

THE PRECIPITATION AND STRENGTHENING BEHAVIOR OF Ni₂(Mo,Cr) IN HASTELLOY® C-22HS® ALLOY, A NEWLY DEVELOPED HIGH MOLYBDENUM NI-BASE SUPERALLOY

Xishan Xie¹, Yanping Zeng¹, Lizhong Kou¹, Jianxin Dong¹, L. M. Pike², Dwaine Klarstrom²

¹University of Science and Technology Beijing, Beijing 100083, China

²Haynes International, Inc, Kokomo, IN 46904-9013, USA

Keywords: Precipitation strengthening, Ni₂(Mo,Cr), HASTELLOY C-22HS® alloy

Abstract

The precipitation and strengthening behavior has been studied in a newly developed high molybdenum Ni-base superalloy, HASTELLOY® C-22HS® alloy, for long time exposures of 1000hrs at 600, 625 and 650°C. The homogeneous precipitation of the long range ordered (LRO) phase Ni₂(Mo,Cr) with an average size on the order of 10nm after a specially designed heat treatment contributes an excellent strengthening effect for this new superalloy. The grain boundary precipitation of high molybdenum containing phases such as M₆C and μ phase has been studied via isothermal exposures in a wide temperature range of 600-1050°C. The T-T-T curve of grain boundary phase precipitation has been also determined. This newly developed Ni-base superalloy with excellent corrosion resistance and high strength can be used in the intermediate temperature range below 650°C.

Introduction

Almost all of the Ni-base superalloys are strengthened by Ni₃M-type γ' and γ'' phases such as Ni₃(Al,Ti) and Ni₃(Nb,Ti,Al). In some applications the alloy is required to possess both high temperature strength and high corrosion resistance. For this purpose a new high molybdenum Ni-base superalloy designated as HASTELLOY C-22HS alloy has been recently developed by Haynes International, Inc^[1]. This new alloy, Ni-21Cr-17Mo, is actually on the base of the ternary Ni-Cr-Mo system^[2]. From the search of experimentally determined Ni-Cr-Mo system phase diagrams, high molybdenum containing phases can be formed such as μ and P phases, but many others are still subjected to debate (with question marks in the phase diagrams) such as ?CrMo₄Ni₅, ?Cr₄Mo₃Ni₃, ?Cr₅Mo₇Ni₈^[3] and ? Cr₃Mo₅Ni₆^[4]. Recent calculated isothermal sections of the Ni-Cr-Mo phase diagram at 500, 620 and 700°C show the existence of P phase and OP6 phase^[5], OP6 stands for Pt₂Mo type phase (such as Ni₂Mo and Ni₂Cr or Ni₂(Cr,Mo)). The high chromium and high molybdenum carbides M₂₃C₆ and M₆C can be also formed respectively because of the existence of carbon in C-22HS alloy.

For understanding the strengthening behavior of this new alloy, the precipitation behavior and microstructural stability have been studied in the temperature range of 600-650°C for 1000 h for the purpose of intermediate temperature applications. Grain boundary precipitation behavior is important to understand for engineering applications. Isothermal exposures have been conducted in a wide temperature range of 600-1050 °C for determination of T-T-T diagram of grain-boundary precipitation.

Experimental Procedure

Nominal chemical composition of HASTELLOY C-22HS® is

HASTELLOY, C-22HS, and C-22 are registered trademarks of Haynes International, Inc.

shown in Table I. Investigated samples for this paper were taken from Φ19mm hot rolled and annealed bar. The specially designed heat treatment is 1080°C mill annealing followed by water quenching + 705°C/16h furnace cooling to 605°C/32h/AC.

Table I. Nominal chemical composition of C-22HS alloy (wt%)

C	Si	Mn	Cr	Mo	Ni	W	Fe	B
0.01*	0.08*	0.8*	21	17	Bal	1*	2*	0.006

* Maximum content.

For detailed understanding of the precipitation strengthening behavior, a study on long time aging of this new alloy after heat treatment has been conducted as shown in Table II.

Table II Heat treatment and thermal exposure of investigated C-22HS alloy

Heat treatment (HT)	1080°C/Annealed/WC+705°C/16h/FC+605°C/32h/AC
Thermal exposure	HT+600°C/10h, 100h, 500h, 1000h/AC
	HT+625°C/10h, 100h, 500h, 1000h/AC
	HT+650°C/10h, 100h, 500h, 1000h/AC

Isothermal exposures have been conducted after super-solvus solution treatment at 1120°C in a wide temperature range of 600 to 1050°C for determination of grain boundary precipitation behavior in C-22HS alloy (see Table III).

Table III. Isothermal aging conditions after super-solvus temperature of 1120°C/1h for C-22HS alloy

Time/h \ Temp/°C	0.1	0.17	0.25	0.33	0.67	22	32	96
1050	√	√					√	
1000	√	√				√		
950	√	√					√	
900	√	√					√	√
850	√	√					√	
800		√	√				√	√
750				√			√	
700					√		√	√
650							√	√
600							√	√

Phase identification and structure analyses have been conducted by means of SEM with EDX, TEM with SAD and EDX. Precipitated phases were also electrolytically extracted and examined by XRD for phase identification and in some cases quantitatively analysed. Mechanical properties of tensile and impact tests were conducted for understanding strengthening effect only.

Results and Discussion

Mechanical Properties

The yield strengths of C-22HS alloy at ambient and high temperature (595°C) in comparison with C-22 alloy are shown in Figure 1.

It can be seen that the yield strengths of C-22HS alloy at both room temperature and 595°C are approximately doubled after aging in comparison with the mill annealed condition (MA). However, C-22HS alloy still possesses very good ductility in the as-heat treated condition. For example, the reduction in area for tensile test at room temperature can almost reach 50%. This is a unique strengthening effect developed in a high molybdenum containing (17%Mo) C-22HS alloy in comparison with C-22 alloy (13%Mo) at almost same level of chromium content (21%Cr).

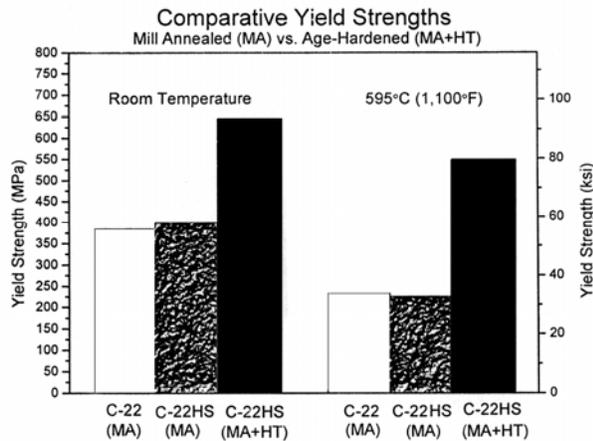
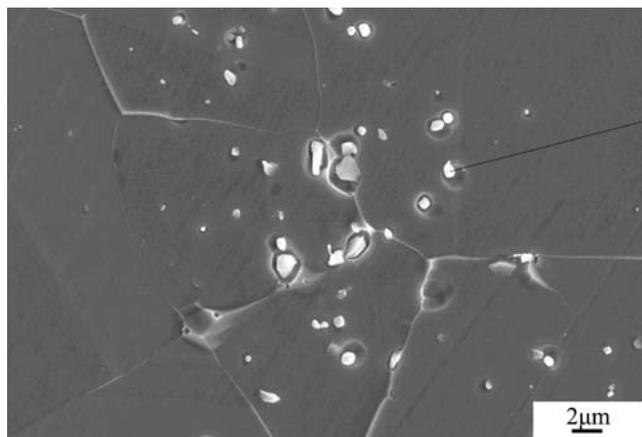


Figure 1. Comparative yield strengths of C-22 and C-22HS

Phase Calculation

The phase diagram based on the nominal chemical composition of C-22HS alloy has been calculated by Thermo-Calc software^[6] as shown in Figure 2. It can be seen that only 2 carbides, $M_{23}C_6$ and M_6C , and 2 high molybdenum containing intermetallic



compounds, $(Ni,Cr)_7Mo_6$ type μ phase and $Ni_{40}Cr_{18}Mo_{42}$ type P phase, can be formed in the FCC Ni-Cr-Mo γ -matrix. However, $M_{23}C_6$ and M_6C carbides often precipitate at grain-boundaries in Ni-base superalloys. Intermetallic compounds μ and P are normally considered as deleterious phases in Ni-base alloys. The strengthening phase in C-22HS alloy must be some kind of finely dispersed distributed phase in the γ -matrix. It will be confirmed as $Ni_2(Mo,Cr)$, a long range order phase in this paper. The stability of the $Ni_2(Mo,Cr)$ strengthening phase after extended long time thermal exposure is the key issue for C-22HS alloy to be used at high temperatures. The purpose of following study is to observe the strengthening phase and to study its precipitation and coarsening behavior at high temperature exposures.

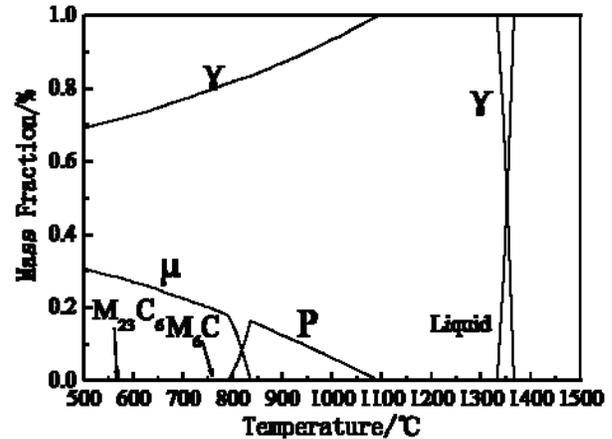


Figure 2. Calculated phase diagram of C-22HS

Structure in the as-HT Condition

Figure 3 shows an SEM micrograph of C-22HS alloy in the as heat-treated (HT) condition. Different size particles are present not only at grain-boundaries, but also randomly distributed in the grains. These undissolved particles after 1080°C MA condition have been electrolytically extracted and identified via XRD as μ and M_6C carbide (see Figure 4). These particles are in a very small amount and quantitatively determined after electrolytical extraction just 0.07%wt only.

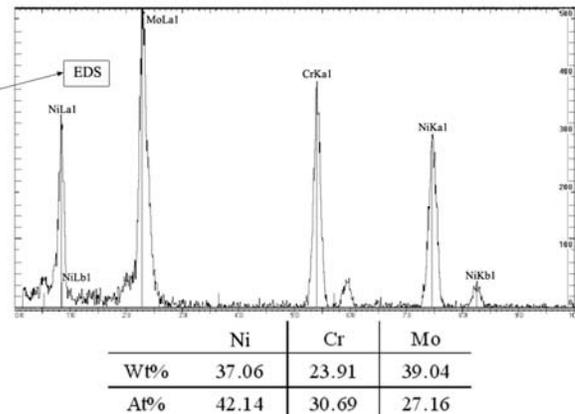


Figure 3. SEM microstructure of C-22HS alloy at as HT condition

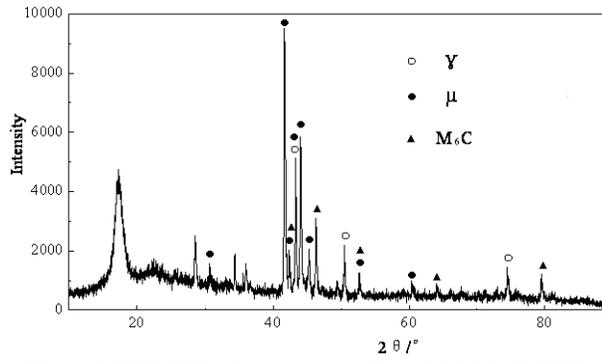
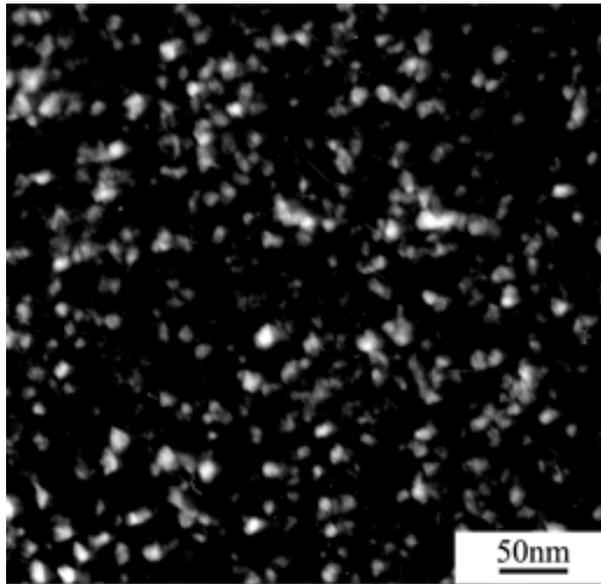


Figure 4. XRD diffraction spectrum of μ and M_6C in C-22HS

Dark field TEM imaging reveals a homogeneous distribution of



fine precipitates in γ -matrix. The average size is on the order of 10nm. Selected area diffraction of these precipitates confirms their identity as the long range ordered phase $Ni_2(Mo,Cr)$, see Figure 5.

In the Ni-Cr system, Ni_2Cr is a LRO stable phase, but Ni_2Mo (Pt_2Mo type) in Ni-Mo system is a LRO metastable phase. However, in Ni-Cr-Mo ternary system chromium can replace a part of molybdenum to increase the stability for forming $Ni_2(Mo,Cr)$ Pt_2Mo -type strengthening phase. The volume fraction of $Ni_2(Mo,Cr)$ strengthening phase in C-22HS in a as heat treated condition was calculated from TEM images and reported as about 25% in the recent paper^[7]. Quantitative determination of $Ni_2(Mo,Cr)$ phase by electrolytical extraction followed by special designed micro-chemical analysis was conducted. However, it failed because of the close chemical potentials of Ni-Cr-Mo γ -matrix and $Ni_2(Mo,Cr)$ phase at electrolytical isolation condition.

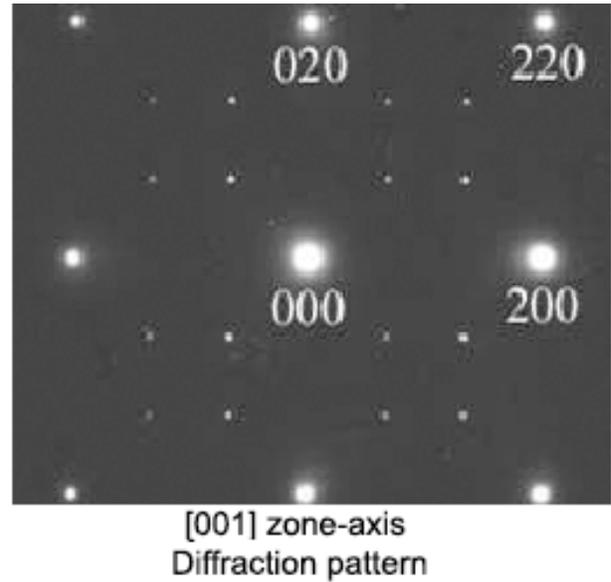


Figure 5. Dark field TEM image and SAD pattern of $Ni_2(Mo,Cr)$ in C-22HS alloy at as heat-treated condition

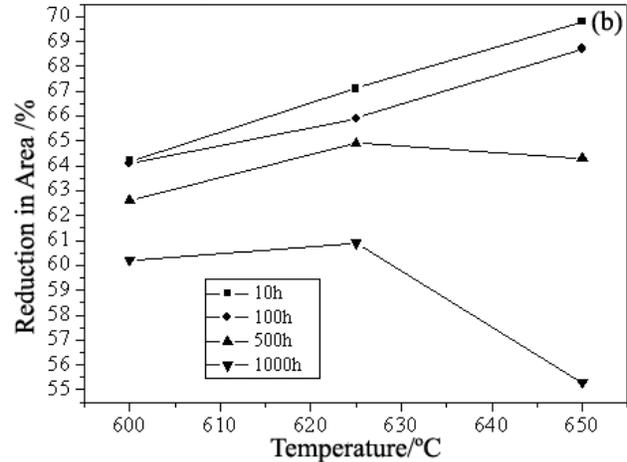
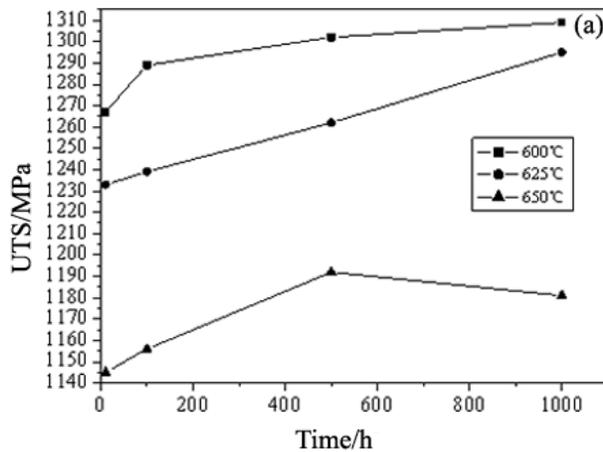


Figure 6. The relationship of room temperature tensile properties with exposure time (1000h) and temperature (600, 625 and 650°C) for (a) ultimate strength, (b) reduction in area

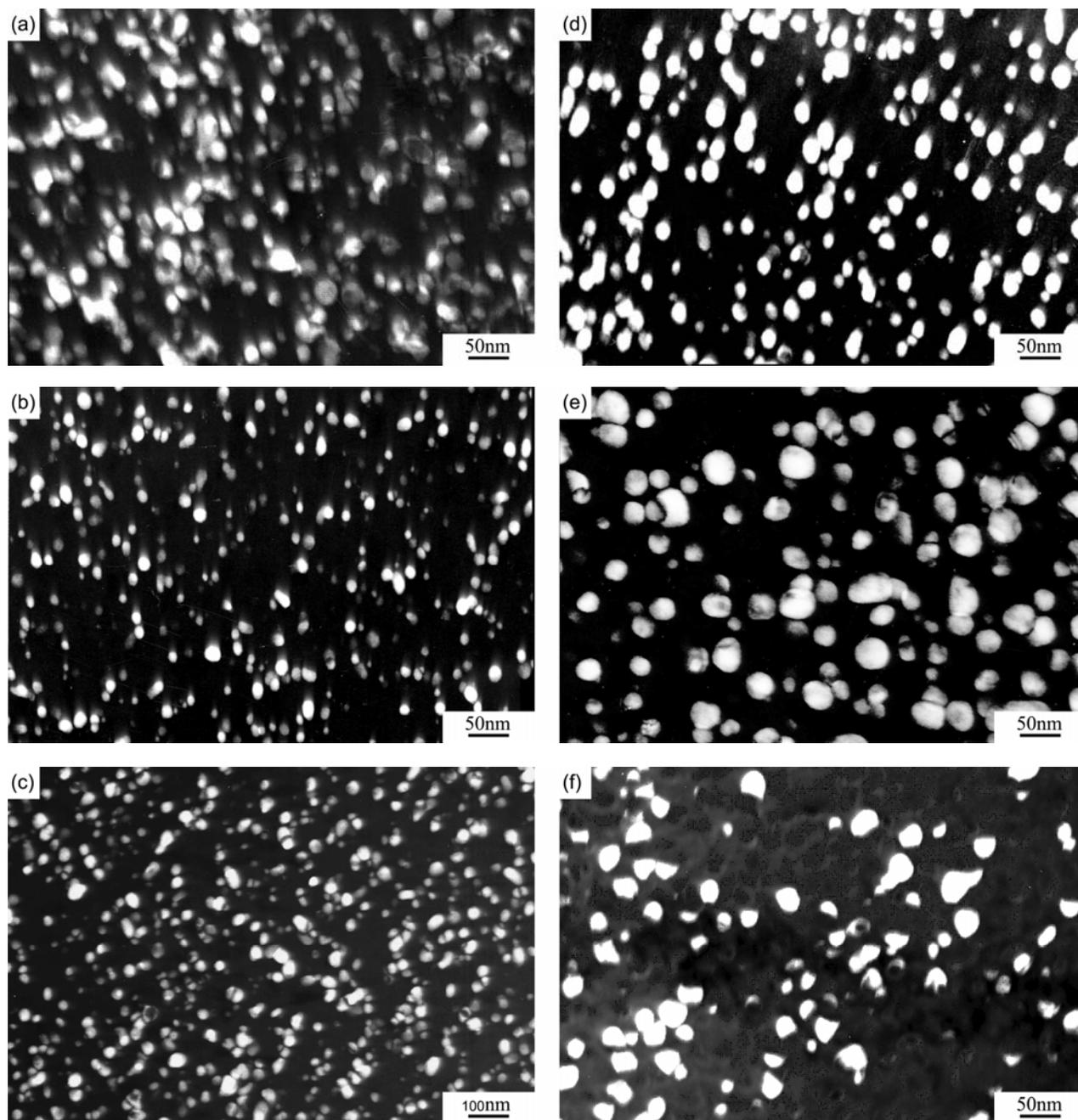


Figure 7. Morphology of dispersively precipitated $\text{Ni}_2(\text{Mo,Cr})$ in C-22HS alloy at different thermal exposures
 (a) AS HT+600°C/1000h; (b) AS HT+625°C/100h; (c) AS HT+625°C/1000h; (d) AS HT+650°C/100h;
 (e) AS HT+650°C/500h; (f) AS HT+650°C/1000h

Long-term exposure at 600, 625 and 650°C

The ultimate strengths of C-22HS alloy continuously increase with the exposure time up to 1000h at 600, 625 and 650°C (see Figure 6a) and ductilities are still very high, for example the reduction in area of tensile testes can still keep above 55% (see Figure 6b).

It shows the unique strengthening effect of $\text{Ni}_2(\text{Mo,Cr})$ fine

particle complementary precipitation during long time aging in the temperature range of 600-650°C.

These LRO phase $\text{Ni}_2(\text{Mo,Cr})$ fine particles are very stable as shown in Figure 7a after 1000h exposure at 600°C. $\text{Ni}_2(\text{Mo,Cr})$ fine particles can still homogeneously distribute in the grains from 100h to 1000h exposure at 625°C (see Figure 7b and 7c). The

dispersively distributed particles $Ni_2(Mo,Cr)$ increase in size with a certain coarsening rate in the time period of 100, 500 and 1000h exposures at 650°C (see Figure 7d, e and f). The average size of the $Ni_2(Mo,Cr)$ phase vs temperature and time at long-term exposure has been quantitatively determined from TEM images as shown in Figure 8. The growth rate of the $Ni_2(Mo,Cr)$

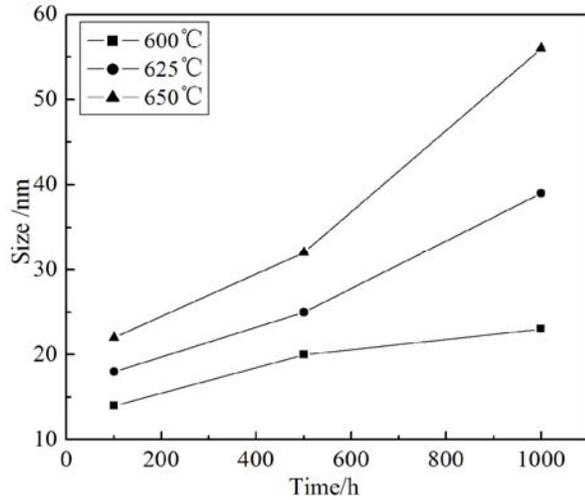


Figure 8. Relationship of the average size of $Ni_2(Mo,Cr)$ phase vs temperature and time at long-time exposure

strengthening phase is very slow at 600°C and only a little bit higher at 625 and 650°C. The average sizes of $Ni_2(Mo,Cr)$ after the 1000h long time exposure at 600, 625 and 650°C are still below 20, 40 and 60nm respectively. These particles sizes can still impart a significant strengthening effect and they are acceptable for engineering application.

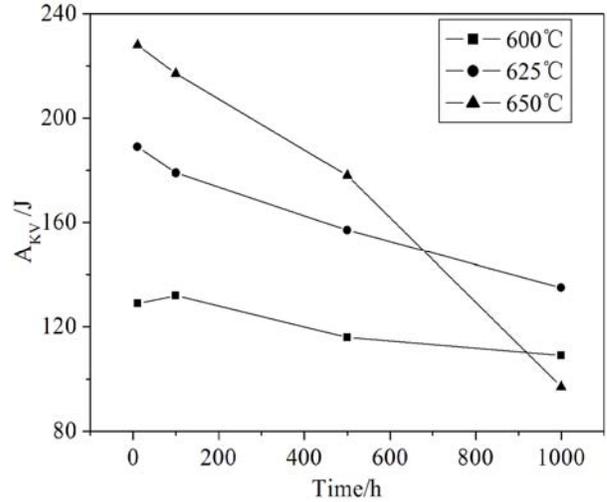


Figure 9. Relationship of Charpy impact energy of C-22HS alloy vs long-term aging time in the temperature range of 600-650°C

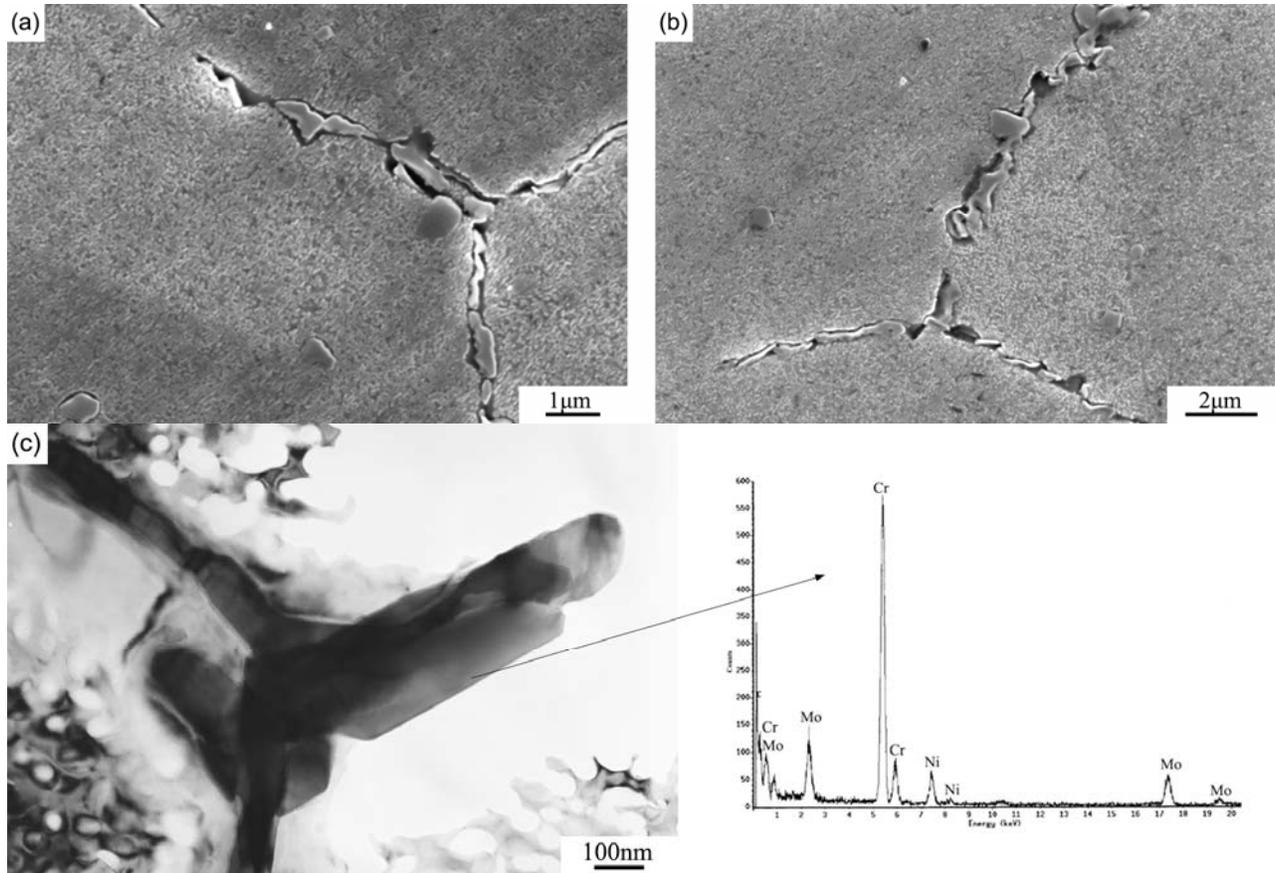


Figure 10. High chromium grain boundary precipitates in C-22HS alloy after 650°C/1000h aging (a) (b) SEM micrograph (c) Bright field micrograph and EDX spectrum of high chromium precipitate

The impact toughness mildly decreases with the exposure time at 600 and 625°C. However, it drops rapidly at 650°C aging after 500h and it is lower than 100J after 1000h exposure at 650°C (see Figure 9). SEM micrograph shows the continuous grain boundary precipitation (see Figure 10) which may be the origin of this drop in impact toughness. Bright field TEM micrograph and EDX spectrum show a high chromium containing precipitate at grain boundaries (see Figure 10c). XRD analysis of extracted residue from C-22HS long-term aged at 650°C for 1000h shows the existence of high chromium carbide $M_{23}C_6$ (see Figure 11).

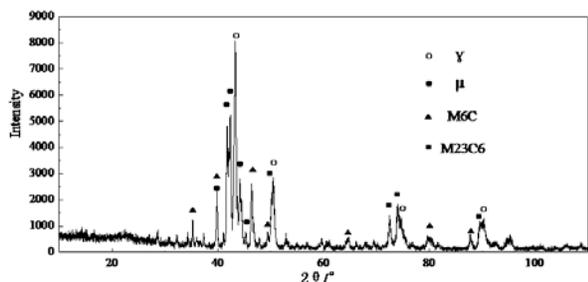


Figure 11. XRD spectrum of extracted residue from C-22HS alloy aged for 1000h at 650°C

T-T-T Diagram of Grain-boundary Precipitation

To understand the grain boundary phase precipitation in C-22HS alloy, isothermal exposures have been also conducted in a wide temperature range (600 - 1050°C) with different times as shown in Table III. A super-solvus temperature of 1120°C was conducted for full dissolution of μ and M_6C phase at mill annealed condition. A T-T-T curve of grain-boundary precipitation was determined by SEM observation as shown in Figure 12.

Grain boundary precipitation is accelerated by increasing temperature as shown in Figure 12 and 13 from 600°C to 750°C. Above 800°C, the grain-boundary precipitation develops very fast and a certain amount of grain-boundary precipitates can be formed at very short time such as only after 10min in the temperature range from 800°C to 1050°C (see Figure 14). An EDX spectrum of grain-boundary precipitates in this temperature range (for example 900°C/96h) shows very high molybdenum content (see Figure 15). It reminds us that the grain boundary precipitates in the temperature range of 600°C-1050°C might be high molybdenum containing μ phase and M_6C carbide. The detail work on grain-boundary precipitation will be studied further.

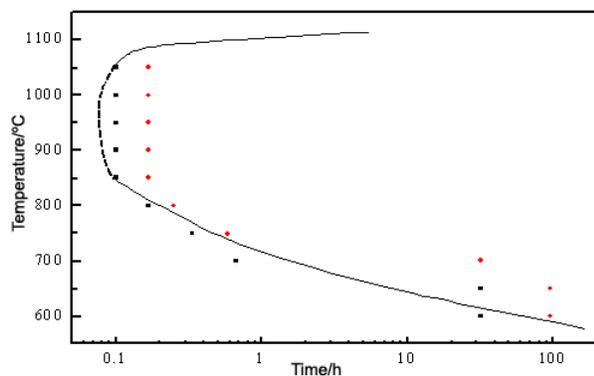


Figure 12. Time-Temperature-Transformation diagram of grain boundary precipitates in C-22HS

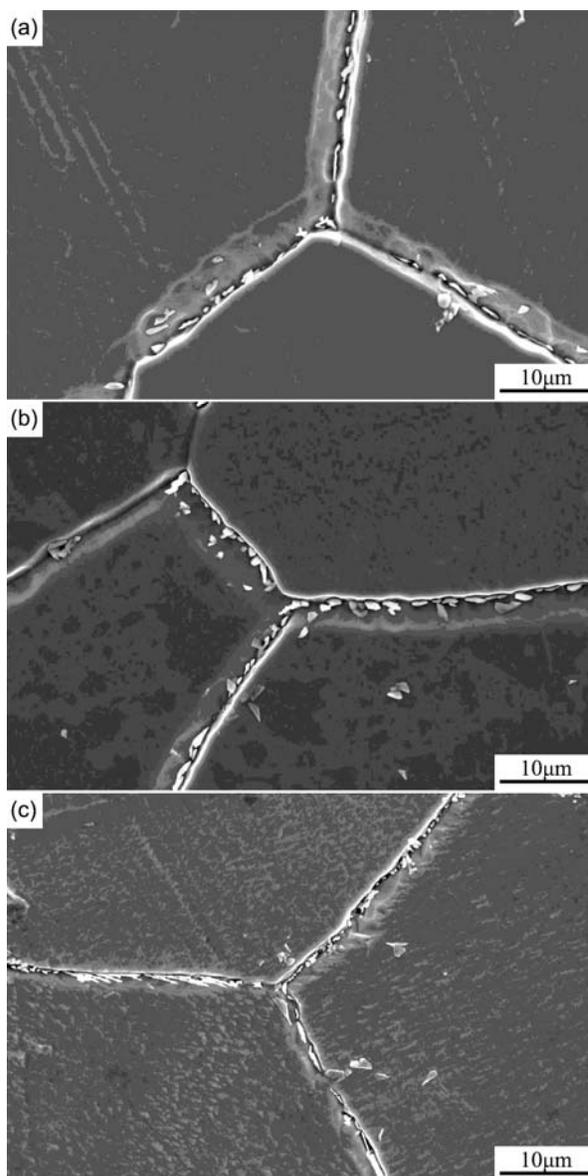


Figure 13. Grain-boundary precipitation at iso-thermal treatment of C-22HS alloy after (a) 600°C/96h (b) 700°C/32h (c) 750°C/35min

Conclusions

1. Three high molybdenum containing phases μ , M_6C and Pt-Mo type $Ni_2(Mo,Cr)$ have been identified in the newly developed Haynes C-22HS[®] superalloy. A high chromium carbide, $M_{23}C_6$, has been also found after 650°C/1000h aging.
2. The new alloy possesses high strength as a result of the strengthening effect of the Pt₂Mo-type long range ordered $Ni_2(Mo,Cr)$ phase precipitated using a specially designed heat treatment condition of 1080°C/annealed/WC + 705°C/16h/FC + 605°C/32h/AC.
3. The Pt₂Mo-type long range ordered $Ni_2(Mo,Cr)$ phase possesses a unique strengthening effect because of its fine disperse precipitation in the Ni-Cr-Mo γ -matrix. The average size of

$\text{Ni}_2(\text{Mo,Cr})$ in the as-heat treated condition is on the order of 10nm. Its average size can still keep below 20, 40 and 60nm after 1000h exposure at 600, 625 and 650°C, respectively.

4. The T-T-T diagram of grain boundary precipitates has been determined over a wide range of temperatures (600-1050°C).

5. This newly developed, highly corrosion-resistant Ni-base superalloy with high strength, C-22HS[®] alloy, can be used at intermediate temperatures below 650°C.

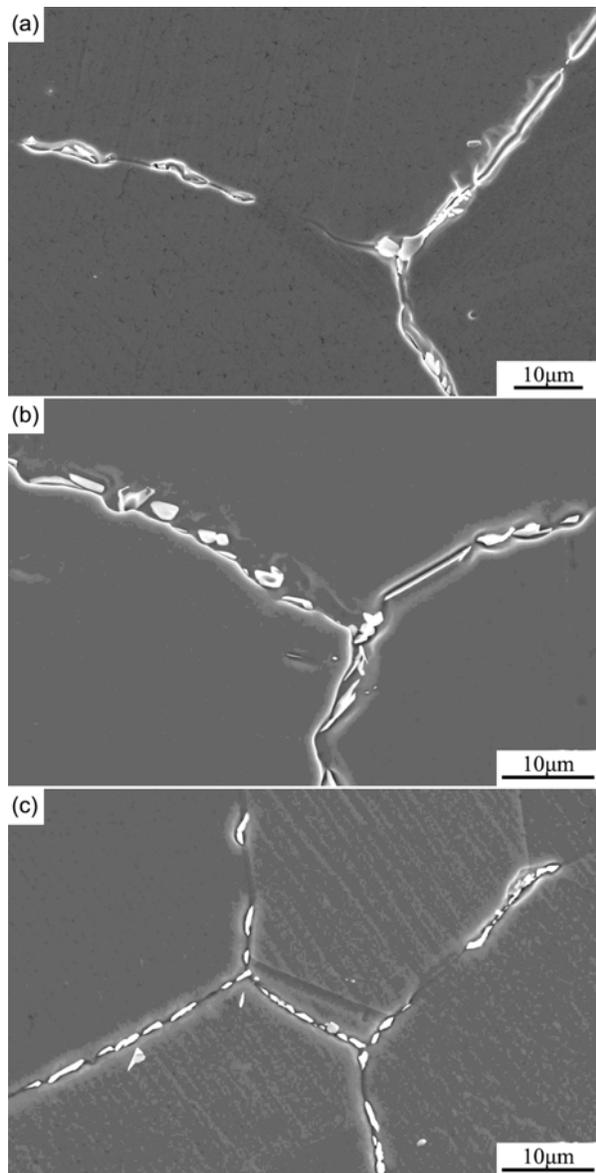


Figure 14. Grain-boundary precipitation at iso-thermal treatment for 10min of C-22HS alloy at the temperatures (a) 950°C (b) 1000°C (c) 1050°C

Acknowledgements

The university authors appreciate the material offering from Haynes International, Inc and financial support for graduate student training.

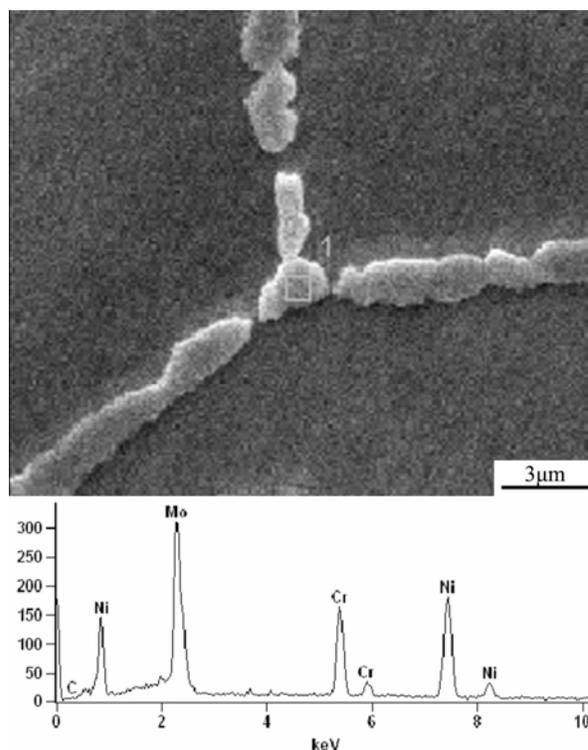


Figure 15. SEM micrograph and EDX spectrum of grain boundary precipitate in C-22HS alloy after iso-thermal aging at 900°C/96h shows high content of Mo (~32.5%wt) and Cr (~19.7%wt)

References

1. HASTELLOY[®] C-22HS[™] Alloy Preliminary Data, Haynes International, Inc (2006).
2. M. Pike, D.L. Klarstrom, "A New Corrosion-Resistant Ni-Cr-Mo Alloy with High Strength", paper No: 04235, NACE International, Houston, TX (2004) 1-5.
3. K.P. Gupta, "The Ni-Cr-Mo System", Phase Diagrams of Ternary Nickel Alloys, Indian Institute of Metals, Calcutta, India 1 (1990) 26-48.
4. J.R. Mihalisin, G.G. Bieher, and R.T. Grant, "Sigma-Its Occurrence, Effect, and Control in Nickel-Base Superalloy". *Transactions of the Metallurgical Society of AIME*, 242 (1968), 2399-2414.
5. T.L. Kanfman, Z.K. Liu, "Modeling of Ni-Cr-Mo bases alloys: Part I-phase stability", *Computer coupling of Phase Diagrams and Thermochemistry*, 30 (2006), 70-87
6. B. Sundman, B. Jansson, and J. O. Anderson, *CALPHAD*, 9 (1985), 153.
7. Y.L. Liu et al., "Strengthening Domains in a Ni-21Cr-17Mo Alloy", *Scripta Materialia*, 56 (2007), 121-124.