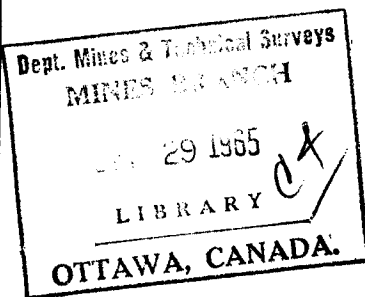




CANADA



**CORROSION BEHAVIOUR OF
URANIUM-BEARING
RESULPHURIZED CHROMIUM
STAINLESS STEELS**

G. J. BIEFER & W. M. CRAWFORD

**DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA**

PHYSICAL METALLURGY DIVISION

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CORROSION BEHAVIOUR OF URANIUM-BEARING RESULPHURIZED CHROMIUM STAINLESS STEELS

by

G. J. Biefer* and W. M. Crawford**

ABSTRACT

In keeping with their much higher sulphur contents, conventional AISI Type 416 and 430F resulphurized chromium stainless steels showed markedly higher aqueous corrosion rates than did AISI Type 430 chromium stainless steel, which has a low sulphur content.

Uranium alloying additions to the resulphurized steels conferred markedly improved corrosion resistance in nitric acid solutions at room temperature when U/S ratios were 3.5/1 or more, the performance of such steels approaching or equalling that of AISI Type 430 stainless steel. However, the uranium alloying additions had only a slight effect upon corrosion behaviour of the resulphurized stainless steels in sulphuric acid, hydrochloric acid and ferric chloride solutions.

Metallographic examinations showed that resulphurized steels with U/S ratios of 3.5/1 or more had predominantly globular sulphide inclusions of undetermined chemistry that had sufficiently high melting points to retain their shapes subsequent to hot-rolling. In contrast, the uranium-free resulphurized steels, subsequent to hot-rolling, showed characteristic sulphide stringers.

Electrochemical measurements indicated that the uranium additions brought about decreased corrosion in nitric acid solutions because of their effect upon anodic polarization behaviour.

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Direction des mines

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COMPORTEMENT À LA CORROSION DES ACIERS INOXYDABLES AU CHROME RESULFURÉS ET CONTENANT DE L'URANIUM

par

G. J. Biefer* et W. M. Crawford**

RÉSUMÉ

Du fait de leur forte teneur en soufre, les aciers inoxydables ordinaires au chrome resulfurés AISI des types 416 et 430F ont présenté des vitesses de corrosion aqueuse beaucoup plus élevées que celles des aciers inoxydables au chrome AISI de type 430, qui ont une plus faible teneur en soufre.

Des additions d'uranium aux aciers inoxydables resulfurés ont amélioré grandement la résistance à la corrosion dans des solutions d'acide nitrique à la température ambiante lorsque les rapports uranium-soufre sont de 3.5/1 ou plus. Le comportement de ces derniers aciers se rapproche de celui de l'acier AISI de type 430 ou l'égale. Cependant, les additions d'uranium n'ont qu'un faible effet sur le comportement à la corrosion des aciers inoxydables resulfurés dans les solutions d'acides sulfurique et chlorhydrique et de chlorure ferrique.

L'examen métallographique a indiqué que les aciers resulfurés avec des rapports U/S de 3.5/1 ou plus contiennent des inclusions sulfurées à prédominance globulaires d'une composition chimique indéterminée à point de fusion assez élevé pour conserver leur forme après laminage à chaud. Par contre, les aciers resulfurés sans uranium, après laminage à chaud, laissent voir les filets de sulfure caractéristiques.

Les mesures électrochimiques ont indiqué que les additions d'uranium réduisent la corrosion dans les solutions d'acide nitrique à cause de leur effet sur le comportement de la polarisation anodique.

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INTRODUCTION

During the period 1959-1960 there was a marked decrease in the demand for Canadian uranium. Consequently, the Canadian government and the uranium industry undertook wide-scale investigations into potential non-nuclear applications of the metal, in an attempt to develop new markets. One area of investigation was the use of uranium as an alloying element in steel. For the past few years, the Physical Metallurgy Division of the Department of Mines and Technical Surveys has investigated the effects of uranium in various types of steel. Results obtained up to April 1962 have been comprehensively reviewed⁽¹⁾.

The effect of uranium upon resulphurized steels was considered to be of particular interest because of thermodynamic evidence that uranium has strong sulphide-forming tendencies, similar to those shown by thorium⁽²⁾. Its monosulphide, US, is much more stable than that of manganese, which is normally added to steels in order to combine with unwanted sulphur (Figure 1).

In research by the Physical Metallurgy Division, the first practical indication of a uranium-sulphur reaction occurred in an early investigation of carbon steels of low sulphur content. Here it was observed that some uranium-bearing steels would not "sulphur-print", thus suggesting that the sulphides were resistant to attack by 2% sulphuric acid⁽³⁾. Subsequently it was observed, for ferritic steels of low sulphur content, that uranium additions conferred minor improvements in corrosion resistance in acids⁽⁴⁾, and the effect of uranium additions in AISI Type 430 stainless steel has been reported in some detail⁽⁵⁾. Since sulphur is known to be detrimental to corrosion resistance, it appeared possible that these favourable trends were connected with the "fixation" of the low amounts of sulphur present.

Other preliminary work on two grades of high-sulphur, free-machining stainless steels (AISI Types 303 and 416) showed that a U/S ratio of approximately 3.5/1 produced sulphides that did not elongate on rolling, but remained globular in shape⁽⁶⁾. These observations led to further research on those properties of uranium-bearing stainless steels which are likely to be dependent on the morphology of the sulphides. In particular, comprehensive investigations were carried out on two important resulfurized grades of the AISI 400 series, the martensitic Type 416 and the ferritic Type 430F, with regard to the effect of uranium upon their machinability, transverse ductility, hot forgeability, and cold formability⁽⁷⁾.

In view of the effect of uranium additions upon the corrosion resistance of other steel types, referred to above, it was decided to extend the research on these steels to include a study of their corrosion resistance. This work is the subject of the present report.

EXPERIMENTAL

1. Materials

It was decided that AISI stainless steel Types 416 and 430F would be examined at two levels of sulphur, 0.15% and 0.30%, with corresponding uranium additions to give target U/S ratios of approximately 0, 1/1, 4/1, and 7/1.

The sixteen heats were prepared in a 50 lb air-melting induction furnace. A basic charge of "Armco" iron was used, along with low-carbon ferro-alloy additions, and final deoxidation was carried out with aluminum (2 lb/ton). Elemental sulphur and uranium were added in quick succession immediately following this, and the heat poured into a hand ladle and thence into a cast iron mould. The uranium was added as pure metal which was wrapped in a small piece of aluminum foil in an attempt to cut down oxidation.

A 70% recovery was obtained. Small test bars were poured with each ingot and drilled for chemical analysis. The compositions of the heats are shown in Table 1.

After cropping, each ingot was forged and rolled to plate $3\frac{1}{2}$ in. wide x $\frac{3}{4}$ in. thick, Type 416 at 1150°C (2100°F) and Type 430F at 1065°C (1950°F). The plates were then given a full annealing treatment of 870°C (1600°F) for one hour, followed by a furnace cooling. One side of each plate was surface-ground in preparation for sulphur-printing and autoradiography.

Sulphur-printing of the plates was carried out in the usual manner, i.e. using a photographic film soaked in 2% sulphuric acid in contact with the plates for about 2 minutes. The effect of the uranium in preventing the production of normal prints was highly significant. In all cases the controlling factor was the ratio of U/S; with no uranium present, the base compositions containing 0.15 and 0.30% sulphur gave vigorous prints. However, as the U/S ratio was increased, a less distinct print was obtained until, at U/S ratios of approximately 7/1, no reaction occurred. It is noteworthy that this effect has not been correlated with markedly improved corrosion resistance when uranium-bearing steels are exposed to sulphuric acid solution for longer periods.

In the production of autoradiographs, the ground metal surface was exposed for 24 hr or more in intimate contact with an X-ray film. This technique showed the presence of uranium by a darkening of the film, caused by radiation emitted by the uranium. The more uranium present, the darker the film, i.e. the lighter a print of the film. The autoradiographs also demonstrated a phenomenon which was found to occur with most uranium-bearing steels and which was attributed to the high affinity between uranium and oxygen, namely, the presence of small areas of high uranium concentration distributed non-uniformly throughout the steel. This has been termed "uranium segregation" and each area of "uranium segregate" is known to be made up of an agglomeration of inclusions thought to be predominantly composed of UO_2 (1).

Figure 2 shows prints of autoradiographs from two plates of Type 416 stainless steel at the 0.30% sulphur level. It will be observed that the occurrence of uranium segregate (white areas) increases with uranium content and that the segregate also becomes more massive. It should be kept in mind, however, that autoradiographs give an exaggerated effect to the size of the segregate, which is actually made up of galaxies of small inclusions. The radiation from each particle plus the scattering of the rays give the deceptive appearance on the film of a single large inclusion.

The occurrence of uranium segregation has been regarded as undesirable, and, for example, in some steels localized corrosion attack has been observed at uranium-rich areas revealed by autoradiographs⁽⁸⁾. Therefore, in the present work, autoradiographs were routinely carried out on metal corrosion coupons, and coupons showing a significant amount of uranium segregation were not used in tests. These precautions were evidently sufficient, as no effects attributable to uranium segregation were observed. It might be noted that, in the period since these heats were made, techniques for adding the uranium have been improved and less "segregated" steels can now be produced.

2. Corrosion Tests

The aqueous corrosion tests were carried out on small rectangular flat specimens, each provided with a hole for suspension during testing. All specimens were cut so that the major faces lay in the plane longitudinal to the direction of rolling. Prior to testing, all surfaces were ground on water-cooled 120 grit silicon carbide papers, then degreased in ultrasonically agitated carbon tetrachloride and dried in acetone. Specimen areas were calculated from measurements made with a micrometer and were usually 10-12 cm². Specimens were weighed, before and after testing, on an analytical balance accurate to ± 0.1 mg.

During tests the specimens were suspended from "Teflon" fluorocarbon resin strips that, in turn, were fastened to a "Lucite" frame that did not come in contact with the test solution. Two to eight specimens were tested simultaneously by immersion in 500 to 2,500 ml of solution held in a pyrex beaker. The tests took place in a room with a controlled temperature of $23^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ($73^{\circ}\text{F} \pm 2^{\circ}\text{F}$).

After immersion in the corrosion test solution for the required period, the specimens were removed, rinsed with tap water, scrubbed lightly with a bristle brush to remove any adherent corrosion film, then rinsed in alcohol and dried rapidly in hot air. The specimens were then reweighed and the surfaces examined, using a stereomicroscope with a maximum magnification of 40X.

3. Electrochemical Measurements

Specimens used in the electrochemical measurements were rectangles with a thin shaft extending along one edge, to permit the flow of electrical current into the specimen while immersed in a test solution. The electrochemical specimens, which had a total immersed area of about 8 cm^2 , were given the same pretreatment as the rectangular corrosion test specimens described above.

The electrochemical test vessel held 1.6 litres of solution in all (Figure 3). It was provided with a platinum auxiliary electrode in a separate compartment, and a second compartment into which purified nitrogen was bubbled, so that the test solution was circulated but no gas bubbles impinged on the steel specimens.

A Luggin probe and a salt bridge were arranged so that the potential of the steel specimens could be measured with respect to a saturated calomel electrode. A vacuum tube voltmeter (Simpson, Model 311) was used for trial potential measurements. A potentiostat (Anotrol, Model 4100) was used to hold the specimens at desired potentials relative to the standard electrode,

by means of an electronically adjusted electrical current which flowed from the specimen to the platinum auxiliary electrode or vice versa. These impressed currents could be measured continuously by means of a potentiometric chart recorder (Westronics, Model 511A/U).

The potentiostat was provided with a linear scanning drive so that "potentiodynamic" experiments could be carried out, i. e., the potential could be varied at a constant rate over a selected range, and the impressed current measured continuously. In the present work, linear potentiodynamic scans were carried out in the potential range -600 mV to +1200 mV, at rates ranging from 2 to 7.2 V/hr; in nitrogenated 10% nitric acid. The scans were always started at a cathodic (negative) potential and the potential was altered in the noble (more positive) direction at a linear rate. The low-current sections of typical scans are reproduced in Figure 4.

The test solutions were routinely prepared in the afternoon and nitrogen bubbled through the solution overnight. The electrochemical specimens were immersed in the solution the next morning and after 1-2 hr of unpolarized corrosion the potentiodynamic scans were started. A single "conditioning" scan over the range -600 mV to +1200 mV was always carried out, but not recorded, prior to tests.

RESULTS

1. Corrosion Tests

The results obtained in corrosion tests in four different corrosion solutions, in terms of weight losses per unit area in 4 hr, appear in Table 2. Each weight loss represents an average of at least 3 determinations, reproducibility being good in all cases. To illustrate the deleterious effect of sulphur upon general corrosion resistance, the results obtained on AISI Type 430 stainless steel, which has a low sulphur content, are also presented.

In 10% nitric acid, as is made clear by the results in Figure 5, there was a striking relationship between corrosion and uranium content. The steels with no uranium, or U/S ratios below 1/1, showed extremely high corrosion rates, the test solutions rapidly developing a brownish colouration. However, at U/S ratios of 3.5/1 or more, solutions remained clear during the tests. Corrosion rates were low, and appeared to become lower with increasing U/S ratios over the range investigated.

The AISI Type 430F steels with the lowest sulphur level were selected for additional measurements in nitric acid over the concentration range 2-90%. The results obtained, in terms of weight losses per unit area in 4 hr, appear in Figure 6. It is seen that, for the uranium-free resulphurized 430F stainless steel, corrosion rates were high in nitric acid solutions in the concentration range 5-20%, and comparatively low at higher and lower nitric acid concentrations. The steels with U/S ratios of 4.2/1 and 7.5/1, on the other hand, exhibited comparatively low corrosion rates in all nitric acid concentrations investigated. The steel with a U/S ratio of 0.6/1 showed markedly improved corrosion resistance, as compared with the uranium-free steel, in 20% nitric acid, but generally exhibited similar behaviour to the uranium-free steel at the other concentrations of nitric acid.

2. Electrochemical Measurements

Using nitrogenated 10% nitric acid as test solution, specimens of each of the AISI Type 430F steels with 0.13-0.14% sulphur were installed in turn in the electrochemical cell, and the vacuum tube voltmeter used to measure their potentials while corroding freely. Steels 5180 and 5181 were found to corrode rapidly, the test solutions soon showing a brownish colouration. Corrosion potentials E_{corr} were variable, and lay in the range -370 to -495 mV. In contrast, steels 5182 and 5183 appeared passive, the test solutions remaining clear. E_{corr} values for these steels were also variable, but lay in the range +20 to +240 mV. However, it was observed that, subsequent

to the first "conditioning" scans from -600 to +1200 mV, all four unpolarized steels showed highly variable positive potentials which appeared to drift, with time, towards the range +200 to +350 mV.

In repeated linear scans upon single specimens of each of the steels, reproducibility was only fair, but it became clear that the "conditioned" steels could nevertheless be divided into two distinct groups. The main features of each group are shown in Figure 4. Steels 5180 and 5181 showed E_{corr} values of about -200 mV, and definite anodic peaks at potentials of about -100 mV. As the potential was made still more positive, two reversals of polarity then followed, from anodic to cathodic, then back again to anodic, thus constituting "cathodic loops"⁽⁹⁾. Steels 5182 and 5183 showed E_{corr} values varying over a considerable range, but did not exhibit definite maxima nor cathodic loops following their single polarity change from cathodic to anodic.

In Figure 7 a number of linear cathodic scans, in the potential ranges -600 to -100 mV and -500 to 0 mV, are reproduced. The points shown on this figure were obtained by the transfer of selected points from the continuous linear curves obtained on the chart recorder. Once again, the differences between steels 5180 and 5181, on the one hand, and steels 5182 and 5183, on the other hand, are obvious, particularly at the more noble (more positive) potentials.

3. Metallographic Examination

Samples of the rolled steels were cut and polished in the plane longitudinal to the direction of rolling, and examination in the unetched condition showed that uranium produced a pronounced change in the morphology of the sulphide inclusions. With sufficient uranium content, the stringer sulphides characteristic of conventional resulphurized steels were replaced by a random dispersion of sulphides that had remained globular through the rolling process. Photomicrographs of three of the groups of heats are shown in Figures 8, 9, and 10. Here, it will be observed that globularization is

predominant at U/S ratios of approximately 4/1. At the higher ratios, in the region of 7/1, a mixture of globular and angular shaped inclusions is obtained. Micrographs for steels 5185 - 5188, which showed the same effect of uranium, are not reproduced, because of the off-standard composition of the uranium-free steel.

Examination of specimens at high magnifications gave striking evidence of changes in the constitution of the sulphide inclusions with the addition of uranium, and showed that more than one type of inclusion was produced. The photomicrographs of Figure 11 are for the low-sulphur group of experimental AISI Type 430F heats, but are representative of other steels of similar U/S ratios. The only major difference noticed between resulphurized steels of similar U/S ratios, but different sulphur contents, is that the inclusions are larger in the steels with higher sulphur contents (cf Figures 8 and 9).

Figure 11a shows the typical sulphide found in the U-free control heat 5180 - grey, monophase, and elongated in the direction of rolling. At a low U/S ratio such as 0.6/1, a similar type persists, but there are also many sulphides, such as that shown in Figure 11b, which seem to have been more resistant to deformation during rolling, and have not elongated completely into stringers. When sufficient uranium is added to bring about a significant morphological change, e.g., a U/S ratio of 4.2/1, the sulphides are not only rounded in shape and randomly dispersed, but many are duplex in character. Figure 11c shows a group of inclusions representative of such a U/S ratio. It contains the following: round, bluish-grey monophase inclusions; a round inclusion with what appears to be a light-grey eutectic set in the grey matrix; and a two-phase type made up of a grey matrix and light-grey, angular-shaped material. Under polarized light with crossed nicols, the latter constituent was observed to be moderately anisotropic and exhibited pleochroism, i.e., changed colour on rotation of the specimen. Utilizing the latter property as a means of identification, heats of high U/S ratios, e.g., heat 5183 (U/S - 7.5/1), were observed to contain much

more of this constituent, which, under reflected light, was either light-grey or very deep bluish-grey in colour, and occurred in many angular shapes, e.g., hexagonal, rhombohedral, rectangular. It was found that, for many of the two-phase inclusions, each phase showed the same pleochroic effect, but at different stages in the rotation, thus suggesting similar material at different orientations. Examples of the different types of inclusions observed at the high U/S ratios are shown in Figures 11d and e. The mixture of round and angular types will be noted and also the appearance of some thin, elongated inclusions.

In this and other work on uranium-bearing resulphurized steels, it has been established that the controlling factor over the shape and character of the sulphides is the ratio of uranium to sulphur. A comparison of the type of sulphides found in samples of similar uranium but different sulphur contents readily demonstrates this. For example, heat 5134, containing 0.99% U, 0.25% S, and $U/S = 3.5/1$, shows completely spherical inclusions (Figure 9) and no sign of the angular inclusions which appear in Heat 5110 (Figure 8) or Heat 5183 (Figures 10 and 11). Both of the latter heats, however, have uranium contents of 1.05%, similar to Heat 5134, but lower sulphur contents of 0.15% and 0.14%, the U/S ratios being of the order 7/1. For these steels of the 0.13-0.16% sulphur level, a similar sulphide type to that of Heat 5134 is attained at much lower uranium contents of about 0.60%, i.e. at U/S ratios of about 4/1 (Figures 8 and 10). The U/S ratio was also observed to control the appearance of the low melting point eutectic constituent UFe_2 . In uranium-bearing steels with a low sulphur content this phase is noticeable, and has been observed to cause hot shortness at uranium contents as low as 0.35%⁽¹⁰⁾. With resulphurized steels, however, it was found that substantially more uranium could be tolerated without either the formation of UFe_2 or the occurrence of hot shortness, and that this "tolerable" uranium level increased in proportion to the sulphur content. UFe_2 began to appear only at U/S ratios in the region of 7/1 and higher. Heats 5110 (1.05% U) and 5183 (1.05% U), which had U/S ratios of 7/1 and 7.5/1 respectively (see Table 1), showed evidence of UFe_2 on metallographic

examination. Other heats of similar uranium content, but higher sulphur content, e.g. Heat 5134 (0.99% U) and Heat 5187 (0.90% U), gave no indication of this phase since the U/S ratios were 3.5/1 and 4.1/1 respectively. Even in Heat 5135, which contained 1.48% U, no UFe_2 was observed because its U/S ratio (4.7/1) was still considerably below 7/1.

Consideration was given to the possible effect of uranium on the general microstructure. From the Fe-U and Fe-C diagrams of Figure 12, however, it is seen that uranium has no solubility in alpha-iron and a limited solubility in gamma-iron of approximately 2% at 1405°C (2560°F) decreasing to zero at 910°C (1670°F). Uranium is a very strong carbide former and there is evidence, from work on an AISI Type 416 stainless steel, that it depletes austenite of carbon and thereby lowers as-quenched hardness⁽⁷⁾. The material used in this investigation, however, was in the softest condition, i.e. annealed, and mechanical tests conducted in a parallel investigation showed uranium to have no significant effect on the strength in this condition. Photomicrographs of etched specimens of AISI Type 416 and Type 430F stainless steels are shown in Figures 13 and 14. The normal microstructure of ferrite and chromium carbides was observed and it was noted that uranium produced little change in this, apart from the fact that the carbides appeared more massive, suggesting some formation of UC.

DISCUSSION OF RESULTS

1. Corrosion Tests

Comparison with the results obtained on AISI Type 430 stainless steel, which has a low sulphur content (Table 2), serves as an indication of the deleterious effect of sulphur on the general corrosion resistance of the two resulphurized chromium stainless steel types investigated. In particular, in 10% nitric acid, uranium-free resulphurized AISI Types 416 and 430F stainless steel showed phenomenally high corrosion rates,

approximating 30 in./year.

Alloying additions of uranium to U/S ratios of 0.4-0.8/1 had comparatively little effect, but steels with U/S ratios of 3.5/1 or more showed strikingly improved corrosion resistance in the nitric acid solutions investigated. Corrosion appeared to be reduced with increasing U/S ratio over the range investigated. At U/S ratios of about 7/1, which corresponded approximately to the stoichiometric ratio between uranium and sulphur, the additions appeared to counteract the deleterious effect of sulphur completely, as corrosion rates in the nitric acid solutions investigated were equivalent to those shown by AISI Type 430 stainless steel, which has a low sulphur content. There are indications, from earlier unpublished work, that even further reductions in corrosion in nitric acid might be obtained by alloying to even higher U/S ratios, as an AISI Type 430F stainless steel with a U/S ratio of 11.2/1 showed reduced corrosion in 5% nitric acid solution, as compared with a similar steel with a U/S ratio of 6.1/1. Further, the steel with the higher U/S ratio appeared shinier after the test, and has retained this advantage in appearance during a subsequent two-year exposure to ordinary laboratory atmosphere.

In contrast with the favourable trends noted in nitric acid, uranium additions did not affect corrosion resistance to an important extent in the other three corrosive solutions investigated. Only slight reductions in corrosion were noted in non-oxidizing solutions of 10% sulphuric and 10% hydrochloric acid. It should be kept in mind, while assessing these results, that the composition of Heat 5185 was too off-standard for it to serve as a suitable uranium-free control for the other steels in its group. In oxidizing 10% ferric chloride solutions, uranium additions had no significant effect upon corrosion.

2. Electrochemical Measurements

In the past decade a number of investigators have carried out theoretical analyses of polarization curves. More recently, N. D. Greene⁽⁹⁾ has reviewed methods which may be used to predict the behaviour of corrosion-resistant alloys from anodic and cathodic polarization curves obtained with a potentiostat. Figure 15, reproduced from Greene's paper, shows three different cases which may occur for a corroding metal which is capable of active-passive transitions (as were the steels of the present investigation in nitric acid). In this figure, the S-shaped curve is a theoretical anodic polarization curve. The lower branch of this curve - i.e. that branch upon which the points A and B fall - represents an anodic dissolution of the metal (expressed in terms of the electrical current produced by the dissolving ions) which increases in rate as the potential is made more noble, in this region. At potentials more noble than that at B, a maximum current density is reached, and the current density then begins to decrease as the potential is made increasingly noble. The maximum current density is termed the critical anodic current density I_c and the potential at the maximum is termed the primary passive potential E_{pp} . The values of both I_c and E_{pp} are important in predicting corrosion behaviour. The vertical part of the S-shaped curve defines the potential range within which the metal is passive, generally corroding at an insignificantly low rate.

The three parallel slanted lines in Figure 15 are theoretical cathodic polarization curves, representative of three different types of corrosion behaviour. In systems corresponding to Case 1, metals corrode at rates which may be relatively high, at active potentials corresponding to the point A. In the present investigation, this appears to correspond to the behaviour observed for the AISI Type 416 and 430F stainless steels in 10% hydrochloric acid and 10% sulphuric acid, because passivity was never observed in these solutions.

Case 2 is representative of active-passive systems in which metals may either corrode, at relatively high rates, at active potentials corresponding to the point B; or corrode at the relatively low rates, characteristic of the passive state, at more noble potentials corresponding to the point D. In the present research, this appears to correspond to the behaviour of steels 5180 and 5181 in 10% nitric acid. Prior to "conditioning", active corrosion potentials were observed ranging from -370 to -495 mV. Passive potentials were variable, but after the "conditioned" specimens had been standing for an hour or more in the unpolarized condition, the values usually lay in the range +200 to +350 mV. The observation of cathodic loops for these two steels in the polarization scans is further evidence, according to Greene⁽⁹⁾, that we are dealing with a system corresponding to Case 2.

Steels 5182 and 5183 always appeared to be passive in nitric acid solutions, which would indicate general correspondence to Case 3 of Figure 15. In keeping with this, cathodic loops were not exhibited in the potentiodynamic scans in 10% nitric acid. Passive corrosion potentials, as determined on unpolarized specimens prior to "conditioning", lay in the range +20 to +240 mV, corresponding to the point E on Figure 15.

However, the cathodic polarization curves of Figure 7 made it clear that differences in corrosion behaviour between steels 5182 and 5183, as contrasted with steels 5180 and 5181, could not be explained in terms of changes of the cathodic polarization curves from Case 2 to Case 3 of Figure 15. Indeed, the uranium additions appeared to shift the cathodic polarization curves in the opposite direction, i.e. from Case 2 towards Case 1. It appeared, therefore, that uranium additions must alter corrosion behaviour primarily by affecting anodic polarization behaviour, i.e. by decreasing the critical anodic current density I_c and/or shifting the primary passive potential E_{pp} so that the anodic maxima lay beneath the cathodic polarization curves, as in Case 3 of Figure 15.

To gain some information regarding values of I_c and E_{pp} for steels 5182 and 5183, weight-loss corrosion tests were carried out for the latter in nitrogenated 10% nitric acid at potentiostatically controlled potentials ranging from 0 to -200 mV. The results of these measurements indicated that E_{pp} was in the vicinity of -100 mV, and the dissolution current density at that potential was calculated to be about 0.08 mA/cm^2 . Bearing in mind that this potentiostatically obtained result cannot be compared directly with the potentiodynamic data of Figure 7, this appears to be a reasonable current density for a point which must be near to I_c , and indicates that the effect of uranium is principally to decrease I_c rather than to shift E_{pp} to some more active value.

It should be emphasized, finally, that changes in the anodic polarization behaviour of these steels, due to alloying with sufficient uranium, can be postulated to occur only in nitric acid solutions. No changes of any consequence were observed to be brought about by uranium additions in the non-oxidizing acids, i.e. 10% hydrochloric and 10% sulphuric acid, or in the oxidizing ferric chloride solution.

3. Metallographic Examination

The significant changes in the morphology of the sulphides, brought about by uranium alloying additions at U/S ratios of 3.5/1 or more (Figures 8-11), corresponded with striking reductions in the corrosion in 10% nitric acid (e.g. Table 2). These results pointed to a change in the chemical composition of the sulphides, from one which is attacked by nitric acid to one which is resistant. Etching of metallographic samples in 5% "Nital" (5% nitric acid in ethanol) and examination under the microscope did in fact show this difference of the respective sulphides in response to attack.

As yet, chemical identification of the various types of sulphides observed in the uranium-bearing steels has not been obtained. However, the controlling influence of the U/S ratio, pointed out previously, does suggest a uranium-sulphur combination. The first appearance of UFe_2 only after a

U/S ratio of about 7/1 is reached suggests that there may be an equal number of uranium and sulphur atoms in some forms of the sulphide, and in fact M. Kawabata et al.⁽¹¹⁾ have used X-ray analysis to demonstrate the presence of US and UOS in uranium-bearing resulphurized austenitic stainless steels. In preparing the monosulphide of uranium, Shalek⁽¹²⁾ observed UOS and UO_2 as impurities arising from oxygen contamination, and noted that UN, and possibly to some slight extent UO_2 , were soluble in US. A eutectic of UOS and US was also noted.

The detection under polarized light of both isotropic and anisotropic inclusions allows further speculation on the compounds of uranium which may be present. Material which exhibits isotropy is isometric in crystallographic structure and, conversely, anisometric substances exhibit anisotropy⁽¹³⁾. In the former category we can include US, UO_2 , UC and UN which are cubic, and in the latter, UOS, which is tetragonal, and the higher sulphides U_2S_3 and US_2 , which are orthorhombic⁽¹⁴⁾. In the present work, as noted previously, constituents were observed which were both isotropic and anisotropic, and thus the presence of compounds in both of the above groups is a possibility.

However, in considering the evidence in favour of a uranium-sulphur combination, the behaviour of the sulphides during hot rolling at temperatures in the range 1050-1200°C (1920-2190°F) is perhaps of greatest significance. In the usual resulphurized steels (e.g. AISI Types 416 and 430F) the sulphides are globular in the as-cast metal. However, they become plastic during hot rolling, and are consequently elongated to stringers such as those shown in Figures 8-11. In steels having U/S ratios of 3.5/1 or more, on the other hand, the sulphides remained globular during rolling, and thus must have had much higher melting points than the usual sulphides. The three uranium sulphides US, U_2S_3 , and US_2 fulfil this requirement, the lowest melting point of the three being 1850°C (3362°F), in the case of US_2 ⁽¹⁴⁾.

There is, therefore, much to suggest a definite uranium-sulphur reaction and substantiate the thermodynamic data of Figure 1. From the

variety of sulphides observed, however, a simple replacement of the (FeMnCr) sulphides with sulphides of uranium is probably not the case. It is more likely that complex combinations of both may occur, with the possibility that the oxysulphide (UOS) and the oxide (UO_2) may also be involved, considering uranium's high affinity for oxygen.

CONCLUSIONS AND FUTURE PROGRAM

The results of this investigation indicated that, by the use of uranium alloying additions, resulphurized free-machining chromium stainless steels can be produced that have the excellent resistance to nitric acid of chromium stainless steel of low sulphur content, such as AISI Type 430 stainless steel. Further work, however, would be required to establish this, as the present work was restricted to corrosion tests in nitric acid at room temperature. In three other corrosive media, namely H_2SO_4 , HCl and FeCl_3 solutions, uranium additions to the resulphurized steels were not significantly beneficial.

The effects noted in nitric acid were apparently due to a chemical combination of uranium with sulphur to form unidentified sulphides that were not only resistant to attack by nitric acid, but were also sufficiently high in melting point to resist deformation during rolling at temperatures in the range 1050-1200°C (1920-2190°F).

It has been decided to suspend further testing of uranium-bearing resulphurized steels until information on their machinability and other pertinent properties is available. A decision will then be made as to whether resumption of research is warranted, taking into account that the demand for Canadian uranium shows signs of increasing in the fairly near future.

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Technical Surveys. The chemical analyses were carried out by the Mineral Sciences Division. Some of the photographs were made by the Photographic Services and the drawings by the Drafting Services, both of the Physical Metallurgy Division.

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GJB:WC:(PES):KW

TABLE 1

Chemical Analyses of Steels

AISI Steel Type	Heat No.	C	Si	Mn	S	P	Cr	Al	N	Total U	Ratio, U/S
416	5107	0.08	0.26	1.06	0.13	0.008	13.55	0.03	0.024	-	0
	5108	0.06	0.26	1.06	0.15	0.012	13.75	0.04	0.025	0.06	0.4/1
	5109	0.08	0.25	1.01	0.16	0.013	13.65	0.04	0.024	0.69	4.3/1
	5110	0.08	0.24	1.00	0.15	0.013	13.55	0.04	0.022	1.05	7.0/1
416	5132	0.09	0.31	0.96	0.33	0.008	14.20	0.03	0.022	-	0
	5133	0.10	0.32	1.00	0.34	0.008	14.05	0.04	0.021	0.24	0.7/1
	5134	0.12	0.27	0.96	0.29	0.008	13.80	0.05	0.019	0.99	3.5/1
	5135	0.13	0.28	0.98	0.32	0.008	13.65	0.04	0.020	1.48	4.7/1
430F	5180	0.08	0.32	1.02	0.14	0.007	16.41	0.02	0.021	-	0
	5181	0.08	0.37	1.03	0.14	0.007	16.27	0.04	0.019	0.08	0.6/1
	5182	0.08	0.36	1.06	0.13	0.008	16.49	0.05	0.020	0.55	4.2/1
	5183	0.07	0.44	1.10	0.14	0.011	16.05	0.05	0.021	1.05	7.5/1
430F	5185	0.05	0.25	0.67	0.11	0.013	16.27	0.03	0.019	-	0
	5186	0.06	0.39	1.16	0.23	0.014	16.17	0.05	0.017	0.19	0.8/1
	5187	0.06	0.43	1.16	0.22	0.017	16.02	0.05	0.019	0.90	4.1/1
	5188	0.06	0.27	1.13	0.22	0.018	16.50	0.07	0.018	1.57	7.1/1
430	5555	0.13	0.96	1.14	0.019	0.020	17.29			-	-

TABLE 2

Corrosion in Various Solutions at Room Temperature

AISI Steel Type	Heat	% U	% S	Ratio U/S	Average Weight Loss in 4 hr, mg/cm ²			
					10% HCl	10% H ₂ SO ₄	10% FeCl ₃	10% HNO ₃
416	5107	-	0.13	0	23	36	53	270
	5108	0.06	0.15	0.4/1	20	30	52	260
	5109	0.69	0.16	4.3/1	18	30	49	0.23
	5110	1.05	0.15	7.0/1	20	32	51	0.10
416	5132	-	0.33	0	30	55	58	250
	5133	0.24	0.34	0.7/1	24	39	48	230
	5134	0.99	0.29	3.5/1	20	35	50	0.86
	5135	1.48	0.32	4.7/1	22	39	50	0.44
430F	5180	-	0.14	0	34	50	53	270
	5181	0.08	0.14	0.6/1	24	41	51	210
	5182	0.55	0.13	4.2/1	28	45	53	0.32
	5183	1.05	0.14	7.5/1	24	44	43	0.25
430F	5185	-	0.11	0	29	46	52	289
	5186	0.19	0.23	0.8/1	46	77	52	266
	5187	0.90	0.22	4.1/1	27	48	54	0.48
	5188	1.57	0.22	7.1/1	29	48	54	0.12
430	5555	-	0.019	0	8.7	0.08	28	0.13

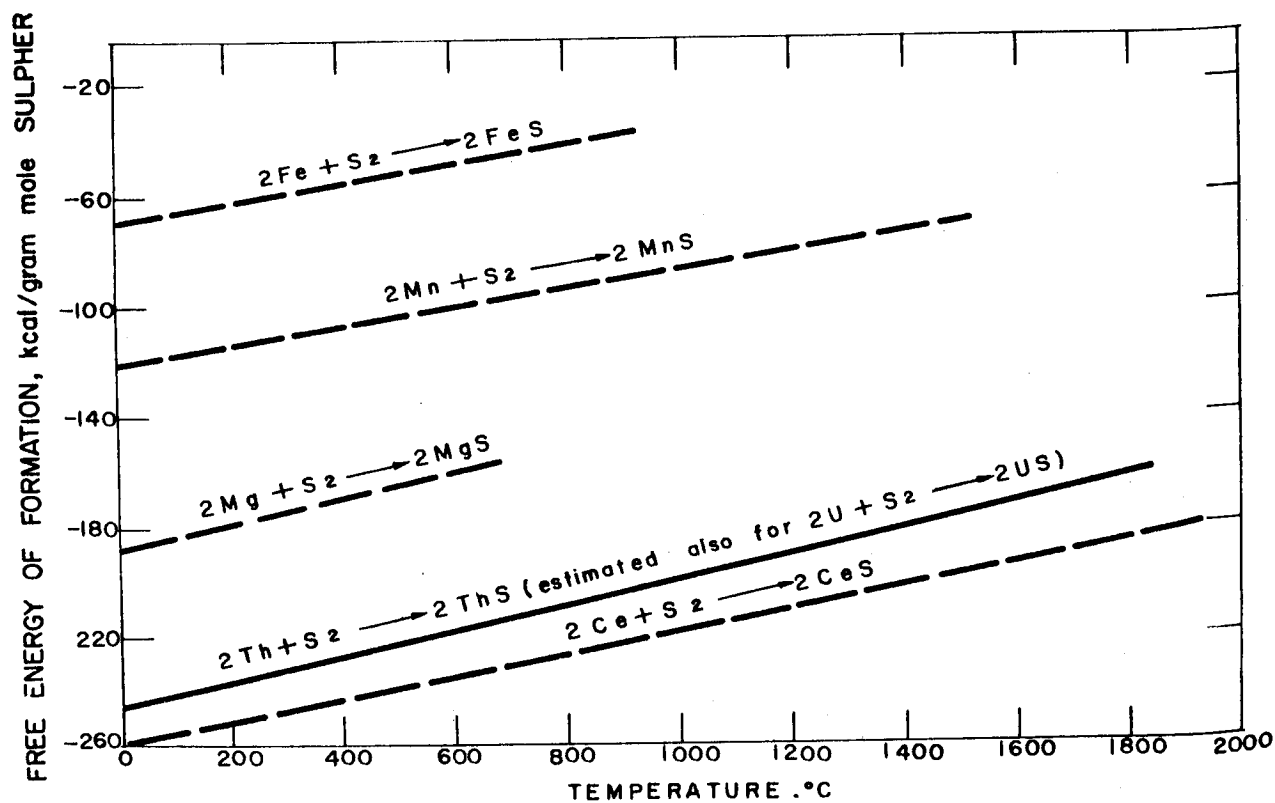
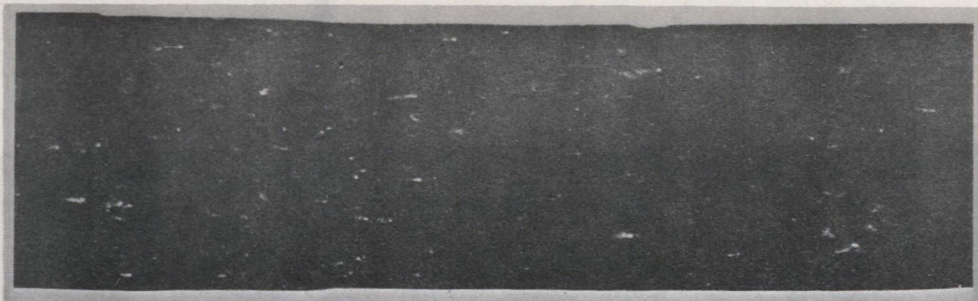
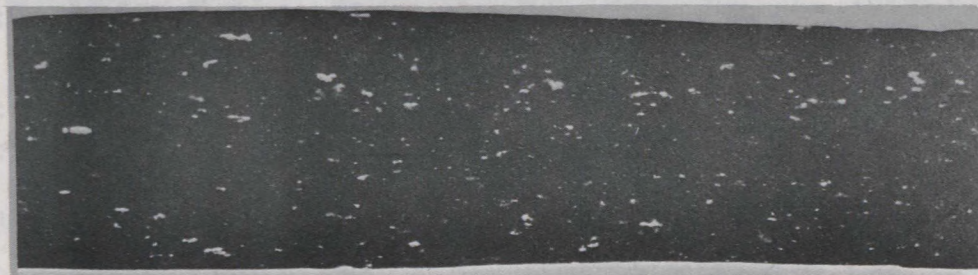


Figure 1. Relationship between the standard free energy of formation of sulphides and the temperature. The stability of sulphide tends to increase with the increase in negative values. (Reproduced from reference 2)



Heat 5133 U/S = 0.7/1



Heat 5134 U/S = 3.5/1

Figure 2. Photographic prints of autoradiographs of uranium-bearing AISI Type 416 stainless steels with 0.29-0.34% sulphur. The light areas are uranium-rich. About $\times \frac{1}{2}$.

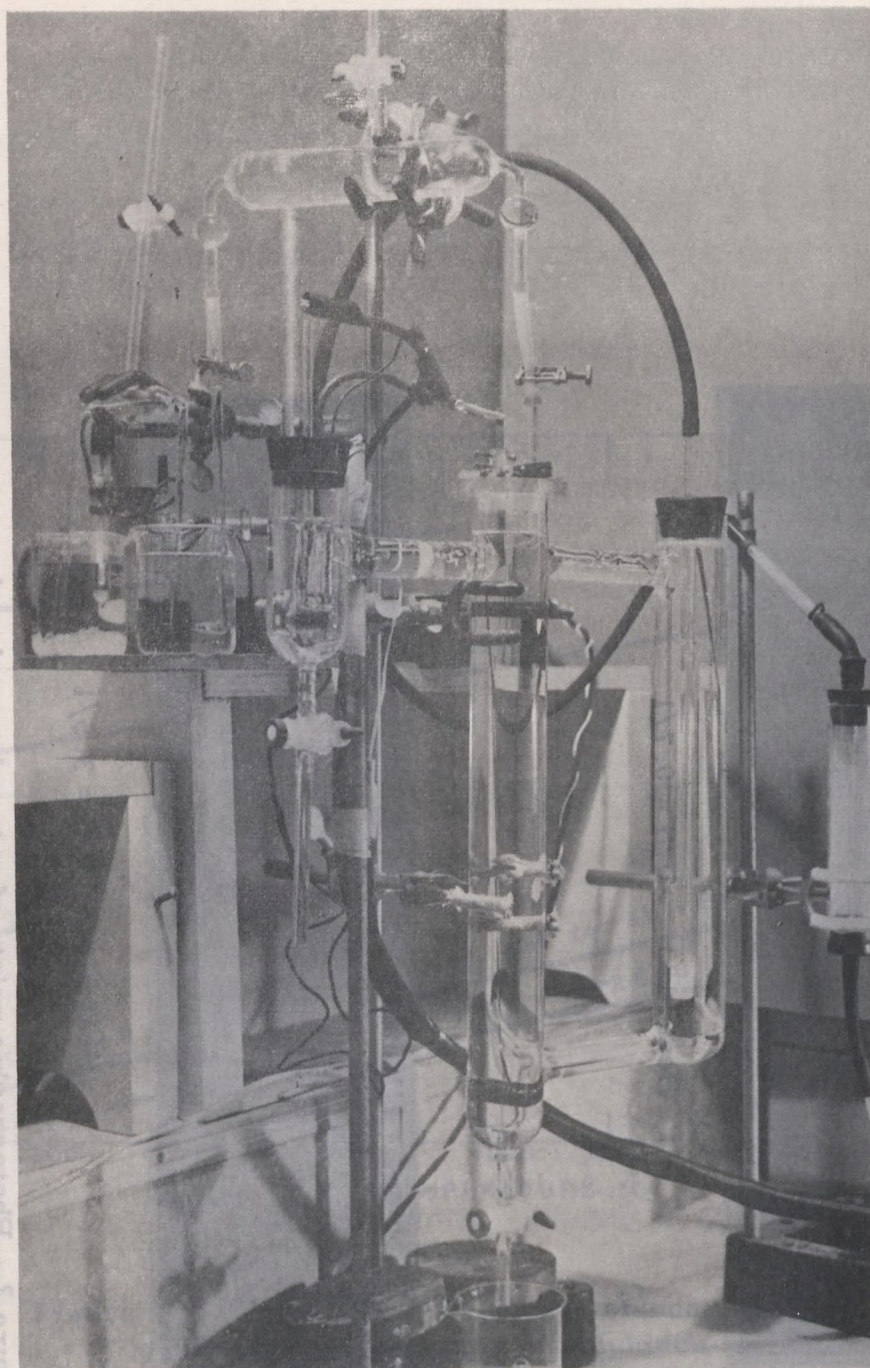


Figure 3. Test vessel used in the polarization measurements. The platinum auxiliary electrode is in the left-hand arm of the vessel, and the sintered glass diaphragm used to bubble nitrogen into the solutions is in the right-hand arm. The specimen and probe are in the centre arm. The probe is connected, through the salt bridges shown at the upper left, to the saturated calomel electrode.

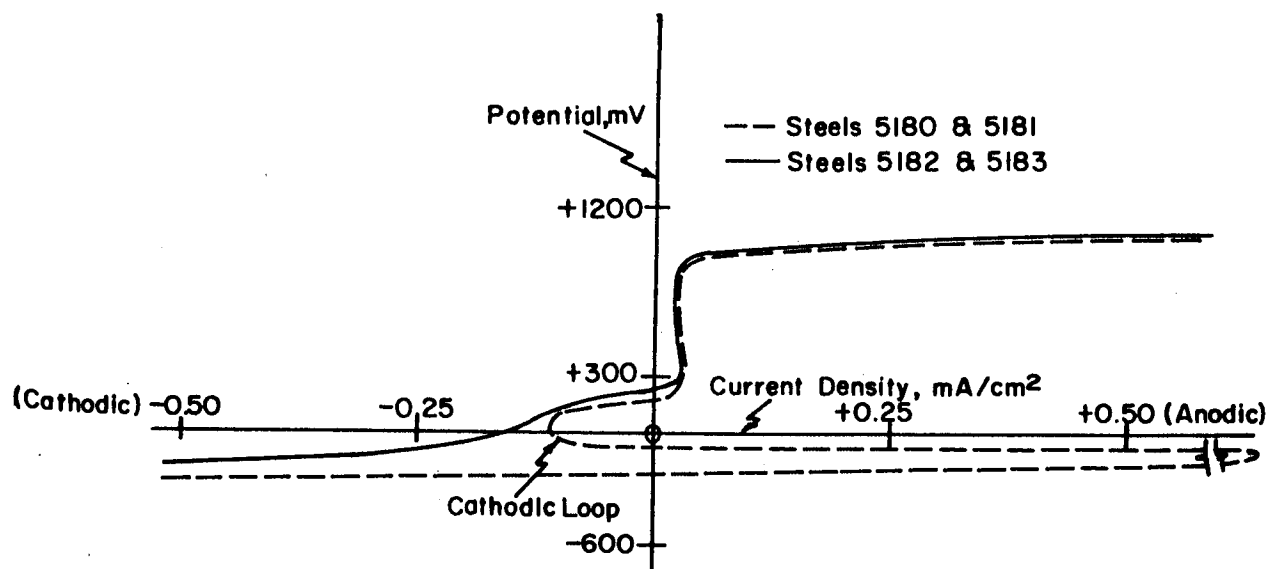


Figure 4. Model potentiodynamic scans, showing the main features differentiating Steels 5180 and 5181 from Steels 5182 and 5183. (For U/S ratios, see Table 1).

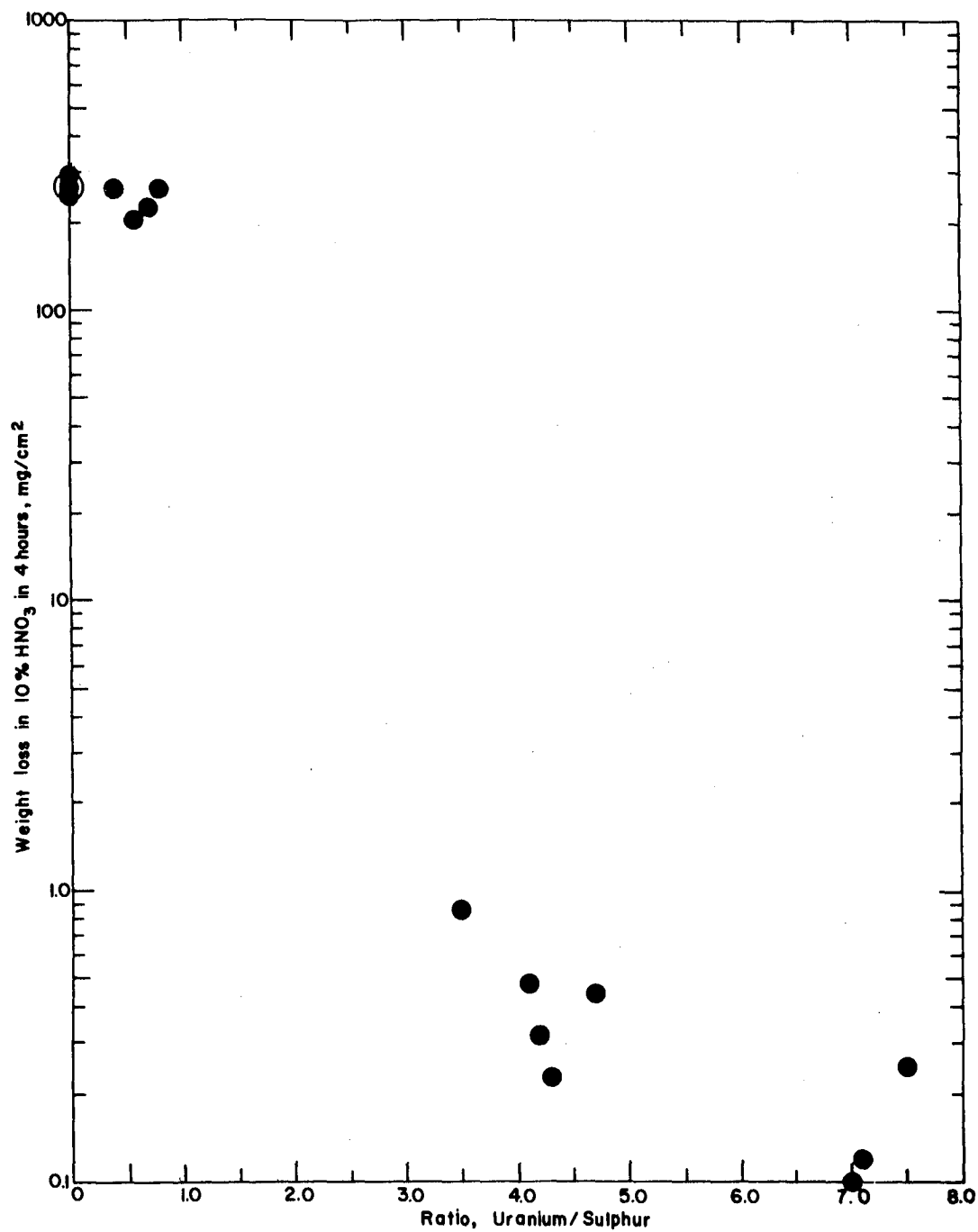


Figure 5. Corrosion of uranium-bearing AISI Type 416 and 430F stainless steels in 10% nitric acid solution.

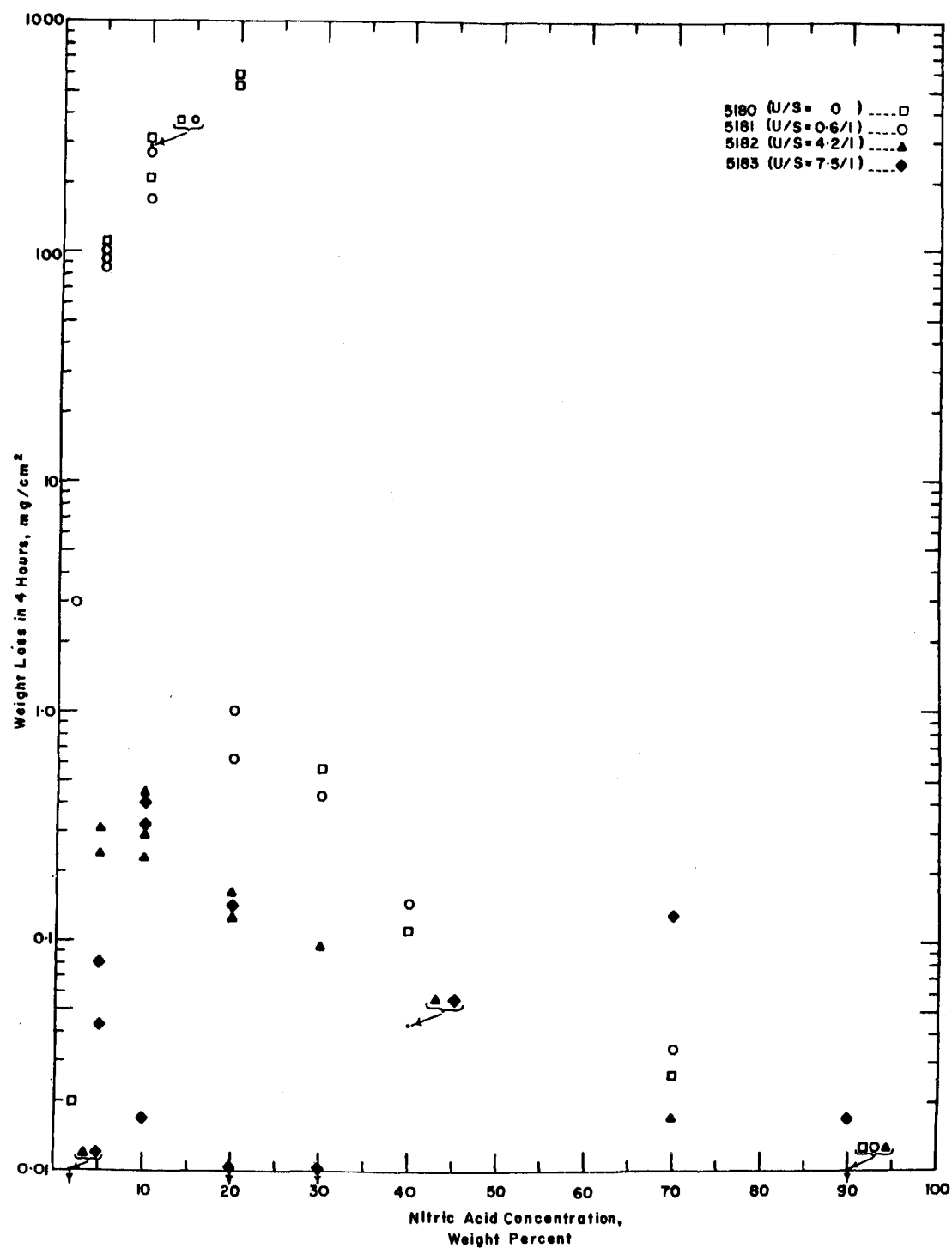


Figure 6. Corrosion of uranium-bearing AISI Type 430F stainless steels, containing 0.13-0.14% sulphur, in nitric acid solutions.

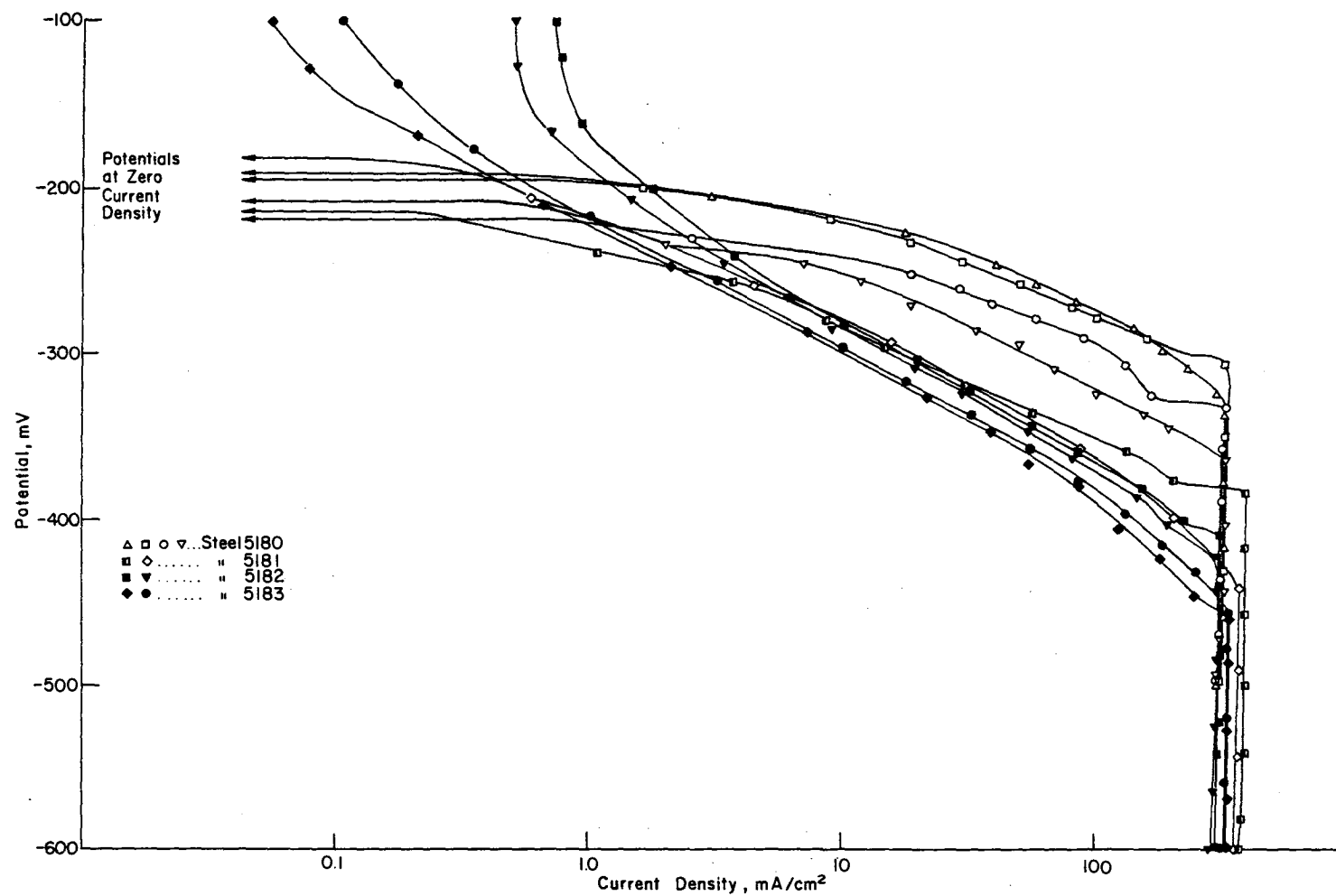


Figure 7. Cathodic polarization curves for AISI Type 430F stainless steels, containing 0.13-0.14% sulphur, in nitrogenated 10% nitric acid solution. For U/S ratios, see Table 1.



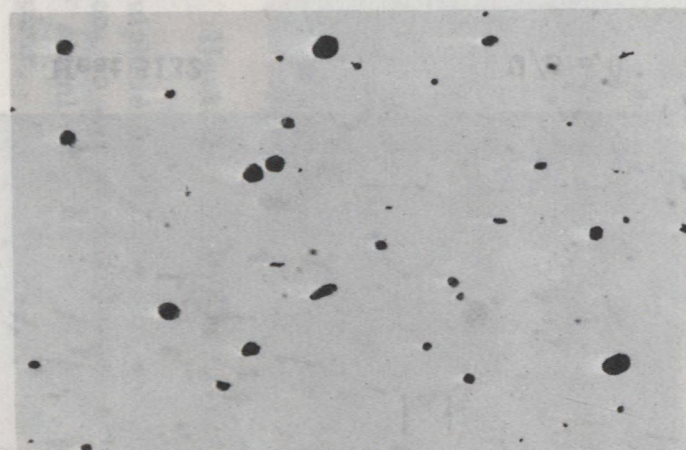
Heat 5107

U/S = 0



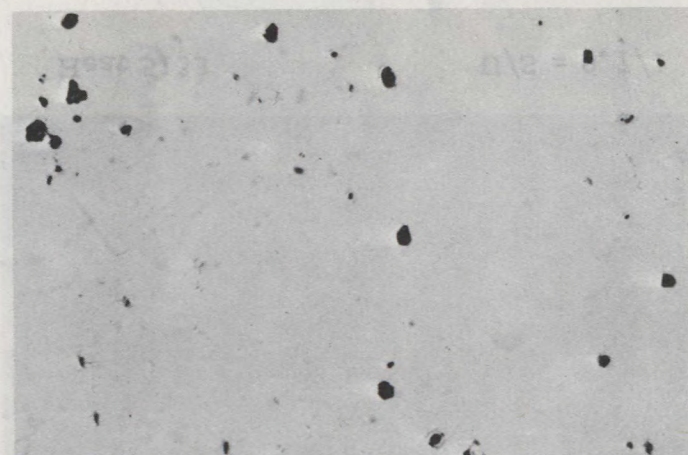
Heat 5108

U/S = 0.4/1



Heat 5109

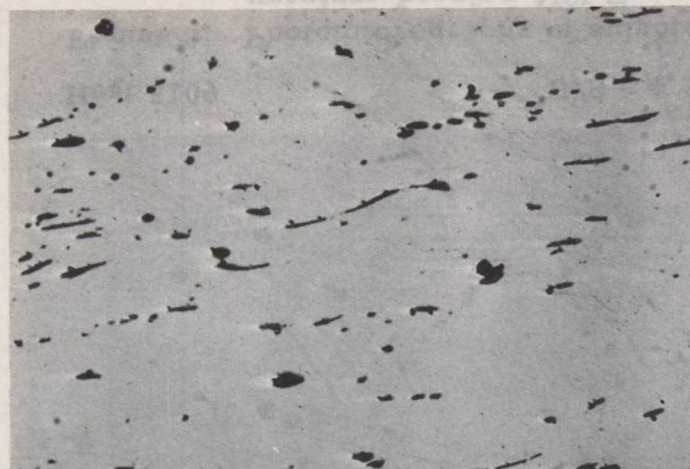
U/S = 4.3/1



Heat 5110

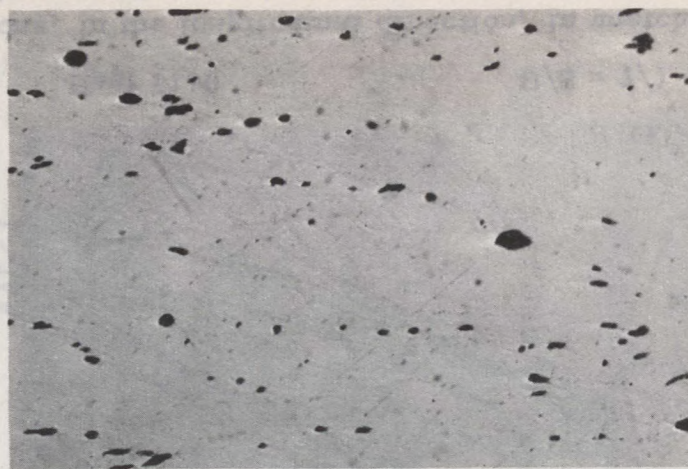
U/S = 7/1

Figure 8. Photomicrographs of sulphide inclusions, in the longitudinal direction, in unetched uranium-bearing AISI Type 416 stainless steels containing 0.13-0.16% sulphur. X250.



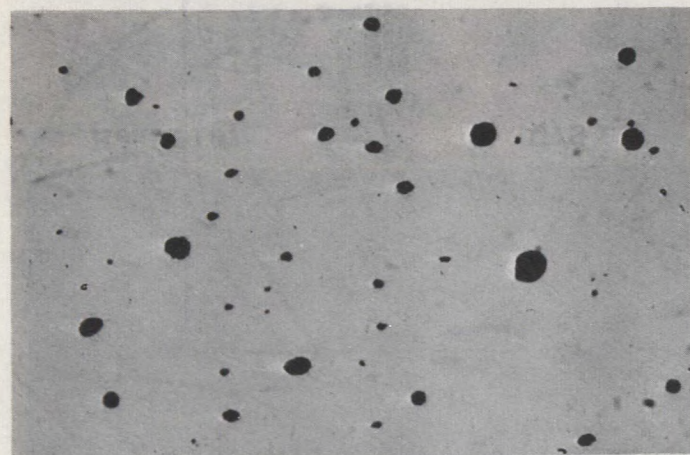
Heat 5132

U/S = 0



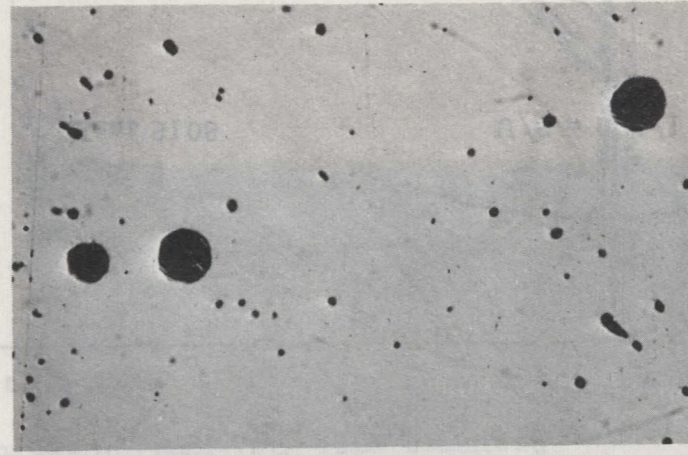
Heat 5133

U/S = 0.7/1



Heat 5134

U/S = 3.5/1



Heat 5135

U/S = 4.7/1

Figure 9. Photomicrographs of sulphide inclusions, in the longitudinal direction, in unetched uranium-bearing AISI Type 416 stainless steels containing 0.29-0.34% sulphur. X250.

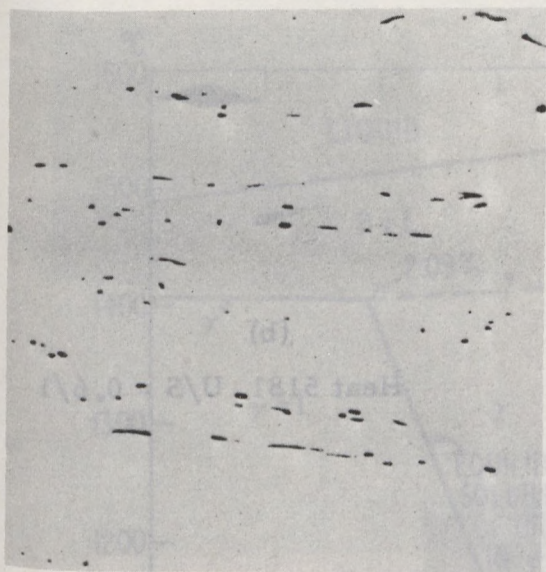
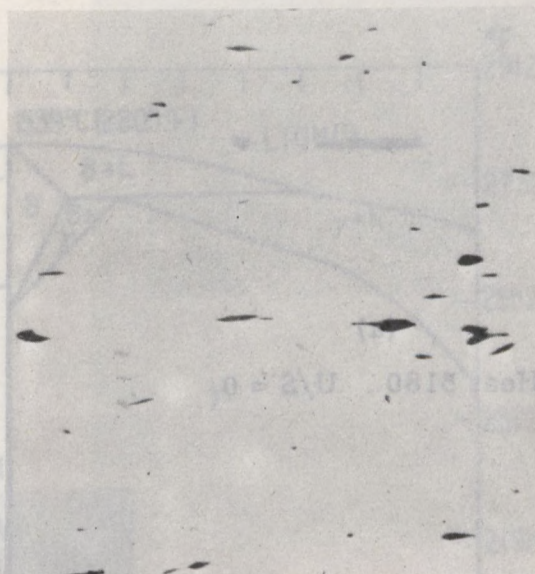
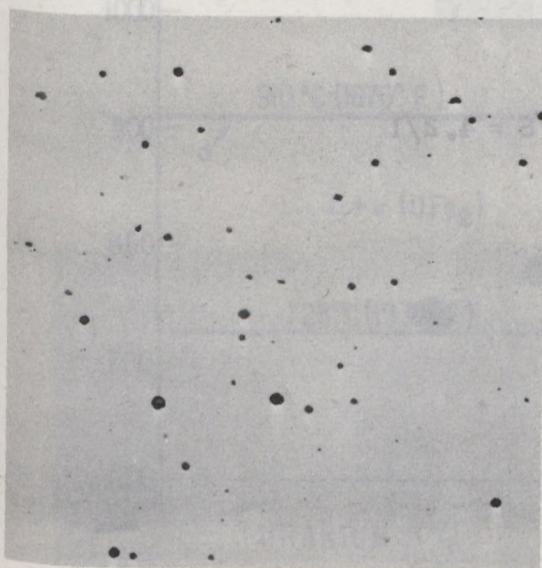
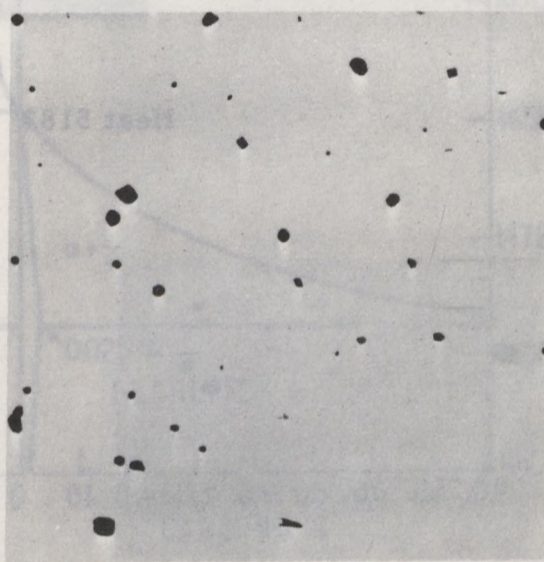
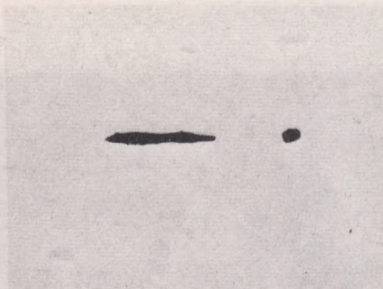
Heat 5180 $U/S = 0$ Heat 5181 $U/S = 0.6/1$ Heat 5182 $U/S = 4.2/1$ Heat 5183 $U/S = 7.5/1$

Figure 10. Photomicrographs of sulphide inclusions, in the longitudinal direction, in unetched uranium-bearing AISI Type 430F stainless steels containing 0.13-0.14% sulphur. X250.



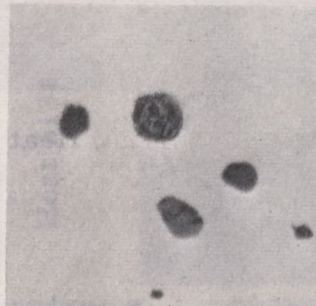
(a)

Heat 5180 U/S = 0



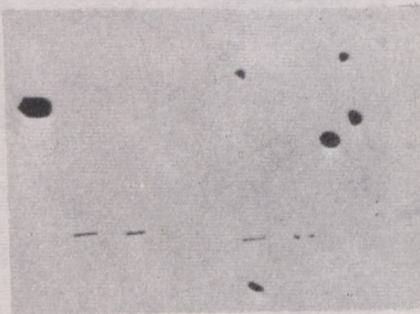
(b)

Heat 5181 U/S = 0.6/1



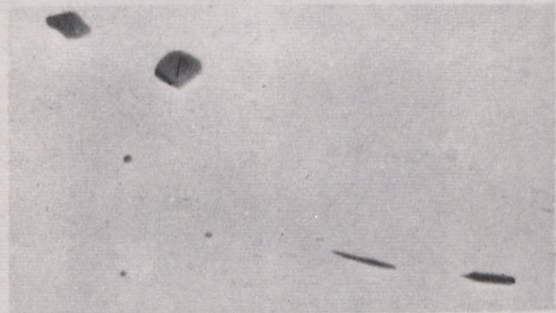
(c)

Heat 5182 U/S = 4.2/1



(d)

Heat 5183



(e)

U/S = 7.5/1

Figure 11. Photomicrographs of different types of sulphide inclusions, in the longitudinal direction, in unetched uranium-bearing AISI Type 430F stainless steels containing 0.13-0.14% sulphur. X1200.

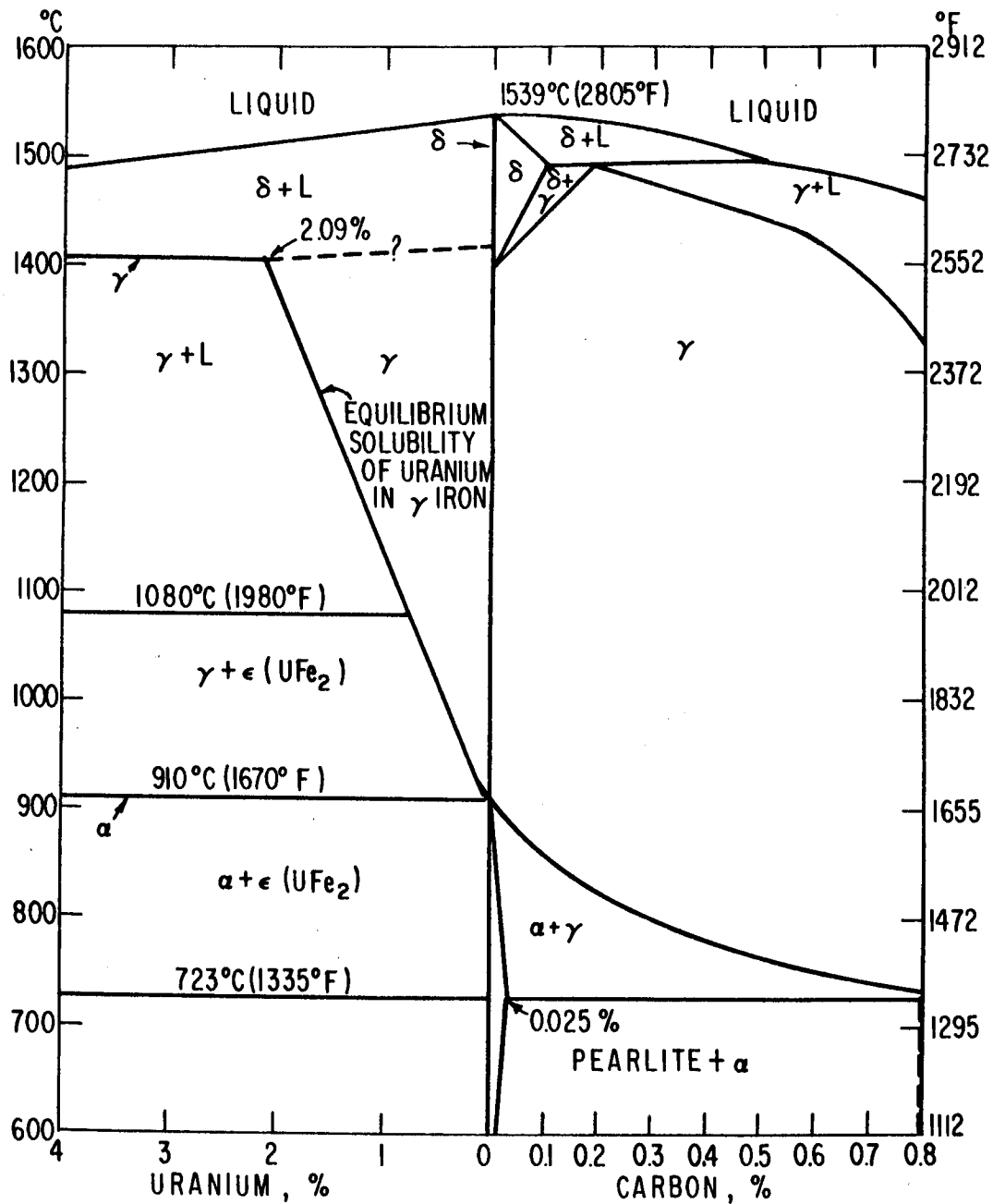
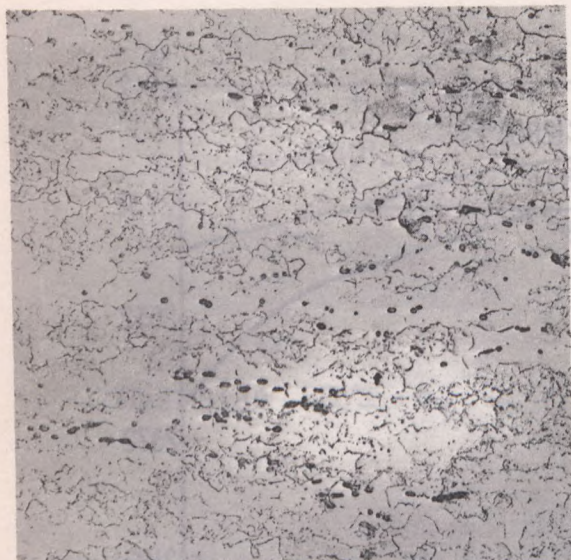
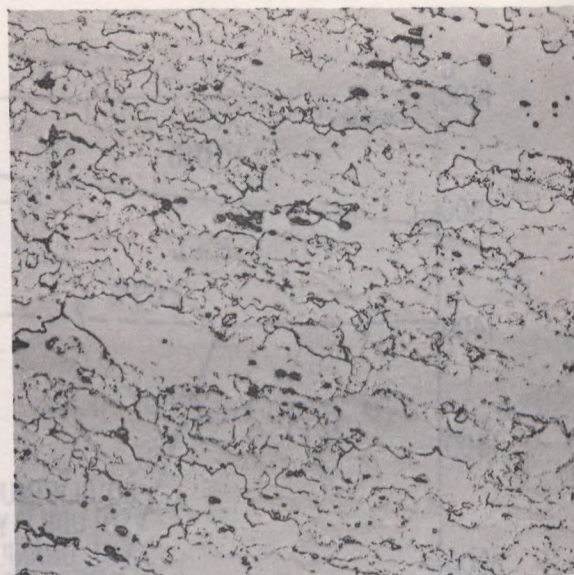


Figure 12. Iron-uranium and iron-carbon phase diagrams.
(Reproduced from reference 3).



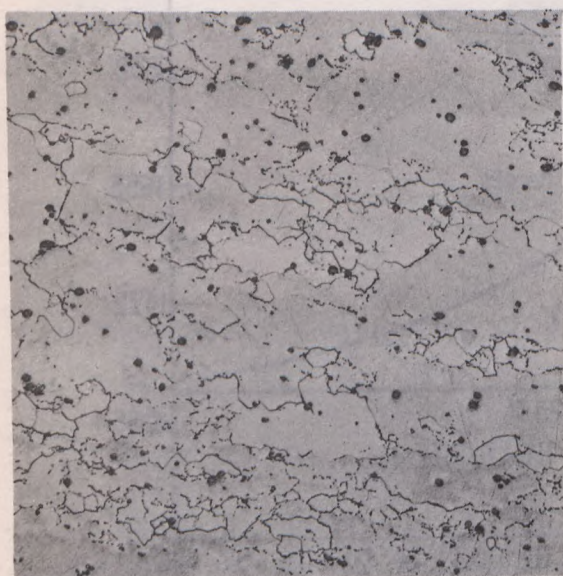
Heat 5107

U = 0



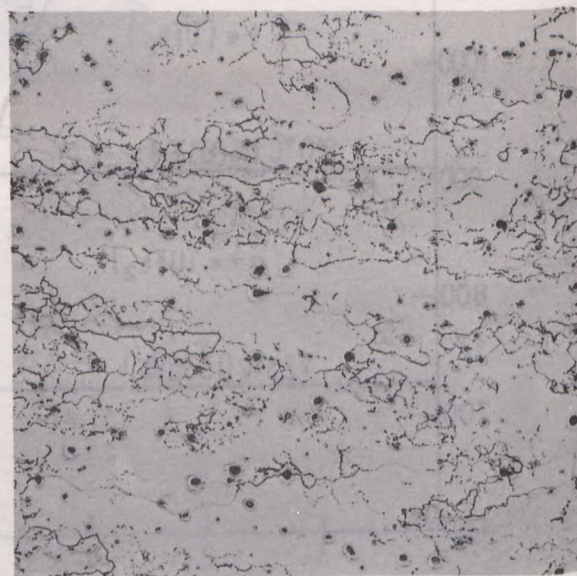
Heat 5108

U = 0.06%



Heat 5109

U = 0.69%

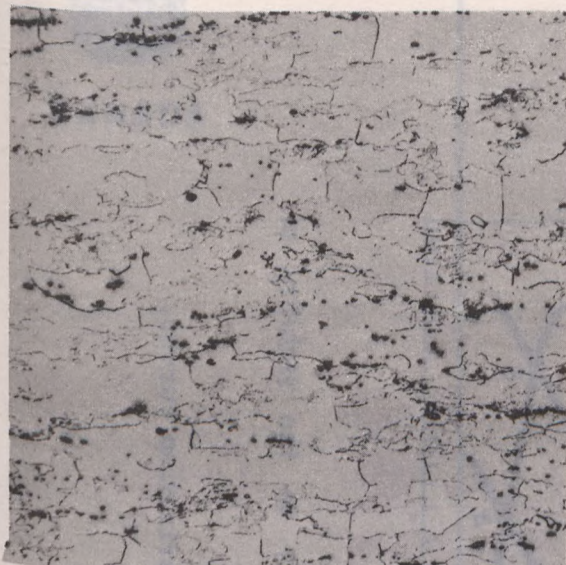


Heat 5110

U = 1.05%

Figure 13. Microstructures, in the longitudinal direction, of uranium-bearing AISI Type 416 stainless steels containing 0.13-0.16% sulphur. (Etched in Vilella's reagent) X100.

Figure 11. Photomicrographs of different types of sulphide inclusions, in the longitudinal direction, in unetched uranium-bearing AISI Type 430F stainless steels containing 0.13-0.14% sulphur. X1200.



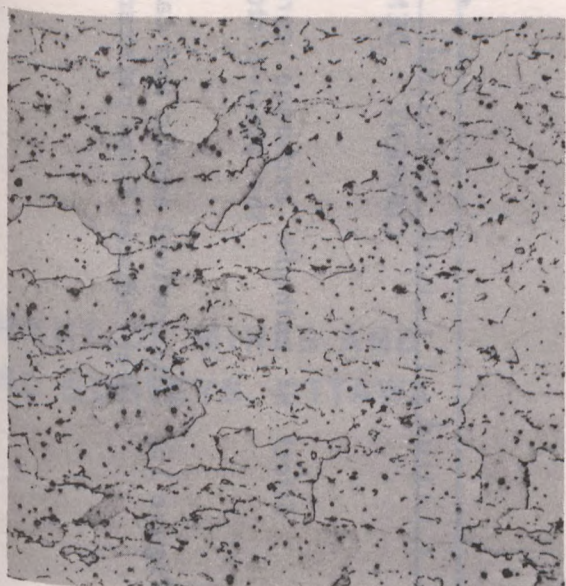
Heat 5180

U = 0



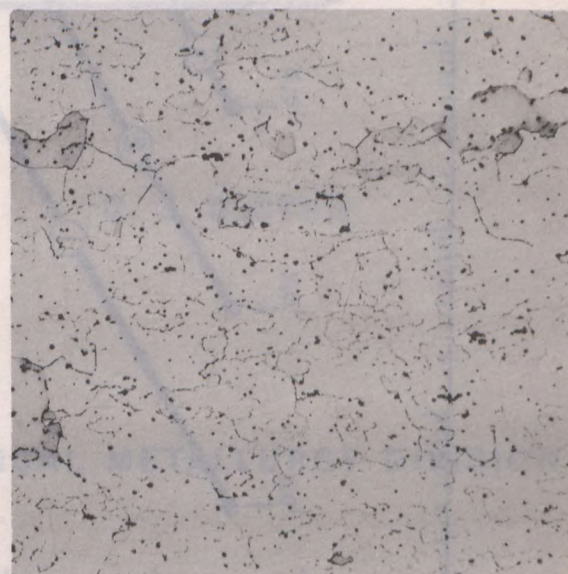
Heat 5181

U = 0.08%



Heat 5182

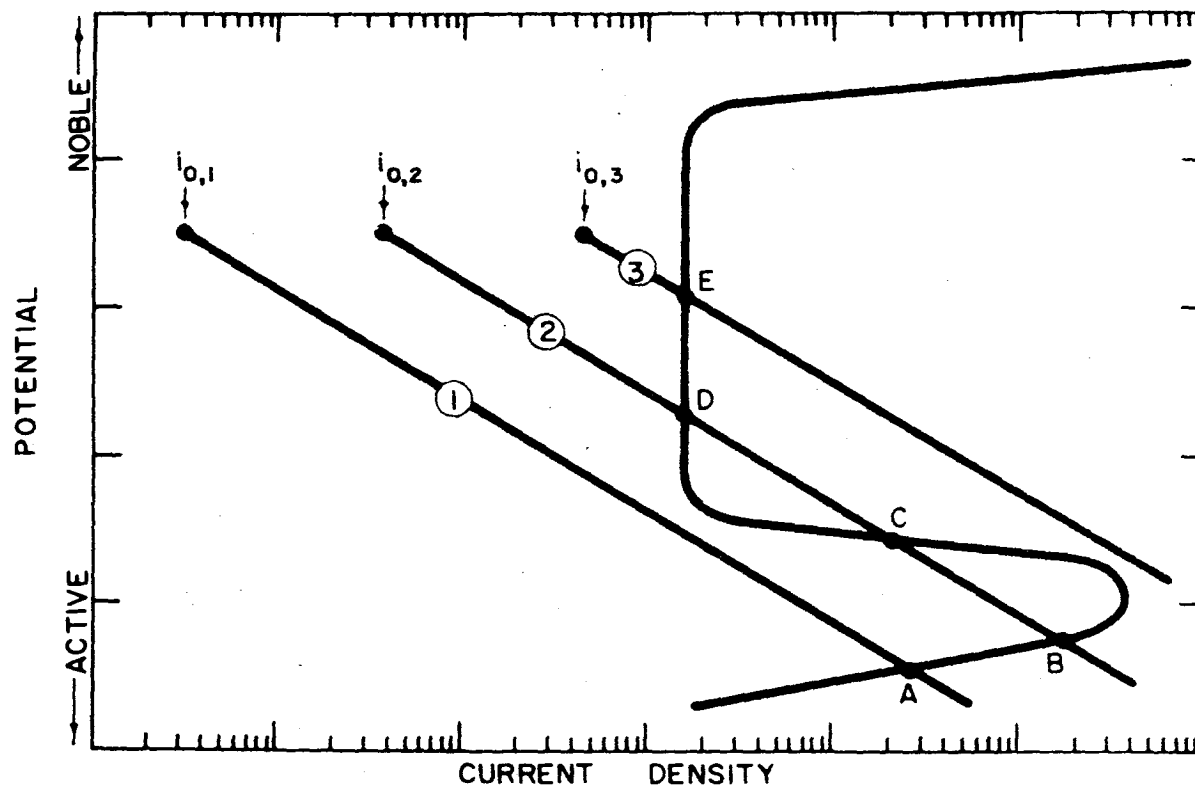
U = 0.55%



Heat 5183

U = 1.05%

Figure 14. Microstructures, in the longitudinal direction, of uranium-bearing AISI Type 430F stainless steels containing 0.13-0.14% sulphur. (Etched in Vilella's reagent) X100.



Effect of cathodic exchange current density on the stability of the passive state.

Figure 15. Theoretical anodic and cathodic polarization curves.
(Reproduced from reference 9)