A LOW-THERMAL EXPANSION, HIGH STRENGTH Ni-Mo-Cr ALLOY

FOR GAS TURBINES

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Abstract

A low-thermal expansion, high strength Ni-Mo-Cr alloy, HAYNES® 242™ alloy, has been developed for gas turbine applications. The hardening response and microstructures of a series of experimental Ni-Mo-Cr alloys were investigated to define the chemical composition of the alloy: Ni-25Mo-8Cr. The standard heat treatment of the alloy results in the homogeneous formation of the Ni₂(Mo,Cr) superlattice domains approximately 10 nm in size. The formation of a large volume fraction of the Ni₂(Mo,Cr) phase, isotypic with Pt₂Mo, is responsible for the strengthening of the alloy which is accompanied by only a modest decrease in the ductility. Prolonged aging at 650°C, up to 4000 hours, coarsens the domains without loss of strength. The paper presents a brief account of the development and physical metallurgy of the alloy.

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Introduction

HAYNES® 242™ alloy is the latest development based on the Ni-Mo-Cr system(1). Its chemical composition and the attendant long-range ordering (LRO) reaction manifest a combination of low-thermal expansion and high strength characteristics. The alloy is suitable for gas turbine components requiring these attributes such as seal rings, containment rings, casings, etc. A continual push to use higher operating pressure and temperature imposes ever increasing demands on the properties of such components. Based on extensive bench testing during the last 3-4 years, it has been specified for seal ring components in several engines. Additional trials are in progress for its application in higher-thrust engines by manufacturers in the U.S.A. and abroad.

An introductory account of the alloy and some of its properties, including thermal expansion, were reported earlier(2). Its thermal expansion characteristics are essentially dependent on the composition (Ni-25Mo-8Cr), and, as such, are slightly inferior to HASTELLOY® alloy B (Ni-27Mo-5Fe) but superior to HASTELLOY alloy S (Ni-15Mo-16Cr). The oxidation resistance of the alloy, based on the static as well as the burner-rig tests, were reported in (3,4) and these tests suggest it is suitable for service in uncoated condition at up to 760°C. The objective of this paper is to discuss the development and physical metallurgy of 242 alloy.

Background

The Ni-Mo and Ni-Mo-Cr systems are the basis for many of the HASTELLOY alloys. In the annealed condition, Ni-Mo alloys possess a disordered fcc structure. However, when aged at intermediate temperatures, they form a variety of ordered phases including Ni_4Mo , Ni_3Mo (DO_{22}) and Ni_2Mo (isomorphous with Pt_2Mo). The superlattices bear a close relationship to each other and can be derived from the fcc lattice by atomic rearrangement on the (420) fcc planes. The atomic arrangements and the crystal structures have a profound effect on the morphologies of the phases as well as the deformation characteristics of the alloys. Whereas Ni_4Mo , DO_{22} and Ni_2Mo structures can form directly from the disordered fcc, it was postulated that the ordering reaction to the equilibrium Ni_3Mo is sluggish and forms in the following sequence(5): Disordered fcc \rightarrow SRO \rightarrow DO_{22} superlattice \rightarrow $Ni_4Mo + Ni_2Mo <math>\rightarrow$ $Ni_1Mo_5 \rightarrow$ Ni_3Mo .

The Ni, Mo phase, isotypic with Pt, Mo superlattice, is not thermodynamically stable (5-7). In contrast, the Ni-Mo-Cr alloys tend to form relatively stable Ni₂Mo and in a fully ordered state their yield strengths are nearly doubled with only a modest loss of ductility. For example, when aged at 538°C for 8000 hours, the room-temperature yield strength of alloy S increased from 436MPa (63 ksi) to 824 MPa (119 ksi) accompanied by a loss of ductility from 58 to 42%. The strengthening in alloys S, C-4 and C-276 was attributed to the formation of a longrange ordered (LRO) Ni₂(Mo,Cr) phase similar to Pt₂Mo(8). A summary of the ordering reactions in Ni-Mo and Ni-Mo-Cr alloys is given in Table I. The ordering reaction to Ni₂(Mo,Cr) is very sluggish. In a study of ordering transformation in alloy C-276, Johnson(9) showed the formation of Pt, Mo type lattice as the final structure after several thousand hours of aging at 500°C. These observations suggest that Cr tends to stabilize the Pt₂Mo-type superlattice. Based on the diffusivities of Mo and Cr in Ni at 538°C, calculated from data in (10), it is found that the diffusivity of the former is an order of magnitude slower. Therefore, Mo might be the rate controlling species. The role of Mo and Cr in the development of 242 alloy is, therefore, to form the LRO microdomains of Ni₂(Mo,Cr), referred to as A₂B hereafter, within a reasonable time. Furthermore, formation of deleterious phases such as Ni₄Mo, Ni₃Mo

and sigma should be either completely prevented or appreciably delayed. The influence of Mo and Cr was therefore extensively analyzed in the development of the 242 alloy.

Table I. Ordering Reactions in Ni-Mo and Ni-Mo-Cr Alloys

	Ni-Mo Alloys (B, B-2)	Ni-Mo-Cr Alloys (C, C-4, C-276, S)		
1. Ordering Reaction	FCC→Ni₄Mo and/or Ni₃Mo	$FCC \rightarrow A_2B$ (Isomorphous with Ni_2Mo)		
2. Kinetics	Very Rapid	Very Slow		
3. Order-Disorder Temperature	High	Low		
4. Effect on Tensile Strength	Considerable Strengthening Severe loss in Ductility	Considerable Strengthening Moderate loss in Ductility		

Materials and Procedure

A series of experimental alloys with broad ranges of Mo and Cr in conjunction with other elements was prepared in the laboratory. The chemical compositions of the alloys will be indicated in the appropriate places in the next section. No Ni-Mo-Cr ternary diagram exists that would depict the phases studied in this paper, nor is there any guidance in selecting additional alloying elements. The 45-Kg heats were vacuum induction melted, electroslag remelted and subsequently hot worked to plate. Samples from the experimental alloys were annealed at 1066°C, 30 minutes at temperature, followed by water quenching. In order to determine the susceptibility of the experimental alloys to long range ordering, test samples were exposed for 24 hours at 595, 650, 705 and 760°C, respectively. This was followed by hardness measurements and other property measurements. Selected compositions were examined by transmission electron microscopy to confirm the nature of the ordering reaction. Thin foils were prepared using a dual jet polisher in an electrolyte consisting of nitric acid and methanol in a 1:3 ratio at about -30°C. A Phillips 300EM operated at 100 KV was used to examine all foils. All diffraction patterns shown in this paper have been indexed with respect to the fcc matrix.

Results and Discussion

Alloy Development: The hardening response of Ni-(21-29)Mo-(5-12) Cr alloys was investigated by measuring their room-temperature hardnesses after 24-hour aging at 595, 650, 705 and 760°C, respectively. Most alloys showed little or no hardening when aged at 760°C. For those alloys which experienced hardening, peak hardness was generally retained at 595 through 650°C; the magnitude of hardening tended to be a little lower at 705°C. Alloys containing Ni-(21-23)Mo-(5-8) Cr underwent little or no hardening after aging at 650°C/24 hours. Figure 1 shows the hardening response as a function of Mo content for a series of Ni-Mo-8Cr alloys subjected to 650°C/24 hour aging. For Ni-25Mo-8Cr, the magnitude of hardness was about HRC 38-40; for higher Mo alloys the hardness increased and stabilized at HRC 46-47. TEM examination showed that the Ni-25Mo-8Cr alloy underwent ordering to the A₂B phase.

The structure of this alloy is contrasted with those of Ni-27Mo-8Cr and Ni-29Mo-8Cr alloys in Figure 2. The microdomains of A,B appear uniformly distributed; the latter two alloys show

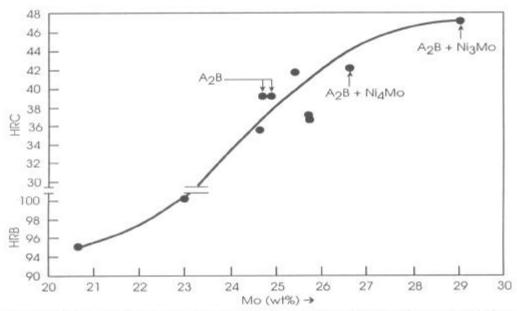


Figure 1: Influence of Mo content on the hardening characteristics of Ni-Mo-8% Cr alloys.

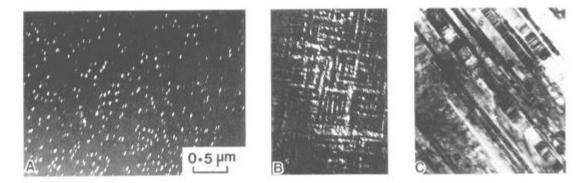


Figure 2: Dark field electron micrographs showing morphologies of various phases:

A. Ni₂Mo in Ni-25Mo-8Cr; B. Ni₄Mo in Ni-27Mo-8Cr; and
C. Ni₄Mo in Ni-29Mo-8Cr alloy.

Ni₄Mo platelets arranged in a plaid mosaic and massive platelets of Ni₃Mo, respectively. As shown in Table I, the presence of Ni₄Mo and Ni₃Mo in platelet morphology is considered very detrimental. A number of compositions showed a mixture of A₂B and Ni₄Mo or Ni₃Mo. It should be noted that the effects of these two phases in small and isolated quantities are not likely to be significant. Based on the microstructural observations, the effect of composition on the structure is summarized in Table II. The formation of coherent LRO A₂B phase is a prerequisite to effecting the hardening response. Furthermore, for commercial development, it would be necessary for A₂B to not degenerate into an embrittling phase after short service. For example, alloy Ni-27Mo-5Cr was found to order to an A₂B-type phase, shown in Figure 3. However, after 1000 hours of aging at 650°C, a mixture of A₂B and Ni₃Mo was observed. When the alloy was aged to 4000 hours, the room-temperature hardness increased to HRC 45. The TEM observations revealed the presence of a mixture of Ni₃Mo and A₂B in the fcc matrix, shown in Figure 4; however, the Ni₃Mo was the predominant phase. This indicated that for this composition the A₂B phase observed after short-time aging was a metastable phase which degenerated upon prolonged exposure. On the other hand, Ni-25Mo-8Cr alloy was found to

harden by the formation of LRO microdomains of A₂B. Additionally, the domains proved stable after prolonged aging. These observations led to the development of HAYNES 242 alloy based on the Ni-25Mo-8Cr composition. The nominal composition of the alloy is given in Table III.

Table II. Microstructural Analysis

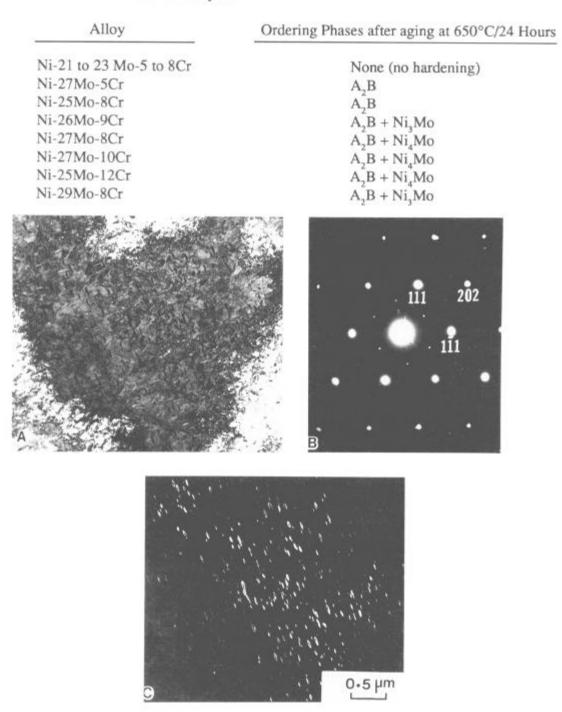


Figure 3: Electron micrographs showing formation of the A₂B domains in a Ni-27-Mo-5Cr alloy: A. BF; B. SADP [101]fcc; C. DF using 1/3 (202)

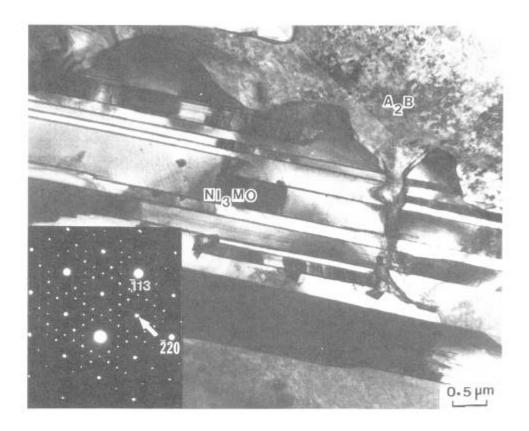


Figure 4: Dark-field electron micrograph showing massive platelets of Ni₃Mo and A₂B in Ni-27Mo-5Cr alloy after aging at 650°C/4000 hours; Inset [110]fcc, arrow is at (111).

Table III. Chemical Composition of HAYNES 242 alloy

Element			Contraction of the last of the		and the same of th		the second secon	the second second second	(inches) and a final party of		
wt%	Bal.	25	8	2*	2.5*	0.8*	0.8*	0.5*	.03*	.006*	.5*

^{*} max.

Heat-Treatment and Microstructure: The hardening kinetics of the Ni-25Mo-8Cr alloy as a function of time and temperature were studied and presented recently(11). It was found that the hardening was most rapid at 650°C. Furthermore, in prolonged aging at 650°C, the hardness was found to increase rapidly during the initial stages, then it became asymptotic after a longer period of time. It was shown that about 90% of the hardening is achieved within 24 hours; therefore this aging treatment was adopted as the standard heat treatment.

In the annealed condition, the microstructure consisted of a disordered fcc matrix, M₆C-type primary and secondary carbides and mu phase. The transmission micrographs showed the presence of weak (1 1/2 0) SRO spots. Dark field examination using the SRO spots showed a mottled appearance presumably on account of the extremely fine domains. In the fully heat-treated condition, 242 alloy exhibited, by design, a large volume fraction of the LRO microdomains of A₂B. Figure 5 shows the typical morphology of the uniformly distributed domains about 10nm in size. The SADP [001]fcc, Figure 5c, shows two variants, while SADP [112]fcc, Figure 5d, shows all three variants of the A₂B phase. A recent paper(12) has sur-

veyed the sequence of phases during ordering of the binary Ni-25%Mo alloys. In most cases, either the Ni₂Mo was metastable or it formed simultaneously with Ni₄Mo in a few minutes to hours at temperatures of 650°C through 860°C, and it finally transformed to the equilibrium Ni₃Mo phase. In 242 alloy, however, no evidence was found for A₂B to Ni₃Mo transformation even after prolonged aging at 650°C. The 242 alloy when aged at 760°C/24 hours resulted in the formation of large clusters of A₂B with a lenticular morphology. Based on these observations, it was postulated that, at less than 705°C, coherent and stable A₂B microdomains

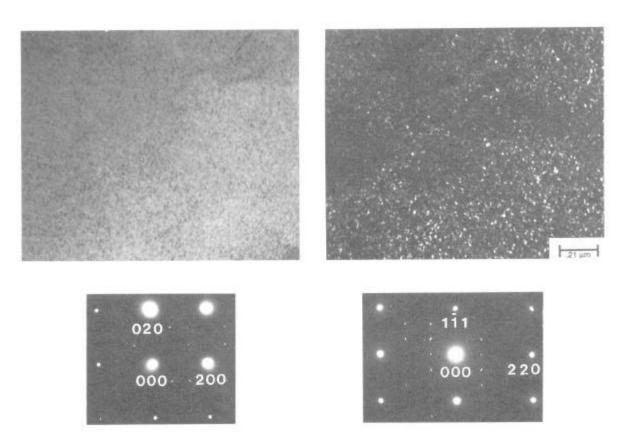


Figure 5: TEM micrographs of 242 alloy annealed plus aged condition (650°C/24 hours): A. BF; B. DF using 1/3 (220); C. SADP [001]fcc and D. SADP [112]fcc.

formed; while at 705-760°C, A_2B formed in the following sequence: matrix \rightarrow SRO spherical A_2B with little misfit \rightarrow ellipsoidal A_2B with greater misfit but still coherent \rightarrow incoherent ellipsoidal clusters of $A_2B(11)$.

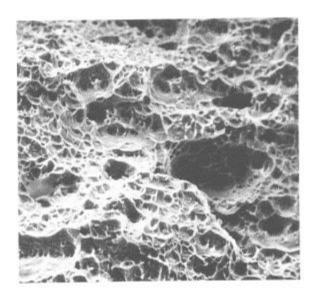
Strength and Stability: The uniformly distributed LRO microdomains of A₂B are responsible for strengthening without loss of ductility in the 242 alloy. The room and elevated temperature tensile properties of the alloy as a function of aging at 650°C for times up to 4000 hours are presented in Table IV. The standard heat treatment, i.e., 650°C/24 hours, caused the room-temperature yield strength to nearly double over that of the annealed state. Further aging caused an increase in the yield strength which was stabilized after 1000 hours. It was recently

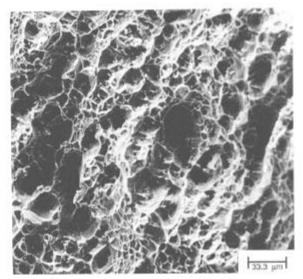
Table IV. Tensile Properties of 242 Alloy, Aged at 650°C

Test Temperature	Aged at 650°C for Indicated Time					
RT	24 Hours	1000 Hours_	4000 Hours			
0.2% YS, MPa (ksi)	776 (112.6)	859 (124.6)	859 (124.6)			
UTS, MPa (ksi)	1262 (183.0)	1346 (195.2)	1363 (197.7)			
% El	38.9	31.9	31.4			
% RA	48.7 44.0		46.1			
650°C						
0.2% YS, MPa (ksi)	578 (83.8)	659 (95.5)	708 (102.6)			
UTS, MPa (ksi)	1034 (150.0)	1045 (151.5)	997 (144.5)			
% El	36.7	21.7	15.0			
% RA	46.7	23.9	17.9			
760°C						
0.2% YS, MPa (ksi)	336 (48.7)	378 (54.8)	601 (87.1)			
UTS, MPa (ksi)	747 (108.3)	744 (107.9)	896 (129.9)			
% El	72.6	64.7	31.0			
% RA	60.7 42.2		45.1			

shown(11) that aging for 4000 hours caused the A₂B microdomains to grow to about 100-300 nm in size. However, this does not cause overaging and deterioration of strength. The heattreated material lost most of its strengthening at 760°C. But, in material subjected to prolonged aging, large domains apparently are retained in short-time tensile tests at 650 and 760°C, thus explaining the higher magnitude of the tensile strengths at those temperatures. The formation of the ellipsoidal ordered domains is not deleterious to the ductility, and so the toughness of the alloy is preserved. This is confirmed by the fiberous appearance of the specimen fracture surfaces for tensile specimens broken at room temperature, as shown in Figure 6. Both scanning electron micrographs suggest fracture by coalescence of microvoids accompanied by considerable ductile dimpling. The large voids are probably associated with tearing in the vicinity of primary carbides. These aside, there is a discernible decrease in the dimple cell size and increase in their numbers.

The microstructural stability can also be monitored by measuring the impact toughness of thermally exposed material. The impact toughness data presented in Table V indicates that 242 alloy, after prolonged exposure at 650°C, did not form an embrittling phase, particularly the equilibrium Ni₃Mo phase with a platelet morphology. These results are contrasted with those of alloy B, known to form Ni₃Mo, and alloy S which also formed A₂B after prolonged aging.





Annealed (1066°C/WQ)

Annealed + heat treated (650°C/24 hours)

Figure 6: Scanning electron micrographs of fracture surface of tensile samples of 242 alloy broken at room temperature.

Table V. Thermal Stability of 242 alloy vs. alloys B and S

Alloy		V-Notch Charpy Impact Toughness, Joules (ft-lb) Condition					
	88						
	Ir	nitial	650°C/10	000 hours	650°C/40	000 hours	
242	90	(66)	56	(41)	42	(31)	
В	120	(88)	120	(88)	8.2	(6)	
S	191	(140)	116	(85)	91.5	(67)	

Initial condition for 242 alloy - Annealed + Heat Treated 650°C/24 hours For B and S - Annealed

Summary

The development of a Ni-25Mo-8Cr alloy for gas-turbine application, HAYNES 242 alloy, was described. The chemical composition of the alloy was defined based on the hardening response and microstructural examination of experimental Ni-Mo-Cr alloys. The formation of apparently stable, uniformly distributed Ni₂(Mo,Cr) microdomains, approximately 10 nm in size, is responsible for the strength and stability of the alloy. The Ni₂(Mo,Cr) phase apparently does not transform into an embrittling phase as indicated by the good toughness values in exposures up to 4000 hours at 650°C. The 242 alloy offers substantial improvement over existing Ni-Mo-Cr alloys and a unique combination of low-thermal expansion and high strength.

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