Atlas of Microstructures

AF234/7226/MSchü

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Table of Contents

Creep Rupture Samples

- 1675°F/913°C

- 1800°F/982°C

- 1920°F/1050°C

- 2012°F/1100°C

Introduction

Up to and through the 1940's, furnace tubes were typically fabricated from wrought chromium steels and/or austenitic stainless steel alloys. Having rather low carbon concentrations, these alloys had poor creep strength and limited service lives. To increase tube life, greater carbon concentrations were required to promote precipitation hardening upon elevated temperature exposure. The increased carbon concentrations, however, generally resulted in excessive work hardening during conventional processing of wrought materials. The use of centrifugal casting, pouring molten metal in a horizontal spinning mold, allowed founders to develop high carbon alloys as the molten metal solidified into near final shape without the need for subsequent metal working operations. Thus, refinement of centrifugal casting processes was the gateway to further alloy development and more aggressive furnace operations.

The first widely used centrifugal cast alloy for steam-methane reformer tube applications was HK40 in the 1950's timeframe. HK40 is essentially the cast equivalent to wrought 310 stainless steel nominally containing 25 wt% chromium, 20 wt% nickel, with iron as the balance. However, HK40 nominally contains 0.40 wt% carbon while wrought 310 stainless steel contains only 0.08 wt% carbon. The increased carbon content and precipitation of primary carbides resulted in HK40 having greatly improved high temperature strength as compared to wrought 310 stainless steel. In the 1960's, the cast HP alloys (nominally 25 wt% chromium, 35 wt% nickel, 0.50 wt% carbon, with iron as the balance) were developed to provide greater creep strength as compared to HK40.

The HK and HP alloys rely on precipitation of $M_{23}C_6$ and/or M_7C_3 carbides (where M is primarily chromium) for elevated temperature creep strength. The precipitated chromium carbides in the HK and HP alloys tended to coalesce as exposure temperatures approached 1800°F (982°C). The carbide coalescence decreased the creep strength and, therefore, limited the strength of these alloys at elevated temperatures. Microstructural changes that occur in the HK and HP alloys with extended aging time and temperature have been well documented by Battelle Columbus Laboratories[1]. The Battelle data has proven to be a valuable resource in estimating reformer tube exposure conditions associated with reformer tube failure analyses and remaining life assessments.

User demand for higher temperature/stronger alloys fueled continued alloy development resulting in the introduction of the HP-modified alloy in the 1970's. The HP-modified alloy had the same nominal chemistry of the HP alloy along with the addition of typically 1 wt% niobium. The niobium addition results in precipitation of $M_{23}C_6$, M_7C_3, and MC type primary carbides upon solidification. In the $M_{23}C_6$ and M_7C_3 carbides, niobium substitutes for some of the chromium with the complex niobium-chromium carbides being more stable at elevated temperatures as compared to chromium carbides. In the HP-modified alloy, niobium is the primary carbide forming element in the MC type carbides.

In the 1980's, the demand for more severe design conditions and/or design lives in excess of 100,000 hours led to the introduction of the HP-micro-alloyed material. HP-micro-alloyed (or commonly designated as HPMA) material was based on the HP-modified chemistry with "micro" additions of alloying elements. In general, micro-alloying refers to intentional alloying additions at a concentration of 0.10 wt% or less. Titanium is the most common micro-alloying addition with other micro-alloying additions including zirconium, tantalum, or tungsten. Rare earth elements such as lanthanum, cerium, and/or yttrium may also be added. The micro-alloying additions provide a fine dispersion of MC type carbides that are stable at temperatures well in excess of 2,000°F (1093°C).

In the 1990's, the 35Cr/45Ni alloy family grew in popularity. The 35Cr/45Ni alloy has similar creep strength to the HPMA alloy but with notably improved carburization resistance. The excellent carburization resistance made the 35Cr/45Ni alloy well suited for ethylene pyrolysis furnace tubes.

As outlined above, alloy development has continued in centrifugally cast heat resistant alloys allowing users to design for and operate at more severe conditions. Unlike the HK40 and HP50 alloys, there is virtually no published data on the microstructural changes that occur in the HP-modified, HPMA, or 35Cr/45Ni alloys upon long term aging. In an effort to address industry need, the Materials Technology Institute (MTI) sponsored the Atlas of Microstructures project. The specimens analyzed in the Atlas of Microstructures were foundry stress rupture specimens generously donated by MetalTek International, Duraloy Technologies, Kubota Metal Corp., and Manoir Industries. In addition, service exposed samples, having longer aging times than the foundry stress rupture specimens, were donated by operating companies including Air Products & Chemicals, Syncrude Canada, Eastman Chemical, and MetalTek International. The thorough, detailed microstructural analyses were completed at the Karl-Winnacker Institut der DECHEMA in Frankfurt, Germany.

The Atlas of Microstructures documents microstructural changes with increased aging time and temperature, identification and chemical composition of precipitated phases, as well as diagrams characterizing the kinetics of phase transformation for the HP-modified, HPMA, and 35Cr/45Ni alloy classes. This MTI Atlas of Microstructures bridges the gap from the Battelle project from the early 1970's to the most important alloys used in the petrochemical industry today.

Description of the Test Specimens

Creep rupture test specimens

The specimens that had been taken from creep rupture tests can be summarized with regards to their exposure conditions and their chemistry in Tables 1-6. For each of the three materials investigated an as-delivered (as-cast) specimen as reference sample was available. For alloy 35Cr/45Ni and alloy HP Modified twelve creep specimens had been supplied for the investigations. For alloy HPMA sixteen creep specimens existed. The test temperatures varied between 1675 and 2100°F (913 and 1149°C), the maximum exposure times reached 12,289 h. The stress range was between 1.0 and 8.5 ksi (6.9 and 58.8 MPa). The scatter of the chemical compositions was in the allowed range for these materials.

continued on page 8

Table 1: Alloy 35/45 Exposure Conditions

Sample_ID Dechema	Sample MTI	Test-Temp °F	Test-Temp °C	Stress Ksi	Stress MPa	Expo. Time hrs
A234_003	35/45-1 (c)	as cast	as cast			
A234_004	35/45-2	1800	982	3.30	22.8	1,509
A234_005	35/45-3	1800	982	2.90	20.0	7,217
A234_006	35/45-4	1922	1050	3.40	23.4	367
A234_007	35/45-5	1900	1038	2.09	14.4	2,023
A234_008	35/45-6	1900	1038	1.60	11.0	6,331
A234_009	35/45-7	1900	1038	1.54	10.6	10,247
A234_010	35/45-8	2012	1100	2.00	13.8	335
A234_011	35/45-9	2000	1093	1.80	12.4	1,297
A234_012	35/45-10	2012	1100	1.15	7.9	3,545
A234_013	35/45-11	2057	1125	1.60	11.1	277
A234_014	35/45-12	2050	1121	1.00	6.9	2,606
A234_015	35/45-13	2100	1149	1.50	10.3	248

Table 2: Chemistry of Alloy 35Cr/45Ni Stress Rupture Samples

Sample_ID Dechema	Sample MTI	Composition (wt%)								
		Cr	Ni	Fe	Mn	Si	C	Nb	N	Other
A234_003	35/45-1 (c)	35.85	44.59	bal	0.60	1.55	0.38	0.91	0.08	Ti, Zr & W
A234_004	35/45-2	35.12	43.69	bal	1.32	1.83	0.46	0.78	0.06	Ti, Zr & W
A234_005	35/45-3	34.84	44.43	bal	1.46	1.86	0.43	0.83	0.04	Ti, Zr & W
A234_006	35/45-4	32.30	43.40	bal	1.02	1.52	0.41	1.21	0.065	Ti
A234_007	35/45-5	32.39	44.77	bal	1.40	1.85	0.42	1.25	NR	
A234_008	35/45-6	34.34	45.42	bal	1.04	1.30	0.37	1.22	NR	Ti
A234_009	35/45-7	34.41	45.37	bal	1.31	1.78	0.42	1.20	NR	Ti
A234_010	35/45-8	32.30	43.40	bal	1.02	1.52	0.41	1.21	0.065	Ti
A234_011	35/45-9	32.65	44.61	bal	1.37	1.71	0.42	1.14	NR	
A234_012	35/45-10	34.84	44.43	bal	1.46	1.86	0.43	0.83	0.04	Ti, Zr & W
A234_013	35/45-11	32.30	43.40	bal	1.02	1.52	0.41	1.21	0.065	Ti
A234_014	35/45-12	32.59	44.34	bal	1.43	1.82	0.42	1.25	NR	
A234_015	35/45-13	34.84	44.43	bal	1.46	1.86	0.43	0.83	0.04	Ti, Zr & W

Table 3: Alloy HPMA Exposure Conditions

Sample_ID Dechema	Sample MTI	Test-Temp. °F	Test-Temp. °C	Stress Ksi	Stress MPa	Expo. Time hrs
A234_018	HPMA-1 (c)	as cast	as cast			
A234_019	HPMA-2	1700	927	8.00	55.2	183
A234_020	HPMA-3	1700	927	6.00	41.3	2,338
A234_021	HPMA-4	1700	927	5.30	36.6	6,072
A234_022	HPMA-5	1750	954	4.45	34.1	8,359
A234_023	HPMA-6	1800	982	5.97	41.2	177
A234_024	HPMA-7	1800	982	3.51	24.2	2,436
A234_025	HPMA-8	1800	982	3.90	26.9	6,478
A234_026	HPMA-9	1832	1000	3.00	20.7	12,289
A234_027	HPMA-10	1922	1050	3.48	24.0	137
A234_028	HPMA-11	1950	1066	2.80	19.1	2,558
A234_029	HPMA-12	1922	1050	2.32	16.0	4,864
A234_030	HPMA-13	1922	1050	2.08	14.3	11,778
A234_031	HPMA-14	2012	1100	2.39	16.5	105
A234_032	HPMA-15	2012	1100	1.80	12.4	2,714
A234_033	HPMA-16	2012	1100	1.45	10.0	5,580
A234_034	HPMA-17	2012	1100	1.35	9.3	8,990

Table 4: Chemistry of Alloy HPMA Stress Rupture Samples

Sample_ID	Sample	Composition (wt%)								
Dechema	MTI	Cr	Ni	Fe	Mn	Si	C	Nb	N	Other
A234_018	HPMA-1 (c)	25.01	33.79	bal	0.65	1.08	0.45	0.65	0.06	Ti, Zr & W
A234_019	HPMA-2	24.92	34,54	bal	0.78	0.80	0.50	0.49	NR	Ti
A234_020	HPMA-3	24.29	32.51	bal	1.31	1.37	0.42	0.40	NR	W
A234_021	HPMA-4	25.01	33.79	bal	0.65	1.08	0.45	0.65	0.06	Ti, Zr & W
A234_022	HPMA-5	25.01	33.79	bal	0.65	1.08	0.45	0.65	0.06	Ti, Zr & W
A234_023	HPMA-6	25.85	35.25	bal	0.89	1.12	0.47	0.95	NR	
A234_024	HPMA-7	24.38	35.13	bal	0.79	0.85	0.46	1.08	NR	Ti & W
A234_025	HPMA-8	24.49	33.53	bal	0.56	1.14	0.44	0.51	0.05	Ti, Zr & W
A234_026	HPMA-9	24.49	33.53	bal	0.56	1.14	0.44	0.51	0.05	Ti, Zr & W
A234_027	HPMA-10	24.36	33.18	bal	1.37	1.73	0.46	0.83	NR	Ti & Zr
A234_028	HPMA-11	25.11	36.13	bal	0.91	1.33	0.48		NR	Ti & W
A234_029	HPMA-12	25.01	33.79	bal	0.65	1.08	0.45	0.65	0.06	Ti, Zr & W
A234_030	HPMA-13	24.49	33.53	bal	0.56	1.14	0.44	0.51	0.05	Ti, Zr & W
A234_031	HPMA-14	24.36	33.18	bal	1.37	1.73	0.46	0.83	NR	Ti & Zr
A234_032	HPMA-15	24.49	33.53	bal	0.56	1.14	0.44	0.51	0.05	Ti, Zr & W
A234_033	HPMA-16	24.49	33.53	bal	0.56	1.14	0.44	0.51	0.05	Ti, Zr & W
A234_034	HPMA-17	25.01	33.79	bal	0.65	1.08	0.45	0.65	0.06	Ti, Zr & W

Table 5: Alloy HP Modified Exposure Conditions

Sample_ID Dechema	Sample MTI	Test-Temp. °F	Test-Temp. °C	Stress Ksi	Stress MPa	Expo. Time hrs
A234_036	HPNb-1 (b)	as cast	as cast			
A234_038	HPNb-2	1675	913	6.50	44.6	659
A234_039	HPNb-3	1700	927	8.50	58.8	59
A234_040	HPNb-4	1750	955	5.10	35.2	794
A234_041	HPNb-5	1778	970	5.15	25.5	286
A234_042	HPNb-6	1778	970	3.77	26.0	1,185
A234_043	HPNb-7	1800	982	5.40	37.4	191
A234_044	HPNb-8	1800	982	5.42	37.4	4,467
A234_045	HPNb-9	1800	982	5.52	37.4	7,833
A234_046	HPNb-10	1800	982	2.80	19.3	10,637
A234_047	HPNb-11	1850	1010	3.60	24.8	707
A234_048	HPNb-12	1900	1038	2.30	15.8	2,555
A234_049	HPNb-13	1900	1038	1.90	13.1	5,373

Table 6: Chemistry of Alloy HP Modified Stress Rupture Samples

Sample_ID	Sample	Composition (wt%)								
Dechema	MTI	Cr	Ni	Fe	Mn	Si	C	Nb	N	Other
A234_036	HPNb-1 (b)	25.30	34.93	bal	1.29	1.40	0.44	1.06	NR	
A234_038	HPNb-2	25.34	34.88	bal	0.74	1.67	0.43	0.75	0.06	W & Zr
A234_039	HPNb-3	25.26	33.56	bal	0.72	1.23	0.42	0.74	0.06	W & Zr
A234_040	HPNb-4	25.34	34.88	bal	0.74	1.67	0.43	0.75	0.06	W & Zr
A234_041	HPNb-5	25.11	32.85	bal	1.34	1.79	0.45	0.83	NR	
A234_042	HPNb-6	25.11	32.85	bal	1.34	1.79	0.45	0.83	NR	
A234_043	HPNb-7	24.88	33.33	bal	0.84	1.29	0.41	1.18	NR	W
A234_044	HPNb-8	24.86	33.79	bal	0.90	1.37	0.41	1.22	NR	W
A234_045	HPNb-9	24.86	33.30	bal	0.83	1.35	0.42	1.2	NR	W
A234_046	HPNb-10	25.26	33.56	bal	0.72	1.23	0.42	0.74	0.06	W & Zr
A234_047	HPNb-11	25.62	34.75	bal	0.94	1.71	0.48	0.82	0.06	W
A234_048	HPNb-12	25.26	33.56	bal	0.72	1.23	0.42	0.74	0.06	W & Zr
A234_049	HPNb-13	25.26	33.56	bal	0.72	1.23	0.42	0.74	0.06	W & Zr

Metallographic Preparation

From the specimens available sections were taken for metallographic preparation with the surfaces to be investigated oriented parallel to the longitudinal direction of the tensile creep rupture specimens or perpendicular to the longitudinal axis of the tube specimens. Cutting was performed by using a precision sectioning machine with direct water cooling of the specimen. Some of the specimens had been delivered in the embedded state from which smaller sections were taken by saw cutting which were embedded again. Hot embedding in a conductive epoxy resin was used with a diameter of the moulds of 25 mm and after this the specimens were ground on SiC papers of the grades 180, 220, 320, 500, 1000 down to grit 2400 (Struers Standard 43-GB-1984, DIN 69176, Part 1,2,4) with a pressure of 70-80 N and water as a lubricant. Fine polishing was performed with a two step diamond polish of 3 µm and 1 µm followed by the finalizing polish with SiO_2 suspension of size 0.02 µm. The area on the specimen surface to be investigated was marked by four Vickers hardness imprints (HV1) with a distance of 500 µm. Usually these areas were marked in the center of the specimen (in some cases, however, in addition regions close to the surface were investigated after marking).

Investigation Techniques

Differential Interference Contrast Technique (LM-DIC)

For documentation of the microstructure in the light microscope at high magnification (500x and 1000x) the differential interference contrast (LM-DIC) technique[2] was used by which the different phases due to the different hardness reveal certain topographical structures which facilitates distinction of these phases.

Scanning Electron Microscopy (SEM-BSE)

After the LM-DIC investigations the same spot was investigated by the scanning electron microscope using the back-scattered electron imaging technique (SEM-BSE). In this case the differences in contrast of the different precipitates resulting from differences in the density can be used in order to distinguish between the phases.

Electron Probe Microanalysis (EPMA)

As a next step the phases documented by the other two techniques were analyzed quantitatively for selected specimens with regard to their chemical composition. In each case several spot measurements were taken with a beam diameter of 2 µm. The results of these measurements were averaged. From the ratio between the different metals in the precipitates conclusions were drawn on the respective carbide type by taking carbon and nitrogen respectively from the difference of the sum of the determined metal fractions and 100%.

Interference Layer Metallography (LM-ZnSe)

After the EPMA investigations the specimens were coated by a PVD process in an evaporation equipment (Edwards) at a vacuum of about 10^{-3} mbar[3-7]. As a coating material zinc selenide (ZnSe) was used which allowed the comparison of these marked areas in the colored state with the images from the other techniques. The evaporation source consists of a little vessel made of tantalum with ZnSe grains filled into this vessel. By resistance heating the vessel is heated to a point where the ZnSe starts to evaporate. The evaporation rate is controlled by controlling the heating current together with observation of changes of the color of the section surface. When reaching the desired color (violet as a macroscopic color) of the specimen surface the heating current is switched off immediately in order to achieve a reproducible thickness of the interference layer. Since the reflection characteristics change periodically with the layer thickness and manual control of the heating current is not easy this coating technique requires significant experience in order to achieve a suitable interference layer. In some cases the layer had to be removed again from the section surface several times and a new coating had to be applied in order to come to satisfactory results. Due to the small dimensions of the different phases there may be slight deviations between the different photographs taken by the different techniques.

Image Analysis by the False Color Technique (LM-FC)

By the use of the automated image analysis system Leica QWin in combination with an automated laboratory microscope Leica DMLA the different fractions of the precipitations which had been characterized before by the other techniques were measured. For these measurements specimens were used which had been contrasted by the interference layer technique beforehand. An automated program routine was developed by which for each specimen several focused images were taken at representative spots in the specimen center and partially also at the specimen edges at a magnification of 1000x. The images were stored and in a second run the lower and upper threshold values for the RGB (red, green, blue)-colors of the different phases were determined and recorded. Since, during the coating process the ZnSe layer can vary from specimen to specimen, this procedure had to be performed for all specimens at least once. For specimens where the microstructure in the center and in the outer region was different this procedure had to be applied separately for the two regions. The program routine allows manual interaction with the measurement procedure, i.e. artifacts like creep pores or cracks can be eliminated in order not to influence the measurement results. Based on the information in the binary memory, each of the phases was represented by a defined (false) color. For the different types of carbides and other phases the following false colors were selected:

M_7C_3	- purple	M_6C	- red
$M_{23}C_6$	- yellow	$M_2(C,N)$	- green
M(C,N), MN	- blue, cyan	G-phase	- magenta

The matrix was not binarized and was used as a background in true colors behind the false color image.

Development of the Microstructure by Etching (LM-etched)

Finally the interference layers were polished off and sections were etched for 30 seconds at 50°C in etchant V2A (composition: 100 ml H2O, 100 ml HCl 1.19, 10 ml HNO3 1.40, 0.3 ml Dr. Vogel's pickle. Dr. Vogel's pickle is a mixture of organic solvents with Thiourea. It consists of 1-Methoxy- 2-propanol (40-50%), Thiourea (3-5%) and Nonylphenol-ethoxylate (5-7%).

The interesting areas of the specimen were photographed at 200x and 500x magnification. By etching the matrix is partially removed so that edges are formed at the transition from matrix to precipitate. Due to the local reflection situation of the light which hits the surface perpendicularly the edges of these phase boundaries appear dark in the photograph so that all phases have a dark seam and the grain boundaries become visible.

(For more discussion on the etching technique, see the Addendum).