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The formation of eutectic phases and hot cracks in one Ni–Mo–Cr superalloy

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ABSTRACT

The structure and the formation mechanism of brittle eutectic phases and hot cracks formed at grain boundaries were investigated in two Ni-Mo-Cr superalloys with different silicon contents (0.06 and 0.46 wt.%). The eutectic phases and hot cracks can be observed along the rolling direction in the 0.46 wt.% Si heat when heated to 1335 °C or a higher peak temperature up to 1365 °C. Exposure to the higher peak temperatures resulted in the formation of larger eutectic phases and hot cracks in the higher silicon heat. Conversely, there are fewer eutectic phases and smaller hot cracks forming in the low-silicon heat when heated to 1365 °C. The eutectic phases were identified as γ-M_6C' type. Based on the constitutional liquation theory and thermodynamic calculations, it was found that the formation of the eutectic phases and hot cracks is due to the localized melting of primary M_6C carbides and surrounding Si-riched matrix. The degree of elements segregation in liquid films determines whether liquid films solidify into eutectic phases or cause hot cracks. This model can reasonably explain the observed phenomena and contribute to designing appropriate solid-solution treatment process and welding procedure to avoid brittle phases and cracks in the Ni-Mo-Cr superalloy.

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1. Introduction

In the proposed next-generation nuclear reactor concepts, the molten salt reactor (MSR) shows particular advantages such as inherent safety features and higher thermodynamic efficiency [1–3]. The structure materials in the MSR must possess high temperature strength, good radiation resistance and compatibility with the liquid fluoride salt. Hastelloy N is a solution-strengthened nickel-based superalloy invented by Oak Ridge National Laboratory (ORNL) specifically for MSR in the 1950s. It exhibited good high temperature mechanical properties and corrosion resistance in molten salts and had served successfully in the 8-MW Molten Salt Reactor Experiment (MSRE) for four years [4]. In spite of the availability of Hastelloy N, the reported brittle eutectic phases and hot cracks in welds of this alloy may threaten the normal working of the future commercial reactors during the long service life [5–8].

It has been found that the relative susceptibilities of various Hastelloy N heats to weld-metal cracks and base-metal cracks depend on the alloy's melting practice and the silicon content [5–8]. There is additional 0.5%–1% silicon in the air-melted heats of this alloy for deoxidants as compared with the vacuum-melted heats [9]. The circular-groove tests and the open-end slot tests [5] revealed that severe weld-metal cracks and base-metal cracks existed in weld specimens of one air-melted heat (0.32 wt.% Si), while the vacuum-melted heat (no Si addition) appeared to be immune to weld-metal cracks and base-metal cracks. The hot-ductility [7] and mechanical tests [6] found that air-melted heat exhibited a lower tensile strength and ductility than the vacuum-melted heat due to the existence of cracks and porosities. Specifically, the location of failure was at the heat-affected zone in some of these tensile specimens [6]. It was observed that base-metal cracks invariably occurred at eutectic structures present on the grain boundaries. The high restraint during the welding process caused the fracture of eutectic structure or interfacial crack. This led to the formation of base-metal cracks. The eutectic structure was found to be formed during the thermal cycle and originated from the stringer-type M_6C carbides existing in the base metal [8]. It has been reported that there are more stringer-type M_6C carbides in air-melted heats [10]. It seems reasonable that eutectic phases induce the formation of base-metal cracks and cause the deterioration of performances in the air-melted heats.

The study on the solid-solution treatment at different temperatures also showed the effect of the eutectic phases on the tensile properties of the Ni–Mo–Cr superalloy [11]. When solid-solution temperature increased from 1177 °C to 1260 °C, the ductility minimum of air-melted heats (0.62 wt.% Si) decreased to 3.97%. In contrast, vacuum-melted heats (0.015 wt.% Si) exhibited a high ductility minimum for both solid-solution temperatures. It was deduced that the eutectic phases formed in the air-melted heats present in the grain boundaries are likely a contributing factor to the increased embrittlement.

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Due to the important role of the eutectic phases, their composition, structure and formation mechanism have been investigated in earlier studies [8,9,11–13]. In regard to the composition of constituent phases, the eutectic phases were identified as Ni_7Mo_7 [9] and Mo_2Ni_3Si [13] in two different studies. It has also been found that when air-melted Hastelloy N was exposed to temperatures in excess of 1300 °C, as encountered in welding, the stringer-type M_6C carbides did not go into solution but transformed to eutectic phases. In contrast, evaluation of vacuum-melted heats revealed that the carbides did go into solution and that eutectic phases did not form [9]. However, it is not known whether it has a stoichiometric ratio different from M_6C or whether it simply represents another distribution of the same phase. Neither is it known whether the formation of eutectic phases is indicative of grain boundary melting or whether this is a solid-state transformation [11]. So far, there is no consensus on the composition, crystal structure and formation mechanism of eutectic phases in Hastelloy N alloy.

The content of silicon is not the only variable in the studies mentioned above. The effects of melting method (air-melted or vacuum-melted) on the eutectic phases and performances should not be neglected. In this paper, one standard vacuum-melted heat (0.46 wt.% Si) and one low-silicon vacuum-melted heat (0.06 wt.% Si) are used to identify the phase structure and composition of eutectic phases. The purpose of this study is to develop a better understanding of the formation mechanism of eutectic phases and hot cracks which can contribute to designing appropriate solid-solution treatment process and welding procedure to avoid brittle phases and cracks in these alloys.

2. Materials and methods

The materials investigated in this study were two Ni–Mo–Cr alloy heats with different Si contents (referred herein as the low-silicon heat and standard heat respectively). The master alloys were prepared by vacuum induction melting (VIM) of a mixture of pure Ni (99.9%), Mo (99.9%), Cr (99.5%), Fe (99.9%), Mn (99.9%), Si (99.9%) and graphite (99.9%). Ingots were then hot forged into bars with a 20 mm diameter. As shown in Table 1, the chemical compositions (wt.%) of the two heats were detected by optical emission spectrometer (SPECTROMAXx06) and carbon–sulfur spectrometer (LECO CS844), which is identical to that of the standard Hastelloy N [14]. All samples with a 20 mm diameter and 5 mm length were cut from the bars and then solution heated at 1177 °C for 0.5 h, followed by water quenching. The samples were put into the heat-treatment furnace at room temperature and then heated to 1315, 1350 and 1365 °C respectively at a rate of 20 K/min to simulate the weld thermal cycle. When the samples reached the high temperatures, they were taken out and water quenched.

Metallographic samples were prepared by standard metallographic techniques and the polished specimens were immersion-etched with aqua regia for 10 s to reveal the microstructure. The microstructures were examined by using a Zeiss M2m optical microscope (OM) and an LEO 1530VP scanning electron microscope (SEM). The phase identification and crystallographic orientation of the sample were investigated using electron backscatter diffraction (EBSD), which was performed on the Zeiss Merlin Compact SEM equipped with an Oxford Instruments AZtec system. An accelerating voltage of 15 kV was used for these operations. Transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN) equipped with energy dispersive X-ray (EDX) analysis system was used for phase identification and semi-quantitative composition analyses. The EDX experiments were performed in the scanning TEM (STEM) mode using a high angle annular dark-field (HAADF) detector. TEM specimens were prepared by electrochemical polishing at a solution of 5% perchloric acid and 95% alcohol at about 243 K.

Table 1
Measured chemical composition (wt.%) of Ni–Mo–Cr alloys by the carbon–sulfur spectrometer (C) and optical emission spectrometer (other elements), the bold values indicate that the amounts of silicon are the main difference between two heats.

Alloy heat	Ni	Mo	Cr	Fe	Mn	Si	C
Standard heat	71.88	16.6	7.09	3.83	0.52	**0.46**	0.04
Low-silicon heat	71.6	16.7	7.35	4.19	0.44	**0.06**	0.053

Differential scanning calorimetry (DSC) measurements were performed in a Netzsch testing apparatus (STA 449F3) to determine the phase-transition temperature in the samples. The test temperatures ranged from 1300 °C to 1500 °C at a rate of 20 K/min. Commercial Thermo-Calc software (Database TTNI8) was used to calculate the phase diagram in present alloy system.

EPMA–WDS analysis was conducted using a Shimadzu EPMA-1720 in the spot mode, under an accelerating voltage of 15 kV and a probe current of 50 nA. The beam diameter in these conditions was approximately 3 μm. Specimen preparation was the same as for OM and SEM.

3. Results

3.1. Initial microstructures of Ni–Mo–Cr superalloys

The microstructures of the two Ni–Mo–Cr superalloy heats in the solution treatment state are shown in Fig. 1. Their microstructures contain heavily twinned equiaxed grains with an average grain size of about 40–50 μm. There many primary precipitate strings dispersed along the rolling direction in the two heats, which has been identified as M_6C carbides [10]. It is noteworthy that the low-silicon heat contains smaller and fewer carbide strings as compared with the standard one as shown in Fig. 1b. Our previous work manifested that the average carbide area fraction in standard and low-silicon heats was respectively 4.93% and 2.08% [10].

In our previous studies [10,15], it was found that M_6C carbides in the standard heat were rich in Mo, Si, C and depleted of Cr and Fe. The quantitative elemental analysis by EPMA indicated that the content of Si in primary M_6C carbides was 3.87 wt.% [15]. The composition of M_6C carbides in low-silicon heat is similar to that in the standard heat except the absence of Si. The lattice parameters of M_6C carbides were found to be 11.025 Å and 11.108 Å in the standard heat and the low-silicon one, respectively [10]. It seems more reasonable that the replacement of the large-diameter metal atoms, such as Ni and Mo, by the small-diameter silicon atoms leads to the decrease of the lattice parameter of M_6C carbides. So the constituent of carbides in the two heats can be deduced as $(M, Si)_6C$ and M_6C, respectively.

3.2. Evolution of microstructure

The melting points of Ni–Mo–Cr superalloys were measured by DSC to determine the effects of the silicon addition. Fig. 2 shows the DSC heating thermograms of the two heats when heated from 1300 °C to 1500 °C at a rate of 20 K/min, in which four peaks can be observed and marked as A, B, C and D, respectively. The peaks A, B and C are labeled with onset temperature, peak temperature and end temperature. Peaks A and B indicate the melting of the standard and low-silicon heat, respectively. It can be found that both onset temperature and end temperature of peak A are approximately 10 °C lower than that of peak B. The addition of Si leads to the decrease of melting point in the Ni–Mo–Cr based superalloys. There are two additional small peaks marked as C and D in the standard heat. In our previous study on the same heat, the endothermic peak C at 1335 °C was inferred as the transformation point from primary M_6C carbides to eutectic phases in the standard heat [10]. Another weak exothermic peak D can be observed at about 1380 °C, which hides in the big matrix exothermic peak A.

To clarify the phase transformation at 1335 °C, the samples with different silicon contents were heated to three various peak temperatures of 1315, 1350 and 1365 °C and then water quenched. Fig. 3 reveals the microstructures of these samples. As shown in Fig. 3a, it is found that the primary M_6C carbides in the low-silicon heat completely decompose into the matrix when heated to 1315 °C. In fact, it has

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