Assessment of XM-19 as a Substitute for AISI 348 in ATR Service

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SUMMARY

It has been proposed that XM-19 alloy be considered as a possible replacement steel for AISI 348 in the construction of Advanced Test Reactor (ATR) capsules. AISI 348 works well, but is currently very difficult to obtain commercially.

The superior and desirable mechanical properties of XM-19 alloy have been proven in non-nuclear applications, but no data are available regarding its use in radiation environments. While most 300 series alloys will meet the conditions required in ATR, it cannot be confidently assumed that XM-19 can be substituted without prior qualification in a radiation test.

Compared to AISI 348, XM-19 will have an enhanced tendency for phase instabilities due to its higher levels of Ni and, especially, Si. However, transmutation of important elemental components in the highly thermalized ATR spectrum may have a very pronounced effect on its performance during irradiation.

Not only will strong transmutation of Mn to Fe reduce the ductility and strength advantages provided by the higher initial Mn content of XM-19, but the extensive loss of Mn will also release from solution much of the N upon which the higher strength of XM-19 depends. In addition, the combined influence of transmutation and Inverse Kirkendall processes may lead to gas-bubble-covered grain boundaries, producing a very fragile alloy after significant irradiation has accumulated. At present, there are no radiation data available to substantiate this possible scenario.

An alternate proposal is therefore advanced. Since the response of AISI 348 and 347 to radiation are expected to be relatively indistinguishable, the AISI 347 might serve as an acceptable replacement. While AISI 348 is usually chosen for nuclear service in order to reduce the overall radioactivity arising from relatively small amounts of highly transmutable elements such as cobalt, these elements have very little effect on the radiation performance of the steel. In the proposed application, however, the activity induced in this highly thermalized spectrum to large doses (10 to 50 dpa) will be overwhelmed by the activation arising from the major steel components: Fe, Cr, and especially Ni. The mechanical properties, irradiation creep, and void swelling behavior of the two steels should be practically indistinguishable.
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<td>AISI</td>
<td>American Iron and Steel Institute</td>
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<tr>
<td>ATR</td>
<td>Advanced Test Reactor</td>
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<tr>
<td>HFIR</td>
<td>High Flux Isotope Reactor</td>
</tr>
<tr>
<td>INL</td>
<td>Idaho National Laboratory</td>
</tr>
<tr>
<td>ITER</td>
<td>International Thermonuclear Experimental Reactor</td>
</tr>
<tr>
<td>LMR</td>
<td>Liquid Metal Reactor</td>
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<tr>
<td>LWR</td>
<td>Light Water Reactor</td>
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Assessment of XM-19 as a Substitute for AISI 348 in ATR Service

1. INTRODUCTION

The 300 series stainless steel AISI 348 has been used as a structural steel in the construction of experimental assemblies for the Advanced Test Reactor (ATR) located at Idaho National Laboratory (INL). However, due to difficulties in obtaining AISI 348, XM-19 or Nitronic 50 (also a 300 series stainless steel) is being considered as a replacement material for use in future assemblies. In the unirradiated condition, XM-19 has mechanical properties that are considered superior to those of AISI 348, properties that would allow less stringent tolerances in assembly design.

The designers of the International Thermonuclear Experimental Reactor (ITER), a fusion reactor, are also considering the use of XM-19 as a replacement for AISI 316, but only for maximum doses of 3–5 dpa (displacement per atom) and at temperatures of <120°C. The ITER spectrum is not as thermalized as that of ATR.

The ideal situation for assessing such a replacement scenario for ATR application would involve a side-by-side, one-on-one comparison of the response of these two steels to radiation exposure. Unfortunately, such data are not currently available. A relatively scarce amount of published data addressing lower exposure levels on AISI 348 are available, but the majority of data addressing higher doses generated in ATR are not openly published. Even more importantly, no published data are available on the response of XM-19 to radiation exposure. Although this steel has been used in various small components of Light Water Reactors (LWRs) within last decade, no examination of these components has been reported.

Since the composition of XM-19 differs significantly from that of AISI 348, there is a concern that its radiation performance will also differ significantly with respect to phase stability, gas generation rates, and retention of desirable properties.

Faced with the lack of XM-19 irradiation data, the suggested approach to assess its use as a replacement for AISI 348 is to answer the following questions:

- Since the radiation performance of the XM-19 steel is as important or more important than its starting properties, how can its potential performance under radiation be estimated?
- Is the anticipated radiation performance specific to the neutron flux-spectra characteristic of ATR?
- If the uncertainties associated with XM-19 preclude its confident use, are there other better qualified candidates such as 347 and 316 steels, which have much larger published data bases?
- Is it possible to gain new data on the radiation performance of XM-19 in a relatively short time?

This report answers these questions by assessing the potential of using XM-19 as a substitute for AISI 348 in ATR service. Other 300 series stainless steels are also considered in this study.
2. APPROACH

The following actions were taken during this assessment:

1. Reviewed the operating environment and target exposures envisioned for ATR application.
2. Reviewed previously unpublished reports supplied by INL on the radiation response of AISI 348 in ATR.
3. Determined the compositional and metallurgical origins of the superior performance of XM-19 in non-nuclear applications.
4. Using INL-supplied flux-spectra, calculated the anticipated transmutation of XM-19 to ascertain if the compositional origins of the desirable properties might be strongly changed.
5. Reviewed the interaction of compositional and environmental conditions to assess the potential for phase instabilities that might adversely impact material performance.
6. Based on the above actions, provided suggestions on further efforts involving XM-19 or other candidate steels.

The following exposure conditions relevant to this study were supplied by INL:

- Maximum fluence limit: \(4 \times 10^{22} \text{n/cm}^2\), \(E>1\text{MeV}\)
- Temperature Range: 240 to 930°F, with an in-core average of <800°F and an in-core maximum wall temperature of 870°F.

For the purposes of this study, this translates roughly into boundaries of 0 to 70 dpa and 115 to 466°C. These are high doses for the steels under consideration in this report, but relatively low temperatures with respect to potential phase instabilities, especially those of the intermetallic type. Radiation-stable phases usually predominate in this temperature range, with gamma prime competing with G-phase. The latter phase is promoted by higher levels of Mn, Cr, and small amounts of Nb and V and has been observed in AISI 348 irradiated in ATR.

The flux-spectral characteristics supplied by INL were used to determine the dpa levels and the transmutation rates. The neutron exposures and the derived transmutation rates are provided in the attached spread sheet.

Based on INL-supplied flux-spectra, \(1 \times 10^{22} \text{n/cm}^2\) (\(E>1.0\text{MeV}\)) = 17.5 dpa.

Fluence >0.1 MeV is 28.8% of the total.

Fluence >1.0 MeV is 14.4% of the total.

The calculations performed in this study were based on an assumed total flux of 1.00E15 n/cm²/s, but given the relatively long half-lives of the relevant transmutants, the results would not change if another flux was employed.

3. Comparison of AISI 347/348 with other 300 Series Stainless Steels

As mentioned in the introduction, open literature data on the irradiation performance of AISI 348 is limited, with most data at relatively low exposures compared to the exposures envisaged in the current effort.\(^{1,2,3}\) There are, however, somewhat more published data on AISI 347, reaching both lower and higher exposures.\(^{5,6,7}\)
The perceived primary advantage of AISI 348 stainless steel in the nuclear community has been its lower activation due to lower levels of easily activated, long-lived impurities, especially Co. However, after service in highly thermalized neutron spectra these steels are so radioactive that Co reduction does not really improve post-irradiation safety and handling.

Based on the results of examination of the very slight compositional differences between AISI 347 and AISI 348 and the accumulated experience on stainless steels leads to the conclusion that, with respect to void swelling, irradiation creep, and mechanical stability, the two steels are essentially identical.\textsuperscript{8,9} AISI 347 behaves well under irradiation without any greatly significant differences from other 300 series steels, especially AISI 316, which is often employed in LWR and liquid metal reactor (LMR) nuclear environments. These three steels also are less prone than AISI 304 to form martensite and radiation-induced ferrite during deformation.

All of the 300 series steels in the temperature range of current interest are very prone to radiation-induced segregation to sinks, giving rise to phase instabilities that produce radiation-stable Ni and Si-rich precipitates such as gamma-prime and G-phase, in addition to various compositionally modified carbide phases.\textsuperscript{9} Ni is the major source of both helium and hydrogen generation via transmutation at relatively high exposures, especially in highly thermalized spectra such as those found in ATR and HFIR.\textsuperscript{10,11,12}

In the 300 series steels operating in highly thermalized neutron spectra characteristic of ATR, the Mn will strongly transmute to Fe.\textsuperscript{13} Normally, this transformation is not a concern in 300 series alloys since the Mn level is usually low, at 1–2\%, and its loss does not severely impact the stability of the austenite phase.

A second-order consequence affects the stability of MnS precipitates in older, not-so-pure heats of steel. Since very stable MnS precipitates are transformed into not so stable FeS, this transformation releases previously sequestered S and detrimental halides (F, Cl) into the matrix. This process has been proposed as one contribution to irradiation-assisted stress corrosion cracking observed in 300 series steels in water-cooled reactors.\textsuperscript{14,15}

The stability of MnS precipitates is also strongly influenced by a phenomenon designated the Inverse-Kirkendall effect.\textsuperscript{16} This is a radiation-driven process that strongly segregates elements which diffuse by a vacancy exchange mechanism. Slower-diffusing species segregate by default at all sink surfaces (grain boundaries, dislocations, Frank loops, precipitates) with faster-diffusing species being depleted at the sink surface. In a Fe-Cr-Ni-Mn base alloy, Mn is the fastest diffusing species followed by Cr and Fe, with Ni being the slowest. This provides another driving force to dissolve MnS by pumping Mn away from MnS precipitates that are also becoming rich in Fe via transmutation.\textsuperscript{14,15}

In the modern production of steels, the concentration of S and various halides are usually much lower, so the problem of MnS dissolution is not as pronounced. As will be shown later, the Inverse Kirkendall effect strongly changes the composition at grain boundaries with some potential consequences of concern to the current study.

There is additional transmutation of Cr to produce small amounts of V, which leads to a modification of carbide composition, but no identifiable metallurgical consequences or property changes have been observed, especially in alloys already containing measurable amounts of V.\textsuperscript{13} The percentage loss of Cr from the matrix is relatively small and insignificant; therefore it probably can be ignored.

In general, however, none of the 300 series steels experience severe problems arising from transmutation other than the possibility of higher void swelling levels in response to the large He and H generation in highly thermalized neutron spectra, especially at the higher boundaries of the dpa and temperature range defined as relevant to this study.\textsuperscript{9}
As explained in the next several sections, it cannot be confidently asserted that XM-19 will also be relatively unaffected by transmutation, since its desirable properties arise from its rather unique composition compared to that of other 300 series steels.

### 3.1 Advantages of XM-19 (Nitronic 50) Stainless Steel

XM-19 has superior features that make it attractive for non-nuclear applications, including superior corrosion resistance, higher yield strength and ductility, and the ability to absorb a very large amount of deformation over a wide range of temperatures without forming martensite or magnetic phases.

The compositional specifications of XM-19 allow some range of variation. In this study the assumed composition was Fe-22Cr-5Mn-13Ni-3Mo-0.3Nb-0.4N-1.0Si-0.3V-0.04P-0.06C. However, variations within the specification ranges will not substantially alter the conclusions of the report.

While easily-dissolved interstitial impurity carbon is normally viewed as being an effective solid-solution strengthening agent, there are practical limitations on the carbon level arising from considerations of phase stability and grain boundary sensitization. Compared to various 300 series steels the most important compositional feature of XM-19 is the relatively high level of nitrogen.

Nitrogen is a much more effective interstitial impurity in providing structural strength, but it is relatively insoluble compared to carbon, especially in nickel-containing alloys. In 316 LN, for example, the N level is generally lower by a factor of 3–4 compared to that of XM-19, but has induced measurable increases in strength.

Excess undissolved nitrogen in steel will lead to cavities and undesirable precipitates such as Cr₂N during fabrication. However, there is a high probability that undissolved N will also promote earlier and larger amounts of void swelling during irradiation by acting as a stabilizing gas for void embryos, similar to the role exerted by He, H, and O.

Ni, P and C all tend to reduce nitrogen solubility in austenite, while Cr, Mo, Si and V and Mn act to increase the solubility of nitrogen. Cr and Mn are the major contributors to nitrogen solubility, however, and XM-19 has higher than ordinary amounts of both elements.

Mn also promotes austenite stability, aids in flow during casting, and sequesters S and halide impurities, among other benefits. Very importantly, however, Mn strongly increases the stacking fault energy and thereby promotes work hardening, leading to enhanced ductility. There are practical limitations to the addition of manganese, with 5 to 6% selected as optimum for this application.

Both Nb and V will act to sequester C in various carbide phases, a process that usually delays the onset of nickel silicide precipitation.

Considering the foregoing discussion, the major compositional attributes of XM-19 that differ from those of 300 series alloys are associated with synergistic strengthening by dissolved Ni and work hardening by Mn. The prospect of maintaining these attributes are the focus of the following discussion.

#### 3.1.1 Influence of Radiation on Properties of XM-19

Before considering the influence of transmutation some statements can be made concerning the potential radiation performance of XM-19. It should be noted that the Si level is twice that of most 300 series steels used in reactor service (~1.0 vs. ~0.5%). This increased silicon level will lead to an initial delay in the onset of swelling but will strongly foster enhanced formation of nickel silicide phases, especially gamma prime, in the temperature range of interest.18,19,20
The deliberate addition of V will tend to diminish somewhat the impact of Cr to V transmutation, and the levels of P and C are just about right to restrain the onset of swelling in the relevant temperature range.\(^9\) The use of Nb and V to form matrix carbide precipitates also works to minimize the deleterious influence of chromium carbides forming on and sensitizing grain boundaries.\(^21\)

While the 13% nickel level is higher than that of AISI 348 at 11%, the increased generation of He and H will increase in direct proportion of 13/11. Ordinarily, this increase would not be considered significant, adding incrementally (~18%) to already rather large gas generation rates. For the purposes of this study, however, it is not thought to be prudent to overlook this enhanced gas generation.

The increased amount of Ni, working with the larger Si level, will induce a much greater level of radiation-induced phase instability. Therefore, before any solid transmutation is considered, it is already clear that this alloy will be somewhat more immune to problems associated with carbide formation on boundaries, but will be more vulnerable to the impact of nickel silicide phases.

### 3.1.2 Influence of Transmutation on the Composition of XM-19

As shown in Figure 1, the transmutation of XM-19 will produce a significant amount of both helium and hydrogen in ATR. Most of these gases are generated by Ni, initially by high energy neutron reactions. But the isotopic balance of Ni is changed strongly by thermal neutrons, producing the long-lived radioactive isotope Ni-59, which in turn leads to very large increases in the generation rate of both gases. The \(^{14}\)N (n, p) \(^{14}\)C reaction also generates H, but this reaction is not a primary contributor compared to the various Ni reactions. Note that H is initially formed at higher rates (see Figure 1), but as Ni-59 is formed from Ni-58 in this highly thermalized neutron spectrum that He is produced at higher rates than H.

![Figure 1. Generation of high levels of helium and hydrogen in XM-19 as a function of neutron exposure in ATR.](image)

Helium in XM-19 reached ~4,300 appm at the maximum fluence limit of \(4 \times 10^{22} \text{ n/cm}^2, E >1 \text{ MeV}\) and generated hydrogen reaches ~2,200 appm. At these levels, the alloy is becoming a gas-modified alloy whose properties need to be carefully assessed.

Helium is relatively immobile and trapped in the alloy but the hydrogen is more diffusive. While conventional wisdom dictates that the hydrogen will diffuse out of the steel, it was recently shown that the hydrogen is also trapped when there is a high density of helium-nucleated bubbles or voids.\(^{22}\) Even more importantly, in a water-cooled reactor there are many other sources of hydrogen and this non-transmutant hydrogen is also trapped at very high levels in cavities.\(^{22}\) In a publication by Thomas and Beeston,\(^{23}\) AISI 348 at 11% Ni was shown to develop very high densities of voids or bubbles after irradiation to 33 to 39 dpa at 350ºC in ATR. At that time it was assumed that the bubbles were pressurized only by helium.
When compared to AISI 348, however, the gas generation issue in XM-19 is slightly greater than already experienced in ATR operation, being on the order of an 18% increase. Ordinarily this would be considered to be of only second-order influence, but perhaps not in this case.

There are relatively small to insignificant transmutation-induced changes in the contents of Mo, Si, Nb, Cr, N, and C. These changes are not thought to be significant in assessing the impact on phase stability, mechanical properties, irradiation creep, and void swelling of XM-19 alloy. Fe changes the most, rising from 55 to 59% at $5 \times 10^{22} \text{E} > 1.0 \text{MeV}$ as a result of Mn transmutation. V increases from 0.3 to 0.7% over this interval, and there may or may not be consequences on phase stability as a result.

However, the issue of Mn transmutation cannot be so easily dismissed. Note in Figure 2 that Mn decreases strongly with accumulated exposure, reaching a loss of ~75% of the original at the maximum target exposure of $4 \times 10^{22} \text{n/cm}^2$, $E > 1 \text{MeV}$. The impact of such a large decrease in Mn on nitrogen solubility cannot be confidently ignored.

It seems reasonable to assume that a continually increasing supersaturation of nitrogen with unpredictable consequences on alloy phase stability and dimensional stability will develop. In particular, increased dimensional instability may arise from acceleration of void swelling as a result of the combined action of He, H, and N to pressurize radiation-driven cavities.

In addition there might be a compounding of this phenomenon arising from the Inverse Kirkendall effect discussed earlier. At grain boundaries especially, it has been demonstrated that Mn and then Cr will be strongly depleted with primarily Ni increasing at the boundary to make up the difference.\textsuperscript{24,25,26,27,28,29,30} In a Fe-Cr-Mn alloy without Ni, grain boundaries quickly turn to ferrite as Mn moves away. Increasing Ni at the boundary via the Inverse Kirkendall effect will act to further drive N from solution in the vicinity of the boundary. Furthermore, increasing Ni will also lead to higher local generation rates of He and H at the boundary.

It is conceivable that the combined effects of Mn reduction via transmutation and Inverse Kirkendall, both acting to release N, when combined with increased He and H, will act to coat the grain boundaries with a near-continuous film of gas bubbles. Such a development is not unprecedented and would severely weaken the alloy during deformation. In this context the 18% increase in He and H generation rates might be a significant contributor to alloy degradation.

![Figure 2. Decline in Mn content in XM-19 with accumulated neutron exposure in ATR.](image-url)
An example of such matrix development of gas-filled cavities and especially grain bubble boundary coating in an ordinary 300 series alloy without Ni addition is shown in Figure 3.\textsuperscript{31} Note that these micrographs were taken in a specimen irradiated at 70 dpa and 350\textdegree C, almost the exact irradiation condition specified as the upper limit of the current study, but here the nickel level and thermal neutron flux are lower than the XM-19 case and there is no nitrogen. The component from which this specimen was derived was showing a very high level of intergranular failure and contained high amounts of H and He.\textsuperscript{32} Hydrogen on grain boundaries is well known to not be conducive to continued integrity of grain boundaries during deformation.

Figure 3. Gas-filled bubbles observed by electron microscopy in cold-worked 316 stainless steel after irradiation in a commercial PWR to \textasciitilde 70 dpa at 350\textdegree C.\textsuperscript{31}
4. CONCLUSIONS AND RECOMMENDATIONS

While most 300 series alloys will meet the required ATR conditions as well as AISI 348 has served, it cannot be confidently assumed that XM-19 can be substituted without prior qualification in a radiation test. Not only will strong transmutation of Mn to Fe reduce the ductility and strength advantages provided by the higher initial Mn content of XM-19, the extensive loss of Mn will also release from solution much of the N upon which the higher strength of XM-19 depends. In addition, the combined influence of the transmutation and Inverse Kirkendall processes may lead to gas-bubble-covered grain boundaries, producing a very fragile alloy after significant irradiation has been accumulated. While this scenario is somewhat speculative, there are no data to refute the possibility and it should be investigated.

However, rather than use XM-19 to replace hard to obtain AISI 348, it is recommended that serious consideration be given to the use of AISI 347 as a substitute for AISI 348. These alloys are essentially indistinguishable with respect to void swelling, irradiation creep, and mechanical property changes. Whereas AISI 348 is usually chosen for nuclear service in order to reduce the overall radioactivation arising from relatively small amounts of highly transmutable elements such as Co, these elements have very little effect on the radiation performance of the steel. In the proposed application, however, the activity induced in this highly thermalized spectrum to large doses (10 to 50 dpa) will be overwhelmed by the activation arising from the major steel components Fe, Cr, and especially Ni. The mechanical properties, irradiation creep, and void swelling behavior of the two steels should be practically indistinguishable.

It is also recommended that XM-19 be included in ATR or another thermal reactor to assess the validity of the scenario advanced in this assessment. The amount of material can be very small, perhaps even a handful of TEM microscopy disks. The most important criterion is that substantial transmutation be induced to test the validity of mechanisms discussed in this report. If only one temperature condition is available in the test matrix, the upper range temperature should be chosen to maximize the influence of the Inverse Kirkendall effect.
5. REFERENCES


4. Private confidential communications between Frank Garner and two engineers working in different commercial light water reactor programs. One individual stated that XM-19 has been used as “a replacement material in tie rods and nuts for recent repairs of BWR core shrouds. Other applications include reactor coolant pump shafts and/or other bolting applications in the RCS.” The second individual said that the “primary application of the Nitronic material is for thermal shield attachment bolts (replacement) – so conditions are what is experienced outside core barrel. No data beyond material certs (everybody wants to fix the problem but nobody wants to pay for finding what caused the problem). I am aware of only one other application (washers in upper internals region). Like I said, it is not used much - only a handful of plants.”


