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Elaboration, high temperature oxidation test and metallographic characterization of a chromium-vanadium alloy

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ABSTRACT

Neighbour to more common elements for superalloys' base (Co, Ni, Fe), chromium is itself a potentially very interesting element for this role thank to its elevated refractoriness and its beneficial effect on the high temperature oxidation behaviour of many metallic alloys devoted to uses in hot atmospheres. In this work a Cr-10V alloy was elaborated by casting and it was structurally characterized by electron microscopy and X-ray diffraction. Hardness at room temperature and oxidation rate at 1200°C were specified. Melting using a high frequency induction furnace under argon led to total melting and solidification of a {not melted part}-free and a {chemical segregation}-free alloy. This one was of not high hardness and easy to machine. In contrast its oxidation at 1200°C was very fast and almost linear, leading to particularly high final mass gain. In contrast no scale spallation occurred during cooling. Since the high refractoriness, the easy machinability and the absence of scale spallation at cooling are the sole qualities of this alloy, this one must be improved inn terms of high temperature mechanical and chemical properties. Carbides or intermetallic precipitates in bulk and deposition of another alloy on surface may be solutions to succeed in taking benefits of the previous qualities of such alloy. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Chromium;
Vanadium;
High temperature oxidation;
Metallographic characterization.

INTRODUCTION

Many applications need materials able to be used at extremely high temperature. For less than 1200°C as service temperature nickel-based, iron & nickel-based and cobalt-based superalloys^[1-4] are the most common metallic materials which are considered when special requirements concerning low and high temperature toughness must be respected (i.e. ce-

ramic materials excluded). In addition to their high mechanical strength at high temperature these alloys, unfortunately not chemically inert in hot environments, are efficiently protected from oxidation and corrosion by the development of continuous external scales of alumina or chromia oxides^[5, 6]. Contrarily to aluminium (melting point of about 660°C), chromium is a very refractory element ($T_m = 1890^\circ\text{C}$ ^[7]), which possibly allows uses at very high

temperatures if not alloyed with too many other elements. Automatically able to develop an external chromia scale without any limitation it may resist against both hot oxidation and corrosion. However, its crystallographic structure at all temperatures (and notably at high temperature) is Body Centred Cubic (BCC), a not compact network which does not favour high mechanical properties. It is thus necessary to alloy it with at least one other element to promote structural strengthening. In the other hand it can be also possible to decrease a little the density (Cr: $7.1 \text{ g/cm}^{3[7]}$) to decrease too centrifugal stresses in the high speed rotating aeronautical pieces (e.g. mobile blades) or industrial tools (e.g. spinners). Vanadium is a possible alloying element for chromium, with its high melting point temperature only a little under the chromium's one ($1735^\circ\text{C}^{[7]}$), its identical crystalline network (BCC too, which notably allows a total miscibility in one another without formation of possible brittle intermetallic phases), a slightly smaller atomic size (V and Cr are neighbours in the same line of the Mendeleiev's table) and a lower atomic mass (leading to a lower density for solid vanadium at room temperature: $5.96 \text{ g/cm}^{3[7]}$). A disadvantage of vanadium is its rather bad behaviour in hot oxidation^[5,6].

The purpose of this work is to try elaborating by foundry a chromium-vanadium alloy, to specify its as-cast microstructure and its room temperature hardness in this state, and to characterize its behaviour in oxidation at high temperature.

EXPERIMENTAL

A single alloy, a Cr(bal.)-10V (in weight percents), as is to say not too rich in V to favour a good oxidation behaviour, was prepared from pure elements (Cr and V, mainly Alfa Aesar, purity > 99.9wt.%). The Cr and V parts were melted together in a CELES high frequency induction furnace under inert atmosphere (600 mbars Ar) in a water-cooled copper crucible protected from the laboratory air by a silica tube. The alloys were maintained in the liquid state during five minutes after melting to ensure complete chemical homogenization before solidification and solid state cooling. This procedure

was applied a second time (re-melting) to ensure total chemical homogenization since both elements are very refractory. The obtained ingots were then cut.

A part was analysed by Differential Thermal Analysis (DTA) by a double thermal cycle: heating up to 1000°C at $+20\text{K/min}$, heating up to 1490°C at $+5\text{K/min}$, cooling at -5K/min down to 1000°C , reheating up to 1490°C at $+5\text{K/min}$, cooling at -5K/min down to 1000°C , and cooling down to room temperature at -20K/min .

Another part was embedded in a cold resin mixture (resin CY230 and hardener HY256). They were ground with SiC papers from 240-grit up to 1200-grit. After ultrasonic cleaning and water-washing final polishing with $1\mu\text{m}$ hard particles on textile disk was performed until mirror-like state. The metallurgical state and chemical composition of the obtained sample was controlled using a Scanning Electron Microscope JEOL JSM-6010AL (SEM) in Back scattered Electrons Composition mode (BEC) and with the Energy Dispersion Spectrometry (EDS) device equipping the SEM, mainly under an acceleration voltage of 20kV. X-ray maps were also acquired to characterize the chemical homogeneity of the as-cast alloy (possible segregations occurred at solidification). Additionally, X-Ray Diffraction analyses were carried out on the as-cast alloy with a Philips X'Pert Pro diffractometer (used wave length: $1.5406 \text{ Angstr\AA} \text{ms}$, $\text{Cu } k_\alpha$). The hardness was specified by five Vickers indentations under a 30kg-load using a Testwell Wolpert machine, followed by the calculation of an average value and a standard deviation one.

A sample, globally parallelepiped, was cut with approximate dimensions $4 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$, and ground with 1200-grit SiC-paper on its six main faces. Edges and corners were smoothed using the same papers. Placed in a thermo-balance (SETARAM TG-92) under a flow of dry synthetic air ($80\% \text{N}_2$ - $20\% \text{O}_2$), hung to a microbalance, its underwent a heating at $+20\text{K min}^{-1}$ up to 1200°C , an isothermal dwell during 50 hours at this same temperature, a cooling at -5K min^{-1} .

The oxidized surface was characterized by X-Ray Diffraction, surface SEM/SE (Secondary Elec-

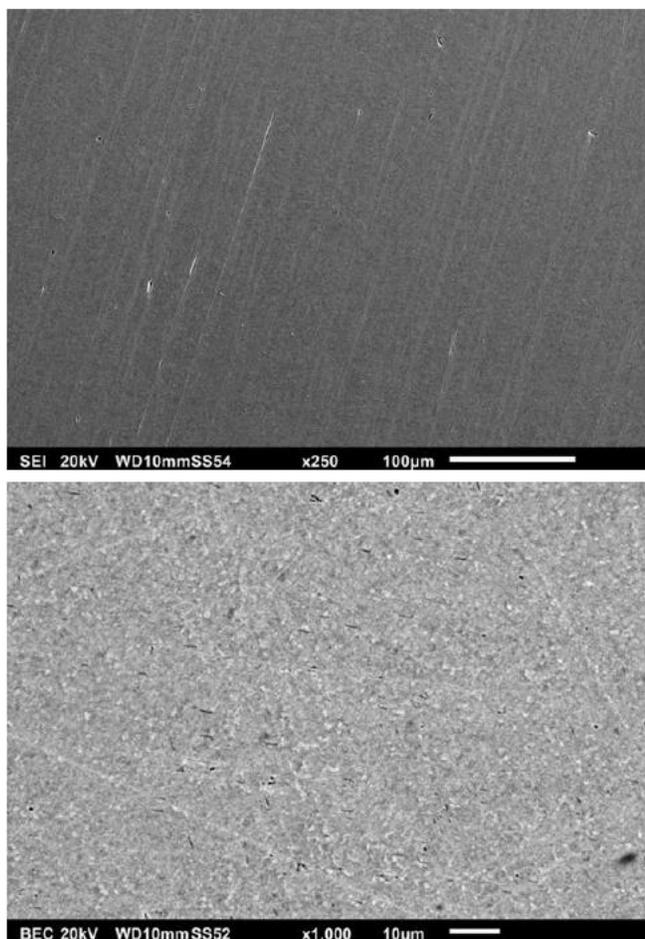


Figure 1 : SEM/BEC micrographs illustrating the as-cast microstructure of the alloy

trons mode) examinations and EDS spot and X-maps, with the same diffractometer and microscope as above.

RESULTS AND DISCUSSION

As-cast metallurgical state and room temperature hardness

As illustrated in Figure 1 the alloy seems being single-phased in its as-cast state. The chromium and vanadium repartitions in the structure are shown in Figure 2 by X-ray maps. The chemical composition seems perfectly homogeneous. No chemical segregation obviously occurred during solidification. The X-ray diffractogram presented in Figure 3 confirms that the alloy is single-phased, on the BCC structure. The five indentations led to rather low hardness: $198 \pm 5 \text{ Hv}_{30\text{kg}}$.

Thermal behaviour at high temperature: refractoriness and oxidation kinetic

The DTA experiments carried out showed that the obtained alloy was really very refractory. The two successive heatings up to 1490°C did not induce any thermal exchange between the sample and the apparatus, demonstrating an exceptional refractoriness of the alloy, observation consistent with the

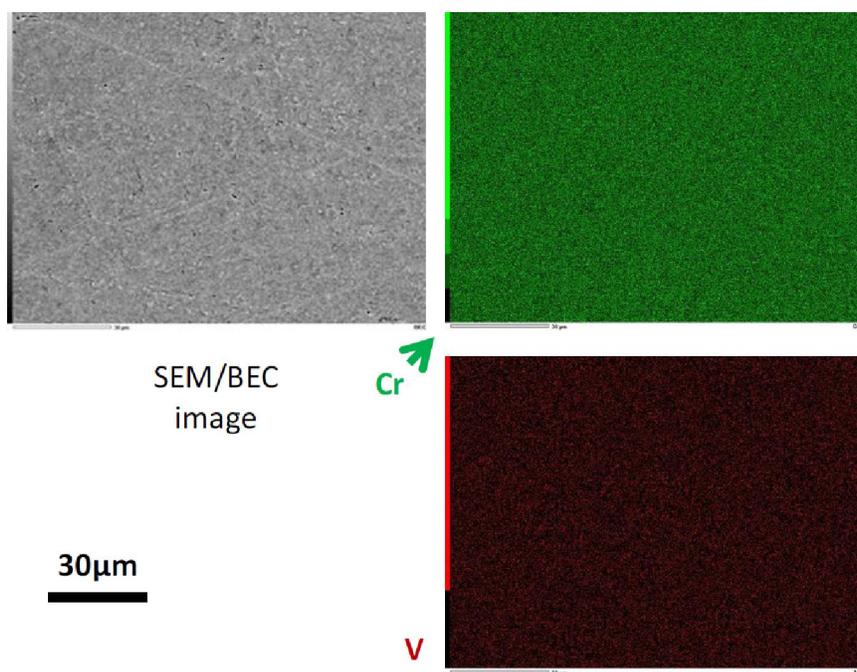


Figure 2 : X-Ray map showing the chemical homogeneity of the obtained alloy in its as-cast state

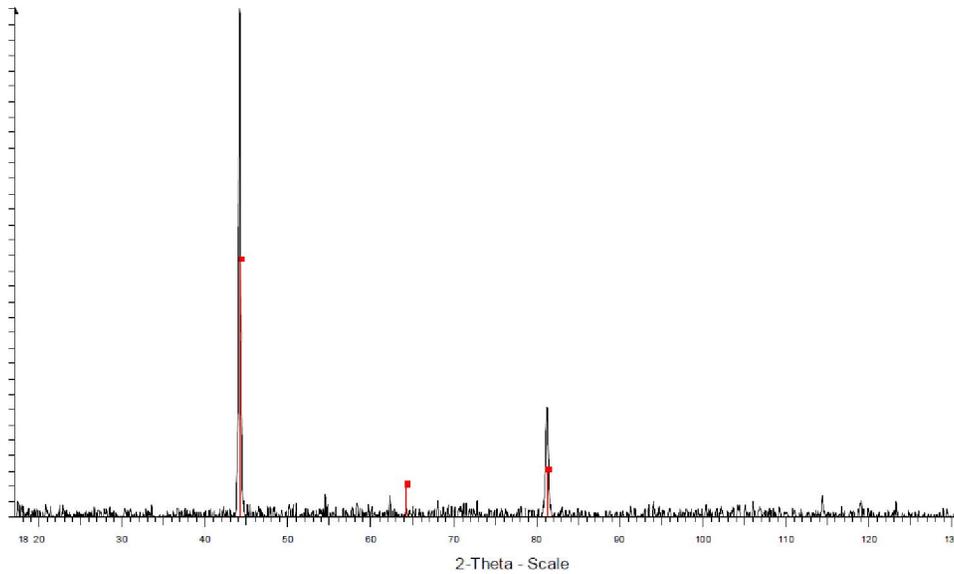


Figure 3 : X-Ray diffractogram showing that only the BCC structure of chromium is present (α phase, BCC, $\text{Im}\bar{3}m$, $a = b = c = 2.89818$ Angströms, $\alpha = \beta = \gamma = 90^\circ$)

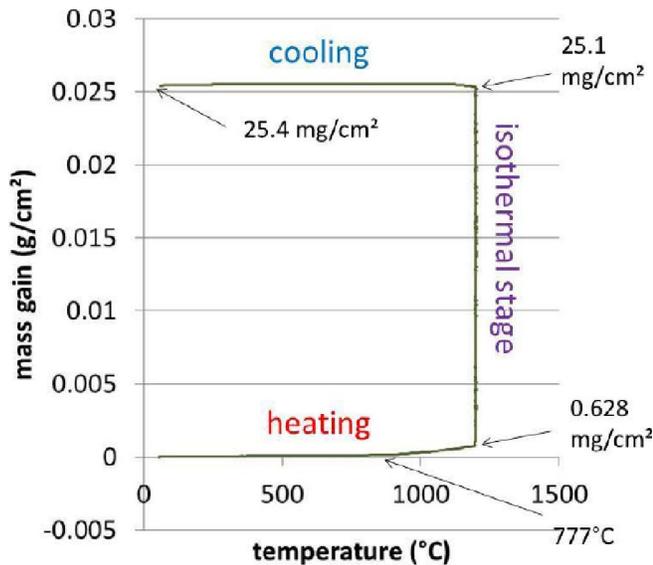


Figure 4 : Evolution of the measured Vickers micro-hardness (top) and of the measured Vickers macro-hardness (bottom) with the increase in chromium content in the case of the cobalt-base binary alloys

binary Cr-V diagram in which all solidus temperatures are above the one of the less refractory element, i.e. vanadium ($T_{\text{mp}} = 1735^\circ\text{C}$).

Since the obtained alloy does not risk any fusion start, high temperature oxidation tests were envisaged. Oxidation at 1200°C in synthetic air was thus performed with thermogravimetry measurement, on fifty hours. The overall thermogravimetric oxidation behaviour of the alloy is presented in Figure 4 with a {mass gain versus temperature}-graph. A correc-

tion from the air buoyancy variation was applied to the obtained mass gain files. One can see that the mass gain became to be detectable by the used thermo-balance when temperature reached about 800°C . The total mass gain achieved during the whole heating is of about 0.63 mg/cm^2 . At the end of the isothermal analysis the total mass gain was about 25 mg/cm^2 . All the mass of oxides formed was kept on the sample until return to room temperature showing that no perceptible scale spallation occurred during cooling.

The mass gain values are more conventionally plotted (versus time) in Figure 5 (top). The obtained curve seems being more linear than parabolic, this explaining the rather high final mass gain (25 mg/cm^2) achieved at the end of the isothermal dwell. Data were also plotted according to the $\{m \times dm/dt = K_p - K_v \times m\}$ -method^[8]. This type of representation confirms that the oxidation kinetic is essentially linear since, except a value of chromia volatilization constant (mass loss), the slope indicates a linear constant (mass gain) equal to almost $10^{-7} \text{ g/cm}^2/\text{s}$ ($9.62 \times 10^{-8} \text{ g/cm}^2/\text{s}$) and a parabolic constant of about $400 \times 10^{-12} \text{ g}^2.\text{cm}^{-4}.\text{s}^{-1}$.

Thermal behaviour at high temperature: surface state after oxidation

The oxidized sample was subjected to X-Ray Diffraction (Figure 6) and SEM examination (Fig-

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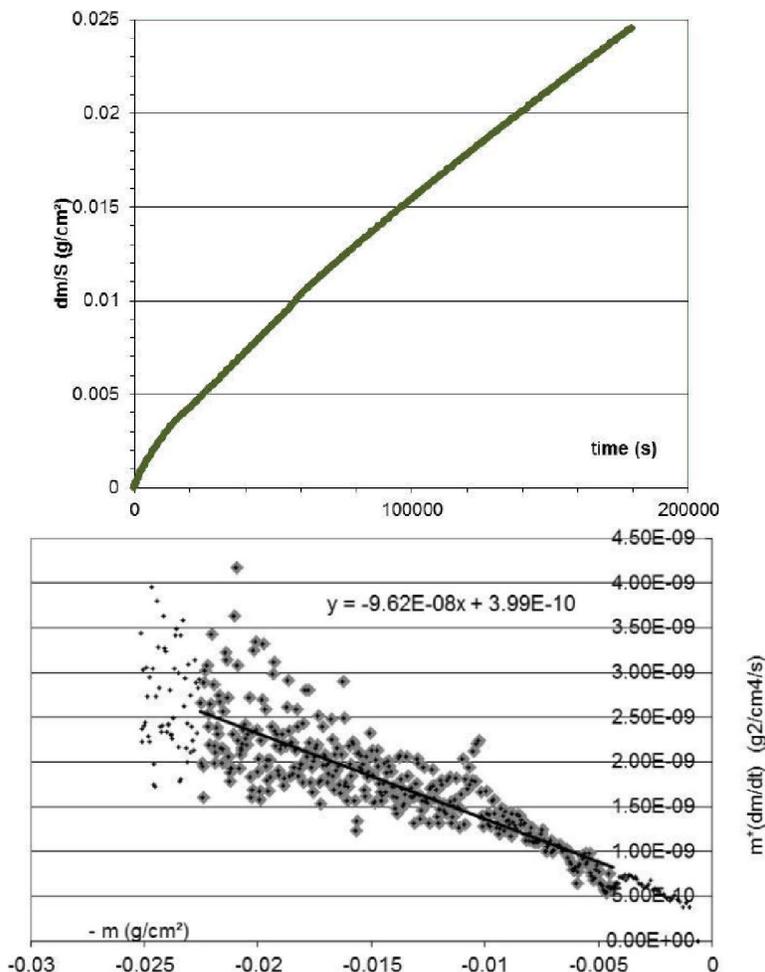


Figure 5 : Isothermal mass gain versus time (top) and $\{m \times dm/dt = K_p - K_v \times m\}$ plot to analyse data by taking chromia volatilization into account (bottom)

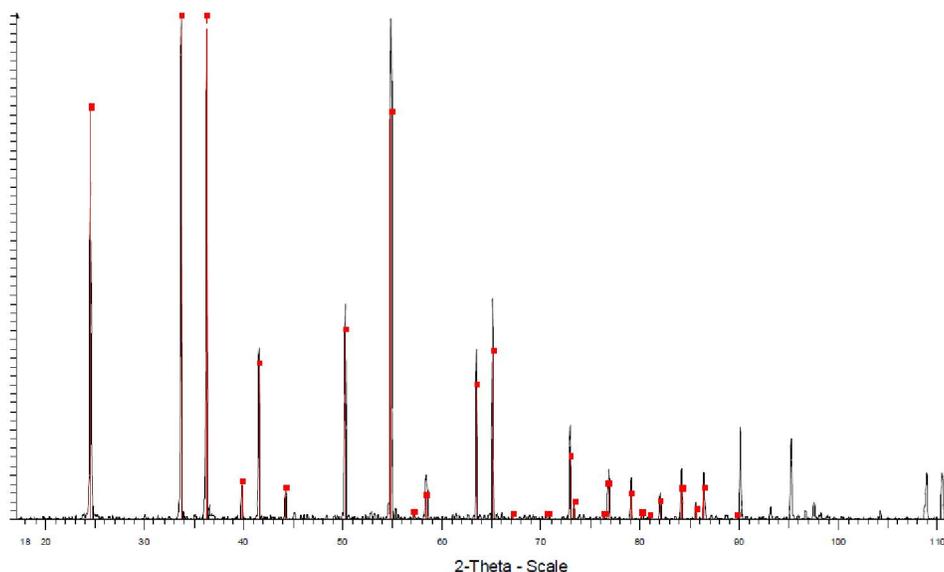


Figure 6 : XRD diffractogram of the oxidized surface: scale principally constituted of chromia

ure 7). The scales are of pure chromia, but rather rough.

General commentaries

It was thus possible to elaborate such a refrac-

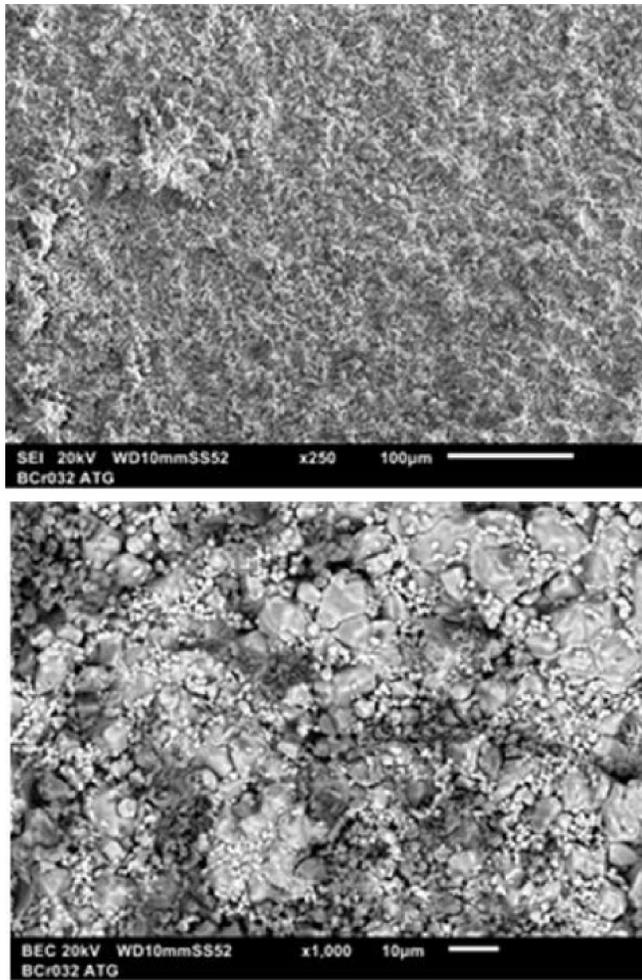


Figure 7 : SEM micrographs of the surface state of the oxidized alloy (50h 1200°C in air), topographically with the Secondary Electrons Imaging mode (SEI, left) and chemically with the BSE mode (right)

tory alloy by foundry, seemingly without not melted parts, thanks to the double-step fusion and the rather long liquid state dwells, despite that the Cr-V system does not present any eutectic reaction.

Cutting, which was rather easy and break-less, allowed to obtain the desired samples. The alloy, in its as-cast state at least, is rather soft, with a hardness of 200 Vickers points only, which was consistent with the good behaviour during cutting. Machining of this alloy and probably of other alloys based on it and reinforced by additional particles should be easy to do. In contrast, such low hardness at room temperature let think that the mechanical properties at high temperature may be not high. In addition, despite the very high chromium content in the alloy, the base of which is this element, the oxidation rate

at high temperature is very high. The parilinear – almost simply linear - character of the mass gain kinetic suggests that the oxidation resistance is very low too. This can be due to the presence of vanadium, an element known to quickly oxidize, but also to the fact that chromium is maybe too present. Indeed the oxidation behaviour of pure chromium is itself known to be bad, and the studied alloy has a composition not far from pure Cr.

No vanadium oxide was found but this can be explained by the gaseous state of vanadium oxide at this temperature. The very irregular state of the chromia scale covering the oxidized sample suggests that gaseous species leaved the alloy and did not allow obtaining and maintaining a protective scale. Despite the exceptionally high Cr content of the alloy, the oxidation behaviour of the studied alloy is catastrophic. Its single advantage is thus its refractoriness.

CONCLUSIONS

By looking to the properties specified in this work, the Cr-10V alloy is not interesting in its present form. Refractoriness and machinability are elevated and good respectively, but the creep resistance (suspected) and oxidation resistance (seen) appear to be not sufficient to envisage a use at high temperature. These two points must be significantly improved. Adding supplementary elements to the global composition needs to be tested, hoping obtaining strengthening particles precipitated during solidification (for example carbides) or by applying specific heat treatment (secondary carbides or intermetallic particles), for example. For the second point, to keep vanadium in the chemical composition, applying an external layer containing chromium too but with a lower activity, ought to obtain more efficient protective chromia scale and to isolate vanadium from the external atmosphere.

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