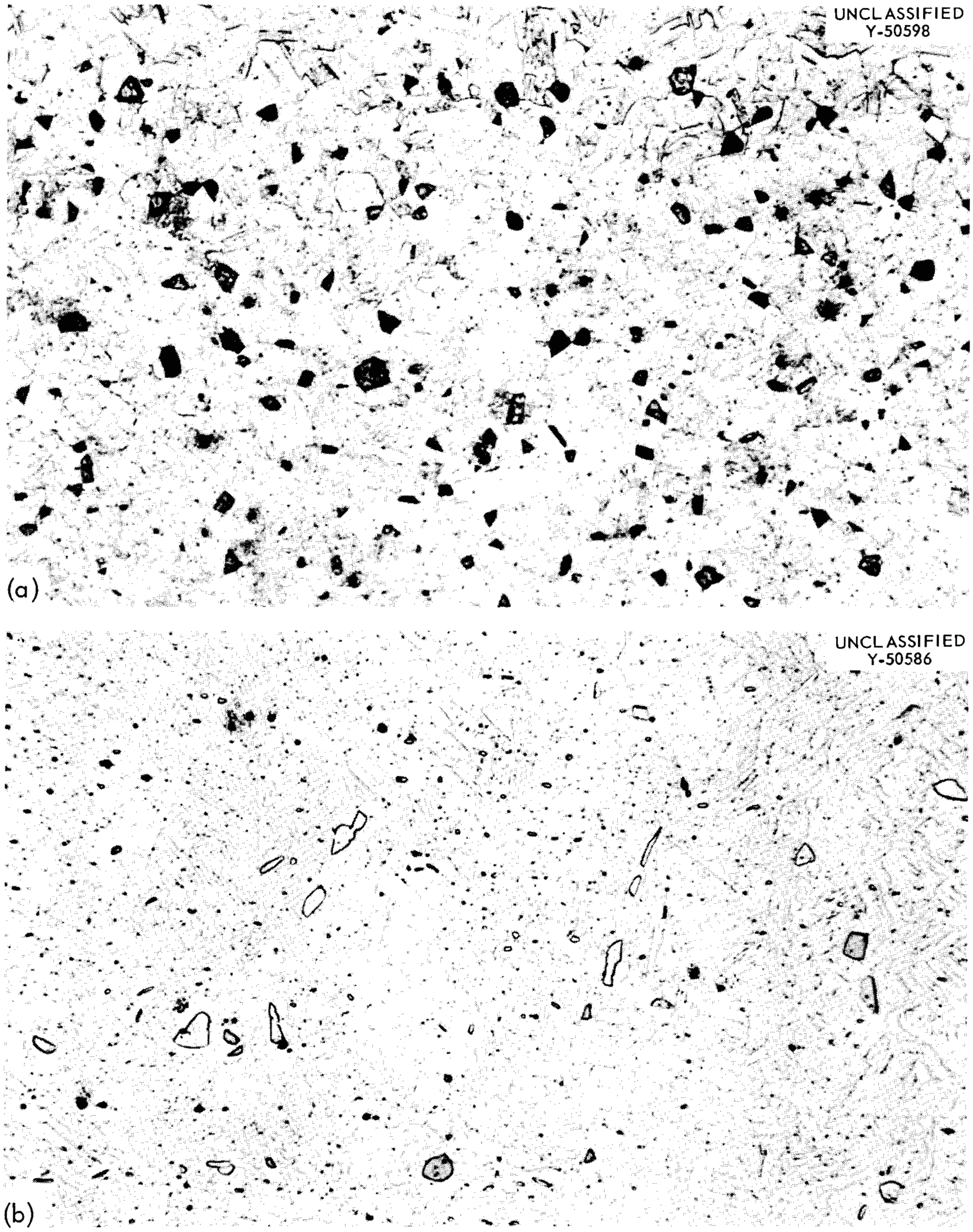


Fig. 11. Photomicrographs of Niobium-Stabilized Steel (18 Cr–8 Ni) Aged 2600 hr at 850°C. (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in glyceria regia. 500X.

temperatures and the resultant ferromagnetism was measured. The force required to pull a magnet from the surface of the specimen is plotted in Fig. 12. It appears that the transformation begins at about 0°C.

Since cold working also promoted the formation of martensite, a specimen was successively cold worked and the resultant ferromagnetism measured. The results are plotted in Fig. 13. After about 5% deformation, the ferromagnetism increases linearly with deformation. It appears that deformation, rather than cooling, is more influential in forming martensite. For example, it requires about 2.25 g to pull a small magnet from a specimen cooled to −196°C and about 5 g are required for a specimen that has been deformed 10%.

A few tensile tests were run to determine what influence the martensitic transformation has on the mechanical properties. The test specimens were small strips of material with welded ends. All specimens failed at the weld so the strain measurements are not accurate. These measurements represent the strain that occurred in the center 1 in. of the specimen at the time failure occurred at the weld. The data in Table 2 show that very little strengthening resulted from quenching in liquid nitrogen and that the strength increased rapidly with cold working; the ductility decreased significantly with cold working. Hence, the martensite formed does not appear to be a brittle product such as is formed in steels with a higher carbon content. However, this steel does appear to have a high rate of work hardening at low temperatures.

Niobium-Stabilized Steel (25 Cr–20 Ni), Cast C-61

It was found that this steel was quite unstable with time over the temperature range of 650 to 850°C. The microstructure after 2600 hr at 650°C is shown in Fig. 14. The black areas are voids thought to have resulted from the etchant attacking the sigma phase. Cold working appears to have promoted the formation of sigma. The microstructure resulting from 2600 hr at 750°C is shown in Fig. 15. Again, cold working has promoted the formation of sigma. At 850°C (Fig. 16) the sigma precipitate is quite coarse and cold working appears to have only a minor effect on its formation.

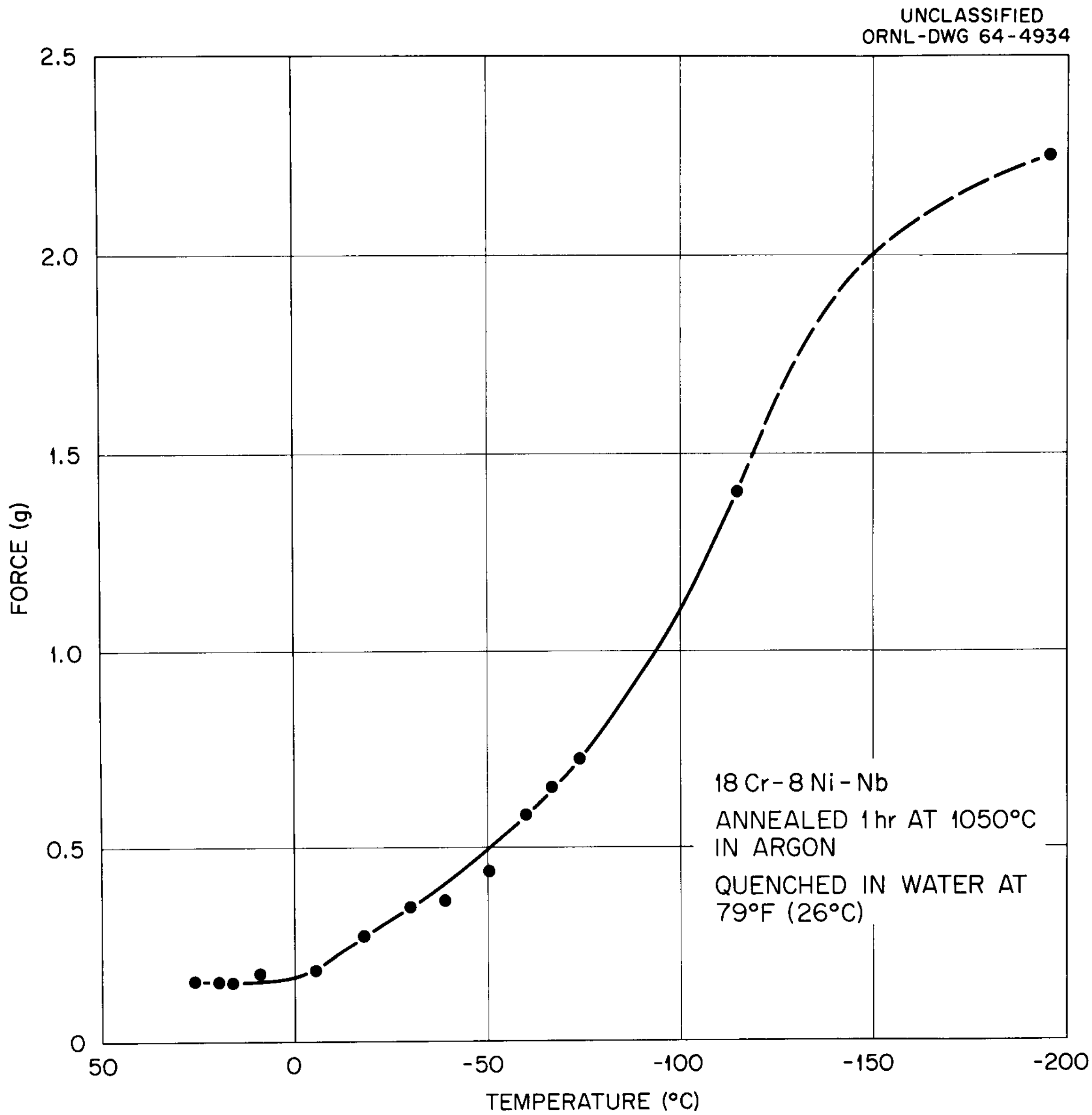


Fig. 12. Annealed Niobium-Stabilized Steel (18 Cr–8 Ni) 1 hr at 1050°C in Argon, Quenched in Water at 26°C.

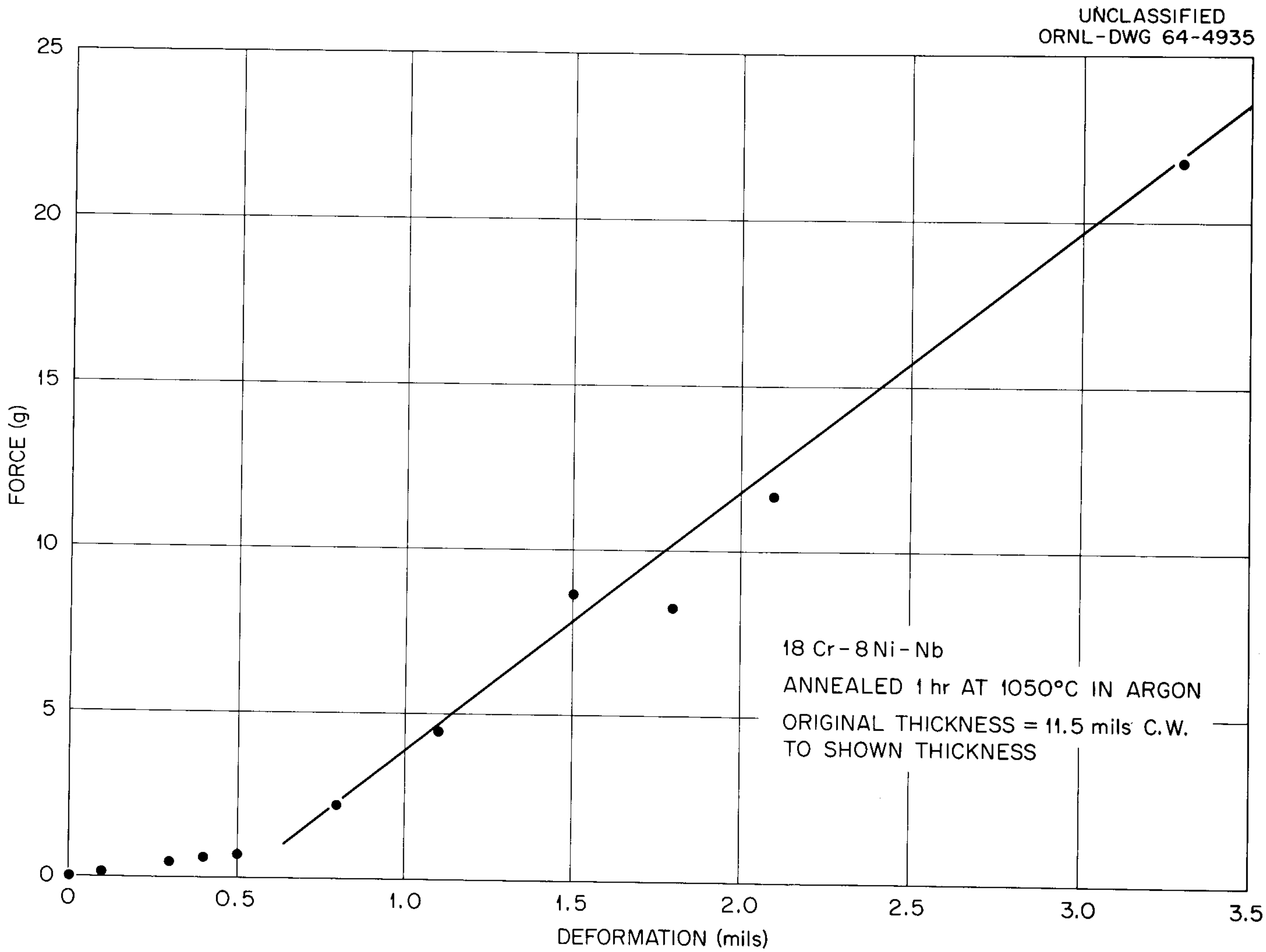


Fig. 13. Niobium-Stabilized Steel (18 Cr-8 Ni) Annealed 1 hr at 1050°C in Argon. Original thickness: 11.5 mils. Cold worked to show thickness.

Table 2. Tensile Properties of Niobium-Stabilized Steel (18 Cr–8 Ni) at 25°C Annealed 1 hr at 1050°C

Pretest Treatment	Yield Strength (psi)	Tensile Strength (psi)	Strain (%)
Water quenched	35,000	99,800	28
Water quenched, cold worked 6%	74,300	117,000	16
Water quenched, cold worked 10%	89,200	135,000	9
Water quenched, cold worked 20%		157,000	1
Liquid nitrogen quenched	35,000	99,800	28
Water quenched, cold worked 10%, liquid nitrogen quenched	94,200	135,000	9
Furnace cooled	33,100	101,700	30
Furnace cooled, liquid nitrogen quenched	39,700	111,700	29
Furnace cooled, cold worked 10%	88,300	134,000	9

Niobium-Stabilized Steel (20 Cr–25 Ni), Cast L16

The as-annealed microstructure of this steel was found to be typical of an austenitic steel (Fig. 17). Aging for 500 hr over the temperature range of 650 to 850°C did not change the microstructure of this steel (Fig. 18). However, it was found that aging for 2600 hr brought about significant changes. Figure 19 shows that aging for 2600 hr at 650°C resulted in the formation of significant quantities of sigma. Cold working, as shown in Fig. 19b, slightly increased the quantity of sigma formed at 650°C. Aging at 750°C for 2600 hr resulted in sigma formation (Fig. 20a), but aging at 850°C (Fig. 20b) did not produce significant quantities of sigma. Cold working did not have any influence upon the formation of sigma at 750 and 850°C.

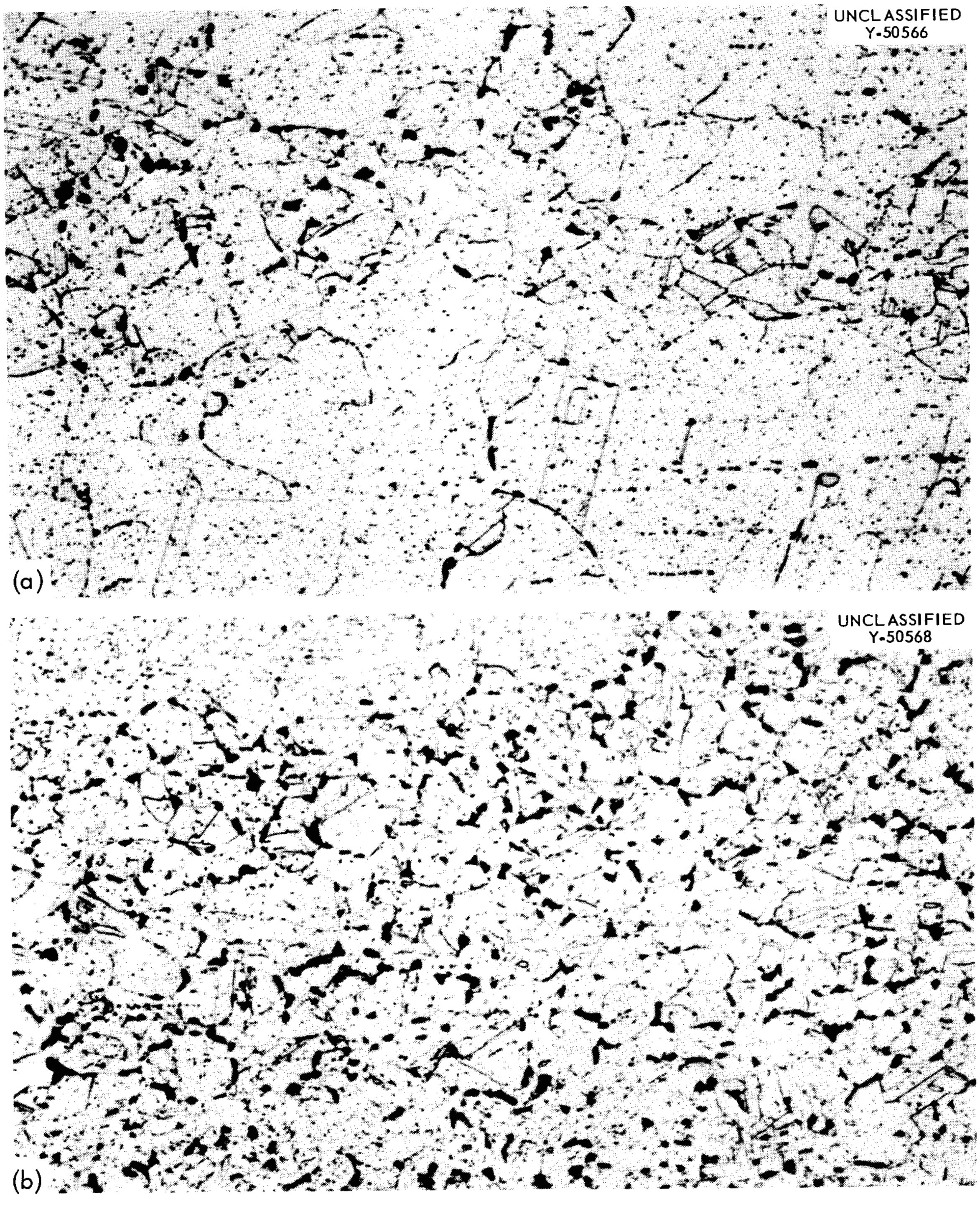


Fig. 14. Photomicrographs of Niobium-Stabilized Steel (25 Cr–20 Ni) Aged 2600 hr at 650°C. (a) Annealed 1 hr at 1050°C prior to aging. (b) Annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in glyceria regia. 500X.

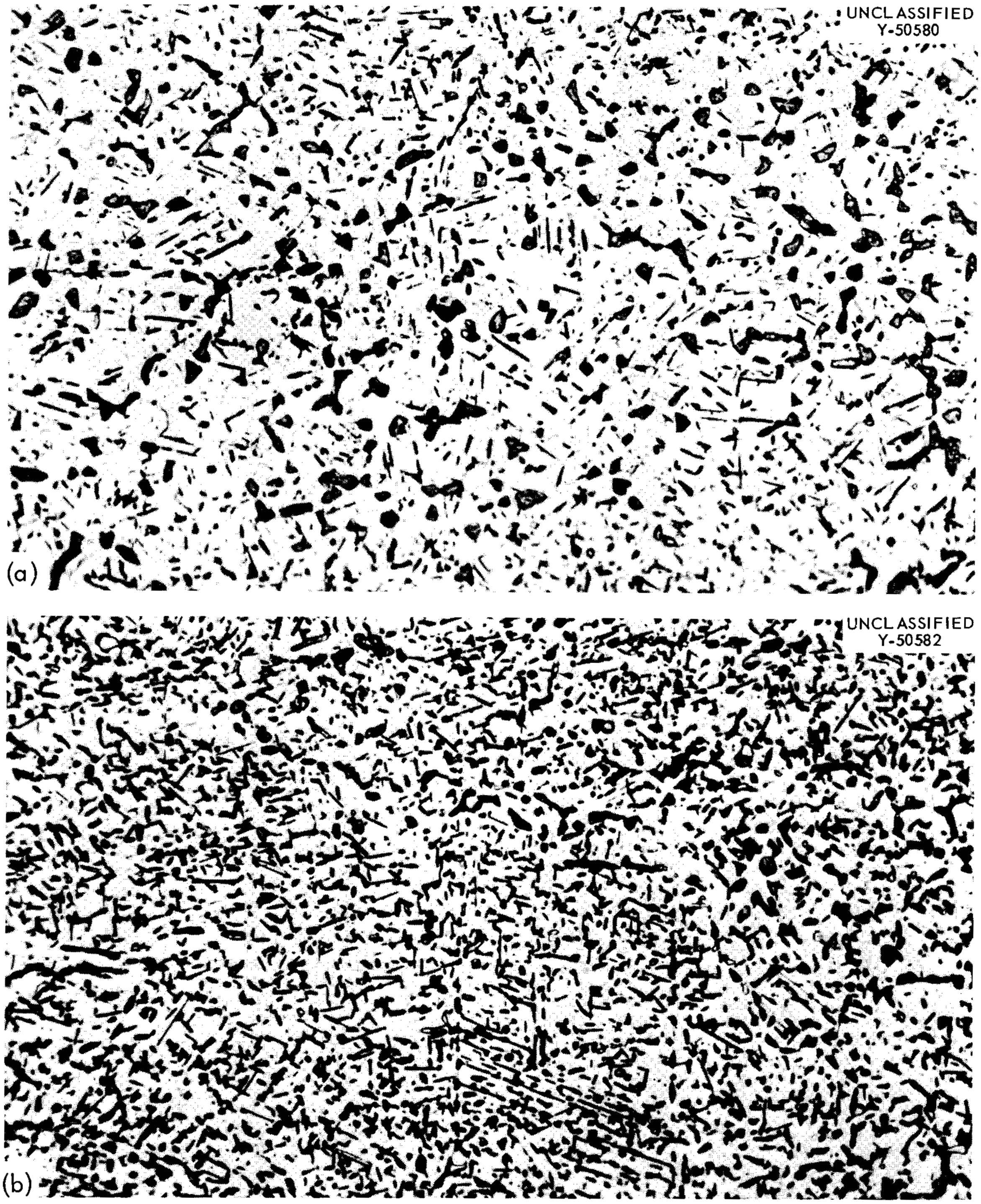


Fig. 15. Photomicrographs of Niobium-Stabilized Steel (25 Cr–20 Ni) Aged 2600 hr at 750°C (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in glyceria regia. 500X.

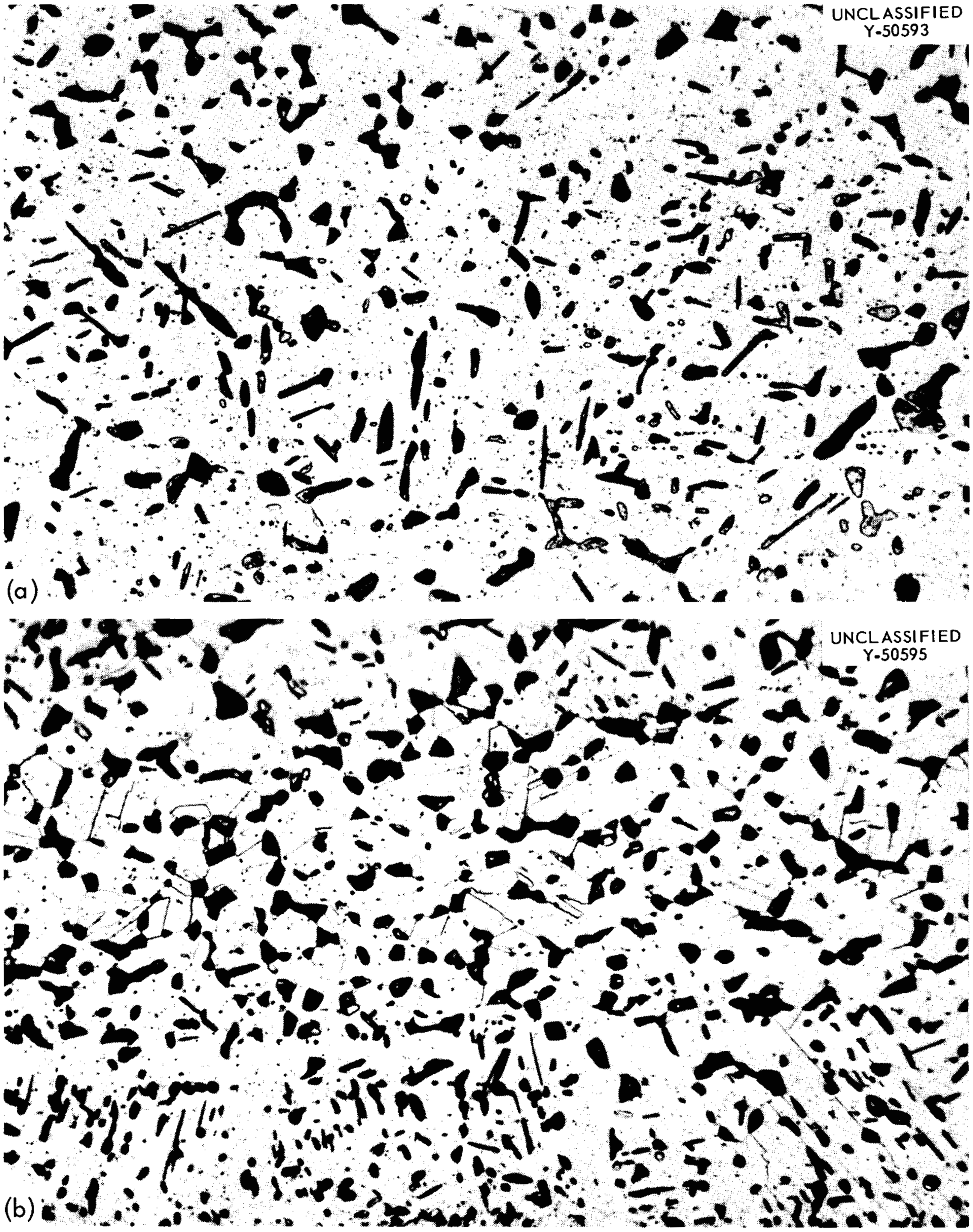


Fig. 16. Photomicrographs of Niobium-Stabilized Steel (25 Cr–20 Ni) Aged 2600 hr at 850°C. (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in glyceria regia. 500×.

Fig. 17. Photomicrograph of Niobium-Stabilized Steel (20 Cr–25 Ni), Cast L16, After Annealing 1 hr at 1050°C. Etched in aqua regia. 500X.

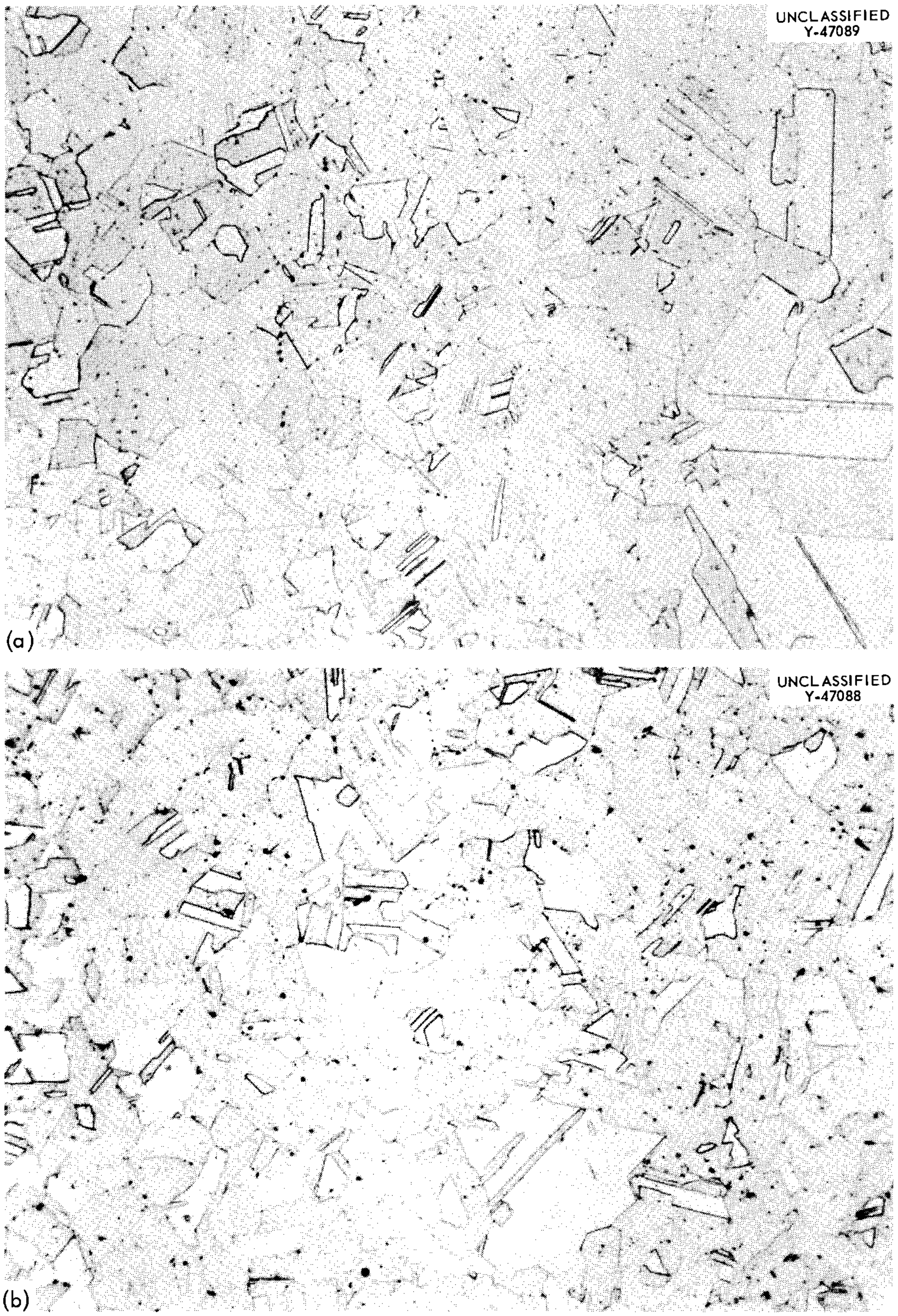


Fig. 18. Photomicrographs of Niobium-Stabilized Steel (20 Cr–25 Ni) Annealed 1 hr at 1050°C and Aged 500 hr. (a) Aged at 650°C; (b) aged at 850°C. Etched in aqua regia. 500X. Reduced 19%.

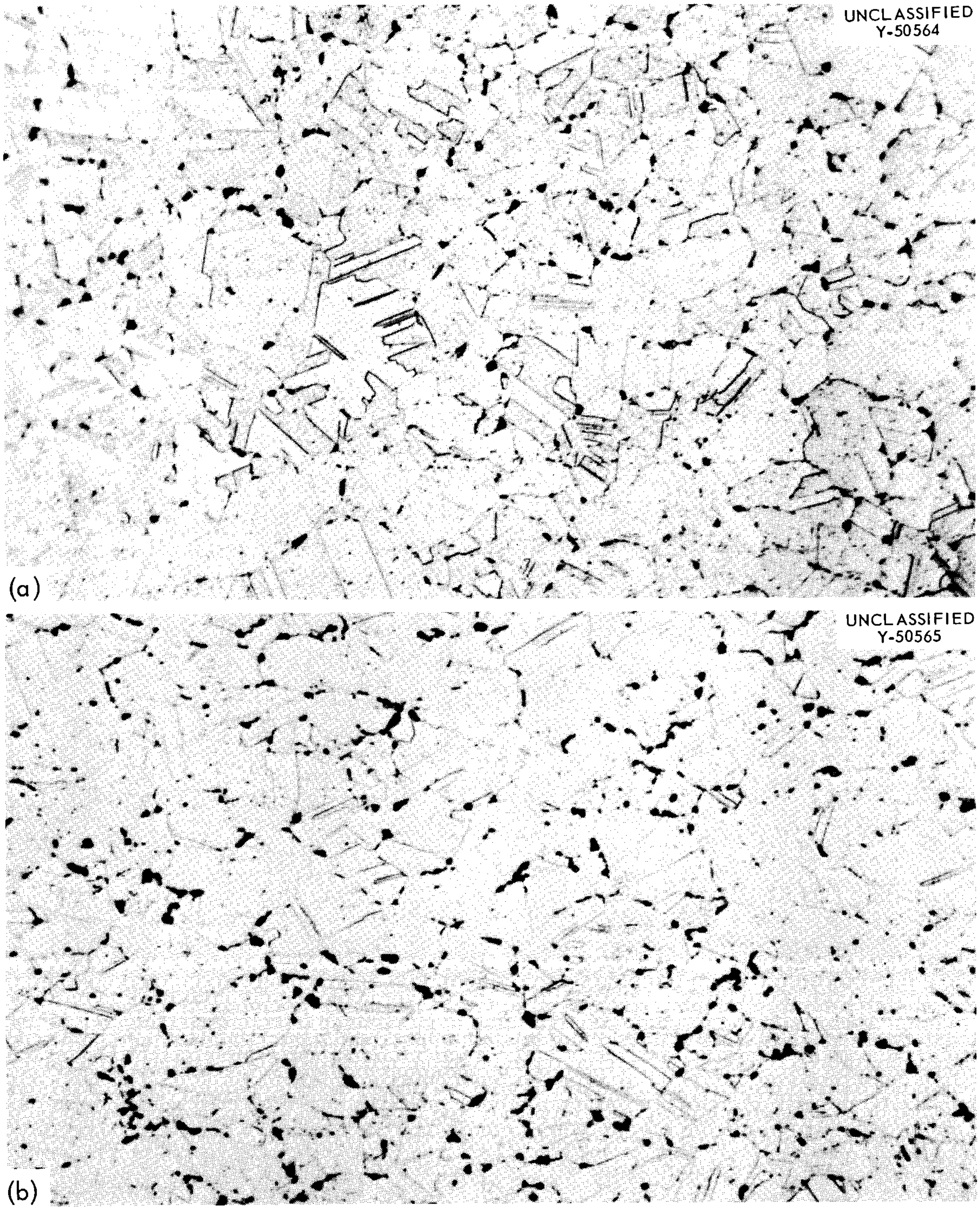


Fig. 19. Photomicrographs of Niobium-Stabilized Steel (20 Cr–25 Ni), Cast L16, Aged 2600 hr at 650°C. (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in glyceria regia. 500X.

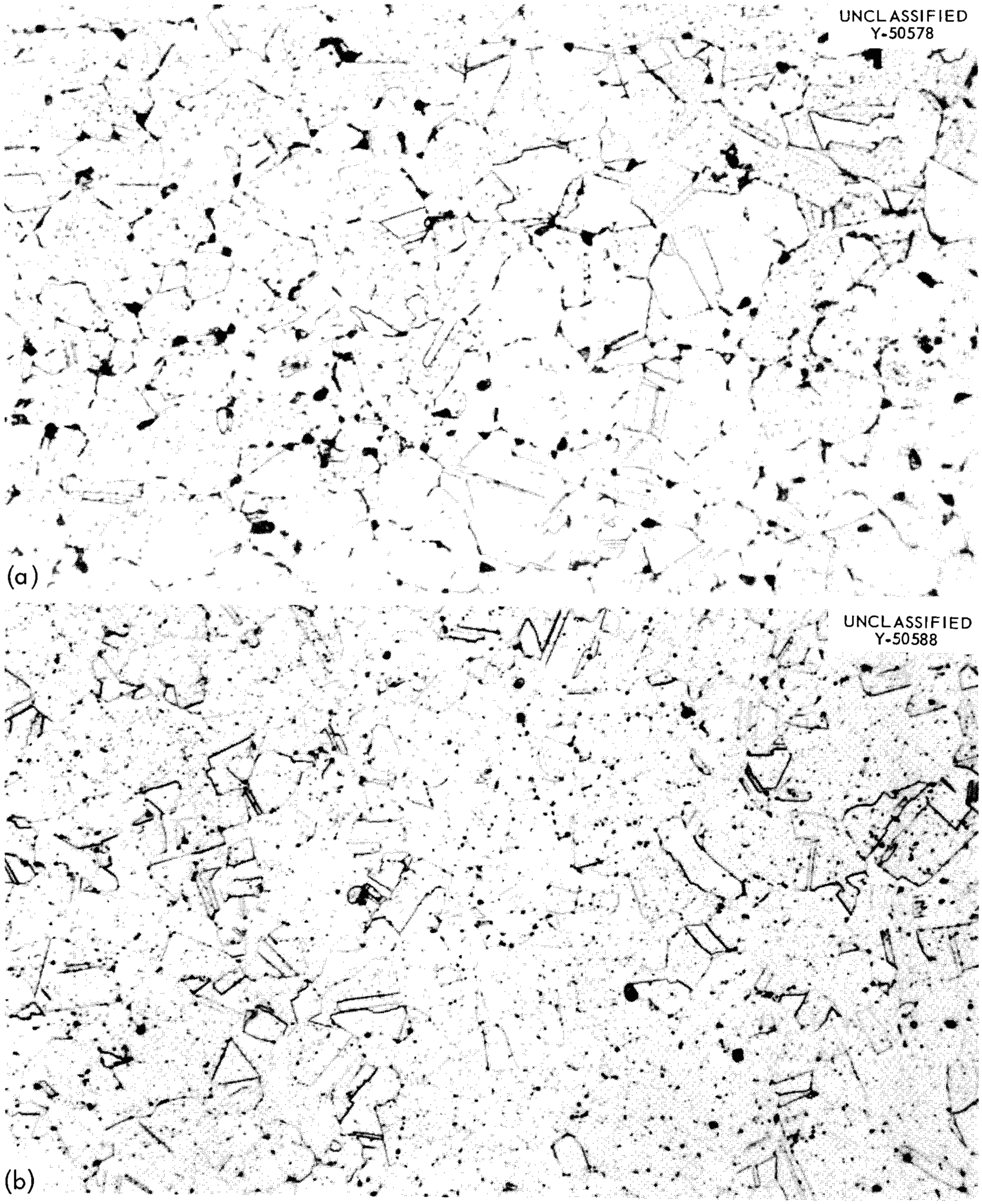


Fig. 20. Photomicrographs of Niobium-Stabilized Steel (20 Cr–25 Ni) Annealed 1 hr at 1050°C and Aged 2600 hr. (a) Aged at 750°C; (b) aged at 850°C. Etched in glyceria regia. 500X.

Niobium-Stabilized Steel (20 Cr–25 Ni), Cast R121

The microstructure of the material in the annealed form was typical of an austenitic steel except for the grain size (Fig. 21). The mixed grain size obtained (ranging from very fine to coarse) was probably due to the uneven working brought about by flattening a tube to make specimens. Aging for 500 hr over the temperature range of 650 to 850°C did not produce detectable amounts of sigma (Fig. 22). Figure 23 shows that aging for 2600 hr at 650°C did produce sigma, particularly in the cold-worked material. Aging at 750 and 850°C for 2600 hr produced progressively less sigma as shown in Fig. 24.

DISCUSSION OF RESULTS

These metallographic studies have shown that the niobium-stabilized steel (18 Cr–8 Ni) is subject to a martensitic transformation and to sigma formation. A survey of the literature shows that the formation of martensite in this steel is, indeed, not surprising. Reed[2] found that niobium-stabilized steel (18 Cr–8 Ni) transforms martensitically upon cooling to a body-centered cubic product, α', and a hexagonal close packed product, ϵ. The formation of the hexagonal close packed phase, ϵ, has been debated. Cina[3] has shown that a total of 24% nickel and chromium must be present in nickel-chromium-iron alloys for ϵ to form. Cina also found that subzero working produced both α' and ϵ in a commercial steel. Carbon was shown to be very influential in reducing the temperature at which martensite was formed. In light of these findings, it is quite surprising that the hexagonal close packed phase, ϵ, was not found in the present steels.

The formation of sigma phase in steels has received considerable attention.[4,5] The literature review by Farrow[4] summarized the available

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[2]R. P. Reed, Acta Met. 10, 865 (1962).

[3]B. Cina, Acta Met. 6, 748, (1958).

[4]M. Farrow, Some Causes of Brittleness in Chromium-Nickel Austenitic Stainless Steels, UKAEA Report No. TRG 564(C), Risley, Warrington, Lancashire, 1963.

[5]Symposium on the Nature, Occurrence, and Effects of Sigma Phase, ASTM Spec. Tech. Pub. No. 110 (1951).

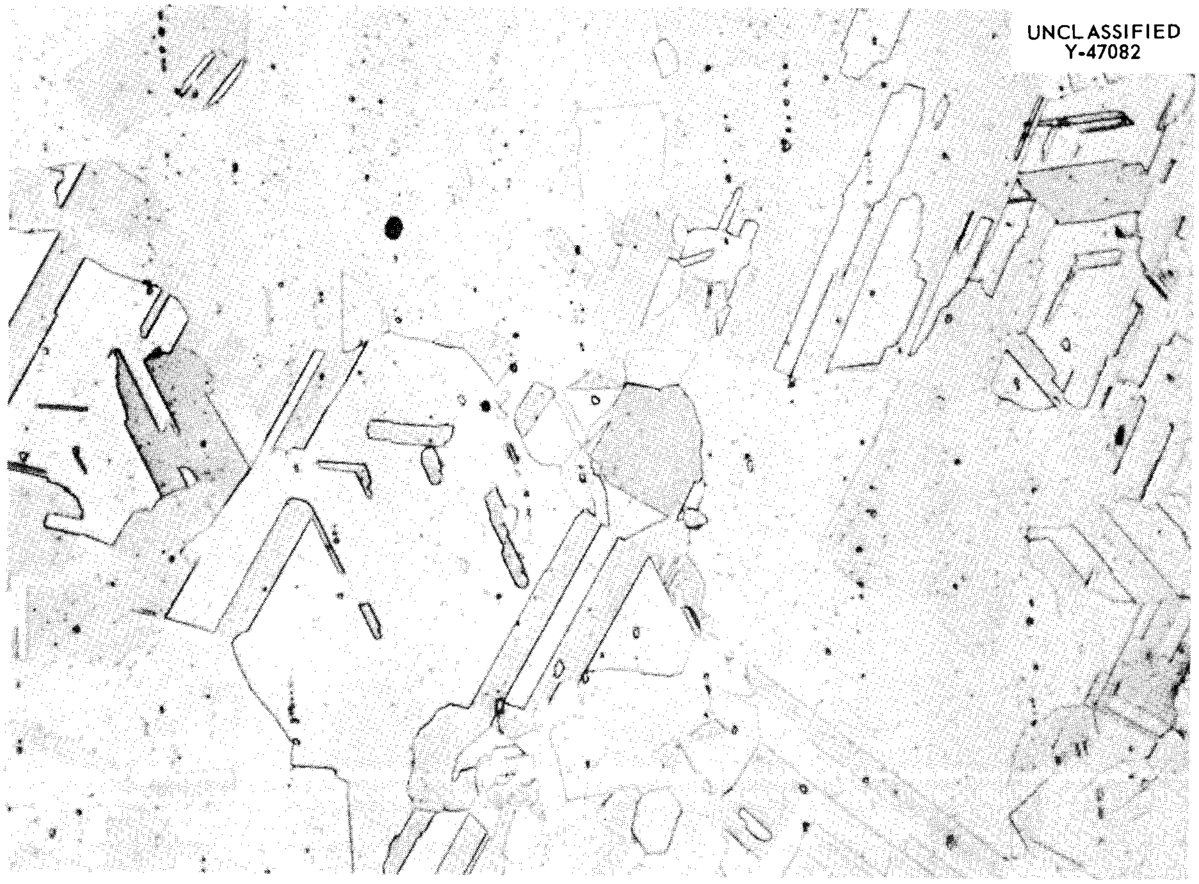

Fig. 21. Photomicrograph of Niobium-Stabilized Steel (20 Cr–25 Ni), Cast R121, Annealed 1 hr at 1050°C. Etched in glyceria regia. 500×.

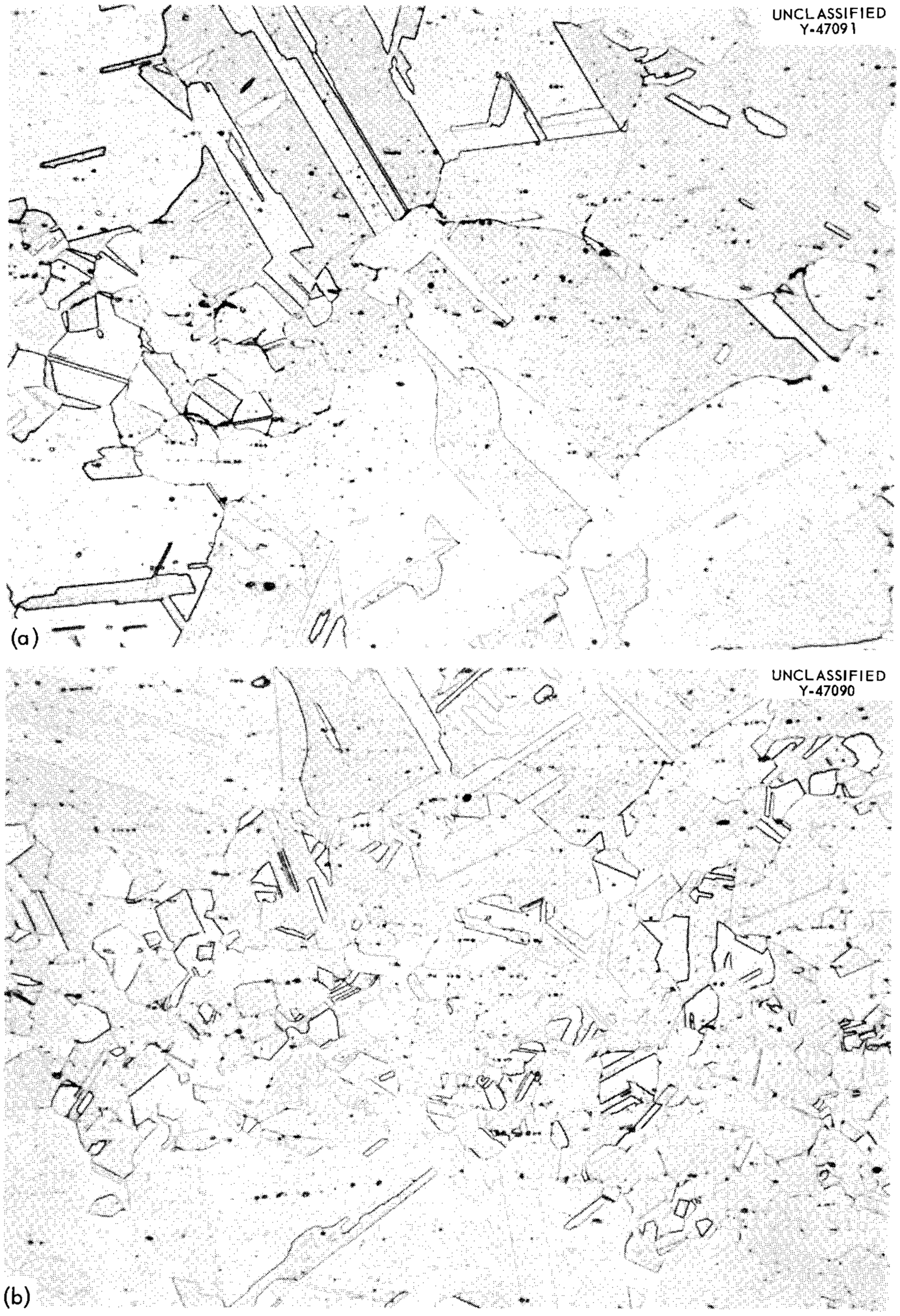

Fig. 22. Photomicrographs of Niobium-Stabilized Steel (20 Cr–25 Ni), Cast R121, Annealed 1 hr at 1050°C and Aged 500 hr. (a) Aged at 650°C; (b) aged at 850°C. Etched in aqua regia. 500×. Reduced 19%.

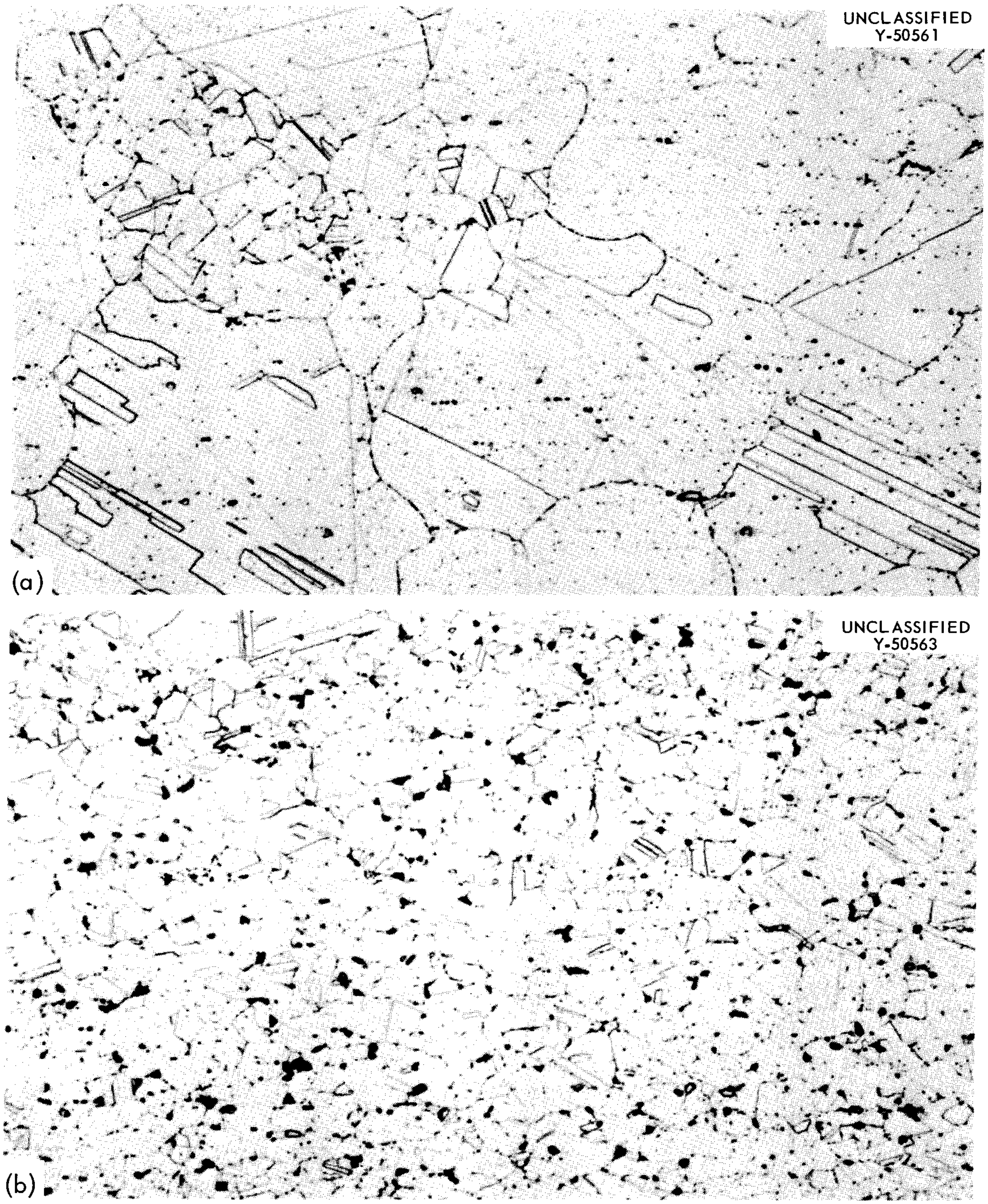

Fig. 23. Photomicrographs of Niobium-Stabilized Steel (20 Cr–25 Ni), Cast R121, Aged 2600 hr at 650°C. (a) Annealed 1 hr at 1050°C prior to aging; (b) annealed 1 hr at 1050°C and cold worked 10% prior to aging. Etched in glyceria regia. 500x.

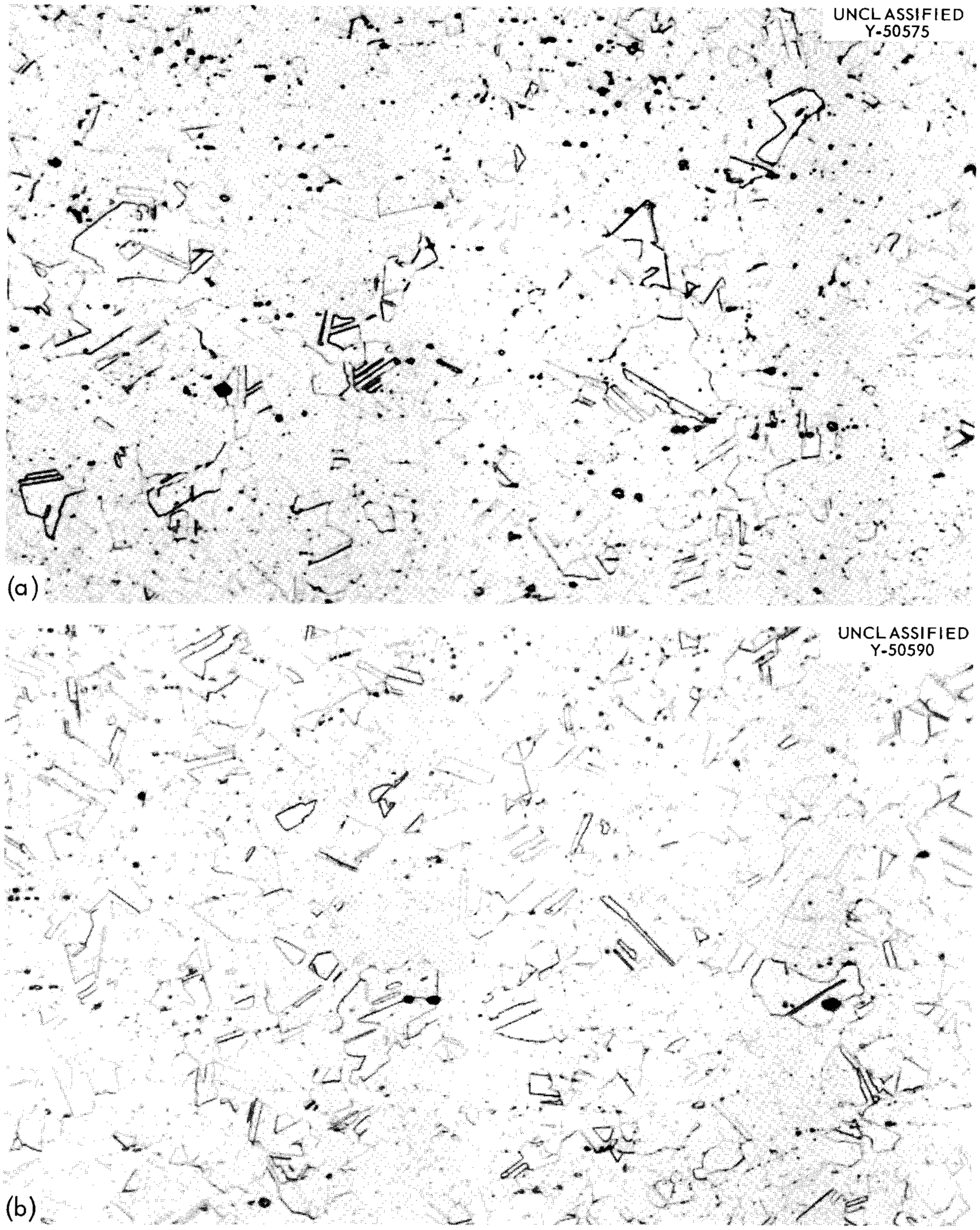

Fig. 24. Photomicrographs of Niobium-Stabilized Steel (20 Cr–25 Ni), Cast R121, Annealed 1 hr at 1050°C and Aged 2600 hr. (a) Aged at 750°C; (b) aged at 850°C. Etched in glyceria regia. 500×.

information on the iron-chromium-nickel ternary systems at 650 to 800°C. At 650°C, the niobium-stabilized steel (18 Cr–8 Ni) is in a sigma field but, at 800°C, lies in an austenitic region. However, the influence of the other alloying elements has not been considered. Farrow's review shows that carbon, nitrogen, and nickel inhibit, whereas chromium, silicon, molybdenum, zirconium, vanadium, aluminum, and tungsten promote sigma formation. Hence, it is not possible to use a ternary diagram to predict whether a commercial steel will form sigma phase. Thus, it is not surprising that the niobium-stabilized steel (18 Cr–8 Ni) forms sigma over the temperature range of 650 to 850°C.

The niobium-stabilized steel (25 Cr–20 Ni) formed profuse amounts of sigma phase. In checking the ternary iron-nickel-chromium diagrams given by Farrow, it is found that the niobium-stabilized steel (25 Cr–20 Ni) falls in a sigma plus austenite field at both 650 and 800°C. Although no mechanical property tests were run on this material, it probably would have been quite brittle at room temperature.[6]

The niobium-stabilized steel (20 Cr–25 Ni) was found to be reasonably resistant to sigma formation, but long times at 650°C produced small amounts of sigma in both heats of material studied. Cast L16 formed significantly more sigma than did Cast R121. Since the ratio of nickel-to-chromium content is about the same for both heats, it is quite likely that the lower carbon content of Cast L16 is responsible for its propensity to form sigma.

The observation was made in several instances that cold working promoted sigma formation. This has been observed by several other experimenters and is rationalized in terms of sigma being formed by a diffusion-controlled process which is accelerated by deformation.

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[6]A. M. Talbot and D. E. Furman, Trans. Met. Soc. AIME **45**, 429 (1953).

SUMMARY AND CONCLUSIONS

A study of the metallography of three niobium-stabilized stainless steels (18 Cr—8 Ni), (20 Cr—25 Ni), and (25 Cr—20 Ni) has revealed several important facts.

1. The niobium-stabilized steel (18 Cr—8 Ni) undergoes a martensitic transformation during subzero cooling or cold working. This transformation does not alter the strength or ductility significantly, but it does appear to result in a higher rate of work hardening.

2. All three of the steels studied form sigma under some aging conditions. The niobium-stabilized steel (25 Cr—20 Ni) is most susceptible to sigma formation, niobium-stabilized steel (18 Cr—8 Ni) is the next most susceptible, and niobium-stabilized steel (20 Cr—25 Ni) is the least susceptible.

3. Cold working increases the rate of sigma formation under most test conditions studied.

Although work has already been initiated on all three of these steels, it appears that the niobium-stabilized steel (20 Cr—25 Ni) is the only alloy worthy of extensive study. The other two steels are quite susceptible to sigma formation and would not be desirable structural materials. In addition, the niobium-stabilized steel (18 Cr—8 Ni) undergoes a martensitic transformation at low temperatures which results in high rates of work hardening and would make fabrication difficult.

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