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The Effect of Long-Term Thermal Exposure at Elevated Temperatures on Microstructures and Mechanical Properties in Centrifugally Casted Iron-Base Alloy.

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Abstract

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This work has an aim to study and investigate the relationship between high temperature exposure conditions on microstructural evolution and mechanical properties in the iron-based alloy, Fe-30.8 Ni - 26.6 Cr alloy, strengthened by carbide precipitation. Two exposure temperatures (900 and 1000°C) with various thermal exposure times are introduced to the as-received alloy. After short-term exposure, it was found that the secondary carbides precipitated early near the primary carbides, which were chromium and niobium/titanium carbide networks. The secondary carbide precipitations were also found in the dendrite cores. The amounts of needle-like carbides and secondary carbide films increased with time and temperature of aging. However, by EDS analysis, the composition of secondary carbides was almost the same as that of primary carbides for 24 hours heating time. However, they continued to change when thermal exposure time increased. It can be summarized that the exposure conditions have effect on shape, size, dispersion and the location of secondary carbides in microstructure and result in the different mechanical properties such as hardness and tensile strength. Under exposure at 900°C, the very fine precipitates of secondary carbide particles located and concentrate in the area close to primary carbide. In case exposure at 1000°C, the coarser secondary carbides dispersed to the cores of dendrites. The needle-like and film carbides were found in heat-treated specimens at both temperatures. The precipitated secondary carbides precipitated after long-term exposure conditions were chromium carbides, which its chemical composition was similar to primary chromium carbide. It could be concluded that the uniform precipitation and dispersion of fine secondary carbides resulted in slightly higher ultimate tensile and yield strengths as well as hardness in the short-term aging. Then both hardness of tensile strength slightly decreased.

Key words : Iron-base alloy, Heat treatment, Aging, Carbide precipitation, Mechanical properties Microstructure

Introduction

The cast iron base alloys are widely used in the petrochemical industries, especially under conditions of long-term exposed at high temperatures in the range of 850 - 1150°C. The low to medium strength at high temperature is not the only one requirement but also the good resistance to surface degradation at such high temperatures such as hot oxidation and corrosion as well as good resistance to thermal fatigue. Most of the alloys in this Fe-Ni-Cr system contain chromium about 15 wt. % to improve surface degradation resistance at elevated temperatures as well as Nickel about 25 wt. % to stabilize the austenitic structure for good strength at high temperatures.

The Fe-30.8Ni-26.6Cr alloy, one of iron-base alloy produced in the form of centrifugally cast tubes, is mainly used in petrochemical industry as material in reformer and pyrolysis furnaces. This alloy has been used instead of expensive superalloys with sufficient high temperature properties such as creep strength. Therefore, many microstructural features have been developed in order to increase high temperature strength in material. The designed microstructure would

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contain a uniform coarsening grain size with beneficial segregation or particle dispersions such as fine and discontinuous carbides of the grain boundaries resulting in higher creep strength and crack growth resistance as well as for fatigue strength.[1] The Fe-30.8Ni-26.6Cr alloy is not a standard alloy, which can be simply classified in HP alloy group but it can be compared to another non-standard HP-35Ni-25Cr alloy. This non-standard iron alloy group consists of more additional elements. These additional elements can be defined as carbide forming elements: niobium, molybdenum, titanium, tungsten and zirconium as well as non-carbide forming elements: aluminum, copper and cobalt for an increase in strength and resistance to carburization. The addition of silicon in very high amount can improve carburization resistance but decreases creep and rupture strength. The carbon content must be carefully controlled to provide strength as carbide precipitation strengthening. However, too much carbon content would decrease the resistance to cyclic thermal shock.[2]

The desired structure of the alloy could be achieved by heat treatment process by means of modified microstructures via a precipitation process of primary and secondary carbides under aging conditions. A number of studies.[3-12] were done subsequently to evaluate the phase changes during heat treatment process and the influence of its microstructure to mechanical strength at both room and elevated temperatures. An improved knowledge of this relationship leads to the development of new aging condition. The tube production using the centrifugal casting technique provides the higher creep properties through the morphological modifications in microstructure and the presence of more stable phases during long-term exposure. The primary eutectic-like carbide network appears to play an important role in resisting grain boundary sliding. Secondary precipitation of fine cube-shaped chromium carbides should act as barriers to dislocation movements. However, there are still very few studies on the microstructural evolution in the Fe-38.8Ni-26.6 Cr alloy to increase mechanical properties by various heat treatment conditions including the investigation of precipitation of secondary carbides and other phase transformations. Therefore, this research study provides an attempt to achieve the optimal microstructure characteristic and mechanical properties. The aging heat treatment programs were systematically performed in the as-received alloy after long-term use. The obtained specimens after various aging conditions were investigated and analyzed.

Material and Experimental Procedure

The Fe-38.8Ni-26.6Cr alloy has a chemical composition by wt. % as shown in Table 1. The as-received alloy was produced by the casting process. The initial alloy was still not proper microstructure and does not have good mechanical properties as desired after this manufacturing. Thus, the following heat treatment is necessary to fulfill the material requirements. Therefore, various conditions according to the tested program were carried out to the alloy as follows:

1) Aging at 900°C for 24, 200, 400, 600, 800 and 1000 hours;

2) Aging at 1000°C for 24, 200, 400, 600, 800 and 1000 hours;

Finally, all tested specimens were observed and analyzed by an optical microscope and scanning electron microscope. To find out the mechanical properties then hardness and tensile tests were carried out.

Table 1. Chemical composition of the alloy (by wt.%; analyzed by Emission Spectroscopy)

C	Si	Mn	Cr	Ni	Cu	Co	Al	Nb	Ti	V	Pb	W	Fe
0.3	1.43	1.40	26.6	30.8	0.05	0.17	0.003	0.68	0.054	0.049	0.005	0.25	38.2

Results and Discussion

Microstructure investigation

Microstructure of as-received alloy

The received microstructure consists of primary carbide networks in austenitic matrix, as shown in Figures. 1 and 2. The dendrite structure indicates the characteristic of casting microstructure. However, no secondary carbide was detected in the microstructure, see Figure. 2. From SEM analysis, it was found that the primary carbide networks could be classified in two types as black and white phases, Figure. 2 Using EDS to analyze the chemical composition of each phase is concluded that the black phase consists of 63.37% of chromium, 9.21% of nickel and 16.58% of Iron. The white phase consists of 0.45% titanium, 36.92% niobium and 9.39 % chromium.

The matrix consists of 38.16% iron, 33.86% nickel, and 23.59% chromium, see Table 2. The alloy consists of 30.8 % nickel, which is high enough to stabilize the austenitic matrix microstructure. The primary carbide networks could form during slow cooling of solidified alloy by the combination among carbon, chromium, niobium and titanium. Titanium and niobium would form as niobium-titanium carbide, which precipitated at higher temperature comparing to chromium carbide (with high ratio between Cr and C).[3] Therefore, the presence of primary carbide precipitation type is M23C6.[4] They usually located near austenitic grain boundary networks.

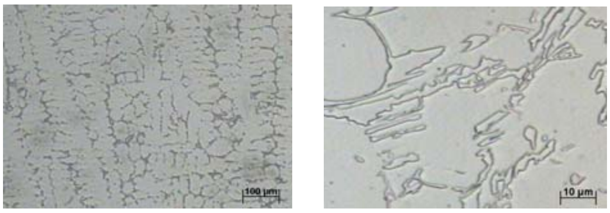


Figure. 1 Microstructure of as-received material; Low magnification (Left) and High magnification (Right)

Table 2. EDS analysis of as-received alloy (by wt.%)

Phase	Fe	Ni	Cr	Si	Nb	Ti	C
Matrix	38.16	33.86	23.59	1.18	-	-	3.21
Primary carbide	16.58	9.21	63.37	0.55	-	-	10.29
Niobium carbide	10.24	9.14	9.39	0.49	36.92	0.45	33.37

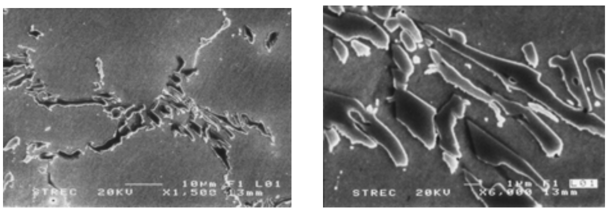


Figure. 2 SEM micrograph of as-received material ; Low magnification (Left) and high magnification (Right)

Microstructure of the alloy after long-term exposure

From SEM micrographs, generally, all microstructures after various thermal exposure conditions were found in similar manner. Most of microstructures consist of primary carbides as the as-received microstructure. However, very fine precipitations of secondary carbides were found locating in the matrix, usually, in areas close to primary carbides, Figures. 3-8. After aging at 900°C the secondary carbide particles concentrated in the zones adjacent to the primary carbides. The amounts of secondary carbide particles increase with exposure time, as shown in Figsure. 3 and 5. Furthermore, the film and needle-like carbides were also observed as well. It should be noted that these secondary carbide particles precipitate in higher concentration near the primary carbide particles and more precipitation disperse toward the dendrite core when exposure times increase. However, when exposure times increased, the previous precipitation of secondary carbide particle would agglomerate to become in coarser sizes and there are more very fine secondary carbides in higher amount in the center of dendrite core. Coarsening needle-like and film carbides are also found.

The microstructures, after aging at 1000°C for various exposure times, are quite similar to those aged at 900°C, Figures. 4 and 6. The secondary carbides are in round shape and precipitate toward the dendrite core. The secondary carbides are in higher concentration comparing to the primary carbides. For exposured microstructure for 24 hours, very fine particles of secondary carbide would agglomerate as coarsening size. However, using SEM investigation in all cases, precipitates free zones (PFZ) were found close to primary carbides because of low chromium content in these areas, where chromium precipitated during previous secondary carbide precipitation.

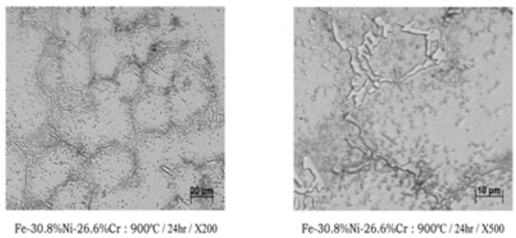
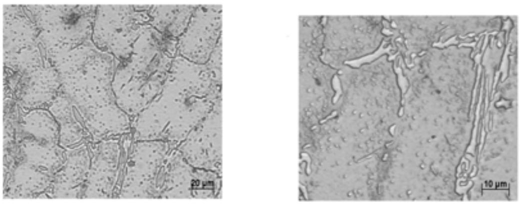


Figure. 3 Microstructure of specimen after aging at 900°C for 24 hours; Low magnification (Left) and High magnification (Right)



Fe-30.8%Ni-26.6%Cr : 1000°C / 24hr / X200 Fe-30.8%Ni-26.6%Cr : 1000°C / 24hr / X500

Figure. 4 Microstructure of specimen after aging at 1000°C for 24 hours; Low magnification (Left) and High magnification (Right)

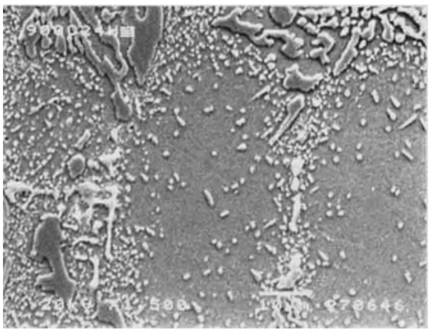


Figure. 5 SEM micrograph of specimen after aging at 900°C for 24 hours

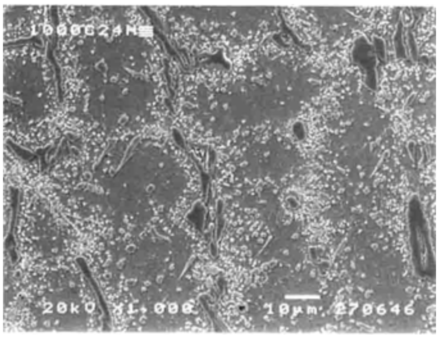


Figure. 6 SEM micrograph of specimen after aging at 1000°C for 24 hours

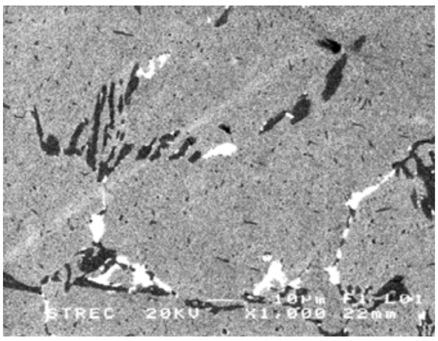


Figure. 7 SEM micrograph of specimen after aging at 900°C for 1000 hours

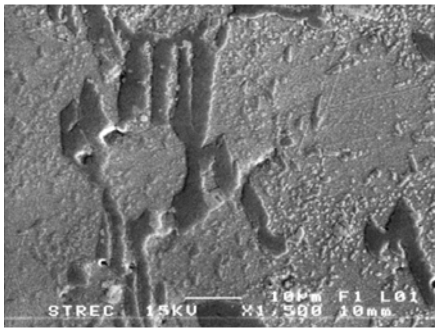


Figure. 8 SEM micrograph of specimen after aging at 1000°C for 1000 hours

Table 3. EDS analysis of individual phases after aging at 900°C for 24 hours (by wt.%)

Elements	Fe	Ni	Cr	Si	Nb	Ti	C
Matrix	37.32	32.24	25.23	1.79	-	-	3.42
Primary carbide	21.42	15.38	52.10	0.96	-	-	10.14
Secondary carbide	13.01	10.97	70.44	0.89	-	-	4.69
Needle-like carbide	15.17	10.79	62.41	0.76	-	-	10.87
Niobium carbide	10.65	10.98	8.73	1.51	37.14	1.74	29.25

Table 4. EDS analysis of individual phases after aging at 1000°C for 24 hours (by wt.%)

Elements	Fe	Ni	Cr	Si	Nb	Ti	C
Matrix	37.28	33.56	24.19	1.08	-	-	3.89
Primary carbide	26.26	9.32	53.26	0.47	-	-	10.69
Secondary carbide	12.80	10.36	70.66	1.17	-	-	5.01
Needle-like carbide	15.75	10.23	68.93	0.79	-	-	4.30
Niobium carbide	9.82	12.42	8.43	1.41	38.12	2.36	27.44

From EDS analysis of specimens after 24 hours exposure in both high temperatures, it was found that there was a slightly increase of chromium amount in the matrix comparing to the as-received condition. This was the result of dissolution of primary carbides in the matrix and then precipitated in form of secondary carbides. Both secondary carbides and need-like carbides after 1000 hours thermal exposure consisted of very similar carbide composition as 24 hours aging ones. In both later precipitated carbides, the amount of iron slightly increased while amount of chromium slightly decreased. Furthermore, it was also observed that the amounts of silicon and nickel increase slightly in niobium carbide due to instability of phases at high temperatures comparing to the as-received ones. It could be summarized that the exposure at high temperatures strongly resulted in precipitation of carbides in terms of distribution, shape and size of secondary carbides, niobium carbides and nickel-niobium silicides. However, it should be noted that after aging for 1000 hours of both elevated temperatures, niobium carbides were not found but the nickel-niobium silicides were appeared.

Table 5. EDS analysis of individual phases after aging at 900°C for 1000 hours (by wt.%)

Elements	Fe	Ni	Cr	Si	Nb	Ti	C
Matrix	37.11	35.05	21.39	1.90	-	-	4.55
Primary carbide	21.38	17.59	55.84	0.41	-	-	4.77
Secondary carbide	20.26	15.39	58.72	0.61	-	-	5.01
Needle-like carbide	17.80	12.62	61.74	0.76	-	-	7.08
Nickel-Niobium Silicide	20.91	35.16	20.46	4.84	11.42	-	7.21

Table 6. EDS analysis of individual phases after aging at 1000°C for 1000 hours (by wt.%)

Elements	Fe	Ni	Cr	Si	Nb	Ti	C
Matrix	36.67	35.47	20.29	0.70	-	-	6.88
Primary carbide	22.91	11.76	53.01	0.58	-	-	11.74
Secondary carbide	15.30	10.82	65.57	0.28	-	-	8.03
Needle-like carbide	15.49	10.67	63.11	1.08	-	-	9.65
Nickel-Niobium Silicide	25.13	23.74	29.00	1.48	10.25	-	10.40

From EDS analysis of specimens after 1000 hours exposure in both high temperatures, it was found that there was no any significant different in chemical compositions of matrixes comparing to the as-received one excepting the carbon amount, which increased. However, it was observed that there were differences in chemical compositions of primary carbides in each condition. After long-term aging, iron and nickel amounts increased but chromium decreased in matrixes due to the precipitation of secondary carbides in matrixes, which utilizing diffused carbon atoms from primary carbides. It could be also concluded that exposured temperature and time had strongly effect on size, shape, distribution, and chemical of each phase in the alloy, see Tables 2-6.

Mechanical tests

The micro-hardness tests of individual phases (matrix and primary carbide) were performed as seen in Figures 9 and 10. Figure 9 shows the effect of long-term exposure in an increase of hardness of the material. No significant difference in micro hardness of matrix was observed between as received and heated specimens. This might be that the investigated areas for hardness tests are very small and no phase transformation of matrix occurred. From results of hardness tests of primary carbides, it is summarized that the hardness of long-term exposed specimens is higher than that of as-received one, Figure. 10 In most cases, there is an increase in carbide hardness reaching to the maximum value at 1000 hours exposure time brought about by increased amounts of precipitates and changes in precipitate size. Therefore, it is concluded that the hardness should strongly relate to morphology of secondary carbides. For high temperature exposure in the temperature of 900°C, there are primary carbides in coarser size than those in the temperature of 1000°C. Hence, the hardness results after the lower temperature heating are higher than those of higher ones. However, it can be summarized that aging at both 900°C and aging 1000°C for 1000 hours provided the similar highest micro hardness of primary carbide in this study. Furthermore, the amount, size and shape of precipitated secondary carbides have also very strong influence to the micro hardness of primary carbides too. Therefore, each exposure temperature condition, which provided its own morphology of precipitated secondary carbides including its precipitation and agglomeration rates during aging, resulted in different values of micro hardness of primary carbides.

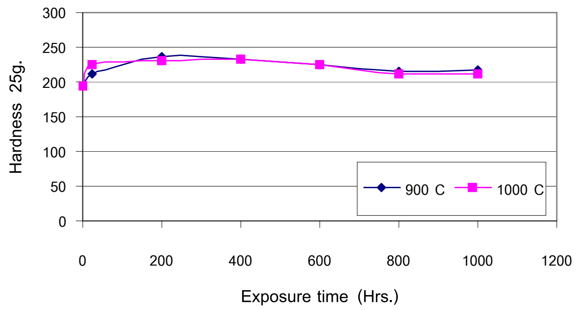


Figure. 9 The relationship between micro hardness tests (HV25g) of matrix and exposure time

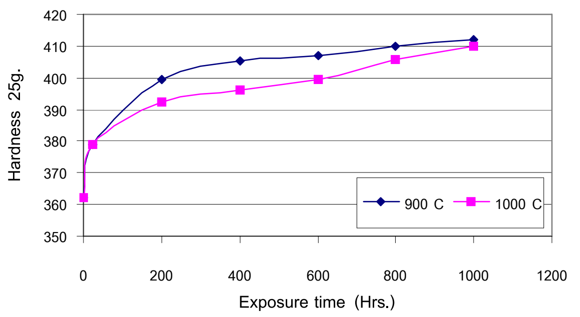


Figure. 10 The relationship between micro hardness Tests (HV 25g) of primary carbide and exposure time

From the tensile test results in Figure. 11, the ultimate tensile strengths of specimens after all long-term exposure were similar and are higher than that of the as-received one. The ultimate tensile strength of specimen aged at 1000°C for 200 hours is the highest, which might be due to higher amounts of finer secondary carbide precipitated particles. Usually, the ultimate tensile strength slightly increased after exposures. The uniform dispersion of fine secondary carbide particles has high efficiency pinning the movement of dislocations resulted in higher strength. In the case of aging at 900°C, ultimate tensile strength did not increase with aging time because of the higher precipitation of brittle needle-like carbides. The ultimate tensile strengths after aging at 1000°C were slightly higher than those after heating specimen at 900°C due to more dispersion and precipitation of secondary carbides. However, after long-term exposure times, the ultimate tensile strength slightly were nearly constant.

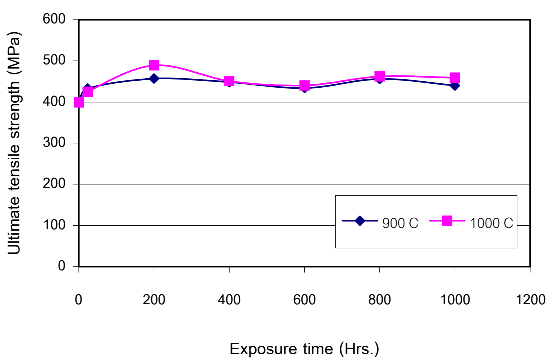


Figure. 11 The relationship between ultimate tensile strength and aging time

Conclusions

1. The secondary carbides precipitated after various exposure conditions are chromium carbide, which its chemical composition is similar to primary chromium carbide.

2. Size, shape and dispersion of secondary carbides depend on aging time and aging temperatures as follows:

2.1 Heating at 900°C, the very fine precipitates of secondary carbide particles located and concentrate in the area close to primary carbide.

2.2 Heating at 1000°C, the coarser secondary carbides dispersed to the cores of dendrites.

2.3 The needle-like and film carbides were found in heat-treated specimens at both 900 °C and 1000 °C just after 24 hours aging.

3. The precipitation and dispersion of fine secondary carbides result in the higher ultimate tensile and hardness comparing to those of as-received condition.

4. The most proper heat treatment condition to maximize tensile strength is aging at 1000°C for 200 hours.

5. Long-term exposure conditions did not provide any significant effect on ultimate tensile and the hardness of matrix results but did so in case of hardness of primary carbides.

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