Influence of heat treatments on the mechanical properties and microstructure of a 50Cr-50Ni niobium containing alloy

G. Caironi, E. Gariboldi, G. Silva, M. Vedani

► To cite this version:

G. Caironi, E. Gariboldi, G. Silva, M. Vedani. Influence of heat treatments on the mechanical properties and microstructure of a 50Cr-50Ni niobium containing alloy. *Journal de Physique IV Proceedings*, 1993, 03 (C7), pp.C7-289-C7-295. 10.1051/jp4:1993746 . jpa-00252164

HAL Id: jpa-00252164

<https://hal.science/jpa-00252164>

Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Influence of heat treatments on the mechanical properties and microstructure of a 50Cr-50Ni niobium containing alloy

G. CAIRONI, E. GARIBOLDI, G. SILVA and M. VEDANI

Politecnico di Milano, Dipartimento di Meccanica, P.zza L. da Vinci 32, 20133 Milano, Italy

ABSTRACT

A heat resisting 50Cr-50Ni niobium-containing casting alloy, particularly developed for petrochemical plants was studied. The alloy combines high temperature strength with fuel ash corrosion resistance. However, during service, the exposure to high temperatures gives rise to precipitation of embrittling phases, strongly depleting the material ductility. Therefore, studies on the thermal aging at 700°C were carried out either in the as cast condition or after heat treatments at 1000, 1075, 1150°C. Alloy modifications were analyzed from a microstructural point of view and through hardness measurements, with the aim of relating them to other mechanical properties. It was found that the thermal treatments, providing a coarse precipitation, were effective in preventing excessive embrittlement levels to be reached.

INTRODUCTION

In petrochemical and power steam plants, economical criteria lead to the adoption of low cost fuels, characterized by highly corrosive ashes. The low melting point of sulfides, chlorides and vanadium oxides in these combustion products, often lead them to be liquid at the operating temperatures. Thus the corrosion rate is increased because of the prevention from forming a protective oxide layer. Furthermore, the conditions are worsened by the high pressure and temperature needed to improve plants efficiency.

The manufacturing of structural components operating in power plants in the afore mentioned environment therefore requires alloys combining good mechanical properties and corrosion resistance. The usual high-temperature materials, such as Fe-Cr-Ni alloys, show inadequate corrosion resistance in the mentioned environment. On the contrary, some Ni-Cr alloys, particularly those with a nickel content in the range 40-70 wt.%, reveal excellent corrosion resistance, especially in vanadium-rich environments [1, 2, 3].

In the present study, a 50Cr-50Ni niobium containing casting alloy featuring high corrosion resistance combined with satisfactory strength has been investigated. Despite the fairly good mechanical characteristics in the as cast condition, the alloy has been reported [2] to having undergone a considerable loss in ductility, particularly during the first days of service. In the present investigation, microstructural evolution during aging at particularly critical temperatures was monitored either in the as cast condition or on samples previously annealed at 1000, 1075, 1150°C. The aim was to follow the development of the first drastic phenomena impairing ductility and to investigate the effects of preliminary structural modifications on the stability of the mechanical properties.

MATERIAL

A nominal 50Cr-50Ni alloy corresponding to the ASTM A560 50Cr-50Ni-Nb alloy and supplied in cast ingots according to ASTM A370 standards was studied. The chemical composition (wt.%) of the material was the following:

Cr	Nb	C	N	Ni
48.31	1.53	0.06	0.05	bal.

The microstructure of the as cast alloy (electrolytically etched in 10 vol.% oxalic acid) is depicted in figure 1a. EDS elemental analysis revealed a microstructure consisting of a γ -Ni phase matrix and of interdendritic regions (about 10 vol.%) rich in α -Cr phase. These latter, containing a limited amount of elongated γ zones, showed boundaries decorated by niobium-containing particles which revealed to be Nb(C, N) compounds. Apart from the above mentioned regions, no α -phase was observed in the matrix. Isolated chromium carbides were detected. The microstructure was almost completely free from lamellar eutectic, confirming the considerable effect of niobium addition on the reduction of this structure [4, 5, 6].

When the alloy is exposed to operating temperatures or to thermal cycles, the non-equilibrium structural condition causes the precipitation of Cr-rich phase in the matrix and of Ni-rich phase in the interdendritic regions [4, 7, 8]. Similar modifications of the alloy microstructure can also be obtained by means of proper heat treatments. These can induce a desired coarse and globulized morphology of the precipitates, thus limiting further precipitation during exposure to high temperature. In the present study three annealing treatments, at 1000, 1075, 1150°C for 1 hour (followed by water quenching), were carried out in order to compare the obtained microstructures and their alterations to those of the basic as cast condition during time.

In literature it has already been pointed out [9] that the most severe operating conditions for as cast components are at 700°C. Consequently, this temperature was chosen to study the microstructural evolutions. Thus, four sets of samples were aged at 700°C for periods ranging from 0 to 192 hours in order to correlate the microstructure with the already known modifications of the mechanical characteristics during the first stage of service of the material in industrial plants.

MICROSTRUCTURAL EVOLUTION

Microstructural observations and quantitative metallographic studies were carried out to monitor the alterations brought about by aging. The relatively low amount of interdendritic regions and the small size of the γ precipitates occurring in these areas prevented any reliable volume content measurement to be carried out. Therefore, the observations were focused only on the precipitation of α phase in the matrix. The particle volume content was measured by means of a point grid counting technique on SEM micrographs (magnification 6000X), obtaining data within 10% accuracy. The shape and size distributions of α precipitates were obtained by applying the De-Hoff modified Schwartz-Saltikov theory [10] on the size distribution of ellipsoidal particles with a fixed axial ratio. According to this method, the α precipitates were assumed to be prolate ellipsoids [11] with the same average axial ratio q (i.e. minor/major axis ratio).

During aging, the above described as cast microstructure rapidly modified (figure 1). In fact, a few hours at 700°C were sufficient to give rise to a massive, oriented and fine α precipitation in the matrix. After 24-hour aging α precipitation had already reached the amount of 53 vol.% and consisted of particles having an average minimum axis and an axial ratio of 0.12 μm and 0.21, respectively. An analogous phenomenon in the α phase of the

interdendritic regions led to the precipitation of much finer and elongated γ phases. Subsequent structural changes consisted of the gradual decrease in precipitation rate (figure 2a) and in the contemporary coarsening and globulization of the precipitated particles.

Figure 1. Microstructural features (SEM micrographs) of the 50 Cr-50 Ni Nb alloy in the as cast condition. a) unaged material, A: Ni-rich matrix, B: Cr-rich interdendritic regions, C: niobium carbo-nitrides; b) and c) microstructures after aging for 48 and 192 hours at 700 °C, respectively.

Figure 2. α -phase precipitate volume content in γ -phase matrix (a) and HRC hardness (b) vs. aging time curves.

The structural modifications brought about by annealing at 1000 and 1075 °C are illustrated in figures 3 and 4, respectively. They mainly consisted of the appearance of a coarse oriented precipitation of α -Cr phase in the γ matrix and of a finer γ precipitation in the α phase. A few μm wide precipitate-free zone around the α -Cr phase was noticed. These areas, together with the spaces in the matrix free from coarse precipitates, revealed to be nucleation sites for secondary finer precipitation during aging. The phenomenon, that was noticed after 24 hours and 72 hours in the 1075 and 1000 °C annealed condition, respectively, had only a slight influence on the overall precipitated particle volume content. Furthermore, the continuum coarsening of particles partially counterbalanced the effects of the secondary precipitation, resulting, after a 192-hour aging, in morphological parameters (D_{av} and q in table I) similar, or even lower, than the initial ones.

Figure 3. Microstructural features (SEM micrographs) of the 50Cr-50Ni-Nb alloy heat treated at 1000°C for 1h. a) unaged condition; b) and c) microstructures after aging for 108 and 192 hours at 700°C, respectively.

Figure 4. Microstructural features (SEM micrographs) of the 50Cr-50Ni-Nb alloy heat treated at 1075°C for 1h. a) unaged condition; b) and c) microstructures after aging for 108 and 192 hours at 700°C, respectively.

Figure 5. Microstructural features (SEM micrographs) of the 50Cr-50Ni-Nb alloy heat treated at 1150°C for 1h. a) unaged condition; b) and c) microstructures after aging for 24 and 192 hours at 700°C, respectively.

The 1150°C solution treatment resulted in a matrix containing only a few isolated and coarse α precipitates and in interdendritic regions with a greater amount of γ zones with respect to the other material conditions (figure 5). The low amount of precipitates in the unaged material did not allowed precise morphological and quantitative measurements. During the first dozen hours of aging, intense precipitation occurred in both phases. The morphological evolution of γ precipitates was similar to that in the as cast condition. Again, the precipitate-free matrix/interdendritic interface which was evidenced after aging for 24 hours, became gradually decorated by the α -Cr constituents. The structural alterations led to a volume content curve similar to the corresponding trend of the as cast condition, though reaching a lower final value (figure 2a).

Table I. Microstructural parameters concerning α precipitation. Dav: average minimum axis of the ellipsoidal particles; q: axial ratio.

thermal treat.	α prec. vol. %		Dav μm		q		γ matrix HV100		α regions HV100	
	0 h	192h	0 h	192h	0 h	192h	0 h	192h	0 h	192h
as cast	0	69	-	0.16	-	0.28	203	449	457	296
1000°C	36	53	0.22	0.19	0.23	0.26	368	410	463	425
1075°C	37	53	0.22	0.22	0.19	0.52	329	370	482	438
1150°C	≈ 4	63	-	0.19	-	0.26	268	358	508	456

HARDNESS

Vickers microhardness tests (applied load on the indenter: 0.981 N) were carried out on matrix and interdendritic regions, before and after aging for 192 hours. The results are summarized in table I. It is worthwhile observing the hardening effect correlated to the amount of α precipitation in the matrix and the opposite effect of γ enrichment in the interdendritic α -rich regions.

Rockwell C hardness tests were performed on the aged samples to follow the overall hardness evolution during exposure time. The results are depicted in figure 2b. The curves followed a trend similar to that of the volume content of α precipitation in the matrix except for the material annealed at 1150°C, where a considerable initial hardness corresponded to a material almost completely free from α precipitates.

DISCUSSION AND CONCLUSIONS

Microstructural observations pointed out that exposure to high temperature, during the examined annealing treatments and/or aging had brought about the contemporary precipitation of α and γ phases in matrix and interdendritic α -rich regions, respectively. This fact, caused by the presence of supersaturated phases in the as cast material, resulted in a global increase of the α phase volume fraction in the microstructure. Thus, the similarity between the evolution curves of the Rockwell hardness and the amount of the α -precipitate could be explained. The occurrence of secondary precipitation in 1000 and 1075°C annealed conditions did not influenced hardness significantly.

The microstructural alterations monitored during the first hundred hours of aging were in good agreement with the mechanical behaviour of the alloy, observed in previous works [3, 4-7, 9]. In table II the mechanical characteristics obtained by the authors [12] for the as cast and 1000°C annealed materials, unaged and aged at 700°C, are reported and compared to the

data by Ennis [9], related to the as cast condition aged at the same temperature.

According to Ennis data [9], the tensile strength of the as cast condition doubled during the first 64 hours of aging. By this time the present study evidenced the occurrence of the most drastic changes in the microstructure. The volume content of α precipitates in the matrix raised from zero to about 60 percent and the hardness of the material, 90 HRB in the unaged as cast condition, overcame 40 HRC. Fracture elongation, as expected, behaved in an opposite manner. The elongated shape and fine size of both α and γ precipitates was responsible for the drastic decrement in ductility of the alloy after the first aging period (table II). The gradual particle coarsening, that is likely to continue for longer aging times, can be related to the limited recovery of ductility, which was observed to begin between 1000 and 5000h [9].

Table II. Mechanical characteristics published in literature or by the authors.

aging time at 700°C (h)	as cast *			as cast **			1000°C X 1h **		
	UTS MPa	YS MPa	Elong. %	UTS MPa	YS MPa	Elong. %	UTS MPa	YS MPa	Elong. %
0	600-800	250-400	22-40	705	448	22.3	891	640	2.6
64	1150-1450	1050-1200	3-5	-	-	-	-	-	-
100	-	-	-	1024	855	0.9	901	735	1.2
1000	900-1000	750-950	<3	-	-	-	-	-	-
5000	800-900	750	2-5	-	-	-	-	-	-

*Ennis [9]; sample diameters: 6.4 mm or 10.2 mm.

**Caironi et al. [12,13]; sample diameter: 6.25 mm, gauge length 25 mm.

Both the fracture elongations were measured from autographic records of the tests.

The annealing treatment at 1150°C resulted in a very limited amount of coarse α precipitates in the unaged samples. However, fine α secondary precipitation rapidly took place during aging. Its nucleation was observed to occur during the transient to the aging temperature. The morphology of the fine precipitates was similar to that of the as cast condition whose greater amount corresponded to greater hardness values.

Heat treatments at 1000 and 1075°C and the following aging had similar effects on the material structure. In both cases, the annealing treatment promoted precipitation. The precipitates, about 40 vol.%, were coarser and more globular with respect to those formed after aging for 192h in the as cast and in the 1150°C heat treated material conditions. Their presence corresponded to the higher strength and lower ductility observed for the 1000°C annealed material (table II). Exposure to 700°C caused a secondary fine precipitation of limited amount and a continuous coarsening of the already present particles which led to the observed slight modifications of mechanical characteristics of the 1000°C heat treated condition after aging for 100 hours and would probably result in a recovery of ductility after longer aging times. As far as the 1075°C heat treatment is concerned, microstructural evolutions similar to those of the 1000°C annealed condition, are likely to give rise to similar modifications of the mechanical characteristics.

ACKNOWLEDGEMENTS

The authors would like to thank FIAS s.r.l. (I-21055 Gorla Min.) for having supplied the materials and the technical information.

REFERENCES

- 1) LEWIS H., J. Institute of Fuels, Jan. (1966),
- 2) PENRICE P.J., STEPLEY A.J., TOWERS J.A., J. Institute of Fuels, Jan. (1966).
- 3) SWALES G.L., Ward D.M., NACE Corrosion '79, Atlanta, Georgia, USA.
- 4) BALBI M., CAIRONI G., SILVA G., TOSI G., Int. Conf. "Monitoring, Surveillance and Predictive Maintenance of Plants and Structures", Taormina, (1989).
- 5) SWALES G.L., WARD D.M., INCO Tecn. Publ.
- 6) OTERO E., MERINO M.C., PARDO A., BIEZMA M.V., Metallographia 21, (1988), 217.
- 7) BALBI M., CAIRONI G., SILVA G., TOSI G., La Fonderia Italiana 9, (1979), 225.
- 8) AYDIN I., BÜLER H.E., RAHMEL A., Arch. Eisenhüttenwass 54, (1983), 461.
- 9) ENNIS P.J., INCO Europe Limited, Sept. (1974).
- 10) DE HOFF R.T., Trans. AIME 224 (1962), 474.
- 11) CATTANEO A., LA MALFA F., Graduation Thesis, Politecnico di Milano - Dipartimento di Meccanica, (1993).
- 12) CAIRONI G., GARIBOLDI E., SILVA G., VEDANI M., II ASM Conf. Heat Treatment and Surface Engineering, Dortmund (D), (1993).
- 13) FIAS s.r.l. (Fonderie Italiane Acciai Speciali), Gorla Minore (I), Technical Datasheet.