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EFFECTS OF AGING CONDITIONS ON MICROSTRUCTURE AND MECHANICAL PROPERTIES IN IRON-BASED ALLOY

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ABSTRACT

The aim of this work is to study and investigate the effect of heat treatment conditions on the microstructure evolution and the mechanical properties in the iron-based alloy, Fe-30.8Ni-26.6Cr strengthened by carbide precipitation. Various aging temperatures (800, 900, 1000, and 1100°C) with various aging times are systematically introduced to the as-received alloy. After aging, it was found that the secondary carbides precipitated early near the primary carbides, which are chromium and niobium/titanium carbide networks. The secondary carbide precipitations were also found in the dendrite cores. The amounts of needlelike 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. It can be summarized that the heat treatment conditions have a great effect on shape, size, dispersion and the location of secondary carbides in the microstructure and result in the different mechanical properties such as hardness, yield strength and the tensile strength.

Keywords: Iron-base alloy, Heat treatment, Secondary Carbides, Mechanical Properties and Microstructure

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INTRODUCTION

The cast iron based alloys are widely used in the petrochemical industries, especially under conditions of long-term exposure 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 a 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 is not a standard alloy, which can be classified in the 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 amounts 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 decreases the resistance to cyclic thermal shock (Ratanamahasaku, 2004)

Generally, such kind of nickel-rich iron-based alloy are better in phase stability than other iron-based alloys, which have lower nickel content. The alloy can be used at elevated temperatures without phase transformation to the brittle sigma (σ) phase during long-term service or processing. The HP iron-based alloy is an austenitic structure at all temperatures thus it is not sensitive to sigma (σ) phase transformation after long-term expose.

However, there are still very few studies on the microstructural evolution in the Fe-38.8Ni-26.6Cr 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 following:

1) Aging at 800 °C for 1, 3, 10, and 24 hours.

2) Aging at 900 °C for 1, 3, 10, and 24 hours.

3) Aging at 1000 °C for 1, 3, 10, and 24 hours.

4) Aging at 1100 °C for 1, 3, 10, and 24 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 (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

1. Microstructure Investigation

1.1 Microstructure of as-received alloy

The received microstructure consists of primary carbide networks in an austenitic matrix, as shown in Figure 1. The dendrite structure indicates the characteristics of the 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 3. Using EDS to analyze the chemical composition of each phase it is concluded that the black phase consists of 70.59% chromium and the white phase consists of 19.93% titanium, 32.60% Niobium and 0.61% chromium.

The matrix consists of 35.74% iron, 31.59% nickel, and 24.54% 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 the solidified alloy by the combination of carbon and chromium, niobium and titanium. Titanium and niobium would form as niobium-titanium carbide, which precipitated at a higher temperature compared to chromium carbide resulting in high ratio between Cr: C (Rodriguez, et al. 2000) Therefore, the presence of primary carbide precipitation type is $M_{23}C_6$ (de Almeida, et al. 2002) They locate near austenitic grain boundary networks.

Table 2 EDS Analysis of As Received Alloy

Phase	Si	Ti	Cr	Fe	Ni	Nb	C, Co & W
White Phase	1.7	19.93	0.61	23.20	21.88	32.60	0.07
TiC (2)	0.14	60.20	5.89	0.75	0.54	0.43	32.06
Black Phase	0.85	-	70.59	15.03	7.7	2.29	1.36
Matrix	2.78	-	24.54	35.74	31.59	1.87	0.24

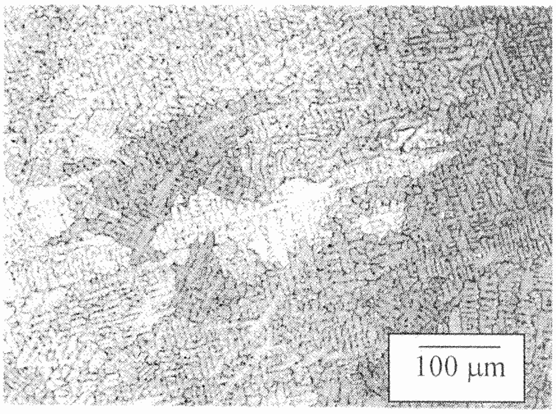

Figure 1 Microstructure of as-received material

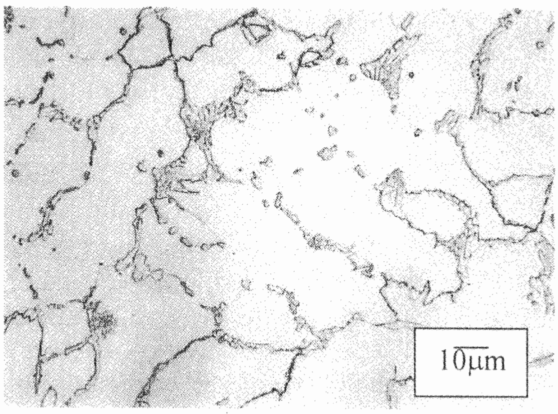

Figure 2 Microstructure of as-received material

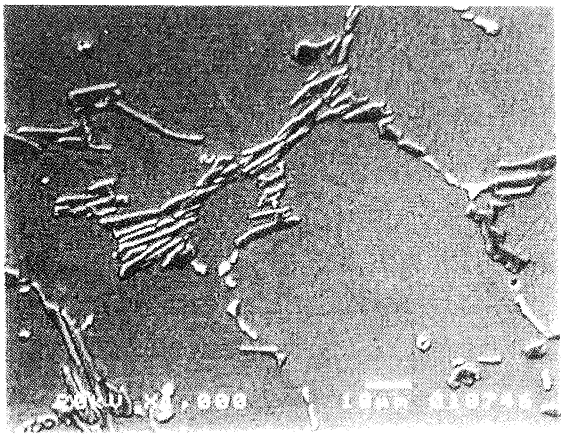

Figure 3 SEM micrograph of as-received material

1.2 Microstructure of the alloy after heat treatment

Generally, all microstructures after various heat treatment conditions were found in a similar manner. Most 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, Figure 4. After aging at 800°C, the secondary carbide particles concentrate in the zones adjacent to primary carbides. The amount of secondary carbide particles increase with time of heat treatment (10 and 24 hours), as shown in Figures 4 and 5. Furthermore, the film and needlelike carbides were also observed, Figures 4 and 5 (respectively). From SEM micrographs, it should be noted that secondary carbide particles precipitate in higher concentrations near the primary carbide particles and more precipitations disperse towards the dendrite core when aging time increases.

After aging at 900°C for various aging times, the heat-treated microstructures are similar to those aged at 800°C but are different in amounts of secondary carbide precipitation. After short-term heat treatment (1 and 3 hours), secondary a carbide are in a high concentration near primary carbides. However, when the aging time was increased to 10 and 24 hours, the previous precipitation of secondary carbide particles would agglomerate to become in coarser in sizes and there are more very fine secondary carbides in the center of the dendrite core, Figure 6. Coarsen needlelike and film carbides are found as well.

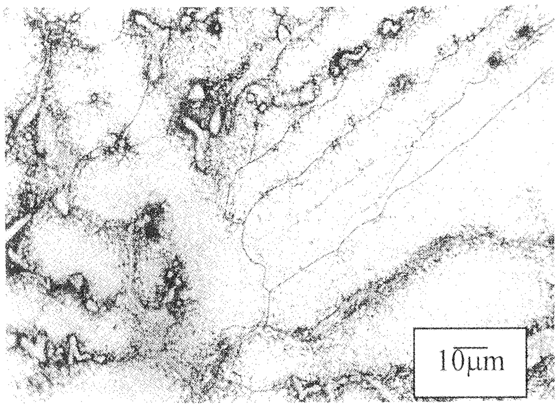

Figure 4 Microstructure of specimen after aging at 800°C for 10 hours

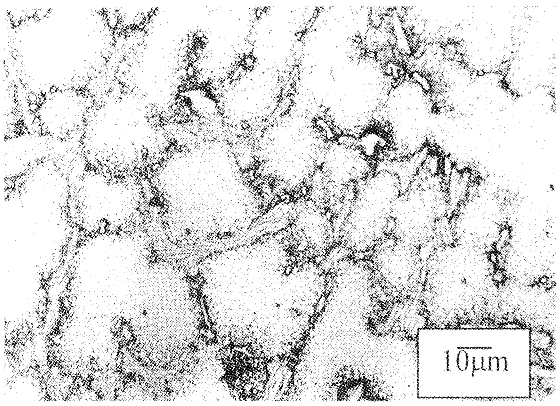

Figure 5 Microstructure of specimen after aging at 800°C for 24 hours

The microstructures, after aging at 1000 and 1100°C for various aging times, are quite similar to those aged at 800 and 900°C, Figure 7. The secondary carbides are round in shape and precipitate towards the dendrite core. The secondary carbides are in high concentration to the primary carbides in case of exposure time of 1, 3, and 10 hours. For aged microstructures of 24 hours, very fine particles of secondary carbide would agglomerate as coarsening size, Figure 8. However, using SEM investigation in all cases, precipitate 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.

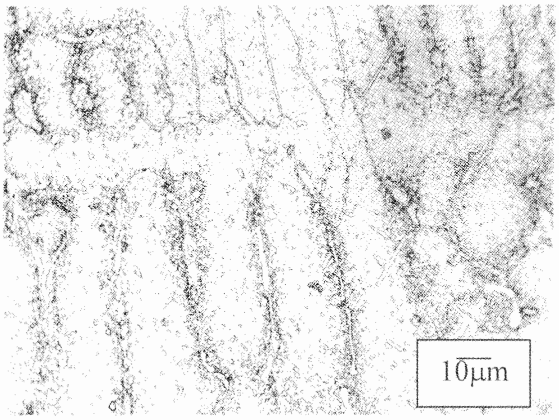

Figure 6 Microstructure of specimen after aging at 1000°C for 24 hours

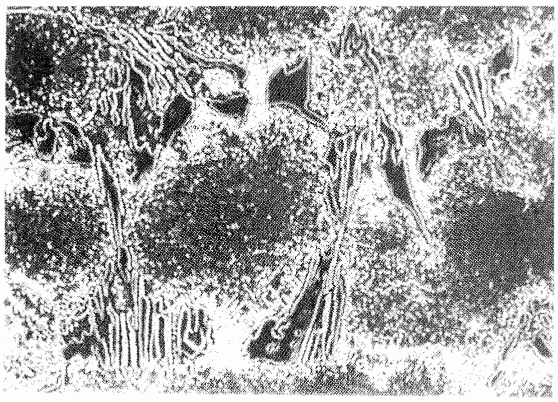

Figure 7 SEM micrograph of specimen after aging at 1000°C for 10 hours

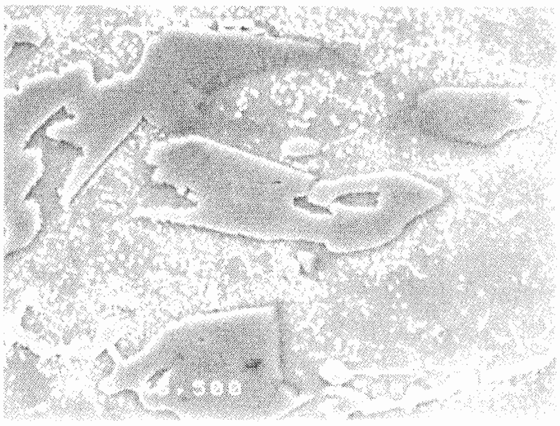

Figure 8 SEM micrograph of specimen after aging at 1000°C for 24 hours

From EDS analysis of primary and secondary carbides as well as in the matrix, it is summarized that the amount of chromium in the matrix decreases after all heat treatment as chromium forms the secondary carbides. However, the amounts of other elements in the matrix are quite constant, see Table 3. Furthermore, it was also found that the amount of chromium (70.72%) in secondary carbides is very close to that of primary carbide (the black phase). This could imply that no significant phase change in the primary carbide after all heat treatment but only loses some amounts by the decomposition of partial primary carbides to secondary carbides. For the needlelike secondary carbide, its chemical composition is as follows: 37.86% Fe, 32.33% Ni, and 27.92% Cr, as can be seen in Table 3.

Table 3 EDS Analysis of individual phases after aging at 1000°C for 24 hours

Elements	Si	Cr	Mn	Fe	Ni	Nb	C, Co & W
Secondary Carbide	0.85	70.72	-	14.86	11.03	0.87	1.64
Needlelike Carbide	1.69	27.92	-	37.86	32.33	-	0.04
Matrix	5.46	29.07	1.46	35.36	29.73	1.11	0.10

After all heat treatment, the chemical composition of primary carbide is almost constant due to no phase transformation, see Tables 2 and 3. However, in another type of primary carbide (the white phase), which consists of 32.6% Nb, 0.61% Ti, 1.7% Si, and 21.88% Ni, the amount of niobium has a tendency to decrease while the amounts of nickel and silicon increase after aging at 800, 900, 1000, and 1100°C for 24 hours. This might be due to the occurrence of phase instability during long-term aging at high temperatures.

Finally, it is summarized that the temperature and time of aging have a significant effect on size, shape, and dispersion of secondary carbides. The most precipitated secondary carbides are the same type as primary carbide, $M_{23}C_6$ (Ratanamahasaku, 2004; Rodriquez, et al. 2000; de Almeida, et al.; Kaya, et al. 2002; Wu, et al. 2000; Piekarsk, 2001; Ibanez, et al. 1993; Barbabela, et al. 1991; Barbabela, et al. 1992; Kenik, et al. 2003; and Barbabela et al. 1991) Furthermore, niobium and chromium also influence the shape of secondary carbides as well (Ibanez, et al. 1993; and Barbabela, et al. 1992). A high amount of niobium and chromium in iron-based alloy induces to needlelike secondary carbide formation at long-term exposed conditions. Therefore, the control of niobium and chromium is very important. The proper and careful control of the amount of both elements reduces the tendency of needlelike carbide formation, which causes brittle fractures later.

Aging time and aging temperature, especially in the range of 800-1000°C, can decrease the amount of niobium in niobium-titanium carbide while increase the amount of nickel and silicon, Table 4. In this temperature range of 800-1000°C, niobium-titanium carbide is not stable and susceptible to the transformation of G-phase or nickel-niobium-silicide ($Ni_{16}Nb_7Si_{16}$) according to previous study (Davis, 1996). However, the G-phase transformation would rarely occur partially because titanium could inhibit the phase transformation. The G-phase probably is considered the weak point for creep-rupture strength.

Table 4 EDS Analysis of primary carbides after aging for various aging time

Specimen	Si	Cr	Ti	Fe	Ni	Nb	C, Co & W
As received	1.7	19.93	0.61	23.2	21.88	32.6	0.07
800 °C 24hr.	2.14	22.25	0.61	25.97	24.63	24.17	0.09
900 °C 24 hr.	5.56	19.94	0.74	12.89	29.96	30.65	0.22
1000 °C 24 hr.	3.23	21.63	0.68	21.94	22.78	29.6	0.15
1100 °C 24 hr.	1.29	16.99	0.81	24.36	21.16	35.32	0.08

2. Hardness tests

From the results of the hardness tests, it is summarized that the hardness the heat-treated specimens is higher than that of the as-received one, Figure 9. In most cases, there is an increase in hardness reaching to the peak value brought about by increased amounts of precipitates and changes in precipitate morphology, as mentioned previously. After the hardness peak is reached, the hardness slightly decreases with continuing particle growth of previously existing secondary carbides for longer aging time (10 and 24 hours). Therefore, it is concluded that the hardness strongly relates to the morphology of secondary carbide. For heat treatment in the temperature range of 800-900°C, there are secondary carbides finer in size and fewer amounts than those in the temperature range of 1000-1100°C. Hence, the hardness results after the lower temperature aging are less than those of higher ones. Furthermore, the micro-hardness tests of individual phases (matrix and primary carbide) were performed as seen in Tables 5 and 6. No significant difference in micro hardness was observed between as received (350.6 HV25g) and heat-treated specimens. This might be that the investigated areas for hardness tests are very small and no phase transformation of primary carbide occurs.

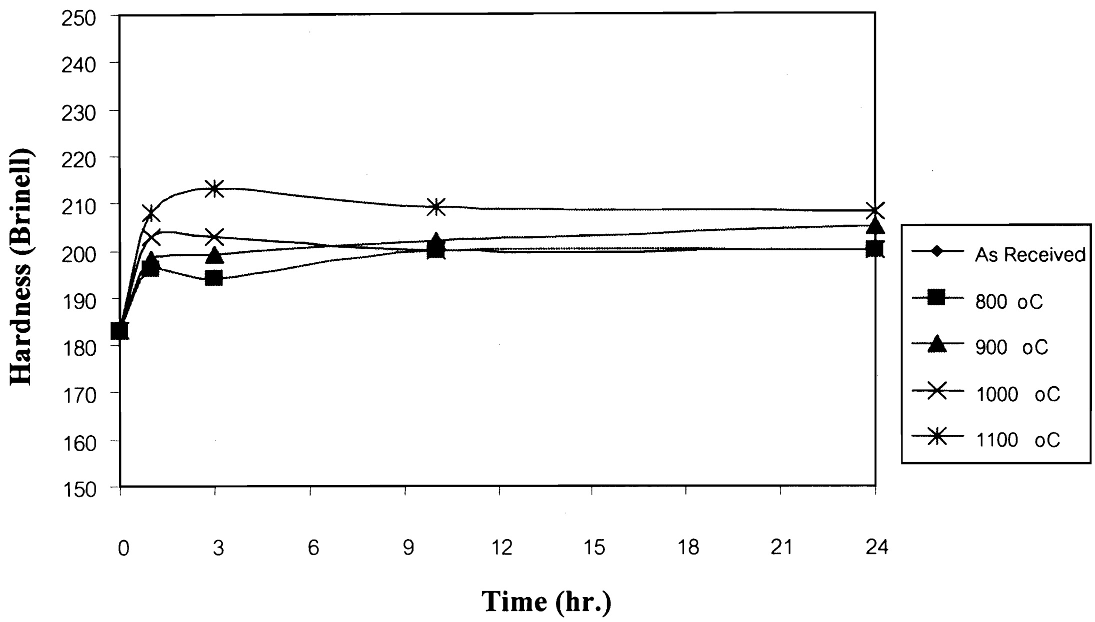

Figure 9 The relationship between hardness and aging time

Table 5 Results of micro hardness tests (HV25g) of primary carbide

Aging Temperature (°C)	Aging Time (hr.)			
	1	3	10	24
800	340	360	327	372
900	348	356	364	364
1000	378	358	351	343
1100	366	365	378	377

Table 6 Results of micro hardness tests (HV25g) of matrix

Aging Temperature (°C)	Aging Time (hr.)			
	1	3	10	24
800	164	169	189	181
900	167	172	181	180
1000	200	198	191	190
1100	226	215	215	195

3. Tensile tests

From the tensile test results in Figure 10, the ultimate tensile strengths of specimens after all heat treatment are similar and are higher than that of the as received one. The ultimate tensile strength of specimen aged at 800°C for 1 hour is the lowest due to fewer amounts of finer secondary carbide precipitated particles. Usually, the ultimate tensile strength slightly increases as aging time increased at the same temperature. The uniform dispersion of fine secondary carbide particles has high efficiency pinning the movement of dislocations resulting in higher strength. In the case of aging at 900°C, ultimate tensile strength does not increase with aging time because the higher precipitation of brittle needlelike carbides resulted in lower ultimate tensile strength than those of aging at 800°C. The ultimate tensile strength after aging at 1000 and 1100°C for 1 and 3 hours are higher than those after aging specimens at 800 and 900°C due to more dispersion and precipitation of secondary carbides. However, after longer aging time, the ultimate tensile strength slightly decreases due to the occurrence of coarser secondary carbide particles and films. It was also found that the ultimate tensile strength behaviour has a similar manner as the hardness behaviour. Considering the yield strength in Figure 11, it is seen that the yield strength has the same trend as the ultimate tensile strength.

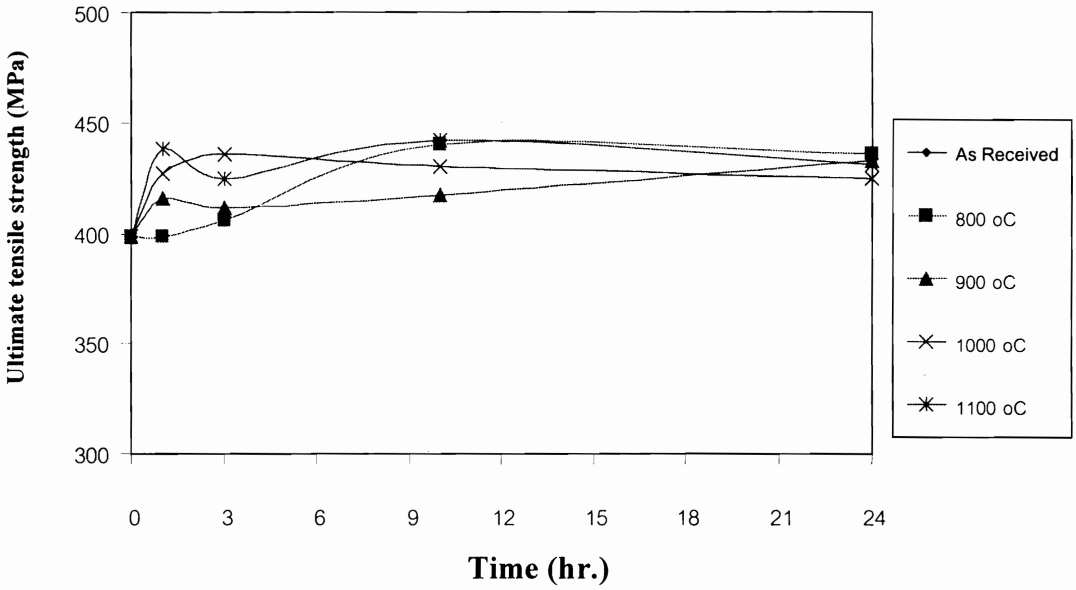

Figure 10 The relationship between ultimate tensile strength and aging time

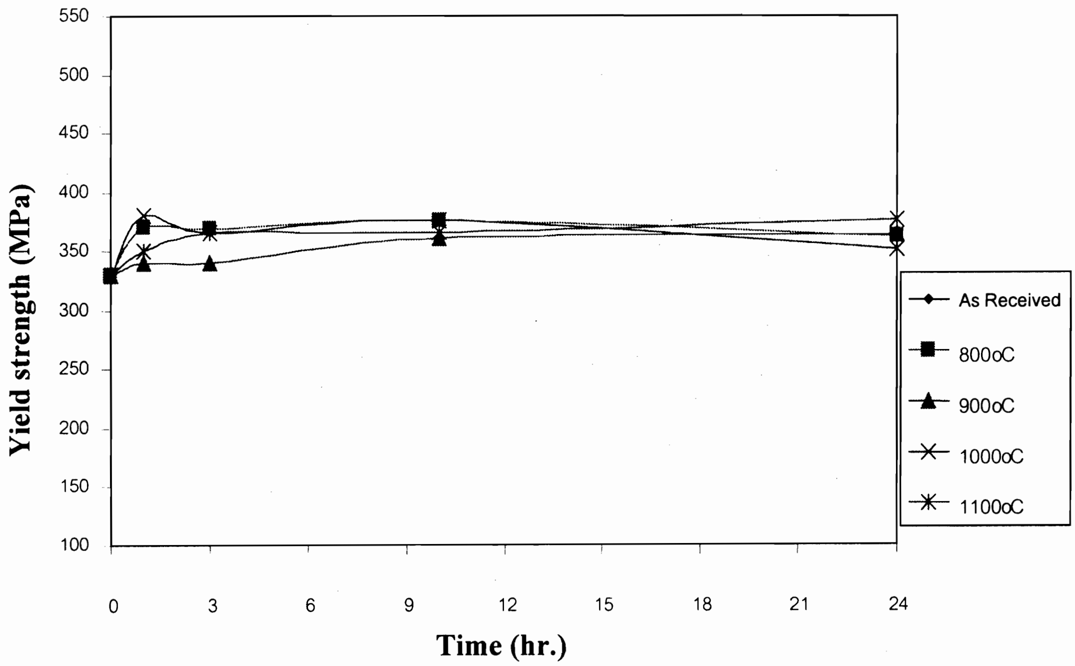

Figure 11 The relationship between yield strength and aging time

CONCLUSION

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

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

2.1 Aging at 800 and 900°C, the very fine precipitates of secondary carbide particles locate and concentrate in the area close to primary carbide.

2.2 Aging at 1000 and 1100°C, the coarser secondary carbides disperse to the cores of dendrites.

2.3 The needlelike and film carbides were found in heat-treated specimens at 900, 1000, and 1100°C.

3. The precipitation and dispersion of fine secondary carbides result in the higher ultimate tensile and yield strengths as well as hardness.

4. The most proper heat treatment conditions to maximize tensile strength is aging at 1100°C for 10 hours.

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