

EFFECT OF HEAT TREATMENT CONDITIONS ON DYNAMIC PARAMETERS OF SECONDARY CARBIDE PRECIPITATION IN CENTRIFUGALLY CAST IRON-BASE SUPERALLOY

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VPLYV PODMIENOK TEPELNÉHO SPRACOVANIA NA DYNAMICKÉ PARAMETRE PRECIPITÁCIE SEKUNDÁRNYCH KARBIDOV V ODSTREDIVO LIATEJ SUPERZLIATINE NA BÁZE ŽELEZA

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Abstract

The aim of this work is to study and investigate the effect of the heat treatment conditions on the microstructure evolution in the iron base alloy strengthened by carbide precipitation. The Fe - 30.8Ni - 26.6Cr alloy, produced in the form of centrifugally cast tubes, was studied by means of scanning electron microscopy (SEM) after various heat treatment conditions. A complete description of the carbide phase precipitation present in the as cast and aged condition was made as a function of time and temperature. After heat treatment, it was found that the secondary carbide 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. From the time-temperature-precipitation (TTP) diagram, it showed that the slowest precipitation rate was at 800°C and the fastest precipitation rate was at temperature of 1000°C. The maximum amount of secondary carbide was 0.7 vol. %. The kinetic study after Johnson - Mehl - Avrami equation showed that the secondary carbide precipitated by the two-step reactions. The first step was volume diffusion, which controlled growth of secondary carbide precipitation with the activation energy of 213.2 kJ/mole. In addition, the secondary reaction was grain boundary diffusion controlling the growth of precipitation with the activation energy of 51.7 kJ/mole. The obtained TTP diagram was established for the aging application and welding of this alloy. It can be summarized also that the heat treatment conditions have a great effect on shape, size, dispersion and the location of the secondary carbides in the microstructures and could result in the different mechanical properties.

Keywords: Microstructural characterization, centrifugally cast Iron-base superalloy, Fe - Ni - Cr Alloy, Time - Temperature - Precipitation (TTP) diagram

Abstrakt

Cieľom tohto článku je štúdium vplyvu podmienok tepelného spracovania na vývoj mikroštruktúry zliatiny na báze železa, ktorá bola spevnená precipitujúcimi karbidmi. Mikroštruktúrne charakteristiky odstredivo odlievaných rúr zo zliatiny Fe - 30,8Ni - 26,6Cr sú študované po rôznych spôsoboch tepelného spracovania použitím riadkovacieho elektrónového mikroskopu. V príspevku je uvedený úplný popis precipitácie karbidickej fázy, tak liateho stavu ako aj stavu po procese starnutia, ako funkcie času a teploty. Po aplikovanom procese tepelného spracovania bolo zistené, že sekundárne karbidy precipitovali v blízkosti primárnych karbidov. Primárne karbidy boli na báze chrómu alebo to boli komplexné karbidy na báze nióbu a titánu. Precipitácia sekundárnych karbidov bola taktiež pozorovaná vo vnútri dendritov. Z diagramu čas-teplota-precipitácia vyplýva, že najnižšia rýchlosť precipitácie bola pozorovaná pri teplote 800°C a najvyššia rýchlosť precipitácie bola zistená pri teplote 1000°C. Maximálne množstvo sekundárnych karbidov, ktoré bolo zistené, bolo na úrovni 0,7 objemových %. Kinetická štúdia využitím Johnson - Mehl - Avramiho rovnice ukázala, že sekundárne karbidy precipitovali v dvoch etapách. Prvou etapou bola objemová difúzia, ktorá kontrolovala rast precipitujúcich sekundárnych karbidov a mala hodnotu aktivačnej energie 312,2 KJ/mol. Následne druhá etapa rastu sekundárnych karbidov bola kontrolovaná difúziou hraníc zŕn a aktivačná energia procesu mala hodnotu 51,7 KJ/mol. Získaný diagram čas-teplota-precipitácia umožňuje jeho použitie pri procesoch starnutia a zvrárania študovanej zliatiny. Na základe dosiahnutých výsledkov je taktiež možné konštatovať, že podmienky tepelného spracovania majú veľký vplyv na tvar, veľkosť, rozloženie a miesto vylúčenia sekundárnych karbidov v mikroštruktúre zliatiny a to môže mať za následok rozdielne mechanické vlastnosti študovanej zliatiny.

Introduction

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 reformer and pyrolysis furnaces. This alloy has been used instead of expensive superalloys with sufficient high temperature properties such as creep strength and corrosion resistance. Therefore, there were many microstructural features that have been developed in order to increase strength at elevated temperature in material [1, 2]. The designed microstructure would 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 [3] as well as for fatigue strength [4].

This type of structure could be possibly 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 previous studies were done before to evaluate the phase changes during heat treatment process and the influence of its microstructure to mechanical strength at both room and elevated temperatures [5, 6]. 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 networks appeared to play an important role in resisting grain boundary sliding. Secondary precipitation of fine cube-shaped chromium carbides should act as potential barriers to dislocation movements.

In this research work, the secondary carbide precipitation behaviour was studied and investigated to find out which mechanism controlling the precipitation process. The optimum heat treatment condition should provide a uniform dispersion of very fine secondary precipitated carbides in microstructure, which could optimized the creep strength at elevated temperature and no any continuous cellular carbides were formed. The obtained TTP diagram could be utilized for the aging application to optimized mechanical properties as well as welding condition for both pre-welding and post-welding of the alloy.

Material and Experimental Procedure

The Fe - 38.8Ni - 26.6Cr alloy has a chemical composition by wt. % as shown in Tab.1. The as - received alloy was produced by the casting process. However, initial alloy was still not proper microstructure as desired after this manufacturing. Thus, the following heat treatment is the attempt trying to fulfill the material requirements. Therefore, various conditions according to the tested program were carried out to the alloy as following: heating with argon gas flow for various time from 5, 10, 30, 60 and 120 seconds; 5, 10, 19 and 30 minutes; and 1, 3, 10 and 24 hours at each elevated temperature of 800°C, 900°C, 1000°C and 1100°C, respectively, then water quenching. All heat-treated specimens were observed and analyzed by scanning electron microscope. Finally, all specimens were measured to find out the percentage volume fraction of secondary precipitated carbides using manual point counting according to ASTM E 562.

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

1. Time - Temperature - Precipitation (TTP) Diagram

The amount of secondary carbides in volume fraction was measured by manual point counting according to ASTM E 562 in the specimens at elevated temperatures (800°C, 900°C, 1000°C and 1100°C) and varying time from 5 seconds to 24 hours. Figure 1 shows the diagram of S-curve relationships between time and volume percentage fraction of secondary carbide. At the first step, reaction occurred very slowly under short exposed time and continuously increasing till the second step, which the faster reaction appeared and continued to the last step, where the equilibrium of system was reached. It also found that the rate was increased when aging at higher temperatures, which could contribute to the higher volume percentage fraction of secondary carbide. However, at the highest aging temperature of 1100°C, the rate of secondary carbide precipitation was significantly decreased. This was probably due to the agglomeration of very fine secondary carbides, which precipitated in earlier step, see Figs. 2 - 9. For aging at 800°C, the reaction occurred most slowly due to the lower of heat energy where carbon diffusion took place slowly providing the least amount of secondary carbide precipitation. For aging at 1000°C, the secondary carbides could maximum precipitate, approximately 0.7 % volume fraction. From Fig. 10, it also found that secondary carbide utilized the minimum time for precipitation under aging at 1000°C while under aging at 800°C, secondary carbides employed maximum time to precipitate.

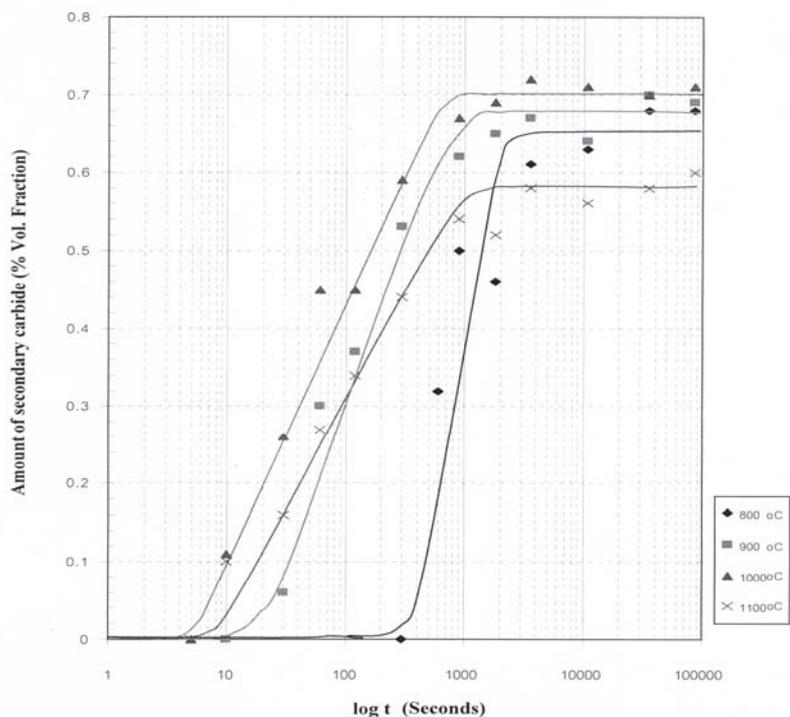


Fig.1 The relationship between % vol. fraction of secondary carbides and aging time (seconds)

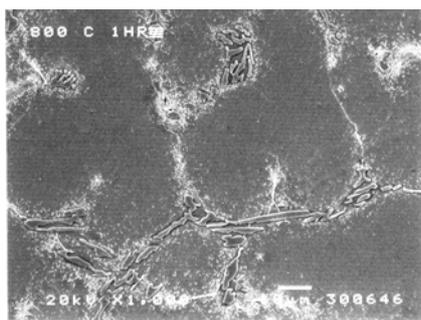


Fig.2 Aging at 800°C/1 hr.



Fig.3 Aging at 800°C/24 hrs.

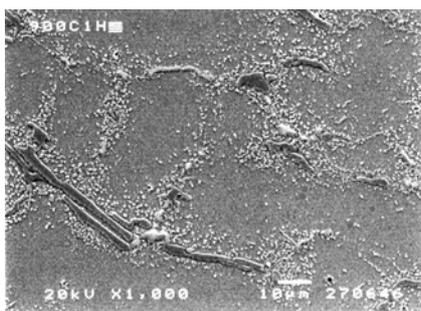


Fig.4 Aging at 900°C/1 hr.



Fig.5 Aging at 900°C/24 hrs.

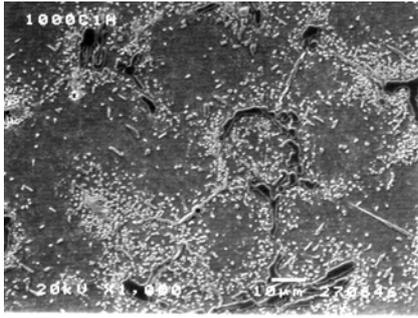


Fig.6 Aging at 1000°C/1 hr.

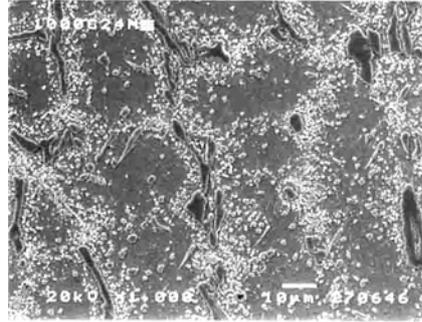


Fig.7 Aging at 1000°C/24 hrs.

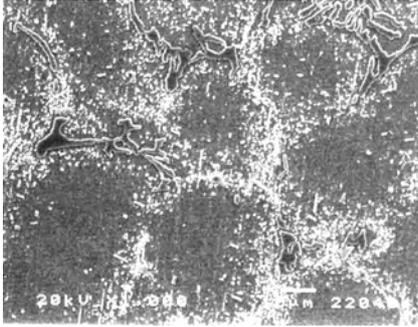


Fig.8 Aging at 1100°C/1 hr.

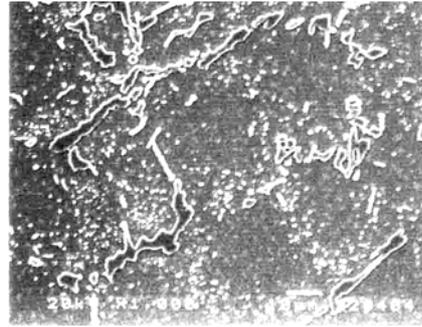


Fig.9 Aging at 1100°C/24 hrs.

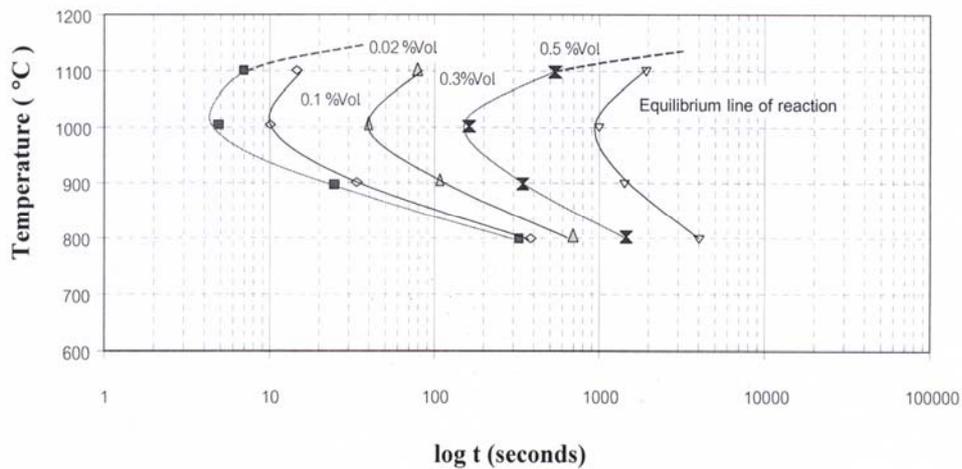


Fig.10 The TTP map showing the precipitation of secondary carbides in the alloy

2. Secondary carbide precipitation according to the equation of Johnson - Mehl and Avrami

Using mathematical relationship according to equation of Johnson-Mehl and Avrami, it can be obtained the precipitation mechanism and the growth of secondary carbides when knowing all parameters in equation (1)

$$f = 1 - \exp(-kt^n) \quad (1)$$

where f is the ratio of volume fraction between secondary and primary carbides at constant temperature, n is growth exponent and k is temperature dependent constant. From this relationship, it can contribute to the secondary carbide precipitation diagram (Fig. 11), which the curve of each aging temperature can be divided in two steps. The change of slope in each curve is referred to the change in reaction from first to second step at 0.22 - 0.26 % volume fraction of secondary carbide precipitation. The n parameter (see Tab. 2) has trend to decrease when temperature is increased as well as increasing when reaction change from first step to second step where size and shape of secondary carbides also changed. In first step reaction, n parameter is in the range of 1 - 4. The nuclei of secondary carbides precipitated in grain edge boundary and grain boundary, see Fig. 2. The n in range of 1- 4 means the nucleation parameter is about 1, which shows the growth of needle-like carbide, (Fig. 7) but amount of this kind of carbide is very low due to the decreasing of reaction rate. Furthermore, it is possible to obtain activation energy of the reaction from the equation of Arrhenius [7, 8] as following:

$$K = k_0 \exp(-Q/RT) \quad (2)$$

Where k is the constant from equation (1), Q is activation energy, R is constant (8.314 J/g-mole - Kelvin) and T is temperature in Kelvin unit. The activation energy obtained from equation (2) is showed in Tab. 3 where the first step used activation energy about 213.2 KJ/g-mole. The growth of precipitation was controlled by volume diffusion mechanism, which the precipitated particles growth in 3-dimensions. The second step reaction needed activation energy about 51.7 kJ/g-mole where precipitate particles growth in 2-dimensions and the growth rate was controlled by grain boundary diffusion mechanism.

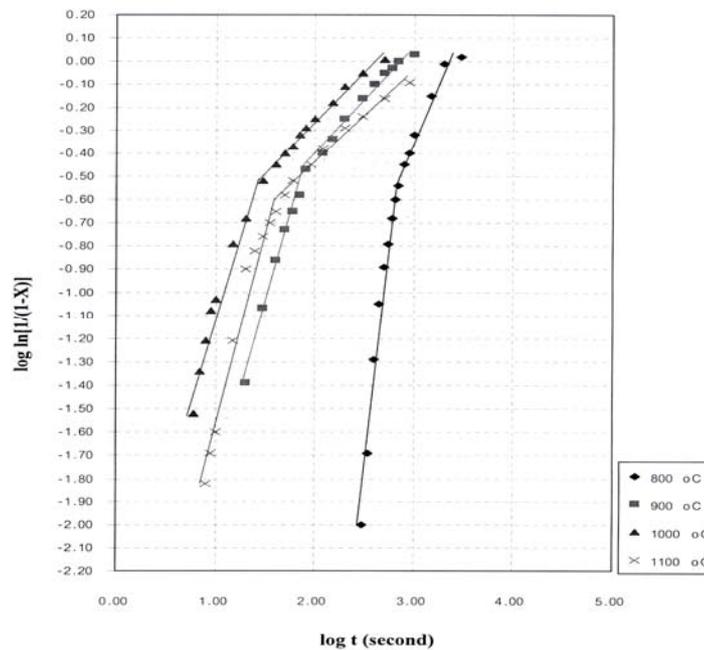


Fig.11 The mathematical relationship of secondary carbide precipitation in the alloy

Table 2 Then parameter (growth exponent), Activation energy (Q), and Arrhenius constant (k_0) of the precipitation of secondary carbide in the alloy

Temperature (°C)		800	900	1000	1100
First step	n	3.7	1.5	1.2	1.8
	Q (kJ/mol)	213.2			
	k_0	9.08 E+11			
Second step	N	0.9	0.5	0.4	0.4
	Q (kJ/mol)	51.7			
	k_0	233.1			

Table 3 The meanings of n according to $f = 1 - \exp(-kt^n)$ [9, 10] of Johnson - Mehl and Avrami's equation

(a) Polymorphous changes, discontinuous precipitation, eutectoid-reactions, interface controlled growth, etc.	
Conditions	n
Increasing nucleation rate	>4
Constant nucleation rate	4
Decreasing nucleation rate	3-4
Zero nucleation rate (saturation of point sites)	3
Grain-edge nucleation after saturation	2
Grain-boundary nucleation after saturation	1
(b) Diffusion-controlled growth (early stages of reaction only)	
Conditions	n
All shapes growing from small dimensions, increasing nucleation rate	>2½
All shapes growing from small dimensions, constant nucleation rate	2½
All shapes growing from small dimensions, decreasing nucleation rate	1½-2½
All shapes growing from small dimensions, Zero nucleation rate	1½
Growth of particles of appreciable initial volume	1-1½
Needles and plates of finite long dimensions, small in comparison with their separations.	1
Thickening of long cylinders (needles), e.g. after complete edge impingement	1
Thickening of very large plates, e.g. after complete edge impingement	½
Segregation to dislocations (very early stage only)	~ 2/3

Conclusions

1. The precipitation of secondary chromium carbides in the alloy can be explained by the equation of Johnson - Mehl and Avrami, which could be divided in two steps. The first step precipitation was controlled by volume diffusion mechanism using 213.2 kJ/g-mole for activation energy and the second step was the growth of precipitation controlled by grain boundary diffusion mechanism using 51.7 kJ/g-mole or activation energy.
2. The **n** parameter according to the equation of Johnson - Mehl and Avrami decreased when increasing temperature and reaction of precipitation changed from first to second step due to the change of morphology of precipitated particles and precipitation mechanism of secondary carbides.

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