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MICROSTRUCTURE STABILITY OF THE DEFORMED AGE-HARDENABLE Ni-Mo-Cr ALLOY DURING LONG-TERM AGEING AT ELEVATED TEMPERATURE

STABILNOŚĆ MIKROSTRUKTURY ODKSZTAŁCZONEGO STOPU Ni-Mo-Cr PODCZAS DŁUGIEGO WYŻARZANIA PRZY PODWYŻSZONYCH TEMPERATURACH

The material used in this study was a commercial nickel-based superalloy containing nominally 25 wt. % Mo and 8 wt. % Cr. The alloy derives its strength from a long-range-ordering reaction. Ageing at 650°C produces very small (on the order of 10 nm) domains of the $\sigma/6$ phase with a $\text{Ni}_2(\text{Mo}, \text{Cr})$ stoichiometry. The conventionally aged material was cold-rolled to a 50% reduction in thickness and then aged at 650°C for 2000 h and 4000 h. The $\text{Ni}_2(\text{Mo}, \text{Cr})$ strengthening phase decomposed into Ni_3Mo - and Ni_4Mo -type phases, Ni-based solid solution and a complex intermetallic P phase. The dominant phase is a plate-shaped Ni_3Mo -type phase while the P phase appears as singular small precipitates.

Keywords: nickel-based alloys, long range ordering, precipitation strengthening

Przedmiotem badań był komercyjny stop na osnowie niklu zawierający 25% Mo i 8% Cr. Wytrzymałość tego stopu zapewniają wydzielenia fazy o uporządkowaniu dalekiego zasięgu. Po konwencjonalnym starzeniu przy temperaturze 650°C, faza uporządkowana, typu $\sigma/6$ i o stechiometrii $\text{Ni}_2(\text{Mo}, \text{Cr})$, tworzy domeny o wielkości rzędu 10 nm. Konwencjonalnie starzony materiał z 50% redukcji grubości, nadaną przez walcowanie, starzono przy temperaturze 650°C przez 2000 h i 4000 h. Stwierdzono, że w materiale tym zanika faza umacniająca $\text{Ni}_2(\text{Mo}, \text{Cr})$, zaś w strukturze występują fazy typu Ni_3Mo i Ni_4Mo , roztwór stały na osnowie niklu oraz złożona faza międzymetaliczna P. Dominująca faza typu Ni_3Mo występuje w postaci płytkowej, zaś faza P występuje w postaci stosunkowo niewielkich, pojedynczych wydzieleni.

1. Introduction

The nickel-base superalloy with 25 wt. % Mo and 8 wt. % Cr, known under its commercial name Haynes[®] 242[™], is an age-hardenable superalloy, developed for applications requiring a combination of good oxidation resistance, strength and a low thermal expansion. It is currently used for various components of gas turbine engines (seals and containment rings, fasteners, casings, etc.). The alloy derives its strength from a long-range-ordering reaction upon the standard ageing (650°C/ 24 - 72 h) which produces very small (on the order of 10 nm) domains of the $\sigma/6$ phase with an $\text{Ni}_2(\text{Mo}, \text{Cr})$ stoichiometry [1]. The strengthening phase is considered as a metastable one. However, quite recent calculations of phase stability in the Ni-Mo-Cr system by the CALPHAD approach predict stability of this phase at temperatures below 620°C for some alloy compositions [2]. A long term thermal stability of this phase is a critical issue in application of this alloy at elevated tem-

peratures. Since its commercial introduction in the early 1990s, the Alloy 242 has been intensively investigated [3], nevertheless, its behavior at elevated temperatures is still weakly recognized so far. Dymek et al. [4] have found that at 650°C the metastable strengthening phase coarsen notably but does not change its crystallographic and ordering characteristics. However, a dramatic deterioration of the alloy's ductility was observed when the tensile test was carried at 650°C. Dymek et al. [5] also found that a combined effect of plastic deformation and subsequent long-term ageing led to the decomposition of $\text{Ni}_2(\text{Mo}, \text{Cr})$ into the stable Ni_3Mo -based phase. In the present work, efforts have been made to comprehensively characterize the nature of this decomposition. Our purpose was to provide a deeper understanding of the morphological, chemical and crystallographic changes occurring in this alloy upon prolonged service at elevated temperature.

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2. Material and experimental procedure

The material used was a commercial Haynes® 242™. Alloy with a nominal composition of 25 wt. % Mo, 8 wt. % Cr, ca. 2 wt. % Fe (present as impurity) and Ni as a base. The alloy was subjected to the standard heat treatment (soaking at 1180°C for 4 h followed by water quenching and ageing at 650°C for 72 h) in order to develop the long-range-order strengthening. The material was subsequently cold-rolled to a 50% and 70% reduction in thickness and then annealed at 650°C for 2000 h and 4000 h. The plastic deformation preceding this annealing was applied to accelerate processes that occur during ageing by enhancing diffusion and making the decomposition of the metastable phase into more stable phases easier. The resulting microstructure was characterized by scanning and transmission electron microscopy (SEM and TEM) supplemented by energy dispersive spectrometry (EDS). The X-ray maps were constructed by the use of an SEM FEI Quanta 200 FEG furnished with the Delphi software provided by the EDAX company. The X-ray phase analysis was also performed.

3. Results and discussion

SEM and TEM studies together with X-ray phase analysis have provided valuable insights into the nature of microstructural evolution during the applied treatments. Samples aged at 4000 h without previous plastic deformation contained only $\text{Ni}_2(\text{Mo,Cr})$ coherent domains – this microstructure and its impact on mechanical properties was discussed in our previous paper [3]. The microstructure of the material plastically deformed and

aged at the same conditions turned out to be quite different. The typical microstructure observed in SEM utilizing the contrast from backscattered electrons is shown in Fig. 1. The micrographs unambiguously show a tremendous change in microstructure with new phases: grey, plate-shaped one, as a dominant feature and small irregularly shaped one, which appear in SEM BSE images as white precipitates. The phases were distributed throughout the sample in a non-uniform manner. There was also a dark phase that was typically adhered to the plate-shaped phase and a deformed matrix. The different contrast among all the phases arose from different chemical composition (atomic number contrast). Table 1 shows average compositions of constituent phases determined by EDS in SEM. The Table also contains data pertaining to the $\text{Ni}_2(\text{Mo,Cr})$ phase which was found in our previous study [3]. Figure 2 shows maps of the K-line intensity of X-ray, displaying the distribution of particular elements within the sample.

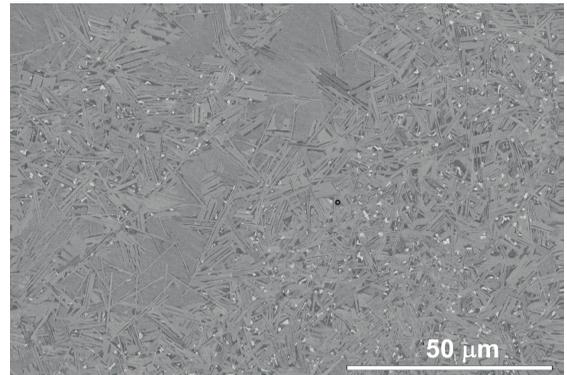


Fig. 1. SEM-BSE micrograph showing microstructure on longitudinal cross-section of the sample after 50% reduction and annealing for 4000 h

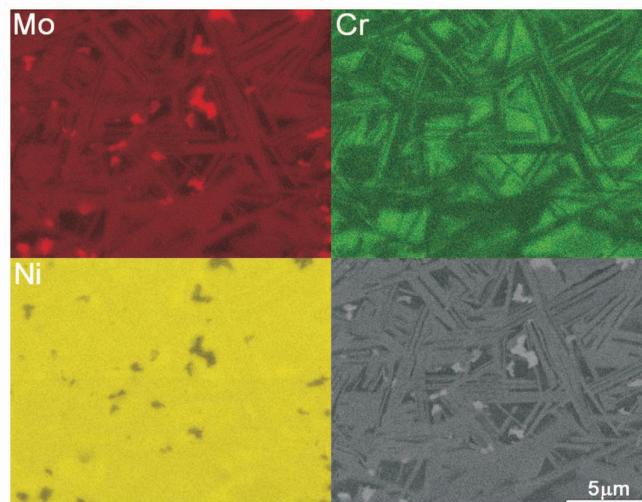


Fig. 2. The characteristic K-line intensity maps of the X-ray and the gray-scale image; the alloy deformed to 50% reduction and annealed for 4000 h

The EDS studies (especially in TEM) indicate that the intermetallic phases in the Ni-Mo-Cr system do not have stoichiometric chemical compositions and the differences in the composition between these phases are too small to unambiguously identify them by EDS alone. Also, identification of the phases by their crystal structure, i.e. diffraction patterns may be confusing since their crystal structures and lattice spacing are related and many of their interplanar spacing are similar. In such cases some morphological differences among the intermetallic phases may be helpful in distinguishing all phases.

The X-ray diffractograms unambiguously revealed peaks corresponding to the Ni₃Mo- and Ni₄Mo-type

phases as well as Ni-based solid solution (Ni_{ss}). Ni₃Mo-type phase may have an oP8 or a tI8 (D0₂₂) crystal structure. The tI8 crystal structure is based on a cubic close-packed stacking. Ruedl described the tI8 (D0₂₂) structure as an intermediate metastable phase preceding formation of Ni₃Mo- and Ni₄Mo-type phases [6]. Also, some well-defined, relatively strong, peaks belonging to another phase or phases could be distinguished in the X-ray patterns (Fig. 3). However, their identification is not unique. The more precise characterization of constituent phases was possible by TEM with the help of selected area diffraction patterns (SADP) and EDS analysis.

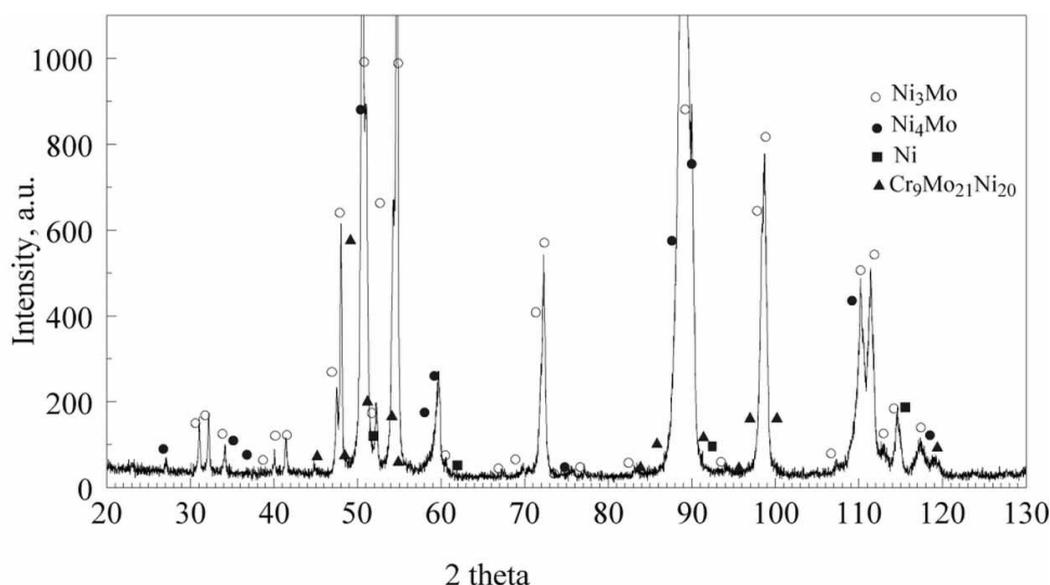


Fig. 3. X-ray diffraction pattern of Alloy deformed to 70% reduction and annealed for 4000 h

Typical microstructure revealed by TEM is shown in Fig. 4. The microstructure is dominated by a long plate-shaped phase parallel to traces of {111}_{f.c.c.} planes. The phase contains numerous stacking faults parallel to the longer edge of the plate which differentiates this phase from the other ones. The chemical composition of this phase coincided with the composition of a grey plate-like phase observed by SEM. Accordingly to this composition the phase may be identified either as Ni₃Mo or a Ni₄Mo-based one depending on partitioning of chromium.



Fig. 4. TEM bright-field image showing microstructure of the sample after 70% reduction and annealing for 4000 h

Some researchers suggest that the Ni₂Mo phase transforms into the Ni₄Mo one rather than into Ni₃Mo [7].

The present results indicate transformation of the Ni_2Mo phase into both of them. Though the SADPs of Ni_3Mo and Ni_4Mo phases are very similar, in our study the majority of SADPs matched better the crystallography of the Ni_3Mo -based phase. The final justification was provided by XRD patterns where peaks from the Ni_4Mo phase were hardly discernable while the peaks from the Ni_3Mo phase were relatively strong (Fig. 3). Thus, the Ni_3Mo -based phase was identified as a dominant phase. Actually, all three of these intermediate phases, Ni_2Mo , Ni_4Mo and Ni_3Mo , are based on a cubic close-packed stacking and are direct superstructures of the disordered f.c.c. matrix. To generate the stacking of the ordered Ni_3Mo ($t/8$) crystal structure, a shear transformation has to take place along the close-packed planes [8]. The results of the present research closely coincide in their characteristics with transformations occurring in Ni-Mo alloys described by Van Tandeloo. It is characteristic that new phases originate predominantly in areas of highly inhomogeneous and localized deformation. This may be explained by the easier diffusion of Mo and Cr atoms in defected microstructure. The new phases only sporadically nucleated in regions of relatively uniform deformation (containing dislocations and twins in one system). In such regions, the $\text{Ni}_2(\text{Mo,Cr})$ phase is still present but the size of its precipitates is much bigger.

The interesting feature in this study is the presence of recrystallized regions that adhered to the plates of Ni_3Mo phase (Fig. 5). These regions were identified as disordered Ni-based solid solution (Ni_{ss}). The chemical composition of this phase was depleted in Mo and enriched in Cr comparing to the nominal alloy composition. The depletion of Mo explains an absence of the $\text{Ni}_2(\text{Mo,Cr})$ strengthening phase.

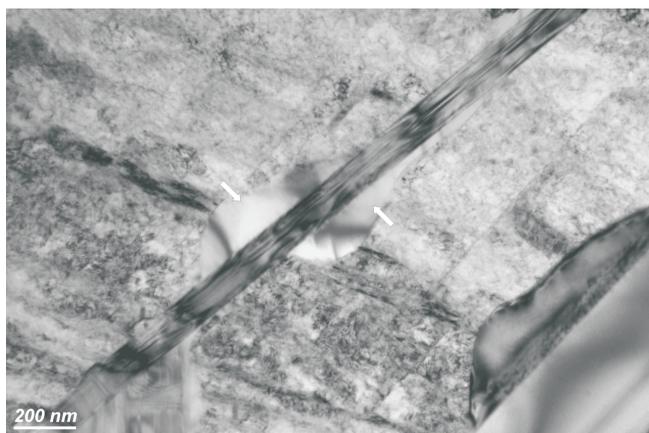


Fig. 5. TEM bright-field image showing microstructure of the sample after 70% reduction and annealing for 4000 h; recrystallized regions are marked by arrows

Yet another phase which is produced upon long-term ageing appeared as precipitates with white contrast in

SEM BSE images (Fig. 1). The phase is enriched with Mo and Cr (Table 1). The Mo-rich phase was also found by TEM. It was characterized by the absence of stacking faults, unlike other intermetallic phases. This phase may be one of the known phases present in the Ni-Mo-Cr system: δ , μ , P or σ [9]. The σ phase occurs at high concentration of Cr and was not considered as a possibility in this particular alloy. According to Raghavan et al. [10], who examined a series of alloys from the Ni-Mo-Cr phase equilibrium diagram, the phase would be identified as the μ phase which was detected at 850°C in alloys with similar composition. Presence of the μ phase was also reported at 700°C by Gozlan et al. [9]. However, the μ phase is usually extensively faulted and the minimum Mo concentration in that phase is 50% (wt.) or higher [10]. Thus, this phase also cannot be considered as explanation for the precipitates. Another possible phase is one of two similar phases: δ (orthorombic NiMo) or P that was described in detail by Shoemaker et al. [11, 12]. The P phase corresponds roughly to the stoichiometry $\text{Cr}_{18}\text{Ni}_{40}\text{Mo}_{42}$. As far as δ phase is concerned, Raghavan et al reported that the chromium solubility in the δ phase is very limited. As this fact is in opposition to our EDS measurements, this phase has been also excluded. The evidence provided by this research makes the P phase the most likely one to match the phase in question. In addition, the justification for the occurrence of the P phase is confirmed by recent modeling of the phase stability of the alloys from the Ni-Mo-Cr system. The work of Turchi et al. [2] presents isothermal sections of the Ni-Mo-Cr phase diagram for low temperatures. The chemical composition of the examined alloy corresponds to the area where the P phase is a one of the potential phases.

TABLE 1

Average chemical composition of constituent phases measured by EDS in SEM

Element	Observed contrast									
	matrix		gray		white		dark		Ni ₂ Mo*	
	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %
Ni	65	71	64	72	42	50	68	71	57	66
Mo	26	18	29	20	46	34	18	12	35	24
Cr	8	10	6	7	11	15	12	15	8	10
Fe	1	1	1	1	1	1	2	2	–	–

* Data from our previous study; measured in TEM (Dymek et al., [4])

4. Conclusions

The Ni-25Mo-8Cr (wt. %) alloy loses its phase stability upon plastic deformation and subsequent exposure at 650°C. The microstructure composed of a mixture of Ni₂(Mo,Cr) strengthening phase and Ni-based solid solution decomposes into a mixture of Ni₃Mo- and Ni₄Mo-type phases, Mo-lean Ni-based solid solution and the complex intermetallic P phase. The dominant phase is a plate-shaped Ni₃Mo-type phase while the P phase appears as singular small precipitates.

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