DUPLEX AND SUPER DUPLEX STAINLESS STEELS

STATE OF THE ART AND FUTURE DEVELOPMENTS

by R. Francis - Corrosion Services Manager
Weir Material Services Limited - Manchester, UK

(Presented at UK Corrosion '91, Manchester 1991)

ABSTRACT

Duplex stainless steels containing over 20% Chromium with molybdenum and nitrogen additions have been around for many years. The 22 Cr type (UNS S31803) have limitations in high chloride environments, such as sea water. 25 Cr duplex and particularly super duplex alloys have improved corrosion resistance and are finding extensive use in the marine environment. The paper describes the current areas where duplex and super duplex alloys are being used by the oil and gas industry. The diversity of components which have been supplied in 25 Cr super duplex stainless steel is covered.

The range of environmental conditions for both sea water and produced/injection waters which are being successfully handled are also presented. The corrosion problems being overcome include pitting/crevice corrosion, stress corrosion cracking and erosion corrosion. Some future developments include an extension of the performance in ever more aggressive operating environments, particularly with regard to limiting velocities in the presence of high solids burdens, and SCC resistance in the presence of high H_2S concentrations. Also described are the environmental conditions in some new or under developed market areas where the combination of high strength and good corrosion resistance of super duplex stainless steel offers the possibility of long service life at low cost compared to alternative materials.

1. INTRODUCTION

The high resistance of 22 Cr, 25 Cr and super duplex stainless steels to pitting, crevice corrosion and stress corrosion cracking is well known. The aim of the present paper is to review the present uses and limits of these alloys and to discuss future developments. These include extending the limits of use in current applications, plus the use of duplex alloys in industries which have made little or no use of these alloys to date.

2. STATE OF THE ART

The composition of the three duplex alloys being considered are shown in Table 1. Because of the proprietary nature of the 25 Cr and super duplex alloys only the main elements are shown, and those listed under others may be present in some alloys. The two main areas of use for high chromium duplex alloys are in the sea water and process fluid systems of offshore oil and gas platforms.

2.1 Seawater Systems

25 Cr duplex and super duplex stainless steels are being used on several North Sea Platforms for pumps and pipes in the sea water cooling system, the water injection system and firewater systems. The 22 Cr duplex alloy is not used in these areas because of its susceptability to crevice corrosion, particularly in chlorinated sea water (1,2). Both 25 Cr duplex and super duplex alloys have been used extensively for sea water pumps and injection pumps, where their high corrosion resistance, cavitation and erosion resistance, as well as high strength and good castability make them an excellent material choice.

Duplex alloys have also been extensively used for sea water pipe work, fittings, flanges, etc. The main potential corrosion problem is crevice corrosion at flanged and threaded joints. Research has shown that as the sea water temperature increases, the chlorine concentration (added to control fouling) permissible before crevice corrosion occurs decreases (1).

Tests over a range of temperatures and chlorine concentrations have shown that super duplex alloys can be used at higher sea water temperatures than 25 Cr duplex alloys (1,3). Super duplex alloys have been shown to have good resistance to crevice corrosion in sea water at 40°C containing 1 mg/l chlorine (3) while a 25 Cr alloy (UNS S32550) suffered deep crevice attack. Tests by Gallagher et al (4) with 0.8 mg/l chlorine at 45°C and 70°C showed no crevice corrosion on any of the 25 Cr and super duplex alloys at 45°C. At 70°C one 25 Cr duplex (UNS S32550) and one super duplex (UNS S32750) suffered crevice corrosion. The other super duplex UNS S32760 and 25 Cr alloys suffered no attack.

2.2 Oil and Gas Process System

In offshore process systems the environment is very different to sea water. The process water contains chlorides, but the concentration can vary from 10,000 mg/l to over 150,000 mg/l. In addition both Co_2 and H_2S are often present, and the pH can vary from about neutral down to about 2.5. All three duplex alloys hve excellent resistance to corrosion in sweet environments, but the presence of H_2 S increases the aggressivity of the process water. The possibility of pitting, crevice corrosion and stress corrosion cracking then arises.

Figure 1 shows some Sumitomo data comparing the relative resistance to pitting of 22 Cr and 25 Cr duplex alloys. The superior pitting resistance of the higher chromium alloy is clearly demonstrated. Figure 2 shows data of Gustaffson et al (5) for pitting of 22 Cr and super duplex, indicating that pitting occurs at temperatures in excess of 60°C for the 22 Cr alloy whereas temperatures of 100 to 200°C are necessary to initiate pitting on super duplex.

The 22 Cr alloy can suffer from SCC at high H_2S concentrations. NACE MRO 175 permits the use of 22 Cr at hardnesses up to 34 HRC at H_2S partial pressures up to 0.3 psi. Figure 3 shows data of Tsuge et al (6) comparing the SCC resistance of 22 Cr and 25 Cr duplex. The results show the superior resistance to SCC of 25 Cr compared to 22 Cr duplex. Table 2 shows some of the current process environments where super duplex (UNS S32760) is being used. Tests have also been carried out to compare super duplex with 25 Cr and 22 Cr alloys (7). The specimens were tested as C-rings loaded to about the 0.2% proof stress and tested at 80°C in a brine containing 46,000 mg/l chloride. The Co_2 partial pressure was 93 bar and three H_2S partial pressures were investigated, 0.125, 0.25 and 0.375 bar. The results are shown in Table 3. It can be seen from Table 3 that the 22 Cr alloy cracked at all of the sulphide concentrations, that the 25 Cr alloy cracked at the two higher concentrations, and the super duplex showed no signs of cracking even at the highest H_2S concentration.

Another corrosion problem which can arise in process environments is erosion at high velocities in the presence of sand. Pumps are designed with high velocities in mind but extreme turbulence can also arise in pipe systems, after sharp bends and partly throttled valves which can lead to excessive metal loss. Super duplex stainless pipe (UNS S32760) is currently being used in an environment with 2.1 bar Co_2 and 0.012 bar H_2S at 110°C and at a velocity of about 30 m/sec. The sand content is believed to be about 3 lbs/1000 bbls. Because of their demonstrated resistance to pitting, crevice corrosion and SCC, duplex and super duplex stainless steels are currently being used for a wide variety of components including pipes, fittings, flanges and pumps.

3. FUTURE DEVELOPMENTS

There are a number of areas where duplex stainless steels, particularly 25 Cr and super duplex, could be used more widely. One requirement for the more extensive use of the more highly corrosion resistant duplex alloys is data to indicate the limits of performance. The following section highlights some of the areas where duplex stainless could be used and explains what is required to prove its suitability.

3.1 Oil and Gas

25 Cr duplex and super duplex alloys have so for largely seen service in the North Sea, where H_2S levels are low. However, in other countries H_2S levels can be over 1000 ppm, particularly in older wells. Data in the previous section has demonstrated the high resistance of super duplex UNS S32760 to SCC at H_2S levels up to 0.375 bar. Further experiments are needed to explore the limits of use of super duplex in terms of both H_2S content and pH. The importance of pH has been demonstrated by Kermani et al (8) who showed that at critical H_2S concentrations a reduction of pH can cause SCC in an

otherwise resistant alloy.

The high resistance to erosion of duplex stainless steels is well known but there is no data to define the limits of use. The effect of both sand content and H_2S concentration on the critical velocity needs to be determined to take maximum advantage of the weight saving possible with duplex stainless steels.

3.2 Flue Gas Desulphurisation

This is an area which is receiving a great deal of attention in the UK. The high resistance to both corrosion and erosion at acid pH makes the 25 Cr and super duplex alloys very suitable for many areas where more costly nickel-based alloys have been used previously. The composition of a typical absorber slurry is shown in Table 4. A super duplex pump of UNS J93380 has been designed and built and has handled a mixture made to the composition shown in Table 4. After about 3000 running hours the pump was stripped for examination, and was found to be in immaculate condition. Alloy UNS J93380 has now been selected for the main slurry pumps at Drax power station.

There are other areas in FGD plant where duplex stainless could be considered, such as gas distribution plates, fasteners, sprinkler heads, slurry centrifuges and ducting applications.

What is required is data to support the use of duplex alloys under the conditions experienced by these components. Unfortunately, such conditions are difficult to reproduce realistically in the laboratory and a suitable pilot rig is really required to obtain reliable corrosion data.

3.3 Chemical Industry

Although some duplex stainless steel has been used by the chemical industry in the past (e.g. UNS S32550), there are opportunities for a greater use of duplex and super duplex pipe, fittings, flanges etc. in corrosive environments. There are many cases where a corrosive environment occasions a material shift from 316 stainless to nickel alloys such as C-276. 25 Cr duplex and particularly super duplex offer a lower cost alternative with a high corrosion and SCC resistance in many environments. Some examples of aggressive environments where duplex alloys could be used include dilute hydrochloric acid (up to ~ 10%), other hot acids containing chlorides, and hot caustic solutions. Because real process environments are not pure chemicals, it is necessary to prove the suitability of duplex stainless steels in the real process liquor, e.g. many stainless steels are resistant to acetic acid but the presence of small quantities of halides can cause rapid localised corrosion of alloys such as 316 SS.

One area where the high strength of duplex stainless steels combined with their high corrosion resistance is of particular value is for pressure vessels. Warburton et al (9) have described the fabrication and testing of a pressure vessel (1.5m dia by 3.5m long) in super duplex UNS S32760. This should lead the way to a wider use of duplex stainless steel by the chemical industry.

3.4 Pharmaceutical Industry

The pharmaceutical industry has similar requirements to the chemical industry, i.e. a lower cost alternative to nickel-base alloys for corrosive solutions such as chlorides, acids and oxidizing agents. In addition to resistance to corrosion and stress corrosion cracking the pharmaceutical industry also demands minimum pick-up by the product of metal cations. Hence it is very important that only very small concentratins of iron, chromium, nickel and molybdenum enter the solution. Recent tests of super duplex UNS S32760 in a chloride solution containing a strong oxidising agent demonstrated not only its resistance to crevice corrosion but also the extremely low pick-up of metal ions by the product. Similar tests in other pharmaceutical products should lead to a much wider use of duplex stainless by the industry.

3.5 Pulp and Paper

The pulp and paper industry includes many environments with moderate chloride levels, high levels of oxidants such as chlorine, temperatures above ambient and acid pH's. Traditionally 317L stainless has been used in the USA, and 904L in Europe, and where more aggressive conditions prevail there has been a tendency to use nickel base alloys. Although 6 Mo austenitic stainless steel has been used in pulp and paper plant in Scandanavia, there is little data on duplex stainless steel. Tuthill et al (10) have reported corrosion data from a previously unpublished field exposure test programme of Haynes International in D-stage chlorine dioxide bleaching plant. The exposure conditions in the five mills are shown in Table 5. The results for alloys 317L, UNS S31254 and UNS S32550 are shown in Table 6.

The results show that in most of the mills 25 Cr duplex (S32550) had a better resistance to both crevice corrosion and pitting compared not only to 317L but also to the 6 Mo austenitic alloy (S31254).

White waters contain chlorides, chlorine and oxidised sulphur species such as thiosulphate. Newman et al (11) have shown that 316 stainless can pit in these environments while 25 Cr duplex stainless steels should give excellent performance in such waters. The combination of high corrosion resistance and high strength of duplex stainless steels means that they are ideally suited for applications such as paper rolls. The wider acceptance of duplex stainless steels by the pulp and paper industry requires more comparative corrosion data in a range of typical environments.

4. CONCLUSIONS

The 25 Cr and super duplex stainless steels are widely used by the oil and gas industry in both sea water systems and process environments containing H_2S and CO_2. The super duplex alloys offer the possibility of extending the use of stainless steels to very sour conditions.

There are also many applications in the chemical, pharmaceutical, flue gas desulphurisation and pulp and paper industries where the combination of high pitting/crevice corrosion resistance, high erosion resistance and high strength of 25 Cr and super duplex stainless steels offers a lower cost alternative to nickel-base alloys.

REFERENCES

1) R. FRANCIS - Stainless Steels 87, York, UK 1987 Inst, Met. p 192

2) E.B. SHONE, R.E. MALPAS, P.GALLAGHER - Trans. I. Mar. E. 100 (1988) 193

3) R. FRANICS - BNF Metals Technology Centre Confidential Report R592/2 Feb 1988

4) P. GALLAGHER, R. E. MALPAS - Paper 113 Corrosion 89 New Orleans, USA April 1989 NACE

5) P. GUSTAFSON, H. ERIKSON - Stainless Steels 86, The Hague Netherlands October 1986 p 381

6) H. TSUGE et al - Metaux Corrosion Industrie Paper 337 1981

7) R. FRANCIS - To be presented at "Sour Service - Problems and Solutions" Aberdeen, November 1991

8) M. B. KERMANI, D. HARROP, M.L.R. TRUCHON, J. L. CROLET - Corrosion 91, Cincinnatti, USA, 1991 NACE Paper 21

9) G. WARBURTON, M. SPENCE, A. STEVENSON - Paper to be presented at Duplex Stainless Steels 91, Beaune, France, October 1991 Paper IVB5

10) A. H. TUTHILL, D. E. BARDSLEY - Proceedings of the Technical Association of the Pulp and Paper Industry, Engineering Conference, Seattle, USA, Sept 1990

11) R.NEWMAN et al - Corrosion 45, 4 (1989) 282

TABLE 1

COMPOSITION OF DUPLEX STAINLESS STEELS

ALLOY	COMPOSITION (WT %)				
	Cr	Ni	Mo	N_2	OTHERS
22Cr	21-23	4.5-6.5	2.5-3.5	0.08-0.2	
25Cr	24-27	4.5-6.5	2-4	0.1-0.25	Cu: up to 2.5
SUPER DUPLEX	24-26	6-8	3-5	0.2-0.32	W : up to 1.0 Cu: up to 1.0

<u>TABLE 2</u>

Some typical conditions currently being experienced by wrought and cast UNS S32760 super duplex stainless steel

	PRESSURE (BAR)			TEMPERATURE
	CO_2	H_2S	TOTAL	(°C)
1	6.0	0.012	240	110
2	2.1	0.2	31	110
3	1.3	0.01	138	80
4	-	0.01	76	55

<u>TABLE 3</u>

Results of SCC tests on C-rings loaded to 0.2% proof stress. Tested at 80°C with 93 bar CO_2 and 46,000 mg/l chloride. (From ref 7)

ALLOY	Pressure H_2S (BAR)		
	0.125	0.25	0.375
22Cr (Cold Worked)	No Crack/ Fine Crack	Crack/Crack	Several Cracks/ Several Cracks
25Cr (Cold Worked)	No Crack/ No Crack	Pits and Fine Cracks/ Pits and Fine Cracks	Several Fine Cracks
Super Duplex (UNS S32760) (Cold Worked)	No Crack/ No Crack	No Crack/ No Crack	No Crack/ No Crack

TABLE 4

Composition of absorber slurry

Calcium Sulphate	10.64 wt %
Calcium Carbonate	0.26 wt %
Chloride	40,000 mg/l
Flyash	0.47 wt %
pH	5.0
Temperature	50°C

TABLE 5

Conditions of test coupons in D stage of chlorine dioxide bleaching mills (from Ref 10)

MILL NO	pH	CHLORINE DIOXIDE* (mg/l)	TEMPERATURE (°C)	CHLORINE (mg/l)
1	3.1-5.5	20-200	68-71	+
3	3.5-4.5	0	60-63	Very Low
4	4-5	0	30-65	130
6	3.1-5.5	20-200	68-71	+
8	4.1	2,300	66	trace

* measured as active chlorine
\+ not reported

TABLE 6

Corrosion of stainless steels in acidic chlorine dioxide bleaching mills (from Ref 10)

MILL NO	EXPOSURE (Days)	ALLOY	CORR. RATE (um/yr)	BASE PLATE PITTING (mm)	CREVICE CORROSION (mm)
1	258	317L	30	YES	YES
		S31254	NR	< 0.61	0.81
		S32550	NR	0.15	0.25
3	270	317L	NR	0.79	0.61
		S31254	-	-	-
		S32550	NR	0.18	0
4	2,000	317L	NR	0.79	0.61
		S31254	-	-	-
		S32550	NR	0.18	0
6	150	317L	NR	< 0.76	< 0.76
		S31254	NR	< 0.76	< 0.76
		S32550	25	< 0.13	0
8	229	317L	NR	< 0.76	< 0.76
		S31254	NR	< 0.38	< 0.38
		S32550	NR	< 0.38	0

NR = not recorded
- = not exposed

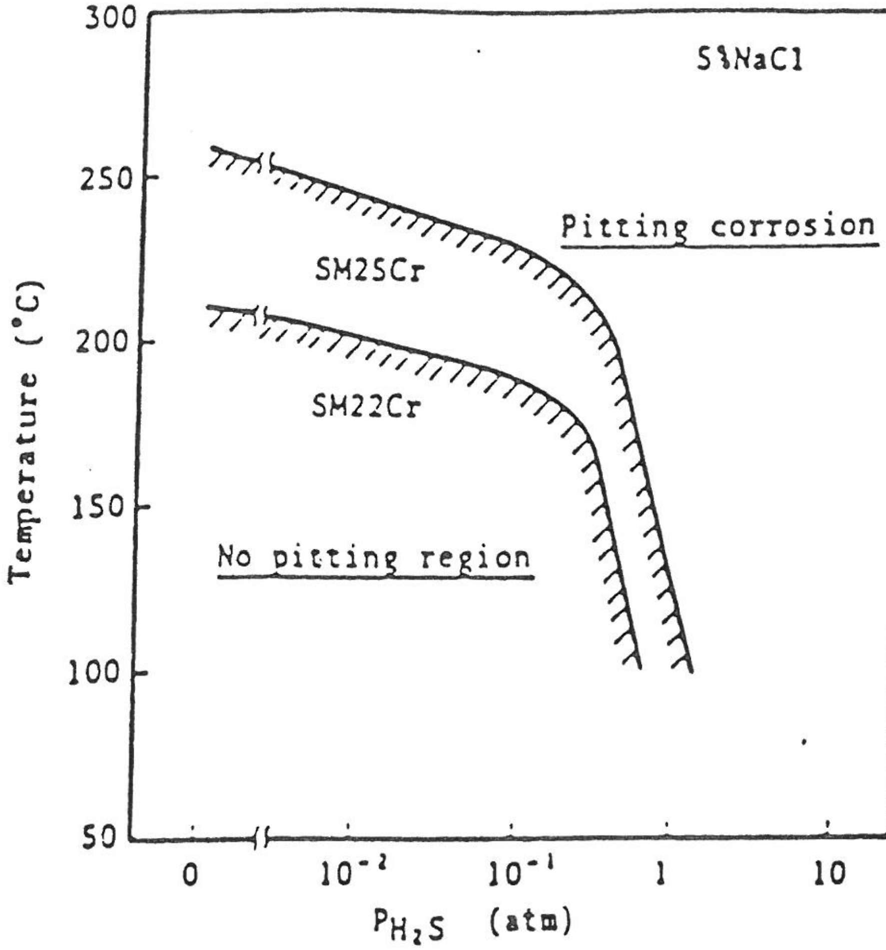


FIGURE 1: PITTING OF 22 Cr AND 25 Cr DUPLEX STAINLESS STEEL AS A FUNCTION OF H_2S PRESSURE AND TEMPERATURE

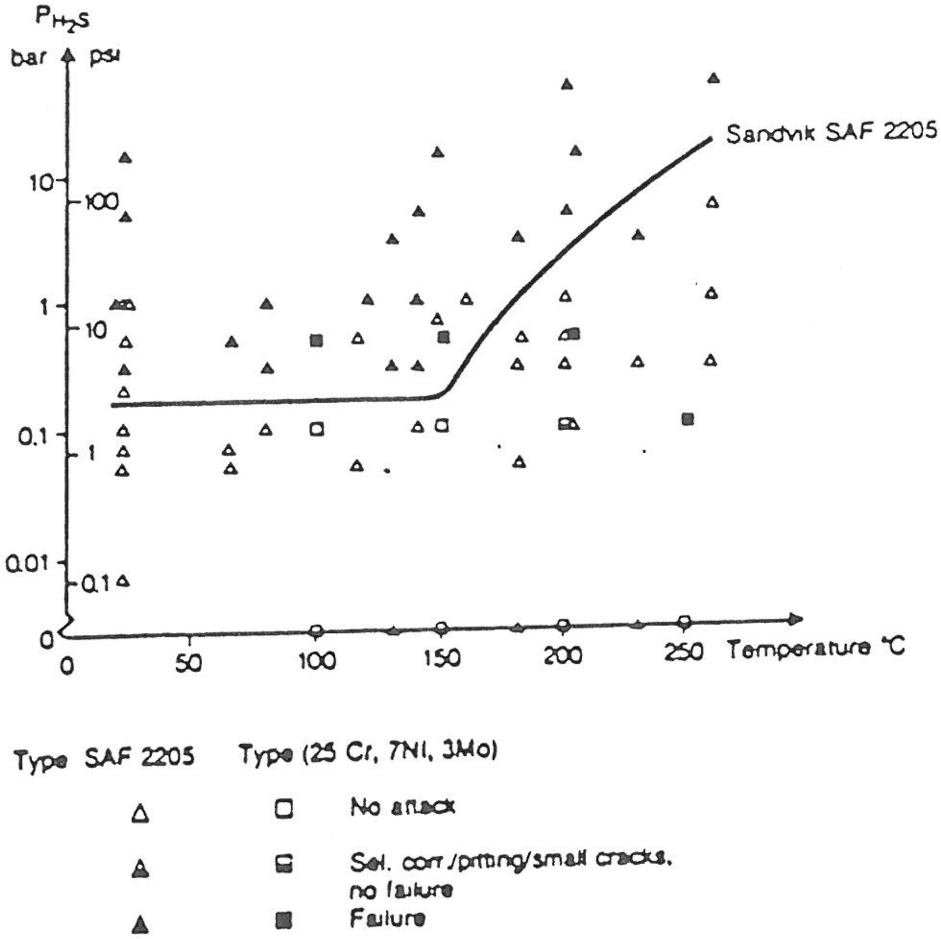
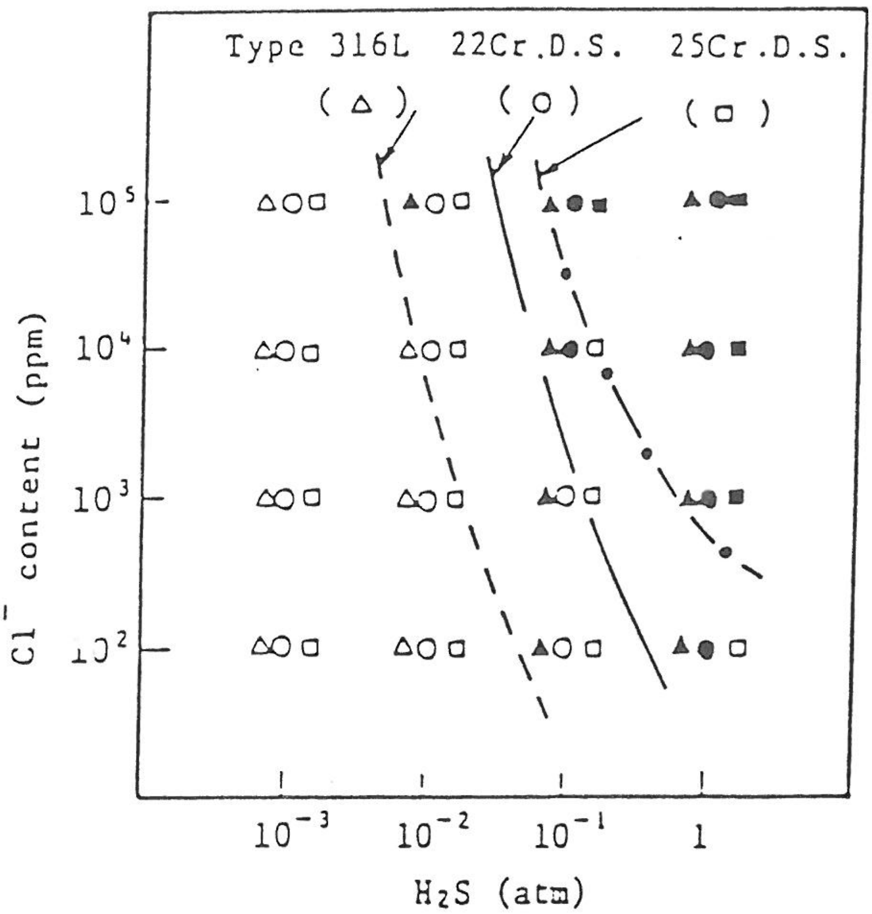


FIGURE 2: PITTING OF DUPLEX STAINLESS STEEL AS A FUNCTION OF H_2S PRESSURE AND TEMPERATURE

FIGURE 3



SCC susceptibility of 22Cr duplex stainless steel in Cl^--H_2S environtemt. ○ : No SCC, ● : SCC (SSRT method: 80°C, strain rate 4.2×10^{-6}/S)