A New Nickel-Base Alloy for Resisting Metal Dusting Attack

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INTRODUCTION

Metal dusting is a carburisation phenomenon that can cause rapid and often unpredicted failure in chemical and petrochemical plants. Processing high temperature gases such as in the synthesis of hydrocarbon feedstocks, methanol and ammonia, as well as in direct iron ore reduction often involves creation of gas streams having high carbon activity with high ratios of carbon monoxide-to-carbon dioxide and low ratios of steam-to-hydrogen. When such gas mixtures are present in the process stream within the critical temperature range of roughly 400-750°C, metal dusting can be a severe corrosion problem. Chemical reactors, furnaces, steam generators and down-stream reformer components can all suffer from this rapid form of material wastage, resulting in costly downtime. In the case of syngas generation, processing conditions and the use of advanced nickel oxide-based catalyst systems have heightened the tendency of synthetic gas streams to promote metal dusting. The technique of injecting sulphur containing species into the gas stream is no longer viable given the likelihood that the catalyst will be poisoned. Higher reforming gas pressures and temperatures in conjunction with lower steam-to-carbon ratios, all combine to make metal dusting conditions more aggressive, and are becoming more common in industry. Until recently, rapid quenching of syngas generated by reformers has been employed in order to minimise exposure of metallic internals downstream to metal dusting conditions. Thus only the material lining in the transfer line must possess appreciable metal dusting resistance. New plant designs, however, employ the use of gas-heated reactors which recover the heat from generated syngas to process more. These reactors typically contain metallic components which are exposed to metal dusting conditions practically throughout. Such extreme conditions necessitate the use of materials possessing a level of resistance to metal dusting which is superior to that of previously commonly-used alloys.

Special Metals Corp. has developed a new material, INCONEL® alloy 693 (UNS 06693), which exhibits excellent performance in metal dusting environments.

CORROSION PERFORMANCE

The nominal compositions for the alloys discussed in this article are shown in Table 1. Figures 1 and 2 show mass change and pit depth for alloy coupons exposed to a laboratory environment generated from CO-20% H_2 at 621°C. Samples were ground to a 120-grit finish prior to exposure and were cycled to room temperature every two weeks for mass change and pit depth measurements. Carbon deposits were first removed using a soft bristle brush. Then samples were ultrasonically cleaned in methanol for more thorough removal of deposits. Pit depth measurements were made using a microscope having a calibrated focusing mechanism. After 15816 hours of testing, INCONEL alloy 693 continued to exhibit excellent resistance. Alloy 693 has been shown repeatedly to possess the best resistance to metal dusting of any alloy tested. Figures 3 and 4 show a comparison of cross sections of alloy coupons from INCONEL alloys 601 and 693 exposed to Special Metals' harsh laboratory environment. The INCONEL alloy 601 exhibited large, hemispherical pits having a maximum depth of about 20 mils (0.51mm) after 6600 hours of exposure whereas the INCONEL alloy 693 exhibited only minor pit-like features extended less than 2 mils (0.05mm) in depth after more than double the exposure period of 15816 hours of testing. A healing layer of oxide was evident at the surface of the minor pitting that was observed in the INCONEL alloy 693 sample.

Similar experience has been reported from in-situ exposures of alloy 693 in industrial syngas environments, by numerous companies. The alloy continues to exhibit excellent resistance after exposure times which have now extended beyond 8000 hours.

Due to its ability to develop a continuous aluminium oxide scale, INCONEL alloy 693 also possesses excellent resistance to oxidation at elevated temperatures. Figure 5 shows results of exposure in air at 1200°C. In addition, resistance to carburising conditions is also excellent, as illustrated in Figure 6.

MECHANICAL PROPERTIES

Corrosion resistance is of prime importance in applications which may cause metal dusting. However, mechanical properties are also an important consideration when selecting a material. The following data are intended to highlight the properties of the newly-introduced INCONEL alloy 693. Table 2 shows room-temperature temperature tensile results for INCONEL alloy 693 before and after intermediate-temperature exposure, showing that reasonable levels of ductility have been retained after as long as 8000 hours of exposure.

Figure 7 shows the elevated temperature tensile properties of alloy 693 hot-rolled rod in the annealed condition. Figure 8 compares the stress rupture properties of alloys 601, 617, 690 and 693 via a Larson-Miller plot. At temperatures below about 900°C alloy 693 possesses greater rupture strength than alloy 601. The properties of the alloy 693 at 982°C are more similar to those expected for alloy 690.

WELDING TRIAL RESULTS

Table 3 shows room-temperature and 649°C tensile results for full-penetration butt welds performed on alloy 693 hot-rolled and annealed plate (20mm thick). All welds were performed using GTAW with a 2% thoriated electrode using 100% argon as the shielding gas. The welding wire diameter was 2.4mm. Transverse 2T side bends were performed for each weld joint, and all bends were acceptable per ASME code standards. Unions joining alloy 693 to itself were made using INCONEL filler metal 52. Welds joining INCONEL alloy 693 to INCOLOY alloy 800 were performed using INCONEL filler metal 82. Welds made joining INCONEL alloy 693 to INCONEL alloy 601 were made using INCONEL filler metal 601. All welds were examined using X-ray photography with no indications detected. Based upon the observed properties, it appears that fracture has occurred in the weld in every sample. For the transverse samples, reduction of area represents a much better indication of the material ductility at the point of fracture. Elongation values for samples tested in the transverse orientation, with the weld placed at the center of the sample, are somewhat biased toward the low end of the range due to the fact that elongation of the sample gage section was not uniform and was likely restricted to the weld metal.

For joining alloy 693 to itself using INCONEL filler metal 52, a last pass using INCONEL filler metal 72 is recommended for enhancement of corrosion resistance at the surface. Figure 9 shows a side bend performed on an INCONEL alloy 693 butt weld (8mm plate) joined using GTAW with INCONEL filler metal 52 and capped at the root and the face with INCONEL filler metal 72.

SUMMARY

INCONEL alloy 693 exhibits a level of resistance to metal dusting environments that is superior to that of any other wrought material tested in Special Metals Corporation's severe laboratory conditions after almost 16000 hours of exposure. In situ exposures of INCONEL alloy 693 in actual industrial environments for times exceeding 8000 hours also confirm the excellent metal dusting resistance of the material. The alloy also possesses excellent resistance to elevated temperature oxidation and carburisation by virtue of its ability to form a continuous aluminium oxide surface layer.

The creep rupture strength of INCONEL alloy 693 is greater than that of INCONEL alloy 601 at temperatures below about 900°C and approximately equivalent to that of INCONEL alloy 690 at temperatures above about 900°C. INCONEL alloy 693 exhibits good retention of room temperature tensile ductility after long-term exposure at intermediate temperatures.

INCONEL alloy 693 is readily welded using conventional fillers and techniques. Successful side bend and tensile results are indicative of sound similar and dissimilar welds.

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Table 1. Nominal Composition (Weight %) for Commercial Alloys

Alloy	**Ni**	**Cr**	**Fe**	**Si**	**Al**	**Other**
INCONEL alloy 693	62	29	4	-	3.1	Nb, Zr, Ti
INCONEL alloy 601	60.5	23	13	0.2	1.4	-
INCONEL alloy 690	59	29	9	0.1	0.3	-
INCONEL alloy 617	55	22	1	0.1	1.2	12.5 Co, 9.7 Mo
INCOLOY® alloy 800/800HT	32	21	45	0.1	0.4	0.4 Ti
INCOLOY alloy MA956	-	20	75	-	4.5	0.5 Y_2O_3, 0.5 Ti
INCONEL® filler metal 82	73	20	1	-	-	2.5 Nb, 3 Mn
INCONEL filler metal 52	59	29	9	0.1	0.8	0.5 Ti
INCONEL filler metal 72	56	43	0.3	-	0.1	0.6 Ti

Table 2. Room Temperature Tensile Properties of INCONEL alloy 693 after Long-Term Exposure at Elevated Temperatures

Exposure Temperature, °C	**Exposure Time, Hours**	**0.2% Yield Strength, MPa**	**Ultimate Tensile Strength, MPa**	**Elongation, %**
As-Produced	As-Produced†	410	834	43.0
As-Produced	As-Produced§	573	907	39.6
593	2000§	759	1111	38.5
649	2000§	762	1121	25.7
704	8000†	709	1108	23.3
760	8000†	463	949	34.8
816	2000§	551	974	24.0

† - Hot-Rolled and Annealed Rod
§ - Hot-Rolled and Annealed Plate

Table 3. Room-Temperature and Elevated-Temperature Tensile Results for INCONEL alloy 693 Welds (20mm Hot-Rolled and Annealed Plate) Performed using GTAW

Temperature °C	0.2% Yield Strength MPa (ksi)	Tensile Strength MPa (ksi)	Elongation %	Reduction Of Area, %	Base Metal(s)	Filler Metal	Orientation	Breakage Location
20	448	648	20.4	38.6	693	52	Transverse	n/a
20	538	696	31.4	56	693	52	Transverse	n/a
649	338	448	23	58.8	693	52	Transverse	n/a
649	324	441	27.6	53.2	693	52	Transverse	n/a
649	324	441	24	54.6	693	52	AWM§	---
649	359	469	26.2	44	693	52	AWM§	---
20	531	669	24.4	64.4	693/800	82	Transverse	n/a
20	483	669	25.2	65.8	693/800	82	Transverse	n/a
649	365	524	22.8	46.4	693/800	82	Transverse	n/a
649	359	524	26.2	48.4	693/800	82	Transverse	n/a
20	469	731	29.8	46.8	693/600	82	Transverse	n/a
20	462	669	28	54	693/600	82	Transverse	n/a
649	352	510	25.8	42.6	693/600	82	Transverse	n/a
649	359	524	32.2	57	693/600	82	Transverse	n/a
20	455	565	13.0	29.0	693/601	601	Transverse	Weld
20	414	621	32.8	47.6	693/601	601	Transverse	Weld
20	407	634	39.0	56.4	693/601	601	AWM§	---
20	393	614	32.0	48.8	693/601	601	AWM§	---
649	345	434	11.4	32.2	693/601	601	Transverse	Weld
649	331	469	21.8	36.4	693/601	601	Transverse	Weld
649	372	510	19.4	47.0	693/601	601	AWM§	---
649	345	469	28.2	35.4	693/601	601	AWM§	---

§ - All Weld Metal.

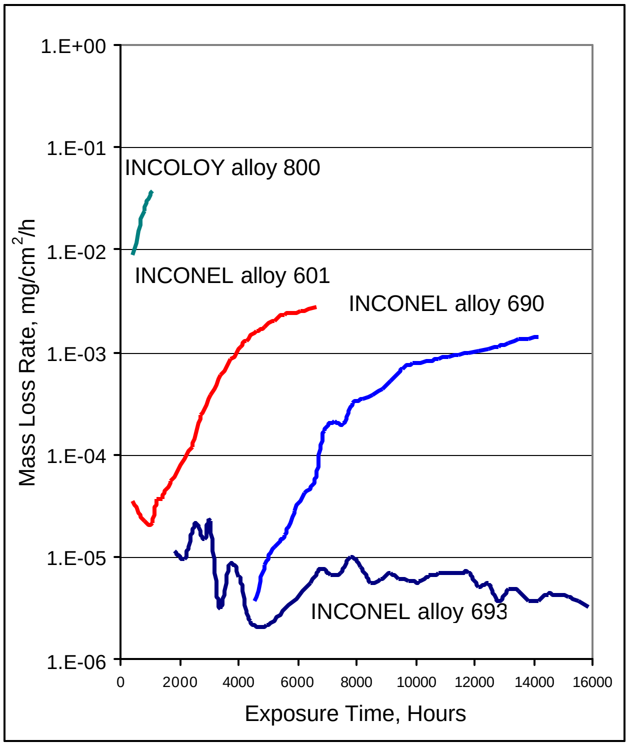

Figure 1. Mass loss rate versus time for samples exposed in CO-20% H_2 at 621°C.

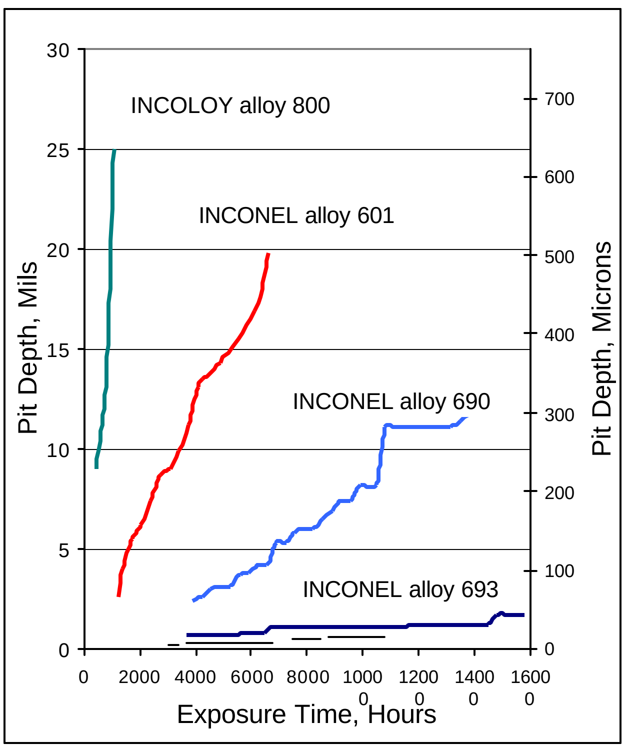

Figure 2. Pit depth versus time for samples exposed in CO-20% H_2 at 621°C.

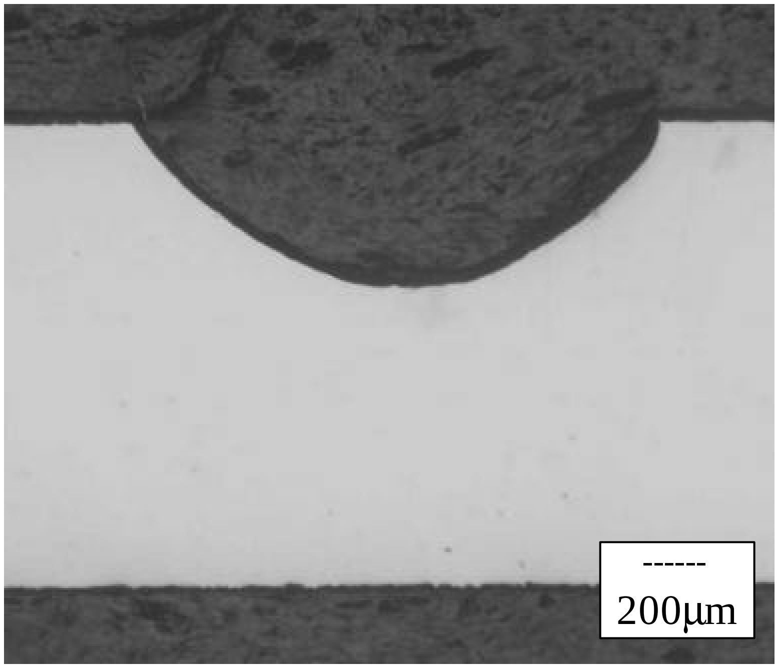

Figure 3. Photomicrograph showing cross section of INCONEL alloy 601after exposure in CO-20% H_2 at 621°C for 6600 hours.

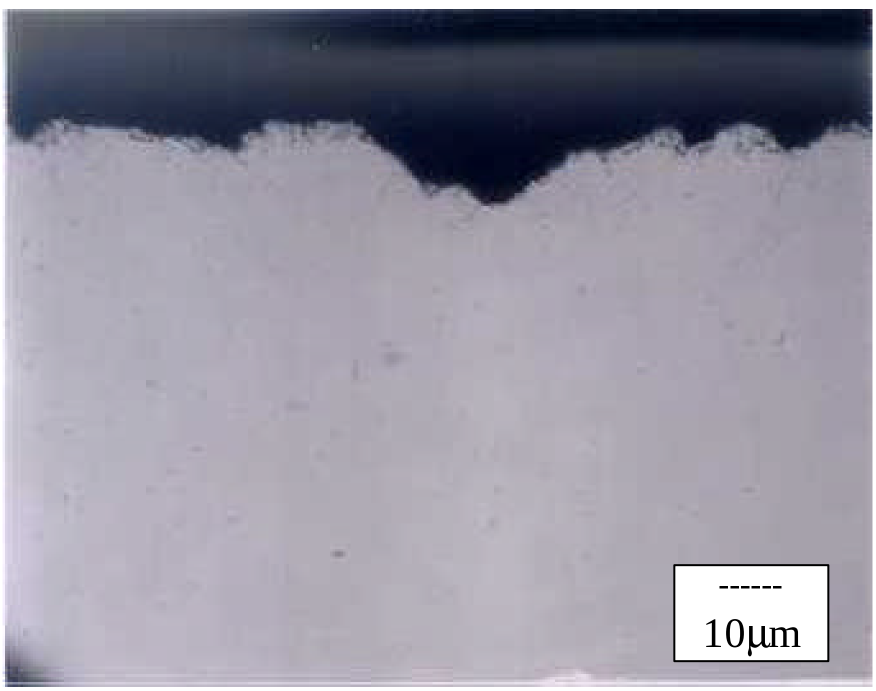

Figure 4. Photomicrograph showing cross section of INCONEL alloy 693 after exposure in CO-20% H_2 at 621°C for 15816 hours.

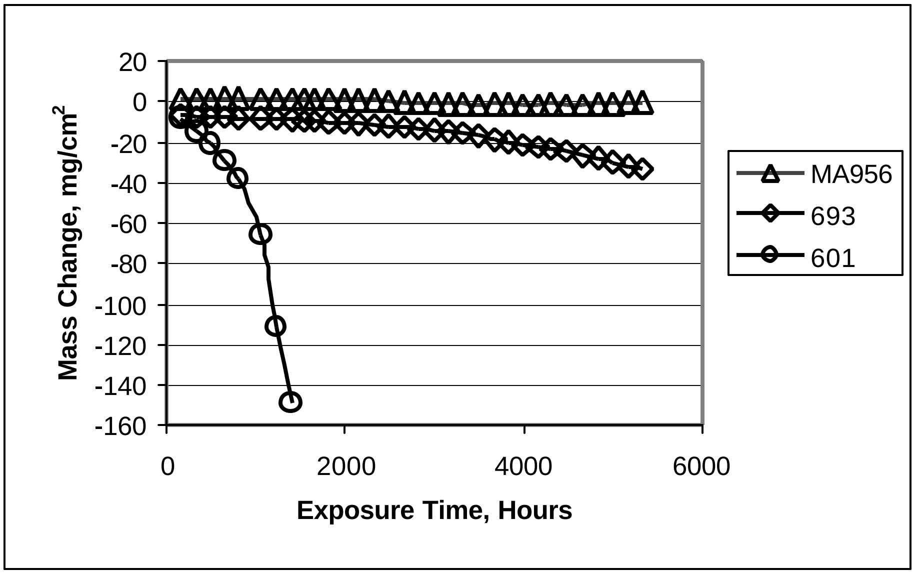

Figure 5. Mass change resulting from cyclic exposure in air at 1200°C. Samples were cycled to ambient temperature and weighed weekly.

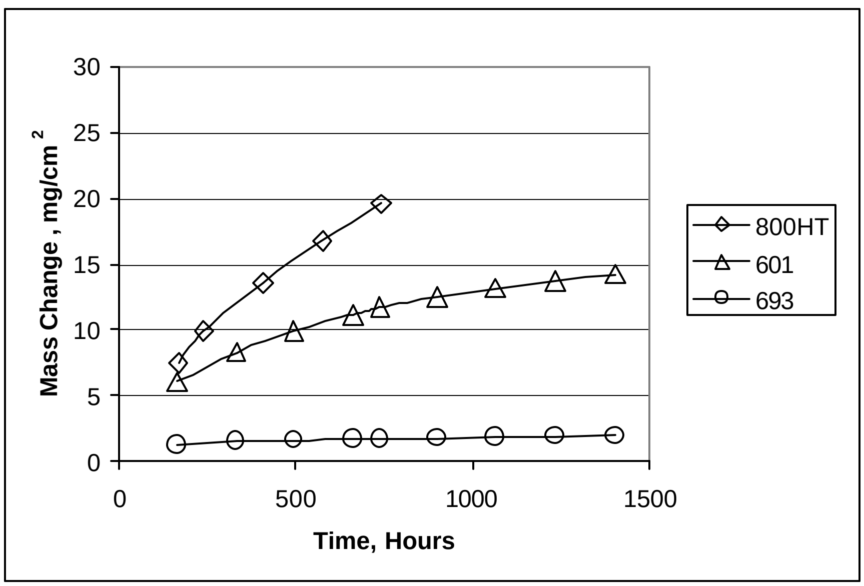

Figure 6. Mass change resulting from cyclic exposure in H_2-5.5% CH_4-4.5% CO_2 at 1000°C. Samples were cycled to ambient temperature and weighed weekly.

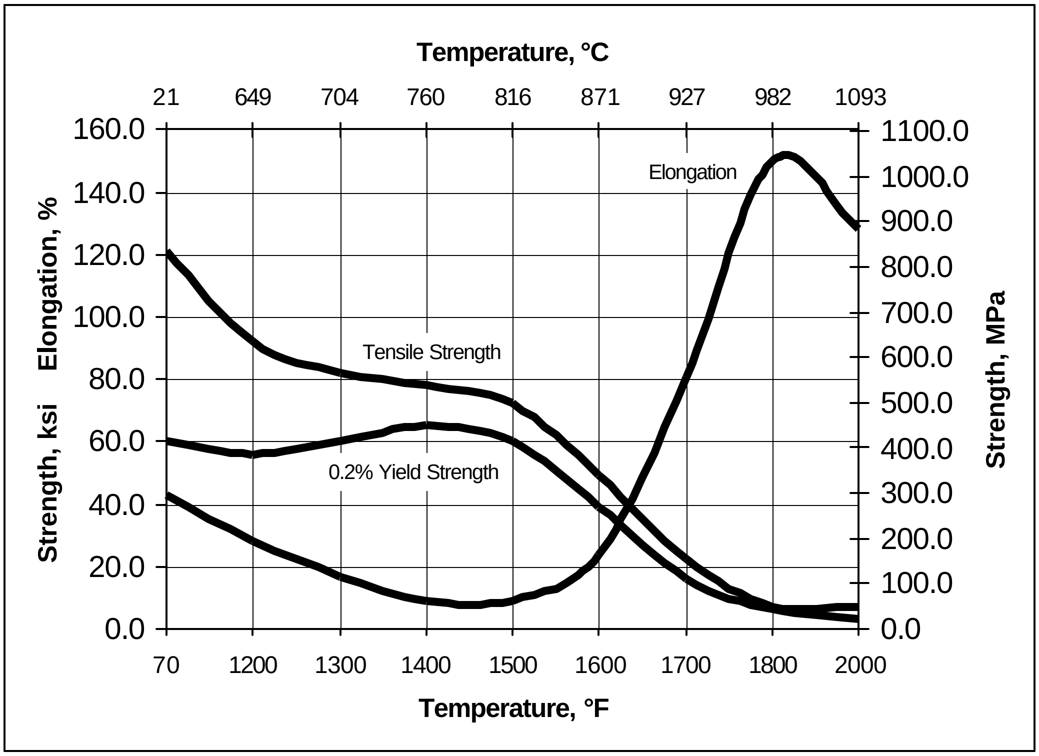

Figure 7. Tensile properties for hot-rolled and annealed INCONEL alloy 693 rod.

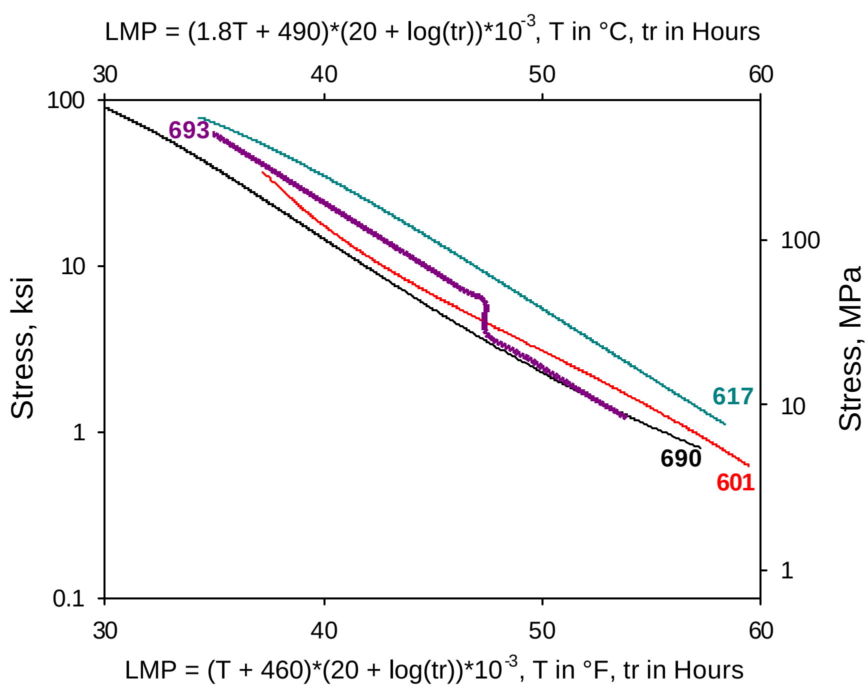

Figure 8. Creep rupture property comparison using the Larson-Miller parameter.

Figure 9. Side bends performed on as-welded butt joint, joining 8mm INCONEL alloy 693 plate using INCONEL filler metal 52 and capping at the root and face with INCONEL filler metal 72.