

## **A new NiCrFe welding product-INCONE FM52MSS provides optimum resistance to PWSCC and DDC**

### **Presenter:**



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# **A new NiCrFe welding product-INCONEL FM52MSS provides optimum resistance to PWSCC and DDC**

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## **Abstract**

Weldments in vessels and components for nuclear power generation must be of especially high quality due to the complexity and criticality of this demanding service. Nickel-based welding products have been used throughout the life of nuclear welding industry because of their excellent resistance to the corrosive environment. From the 1950's thru the early 1980's, INCONEL<sup>®</sup> Welding Electrode 182 (ENiCrFe-3) and INCONEL<sup>®</sup> Filler Metal 82 (ERNiCr-3) were the mainstay welding products for the nuclear power industry. But in the late 1970's primary water stress-corrosion cracking (PWSCC) was encountered as a result of insufficient chromium content in these welding alloys. This brought about the need for a 30% Cr-containing welding electrode 152 (ENiCrFe-7) and Filler Metal 52 (ERNiCrFe-7). These materials were resistant to PWSCC, but they were found to be susceptible to ductility dip cracking (DDC). A patented 30% Cr-containing welding product, INCONEL<sup>®</sup> Filler Metal 52M (ERNiCrFe-7A), has become widely accepted for improvements of DDC resistance over INCONEL<sup>®</sup> Filler Metal 52, however, the applications involving overlays (Pre-emptive weld overlays-PWOL, Structural weld overlays-SWOL, etc.) are insufficiently demanding to highlight the severity of cracking that can occur with higher restraints and heavier section welds. Therefore, a new nickel alloy material with 30% chromium, INCONEL<sup>®</sup> FM52MSS, was developed. The Strain-to-Fracture (STF) test introduced by The Ohio State University welding group has shown substantially improved DDC cracking resistance of INCONEL<sup>®</sup> FM52MSS. This paper discusses the continuing development and performance of the welding material and the results of STF test on this new alloy. The data presented previously have been supplemented with additional information from testing performed on new heats.

Key words: 52MSS, Strain-to-Fracture, PWSCC, DDC.

## **1 Introduction**

In various welding applications, including equipment used in nuclear power generation,

weldments are required that provide resistance to various cracking phenomenon and corrosion environment. This includes resistance not only to intergranular stress corrosion cracking (IGSCC), but to solidification cracking and ductility-dip cracking (DDC) as well.

During the lives of commercial and military nuclear power generation, the nuclear industry has replaced the first generation of nickel alloys that had only 13-17% chromium (ENiCRFe-3) or 18-22% chromium (ERNiCR-3) with a family that now contains about 30% chromium because the weldments using ENiCRFe-3 or ERNiCR-3 are susceptible to primary water stress corrosion cracking (PWSCC) due to their insufficient chromium contents [1-4]. These new families of alloys with 30% chromium are virtually immune to IGSCC, but other issues have been discovered about the welding products of these families. The initial 30% chromium welding products (UNS N06052) contained about 0.50 % Al and 0.50% Ti and had reasonably good general weldability. However, the aluminum content nearly always contributed to floating oxide impurities on many of the weld beads in spite of scrupulous efforts to provide excellent gas shielding. These oxides, if not removed by grinding would often find their way into the interior of multi-pass welds and appear as inclusions which were detectable by radiography or ultrasonic inspection methods. This condition was unacceptable when encountered during the repair of operating nuclear plant components that were radioactively “hot”. In addition, deposits made using these products were found to be susceptible to ductility-dip cracking (DDC).

DDC is a solid-state, elevated temperature phenomenon that has been observed in thick-section, multipass austenitic stainless steel and nickel-based alloy weld metals characterized by large grain size and high restraint. An example is shown in Fig. 1. Early ductility-dip cracking (DDC) that formed in weld metals was usually small, and was often referred to as a ‘micro-fissuring’. Although this type of cracking (DDC) was identified as early as 1961 by Rhines and Wray [5], this term micro-fissuring was indiscriminately applied to both solidification cracking and to DDC until the early 1990’s. The DDC mechanism has been postulated to be the result of “ductility exhaustion” shown in Fig. 2 along the grain boundary with grain boundary sliding and the relative orientation of a grain boundary to an applied strain increasing susceptibility to DDC. That is, with increasing higher-angle grain boundaries relative to the maximum stress direction comes increasing susceptibility to DDC. Although the occurrence of DDC is sometimes unnoticed, in applications where there is low defect tolerance, such as nuclear fabrication, its minimization is highly desirable.

INCONEL<sup>®</sup> Filler Metal 52M (ERNiCrFe-7A) has been reported to have provided improvements of DDC resistance over INCONEL<sup>®</sup> Filler Metal 52, however, the applications involving overlays (PWOL, SWOL, etc.) are insufficiently demanding to highlight the severity of cracking that can occur with higher restraints and heavier section welds[6]. In fact, the advent of much improved weld bead cleanliness presented by 52M had a greater impact on product acceptance than improvements in DDC resistance. Recently a new generation welding material of the 52 family, INCONEL<sup>®</sup> Filler Metal 52MSS, was invented and patented by Special Metals Welding Products Company and AREVA. It has been accepted into AWS A5.14 as classification ERNiCrFe-13 with UNS Number N06055 and is ready for use as F-43 group by ASME Code Case 2142-3. This new

alloy contains about 2.0- 2.5 wt.% Nb and 3.0-4.0 wt.% Mo, which have been shown to improve DCC resistance dramatically, and has reduced aluminum and titanium, which provide the ability to deposit very clean weld deposits without the floating oxide impurities of the previous family. This paper will present the substantially improved DDC resistance of this alloy and the function of Nb and Mo on DDC resistance.

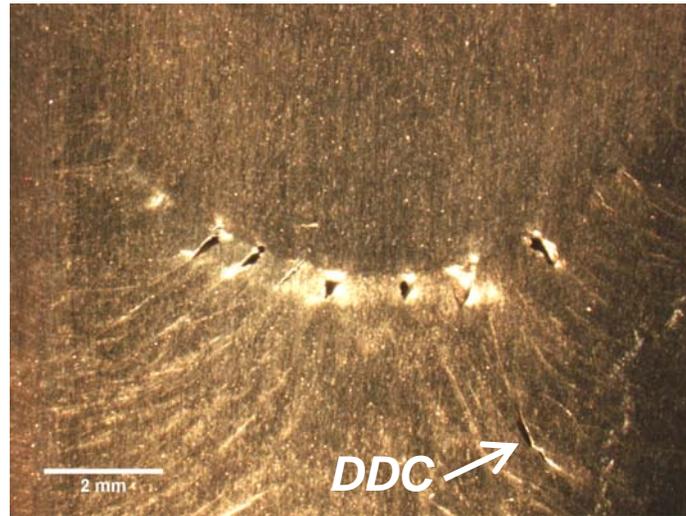


Fig. 1, Ductility dip cracking (DDC) of trailing, solidified portion of transverse restraint test.

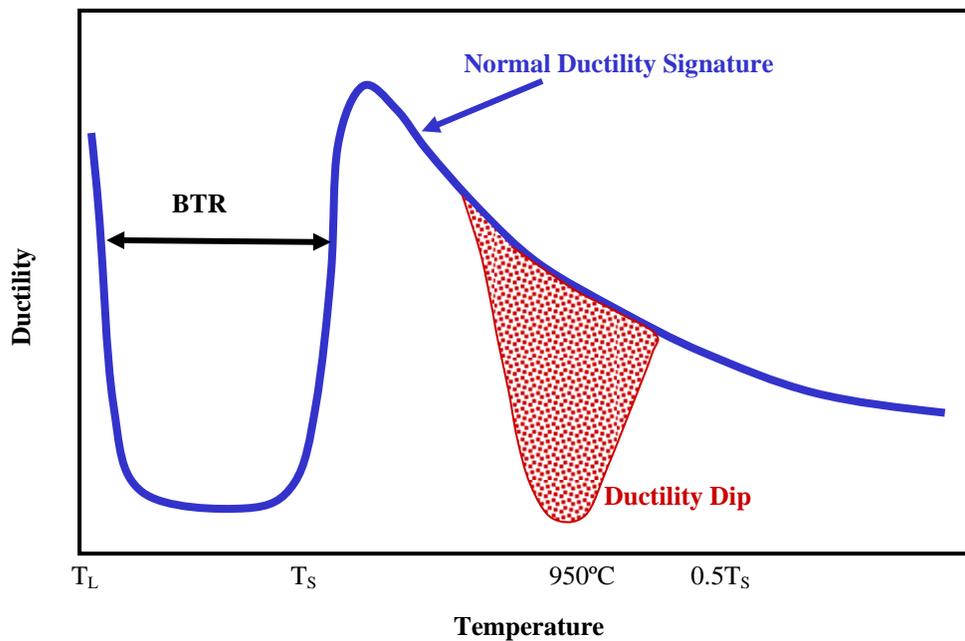


Fig. 2. Schematic that represents the mechanism of ductility-dip cracking.

## 2 Materials and Sample Preparation

Six experimental high-Cr weld metals (denoted as 3W-1, 3W-2, 3W-3, 3W-4, 52MSS (1), and (2)) and two commercial heats of 52MSS (denoted as NX77W3UK and NX79W1UK) with varying contents of Nb and Mo were used in this study. The chemical compositions of these alloys are presented in Table 1. Usually INCONEL<sup>®</sup> Filler metal 52MSS contains ~30% Cr, ~2.5% Nb and ~4.0% Mo and other elements. Other Ni-base filler metals that have been subjected to STF testing are given in Table 1 for comparison also.

Table 1. Chemical compositions of different nickel base filler metals (wt.%)

Element	FM82	FM52	FM52M	3W-1	3W-2	3W-3	3W-4	52MSS (1)	52MSS (2)	NX77W 3UK	NX79W 1UK
C	0.031	0.026	0.02				0.012	0.026	0.024	0.023	0.03
Mn	2.97	0.24	0.80				2.64	0.19	0.79	0.31	0.31
Ni	72.34	58.82	59.54				58.31	54.67	53.46	Bal.	Bal.
Cr	20.57	28.91	30.06				26.8	29.92	30.34	29.49	29.46
Fe	0.95	10.53	8.22				9.04	8.31	8.18	8.49	8.91
Nb	2.5	0.03	0.83	2.19	2.46	2.11	2.53	2.57	2.49	2.51	2.40
Mo	-	0.04	0.01	3.04	1.87	0.75	<0.01	3.83	4.01	3.51	3.20
S	0.002	<0.001	0.001				0.012	0.0013	0.0014	0.0005	0.00015
P	0.004	0.004	0.003				0.006	0.0001	0.009	0.004	0.005
Ti	0.32	0.55	0.224				0.13	0.193	0.188	0.18	0.18
Al	-	0.66	0.11				0.10	0.07	0.218	0.13	0.12
Si	0.16	0.15	0.09				0.39	0.119	0.21	0.11	0.11
Cu	0.01	0.02	0.02				0.01	0.059	0.06	0.05	0.04
Mo-Nb	2.5	0.07	0.84	5.23	4.33	2.86	2.53	6.4	6.5	6.10	5.6

Standard STF dogbone samples were sectioned transversely from the slotted butt joint plates (see Fig. 3), which were made by the automated gas tungsten arc welding (GTAW) and gas metal arc welding (GMAW) processes. The base metal used for these joints was alloy 690. These samples shown in Figure 3 were ground to the final dimension. Then, Autogenous gas tungsten arc (GTA) spot welds were made at the middle of the pre-deposited weld on both sides of the reduced sections using a Jetline Sidebeam unit for arc voltage control and a Miller Dynasty 300LX power supply, as presented in Fig. 3. The circular geometry of this spot gives a radial distribution of grain boundaries so that cracking resulting from the axial strain during the STF test will occur along the most susceptible oriented grain boundaries. Complete details of the STF test are given in Reference 7.

The tested samples were then evaluated for cracks using a stereo microscope up to 30X magnification. The degree of DDC in a given sample is determined by counting the number of cracks in the elongated spot weld of both sides of the sample, then dividing by two. Only cracks that were distinguishable at up to 30X magnification were included in the count. Subsequently, the STF tested samples were prepared for metallographic observation by grinding, polishing and then electrolytic etching in a 10% chromic acid solution at 1.5-2V for 30 s. Scanning electron microscopy (SEM) and EDS analysis was performed on a

Sirion SEM/FEG and Phillips XL-30 ESEM/FEG at 15kV. TEM analyses were performed at 300 kV in a JEOL JEM 3010-URP together with an EDS Noran Voyager system.

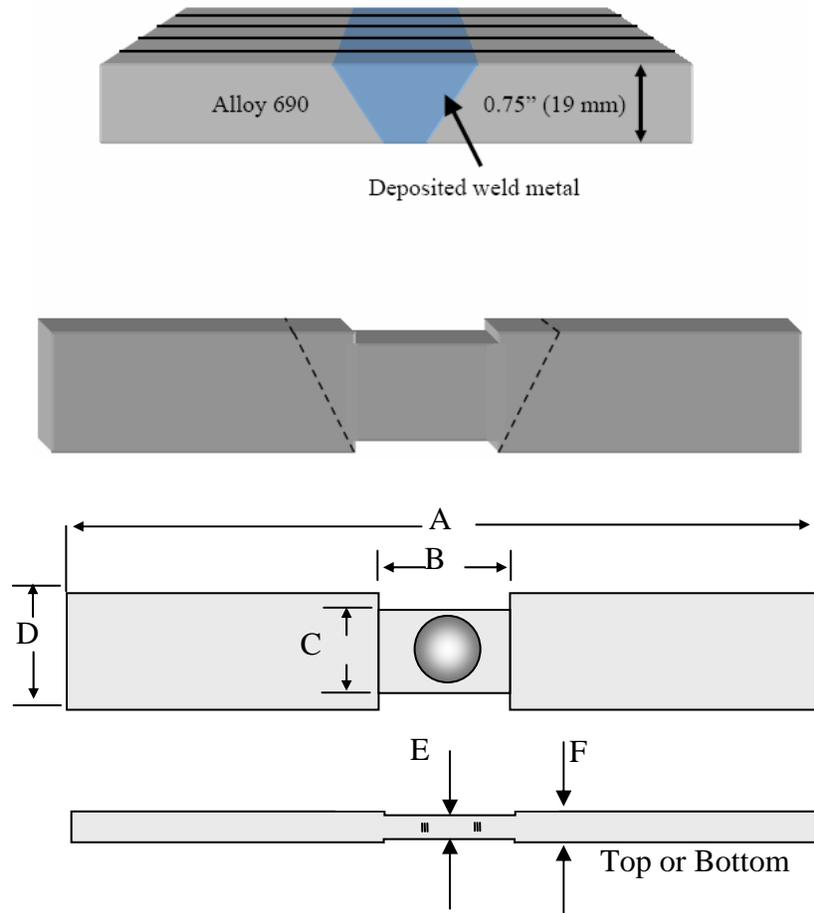


Fig 3. Schematic illustration of strain-to-fracture sample. A = 12.7 cm (5 inches), B = 19 mm (0.75 inch), C = 15.3 mm (0.6 inch), D = 19 mm (0.75 inch), E = Nominally 5.6 mm (0.22 inch), F = 6.4 mm (0.25 inch).

### 3. Results and Discussions

STF test results for an experimental filler metal 52MSS (then identified as 52X-H) are presented in Fig. 4. The numbers in parenthesis represent the number of cracks found on both sides of the tested sample divided by two. The black numbers represent the DDC results of 52X-H and the black solid line represents the approximate threshold strain for cracking for the experimental heat of 52MSS. The threshold strain for cracking for the initial melt of filler metal 52MSS is more than 8% at the most susceptible temperature of 950°C.

The STF results for Filler Metal 52MSS are compared to the STF data published for Filler Metal 52 and Filler Metal 82, as shown in Fig. 5[6-7]. The results indicate that the DDC resistance of the initial heat of Filler Metal 52MSS is considerably higher than Filler Metal

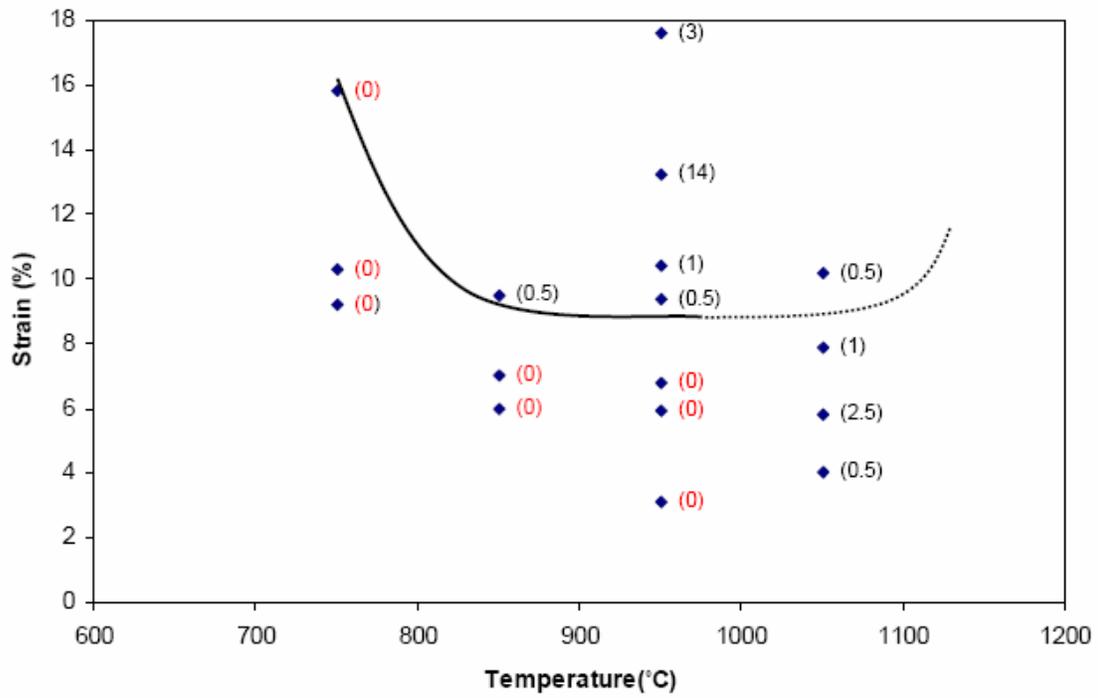


Fig. 4. Initial STF results for Filler Metal 52MSS (then called 52X-H).

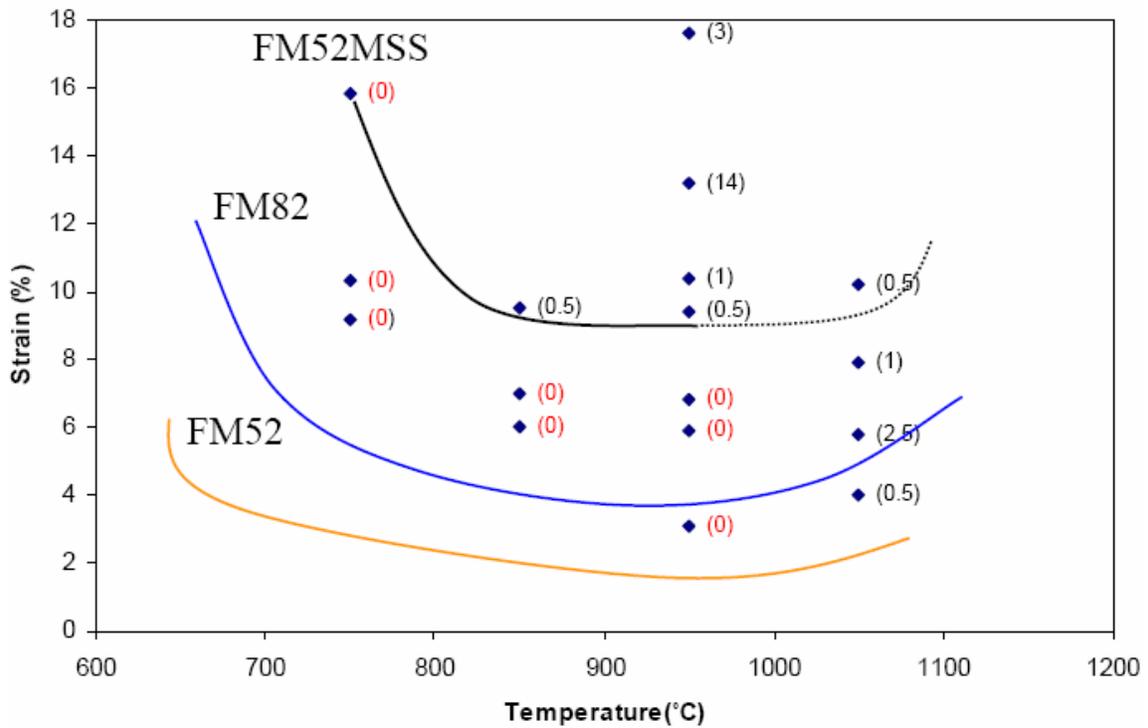


Fig. 5. Comparison of the Filler Metal 52MSS threshold strain for cracking to the STF results of Filler Metal 52 and 82.

52, and over 2 times more crack resistant than Filler metal 82, which is known to be moderately resistant to DDC under high-restraint welding conditions. Because the most susceptible temperature for DDC to occur in 30% Cr Nickel-base welding alloys is at, or near, 950°C, preliminary screening is often performed at this temperature [6].

A comparison of the STF results of different welding filler metals with 30% Cr tested at 950°C is provided in Fig. 6. The horizontal bar in the column above each filler metal represents the threshold strain for cracking for that material while the numbers present the number of cracks. The temperature of 950°C was selected for STF screening testing due to the maximum ductility-dip tendency has been found to occur near this temperature, as illustrated in Fig. 2. In addition, experience has indicated that the cracking response at 950°C correlates well with actual fabrication behavior and provides the most discerning data. Two commercial heats of 52MSS, NX77W3UK and NX79W1UK, show the consistent DDC resistance results. The heat of NX77W3UK has a 12% threshold strain for cracking. For the heat of NX79W1UK, the STF test is still under testing, but the first sample showed no cracking when tested at 10% strain. The threshold strain value for this heat is expected to be higher than 10%. A complete study of solidification cracking has been initiated and results will be published in a subsequent paper..

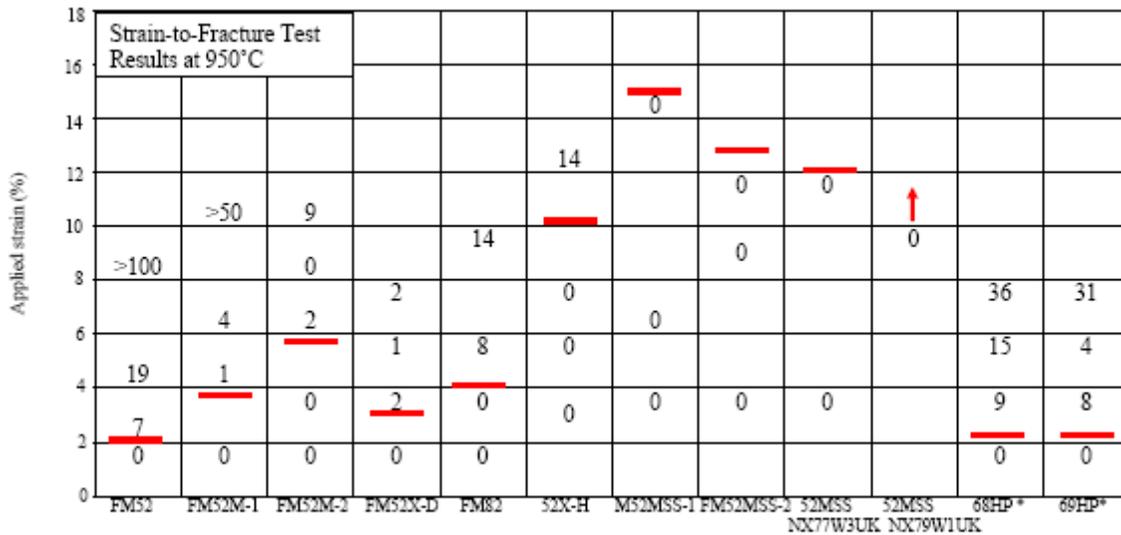


Fig. 6. Strain-to-fracture test results for different nickel-base weld metals tested at 950°C. Some data from reference 7.

The data presented in the Fig. 7 provides the trend of the threshold strain for cracking with the content of Nb and Mo. It is clear that with increasing amounts of Mo in the filler metal when Nb is between 2% and 3%, the threshold strain for cracking increases. It is indicated that the 52MSS family containing 5-6.5% Nb+Mo when %Nb is at least 2%, exhibit the highest threshold strains and the best resistance to DDC cracking. Note that alloy 3W-4 and data points to the left contain no Mo while 3W-3 and alloys to the right have Mo additions and show much improved STF performance.

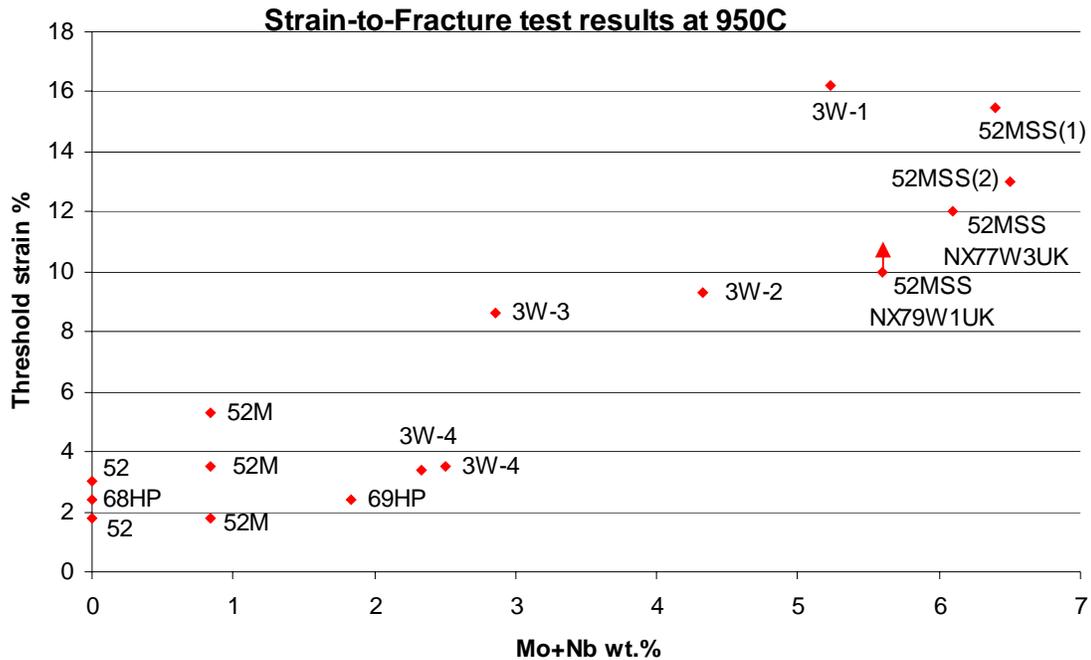


Fig.7. The relationship between threshold strain for cracking and the content of Ni and Mo. The STF results tested at 950°C.

In order to investigate the influence of Nb and Mo on the DDC resistance, microstructural examination of FM52M and FM52MSS was conducted by OSU researchers after STF testing. FM52M contains approximately 0.8% Nb and no Mo, while FM52MSS has a combined total of 6.5% Mo+Nb. Fig. 8 show the patterns of migrated grain boundaries using electron backscattered diffraction (EBSD). It is clear that the boundaries of early 30%Cr nickel-based alloy are generally straight, while the FM52MSS boundaries are extremely serpentine. The straight grain boundaries of early 30%Cr nickel-based alloy were populated with small, Cr-rich  $M_{23}C_6$  carbides as shown in Fig. 9. These  $M_{23}C_6$  carbides form in the solid-state at much lower temperature than that of the NbC (MC) carbide and have no effect on boundary pinning. The SEM image of FM52MSS weld metal shown in Fig. 10 indicates that the Nb-rich M(C,N) precipitates are spread throughout the weld metal interdendritically instead of only in the grain boundaries. These NbC carbides form at the end of solidification before grain boundaries begin to form and migrate. This makes them effective at pinning the migrating grain boundaries, which results in serpentine grain boundaries that create interlocking grains. This structure is much more effective at resisting grain boundary sliding and thus greatly improves DDC resistance.

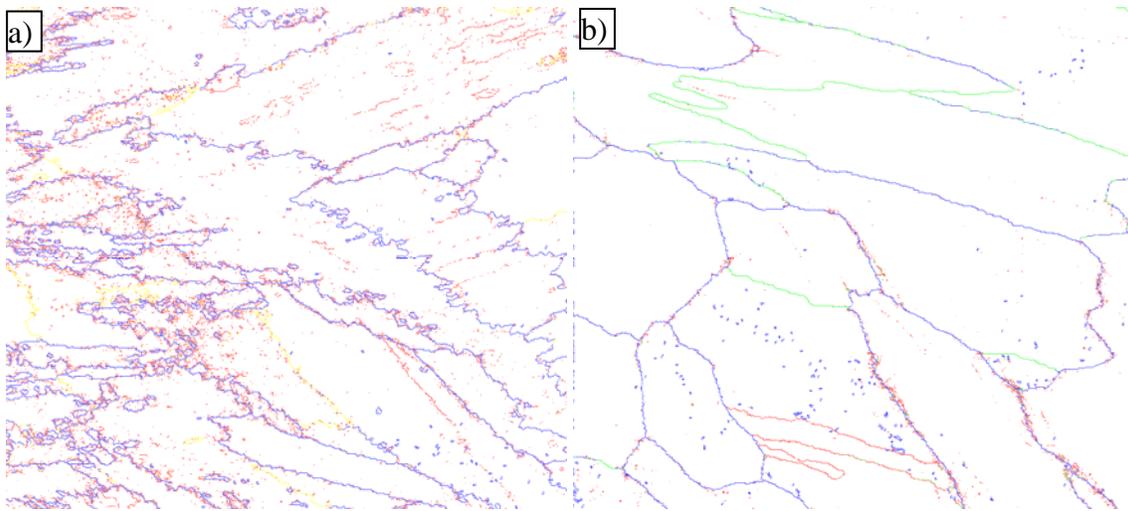


Fig. 8. Electron backscattered diffraction (EBSD) patterns showing (a) serpentine migrated grain boundaries in FM52MSS and (b) the nearly straight grain boundaries of early 30% Cr Nickel-based alloy.

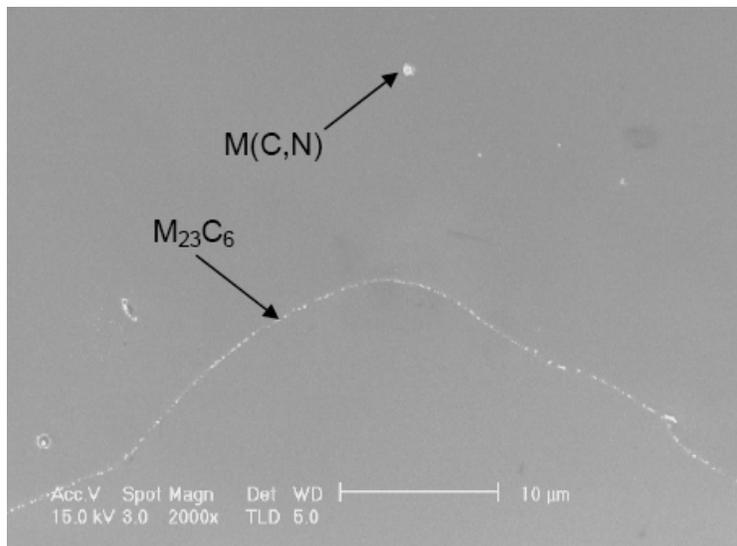


Fig. 9. Undesirable long, straight grain boundaries with nearly continuous  $M_{23}C_6$  carbides in early 30% Cr Nickel-based alloy.

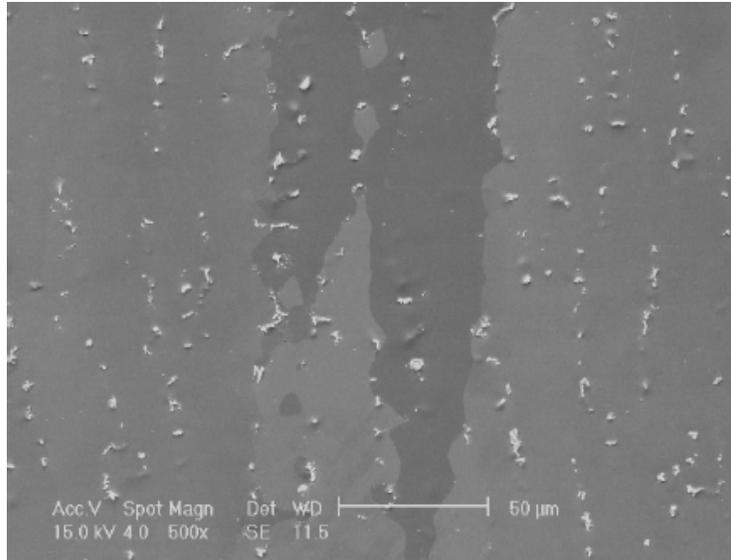


Fig. 10. Backscattered electron SEM image showing visible M(C,N) precipitates in the interdendritic regions and no  $M_{23}C_6$  carbides were observed in the as-welded condition.

Fig. 11 shows the EDS analysis of three locations from the microstructure of 52MSS. Location 3 is the weld metal matrix with similar composition to 52MSS wire. Location 1 and 2 were located on the dendrite boundaries and showed higher content of Nb and Mo, which indicated both Mo and Nb segregate strongly to the dendrite boundaries. The TEM/EDS analysis of the (Nb, Ti)C particle, shown in Fig. 12, indicates that the Nb content in the MC carbide is approximately 75% and that the carbide contains virtually no Mo. A slight Mo enrichment is detected around the MC carbide, resulting from the rejection of the Mo from the solidification boundary during the formation of the MC carbide at the end of solidification. But the test results, shown in the Fig. 7, clearly indicate the beneficial effect of Mo on DDC resistance. Additional work is ongoing to provide a better understanding of the effect of Mo on the interdendritic carbide formation and associated DDC resistance in the weld metal of Filler Metal 52MSS.



Element	Location		
	1	2	3
Ni	41.6 ± 0.6	46.5 ± 0.6	51.4 ± 0.7
Cr	24.0 ± 0.3	28.3 ± 0.3	30.9 ± 0.3
Fe	5.2 ± 0.2	7.0 ± 0.2	8.1 ± 0.3
Mo	7.7 ± 2.1	10.0 ± 2.2	2.6 ± 0.9
Nb	19.1 ± 3.2	5.2 ± 2.0	2.1 ± 1.6
Ti	0.3 ± 0.1	0.3 ± 0.1	0.2 ± 0.1

Fig. 11. SEM/BSE image of 52MSS weld metal with locations indicated for EDS data in the table.

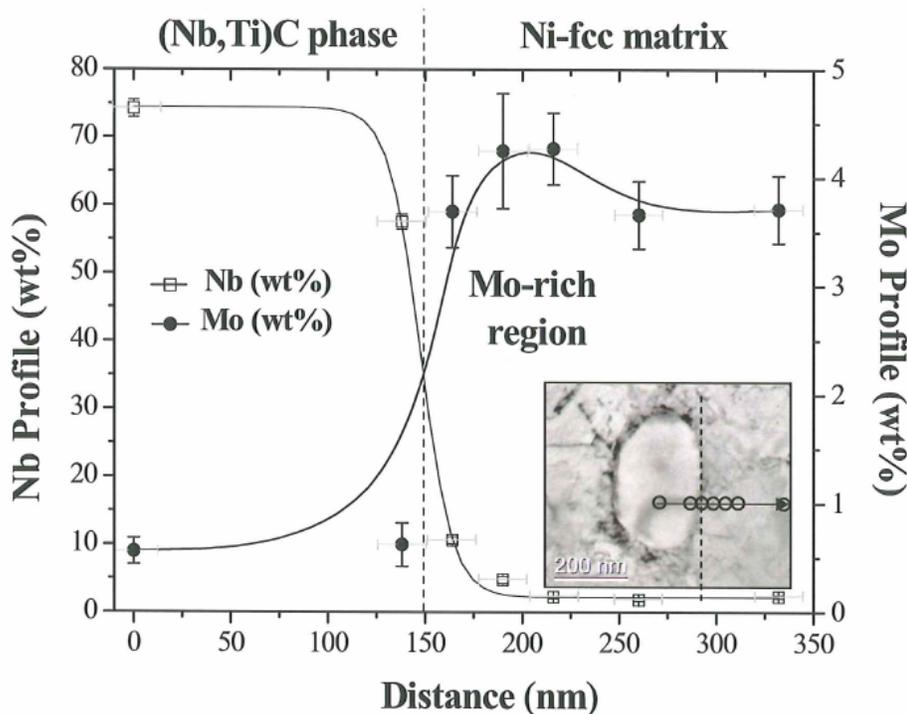


Fig. 12. TEM/EDS analysis showing Nb and Mo composition profile across the MC carbide interface.

#### 4. Summary

The current status of Nickel based alloys for nuclear construction is that 30% chromium-containing nickel-base alloys and welding products are necessary for primary water stress corrosion cracking (PWSCC) resistance. These materials have sufficient resistance to PWSCC, but some weld metals suffer from susceptibility to DDC cracking due to the tendency for long, straight grain boundaries during solidification and cool down.

INCONEL<sup>®</sup> Filler Metal 52M provides reasonable resistance to DDC during fabrication and good resistance to PWSCC in nuclear service. The newest 30% chromium-containing nickel alloy welding product, INCONEL<sup>®</sup> Filler Metal 52MSS, has been shown to provide outstanding DCC resistance and has been found in other research[8] to provide the same excellent PWSCC resistance as INCONEL<sup>®</sup> Filler Metal 52M.

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