Hardness of iron (and/or) nickel-based alloys strengthened by varying fractions of chromium and tantalum carbides

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ABSTRACT

Easiness of machining is of great importance, especially for cast superalloys for which strength at high temperature is sometimes obtained by carbides which may induce an increase in hardness. Knowing how hardness varies versus microstructure is then interesting to predict machinability. Micro- and macro-Vickers indentation was performed on nine {30 wt.%Cr}-containing alloys, based on Fe, both Fe and Ni, or Ni, and containing various fractions of chromium carbides and tantalum carbides. For similar carbon and tantalum contents, the natures and volume fractions of carbides vary with the nature of the base element. The hardness is a function of both the matrix nature and the carbide volume fraction. Hardness increases when the base element is changed from {Fe=Ni} to Fe, then from Fe to Ni. It also increases when the volume fraction of carbides increases, e.g. when the carbon content is higher (0.4 wt.% instead 0.2), or if tantalum is also present in the alloy (between 2.5 and 6 wt.%). The hardness can be lowered after an exposure of 50 hours at high temperature.   © 2008 Trade Science Inc. - INDIA

INTRODUCTION

The hardness of carbon-containing Fe-based alloys is generally of a great interest. For the most important of them, there are steel and cast iron, the hardness of which is governed by the carbon content (among other important parameters), since it can considerably vary with the quantity of carbides (cementite Fe_3C in most cases) present in pearlite or ledeburite for example. In this way hardness measurements allow controlling or characterizing the microstructure of conventionally cast pieces[1], rapidly solidified alloys[2] or even quenched alloys[3]. When chromium is additionally present in Fe-based structural alloys[4] or in hardfacing coatings Fe-based alloys[5], high values of hardness can be obtained, because of the existence of interdendritic chromium carbides in high quantities, for example. The hardness of nickel-containing Fe-based alloys (e.g. austenitic steels) and of Ni-based alloys (e.g. superalloys for service at high temperature), is also often to be taken in consideration, notably to predict their easiness of machining. However, it seems that there are not numerous works concerning the hardness of these types of alloy when used as structural materials. Such studies are predominantly focused on coatings, as Ni-WC or Ni-Cr_3C_2 deposited by different techniques, with a special atten-

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tion to wear resistance[6–9].

In addition to iron, chromium or tungsten, other elements can act as carbide-formers, with significant consequences on the hardness of the concerned alloys. Among them there is tantalum, which is often used in refractory metallic alloys designed for uses at high temperatures (1,000°C and more). It allows improving their mechanical resistance, notably against creep deformation[10]. Indeed it acts as strengthener element both by hardening matrix in solid solution and by forming primary and secondary TaC carbides which are highly stable up to very high temperatures[11]. Since tantalum is a strong carbide-former element, it tends to favor high carbides fractions in most cases, which can cause a high level of hardness. This can be useful for resistance against abrasion and wear, while, on the contrary, this can also cause some difficulties for machining.

Tantalum is principally met in cobalt-base alloys or superalloys[12,13], but one can also find it in iron-based, iron and nickel-based and nickel-based alloys and superalloys. In that ones, it can induce, during solidification, the development of an interdendritic network of TaC carbides which can bring them good mechanical properties at high temperature, in addition to a high level of refractoriness which is moreover higher for the Fe-based alloys[14] than for alloys based on both Fe and Ni[15]. In Ni-based alloys, tantalum tends to be shared between carbides and matrix[16], the latter being hardened by this heavy element present in solid solution. Since the presence of tantalum in alloys may modify the hardness of alloys based on iron, on nickel, or on these two elements together, the indentation-behavior of carbides-strengthened chromium-containing {iron and/or nickel}-based cast alloys, is studied here for two levels of both carbon content and tantalum content.

EXPERIMENTAL

Three {Fe-30wt.%Cr}-based alloys called Fe[1] (low carbon, low tantalum), Fe[2] (high carbon, low tantalum) and Fe[3] (high carbon, high tantalum), three {Fe≅Ni, 30 wt.%Cr}-based alloys (analogously called FeNi1, FeNi2 and FeNi3), and three {Ni, 30 wt.%Cr}-based alloys (Ni1, Ni2 and Ni3) were induction melted and cast under 0.3 bar of argon, from pure elements (Fe, Ni, Cr, Ta: Alfa Aesar, purity >99.9 wt.% and C:

graphite). Three (10mm×10mm×3mm) samples were cut from the obtained 100g-ingots, polished up to 1,200 grit paper, and then exposed to 1,000°C, 1,100°C and 1,200°C during 50 hours in air, before cooling down to room temperature at about 10 K min⁻¹. After cutting, embedding and polishing (up to a mirror-like surface state), mounted samples were available for metallographic examination. They were directly characterized by electronic instruments, since two types of carbides were expected:

Scanning electron microscope (SEM) in back scattering electrons (BSE) mode for the general examination of microstructure, global chemical analysis by using its energy dispersion spectrometry (EDS) device, and micrographs for image analysis; SEM apparatus type: Philips XL30;

Electron probe micro-analysis (EPMA) in wavelength dispersion spectrometry (WDS) for carbide identification; microprobe type: Cameca SX100.

Before hardness measurements, these samples were etched during 1 minute with a Groesbeck solution (4g $KMnO_4$ and 4g NaOH in 100mL of distilled water) in order to reveal the interdendritic carbides. Vickers micro-indentation was performed in matrix with a load of 8 g (five measurements with calculation of the average value and the standard deviation) while Vickers macro-indentation was realized, with a load of 30 kg, in three locations in the middle of the bulk (also followed by calculation of the average value and the standard deviation).

In order to better know the microstructure changes during cooling and then the phases present at room temperature, thermodynamic calculations were run with the N-version of the Thermo-Calc software and the SSOL database completed with the descriptions of systems involving Ta[17].

RESULTS AND DISCUSSION

Obtained chemical compositions and microstructures of the alloys

The chemical compositions of the obtained alloys are listed in TABLE 1. They are the average values of EDS measurements performed with the SEM on three locations randomly chosen in the middle of the samples'

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Fe3   FeNi3   Ni3

Fe2   FeNi2   Ni2

Fe1   FeNi1   Ni1

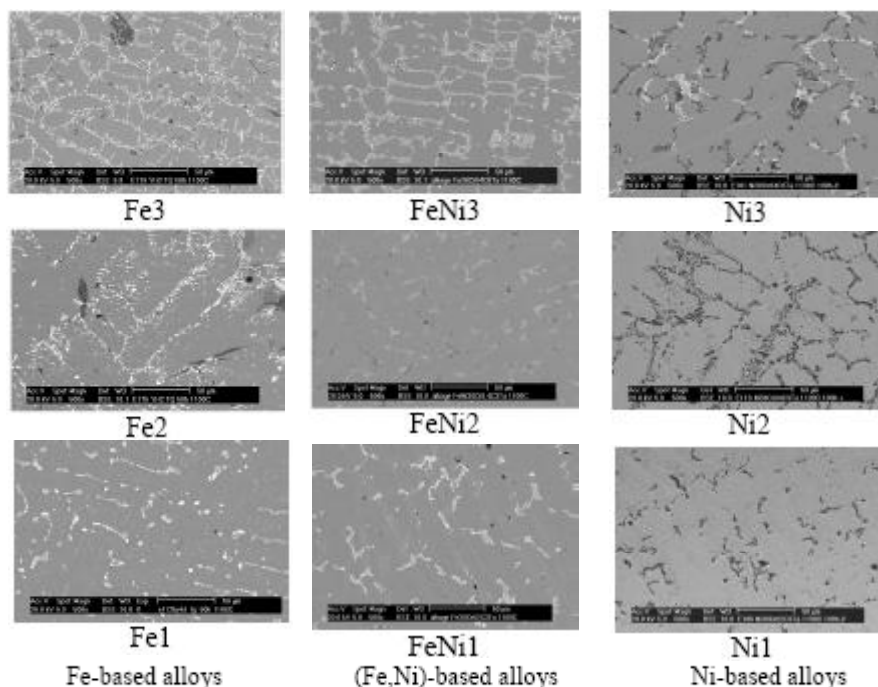Fe-based alloys   (Fe,Ni)-based alloys   Ni-based alloys

Figure 1: Microstructures, after aging at 1,100°C for 50 hours, of all the (Ta,Cr)-containing Fe, (Fe,Ni) and Ni-based alloys (SEM micrographs taken in BSE mode)

bulk. The standard deviation is of the same level as the precision of the EDS analysis, i.e. ±1wt.% for Ni, Cr and Ta. The carbon contents were not measured because of the too small atomic weight of this element and its too low targeted content. But since it was previously verified that this type of elaboration of carbon-containing similar alloys (with these levels of C content) usually led to carbon contents equal to the targeted values (determination done by spark spectrometry analysis), it was supposed here that it is also the case for the present alloys. This is qualitatively confirmed by the carbide fractions which were obtained here. Thus, all chromium contents are close to 30 wt.%Cr, and the "low" tantalum contents are close to 2.5 wt.% while the "high" tantalum contents are close to 6 wt.%Ta.

The microstructures (figure 1) are all composed of matrix, of the BCC type for the Fe-based alloys and of the FCC type for the {Fe,Ni}-based and Ni-based alloys, which contains more or less great parts of Cr and of Ta in solid solution. The samples also contain carbides, interdendritic primary ones, and sometimes (mostly after aging at 1,000°C) also fine secondary carbides dispersed mainly along the interdendritic spaces. Carbides are tantalum carbides and chromium carbides. The first ones are more present in the Fe-based and

TABLE 1: Chemical composition of the alloys analyzed by electron dispersion spectrometry (in wt.%)

Alloys	Fe	Ni	Cr	Ta	C
Fe3	Bal.	-	29.2	6.2	$\cong 0.4$
Fe2	Bal.	-	29.7	2.4	$\cong 0.4$
Fe1	Bal.	-	29.8	2.1	$\cong 0.2$
FeNi3	Bal. (31.2)	32.5	29.5	6.4	$\cong 0.4$
FeNi2	Bal. (32.8)	34.0	30.0	2.8	$\cong 0.4$
FeNi1	Bal. (33.1)	34.2	29.6	2.9	$\cong 0.2$
Ni3	-	Bal.	30.6	5.4	$\cong 0.4$
Ni2	-	Bal.	31.9	2.7	$\cong 0.4$
Ni1	-	Bal.	30.9	2.0	$\cong 0.2$

(Fe,Ni)-based alloys, especially for the highest values of the {wt.%Ta/wt.%C} ratio (i.e. Fe1, Fe3, FeNi1 and FeNi3), and sometimes the sole type of carbide present. In compensation, the chromium carbides are predominantly present in the Ni-based alloys, and the sole carbides present in some cases. When it was possible to perform EPMA on carbides (when these ones had a sufficient size), EPMA measurements confirmed that tantalum carbides are TaC, while chromium carbides are essentially $M_{23}C_6$ in the Fe-based and {Fe, Ni}-based alloys. In the Ni-based alloys chromium carbides are M_7C_3 for 1,200°C (i.e. after cooling from 1,200°C), $M_{23}C_6$ for 1,000°C and a mix of the two types for 1,100°C.

Following the temperature of the aging treatment,
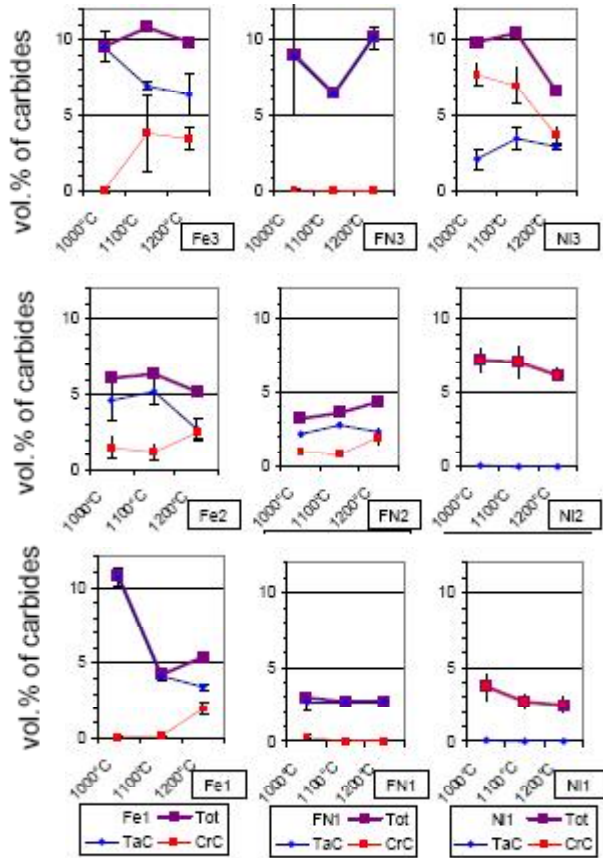
Figure 2: Surface fractions of tantalum carbides ("TaC"), of chromium carbides ("CrC") and sum of the two ("Tot") (image analysis, average of 3 values ± standard deviation)
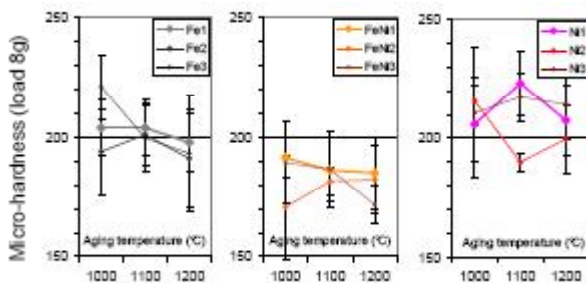
Figure 3: Micro-hardness (load 8 g) of the nine alloys for the three aging temperatures (average value and standard deviation from 5 measurements)

the morphologies of carbides can be different. Indeed, already at 1,100⁰C, but particularly at 1,200⁰C, chromium carbides obviously became coarser or blockier, while tantalum carbides became fractioned. The acicular or elongated shape of primary carbides is then more or less lost while secondary carbides have disappeared, for these temperatures.

Determination of the carbide fractions in the alloys
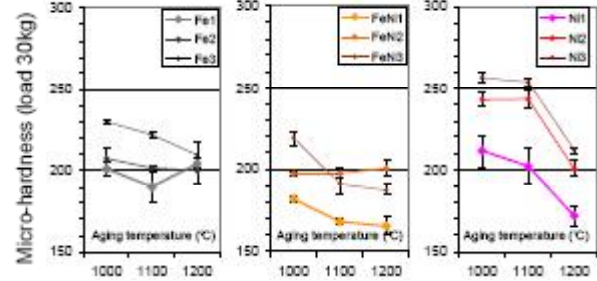
Figure 4 : Macro-hardness (load 30kg) of the nine alloys for the three aging temperatures (average value and standard deviation from 3 measurements)

Generally several types of carbides are present in the studied samples, and etching leads, for the different carbides, to colored results which are not different enough to allow good conditions for quantification by image analysis. Then, it was preferred to analyze SEM micrographs taken in BSE mode, since they led to sufficiently good differences of gray level between tantalum carbides (white), chromium carbides (dark) and matrix (gray but clearer than chromium carbides). The results are graphically presented in figure 2 for the nine alloys and the three aging temperatures, for chromium carbides, tantalum carbides and for the two carbides together.

The fractions of TaC and of chromium carbides are not the same after aging at two different temperatures, and generally the total carbide fraction, which will be later on consideration for the analyze of the hardness results, tends to decrease when the aging temperature increases. The carbide fractions are logically the highest for the highest carbon contents, and they also tend to slightly increase when the tantalum content becomes higher. For similar C and Ta contents, the total carbide fractions are higher for the Fe-based alloys (in which they are mainly TaC) and for the Ni-based alloys (which mainly contain Cr-carbides), than for the {Fe,Ni}-based alloys (mainly TaC).

Hardness measurements

Micro-indentation with a load of 8 g was first performed in the matrixes of all samples (five measures per sample). The results, graphically presented in figure 3, show a significant general dependence of the average hardness on the type of matrix. More precisely, the hardness of the austenitic {Fe, Ni} matrix is obviously lower

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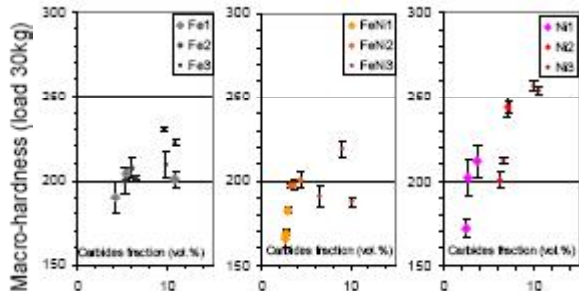
Figure 5: Macro-hardness (load 30kg) of the nine alloys versus the volume fraction of carbides (average value and standard deviation from 3 measurements)

than the hardness of the ferritic Fe matrix, and also than the one of the austenitic Ni matrix, while the Ni matrix is slightly harder than the Fe one. However, a great dispersion of the results obtained in the same sample exists, as shown by the ranges of uncertainty. It is the reason why no relationship between matrix chemical composition and micro-hardness was studied.

Fortunately the results of Vickers macro-indentation with a load of 30 kg were not so dispersed (figure 4) and they showed more clearly the role of the microstructure of the whole alloy (this microstructure resulting from both its global chemical composition and the temperature at which it was aged). The same hierarchy as seen above for the micro-hardness values obviously exists too for macro-hardness. Indeed, the {Fe, Ni}-based alloys are less hard than the Fe-based ones, while the highest hardness values are generally reached with the Ni-based alloys (especially for alloys with 0.4 wt.%C). It can be better seen that an increase in carbon content and also in tantalum enhances the hardness of the alloy while, on the contrary, an increase in temperature of the aging treatment induces a softening, especially for 1,200⁰C.

General commentaries

Depending on the base element (which imposes the crystallographic nature of matrix), the carbon and tantalum contents (which act on both the nature and the density of carbides) and the temperature of the aging treatment (which influences mainly the morphologies of carbides), the Vickers macro-hardness can vary over a range of almost one hundred hardness points. The hardness of the Fe-based alloys are all higher than the one of a binary Fe-30 wt.%Cr alloy elaborated by the same

way (about 175 Hv_{30kg}), while the ones of the Ni-based alloys are all higher than the hardness of a binary Ni-30 wt.%Cr alloy (about 120 Hv_{30kg}). Then, with their high Vickers hardness values, which belong to the[1,330; 1,650] range[18], the presence of carbides is responsible of the increased hardness of these alloys.

In other studies it was found that ternary {Fe-30 wt.%Cr}-based alloys display, after a 50h-exposure to 1,000⁰C, 1,100⁰C and 1,200⁰C, average values comprised between 155 and 180 Hv_{30kg} for 0.2 wt.%, and between 190 and 205 Hv_{30kg} for 0.4 wt.%. Then, the hardness of, on the one hand the Fe1 alloy (200 to 204 Hv_{30kg}) and of the other hand Fe³ (210 to 230 Hv_{30kg}), are increased by the presence of TaC carbides instead $Cr_{23}C_6$, although the two carbides display almost the same Vickers hardness. This is due to the volume fractions of carbides that are significantly higher in the Fe¹ and Fe³ alloys:

- From about 11 vol.% for 1,000⁰C down to 3 vol.% for 1,200⁰C in Fe1, against almost 0 vol.% in a Fe-30Cr-0.2C alloy,
- Between about 9 and 11 vol.% in the Fe³ alloy, against 3-5 vol.% in a Fe-30Cr-0.4C alloy.
- In the same way ternary {Ni-30 wt.%Cr}-based alloys display, after a 50h-exposure to 1,000⁰C, 1,100⁰C and 1,200⁰C, an average hardness belonging to the [150; 200 Hv_{30kg}] range for 0.2wt.%, and to [180; 225 Hv_{30kg}] for 0.4wt.%. The hardness of, on the one hand Ni1 alloy (170 to 210 Hv_{30kg}), and of the other hand Ni3 (210 to 260 Hv_{30kg}), are higher than for the ternary alloys with the same carbon contents. Here too this is due to the volume fractions of carbides that are significantly higher in the Ni1 and Ni3 alloys: - between 2.5 and 3.8 vol.% in the Ni1 alloy, against almost 1-2 vol.% for a Ni-30Cr-0.2C alloy,
- Between about 6.5 and 10 vol.% in the Ni3 alloy, against 3-6 vol.% for a Ni-30Cr-0.4C alloy.

The hardness of all the alloys of the present study is plotted versus the total carbide fraction in figure 5, for the three aging temperatures together.

The points corresponding to the highest hardness for each alloy, which often correspond to an aging done at 1,000°C only, can be considered as varying linearly with the volume carbide fraction (more for the Fe-based and the Ni-based alloys than for the {Fe,Ni}-based alloys). The slopes of these straight lines, i.e. the rates

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of increase in hardness versus the carbide fraction, are about 6 Hv_{30kg} vol.%$^{-1}$ for the Fe-based and {Fe,Ni}-based alloys, and maybe a little higher for the Ni-based alloys: 6.7 Hv_{30kg} vol.%$^{-1}$. Almost all the other spots, which correspond to the aging at the two highest temperatures, are under these straight lines; this reveals the softening effect of the coarsening and fragmentation phenomena. These ones probably act by a decrease in the degree of continuity of the interdendritic carbides, then a reduction of the resistance of these carbides against stresses due to indentation (then a matrix more exposed to these solicitations).

CONCLUSIONS

The presence of carbides in cast alloys and super-alloys allow them to resist mechanical stresses at high temperature and it also induces an increase in their hardness at room temperature, which can complicate their machining. Even for iron, iron-nickel and nickel alloys, which are less hard than cobalt-based alloys for example[19], carbides can lead to hardness which can approach 250 Hv_{30kg}. Fortunately, these ones can loose several tens of Vickers units by applying a sufficiently long treatment at a temperature high enough.

In addition, to predict the average level of hardness, it is more the obtained volume fraction of carbides than the carbon content that must be taken in consideration, because of the difference of carbide-forming power of elements, here Cr and Ta, and the ability of a matrix to favor or not high fractions of carbides, notably during solidification.

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