

Refractory Hard Alloys Elaborated by Casting of Ternary (Co, Ni Fe)-30Cr-2.5 to 5 wt% C Compositions

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Abstract

Three series of ternary alloys of the {M-30Cr-xC}-type with M = Co, Ni or Fe and x ranging from 2.5 to 5 wt% were elaborated by casting. Their microstructure characterizations by XRD and SEM show that very high volume fractions in chromium carbides (even more than 50%) may be obtained in a metallic matrix by this way. However graphite may also appear in very low quantities in the carbon-richest alloys. The hardness increases with the carbon content (up to 1000 Hv_{30kg}) but it may be a little lowered when graphite is also present. The results show that very hard alloys may be simply obtained by casting of rather cheap elements.

Keywords

Cast Co-Based Alloy, Cast Ni-Based Alloy, Cast Fe-Based Alloy, Chromium Carbides, High Hardness, Graphite

1. Introduction

Many industrial applications require very hard materials keeping however a minimal fracture toughness, to efficiently resisting wear. As temperature may increase in service because intense friction on long time, good refractoriness is additionally demanded as well as good resistance to hot corrosion. With their high melting points and their rather low cost, cobalt ($T_f = 1490^\circ\text{C}$, [1]), nickel ($T_f = 1455^\circ\text{C}$, [1]) and iron ($T_f = 1535^\circ\text{C}$, [1]) may be considered for such use since it is possible to efficiently harden them by carbides (high hardness [2]) in low amounts as for carbides-strengthened superalloys [3]-[5] or in much higher quantities as for some cutting tools and hard-facing coatings [6]-[8]. It is additionally possible to bring such alloys high resistance against hot corrosion by addition of chromium [9] [10].

Chromium is beneficial for both chemical resistance (chromia-forming behavior) and mechanical resistance (strong carbide-former element) at low temperature as well as high temperature. Thus simple alloys containing amounts in Cr and in C high enough to combat simultaneously corrosion and wear, already used as coatings, may be also interesting as structural materials, with the same properties, since they may be elaborated and

shaped simply by foundry.

To explore the microstructures which may be obtained by this way (nature, shape and volume fractions of carbides, continuity of the metallic matrix) as well as the achievable levels of hardness three series of ternary alloys, of the {M-30wt% Cr-2.5 to 5wt% C}-type were elaborated and characterized.

2. Experimental

2.1. Elaboration of the Alloys

Six cobalt-based alloys Co(bal.)-30Cr-xC ($x = 2.5, 3, 3.5, 4, 4.5$ and 5 , all contents in wt%), six nickel-based alloys Ni(bal.)-30Cr-xC ($x = 2.5, 3, 3.5, 4, 4.5$ and 5 , wt%) and three iron-based alloys Fe(bal.)-30Cr-xC ($x = 2.5, 3.5$ and 4.5 , wt%) were obtained by melting pure elements (Alfa Aesar, >99.9 wt%) together in order to obtain one ingot per alloy, each weighing about 40 g.

The used furnace was a High Frequency Induction one (CELES). The operating parameters and thermal cycles were:

- inert atmosphere of 300 mbars (pure Argon), voltage up to 4 kV and frequency of about 110 kHz.
- heating up to about 1600°C, dwell during three minutes in the liquid state, cooling of about 15 minutes down to room temperature.

2.2. Metallographic and Hardness Characterization

The ingots were cut for preparing samples to be embedded in resin and polished, and to be subjected to indentation tests. Ingots' were sawed using a Delta Abrasimet Cutter (Buehler). The obtained parts were embedded in a cold resin mixture (resin CY230 + hardener HY956, ESCIL). Grinding was performed using successive SiC papers (from 120-grit up to 1200-grit). After intermediate cleaning by ultrasounds under water the samples were polished with textile disk enriched with 1µm hard particles until a mirror-like surface state.

The microstructure observations were realized using a Field Electron Gun-Scanning Electron Microscope (FEG-SEM, Hitachi S4800) under an acceleration voltage of 15 kV, essentially in the Back Scattered Electrons (BSE) mode. The control of the chemical compositions was achieved with the Energy Dispersion Spectrometry (EDS) apparatus equipping the SEM. The SEM/BSE micrographs were subjected to image analysis using Photoshop CS software (Adobe) to measure the surface fractions of the carbides and of any other possible phase.

X-ray Diffraction runs (XRD) were performed using a X'Pert Pro diffractometer (Cu alpha, 1.5406 Angströms) to identify the present phases.

Differential Thermal Analysis (DTA) was performed on all alloys to specify their temperature melting range, and especially their fusion start temperatures.

Vickers indentations were carried out on all the alloys using a Testwell Wolpert machine under a load of 30 kg. Five values per alloy led to an average and a standard deviation for each of them.

3. Results and Discussion

All the alloys were successfully obtained by casting, without presence of any visible not melted parts. The DTA runs carried out on small parts (about $3 \times 3 \times 7 \text{ mm}^3$) taken apart during cutting effectively showed that the mushy states of all the studied cobalt-based, nickel-based and iron-based alloys are comprised in the [1150°C; 1360°C], [1210°C; 1500°C] and [1190°C; 1390°C] temperature intervals, respectively. Consequently all these alloys can be easily synthesized by classical foundry.

The obtained metallographic and hardness results will be presented thereafter in successive figures in which all data are provided beside a SEM/BSE micrograph illustrating the microstructure.

3.1. Cobalt-Based Alloys

The results concerning the cobalt-based alloys are presented in **Figure 1** for the three carbon-lowest ones and in **Figure 2** for the three carbon-richest ones.

The microstructures of the first two cobalt alloys (with 2.5 and 3.0 wt% C) are typically hypo-eutectic. Indeed dendrites of the cobalt solid solution are clearly visible. In the other areas there is seemingly a eutectic compound of matrix and carbides (darker than matrix in BSE mode). When the carbon content increases the hyper-

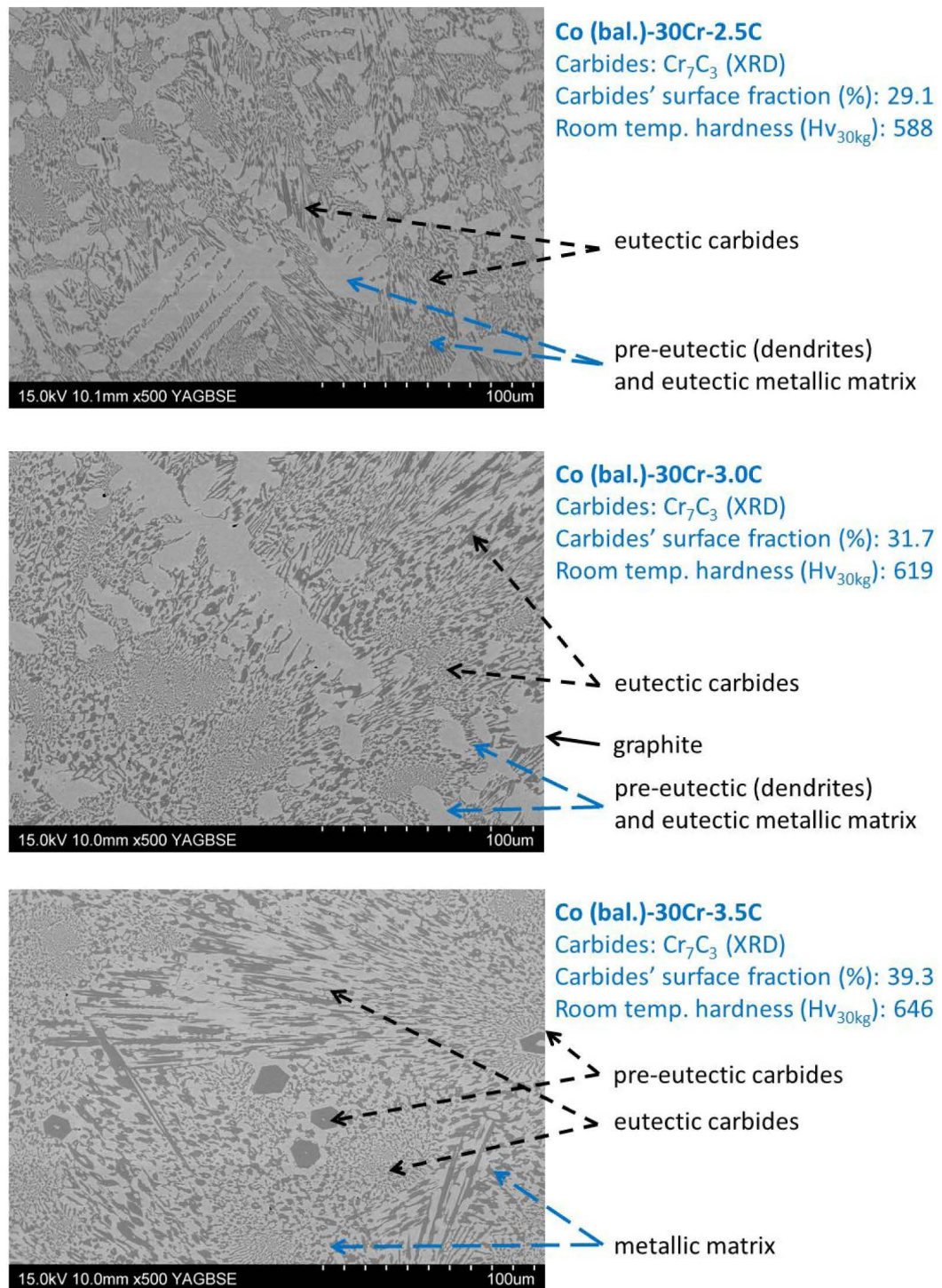


Figure 1. Results concerning the Co(bal.)-30Cr-xC alloys for x = 2.5, 3.0 and 3.5wt% C.

eutectic character appears with the third alloy (3.0 wt% C). Indeed the matrix dendrites are absent and replaced by another pre-eutectic phase, angular blocky compact chromium carbides, the volume fraction and size of which increase with the carbon content. The total surface fraction of eutectic (and pre-eutectic if any) carbides increases from about 29% to about 52% when the carbon content increases from 2.5 to 5 wt% C. These carbides are obviously Cr_7C_3 only in all the six alloys, as revealed by XRD. One must mention too that another phase

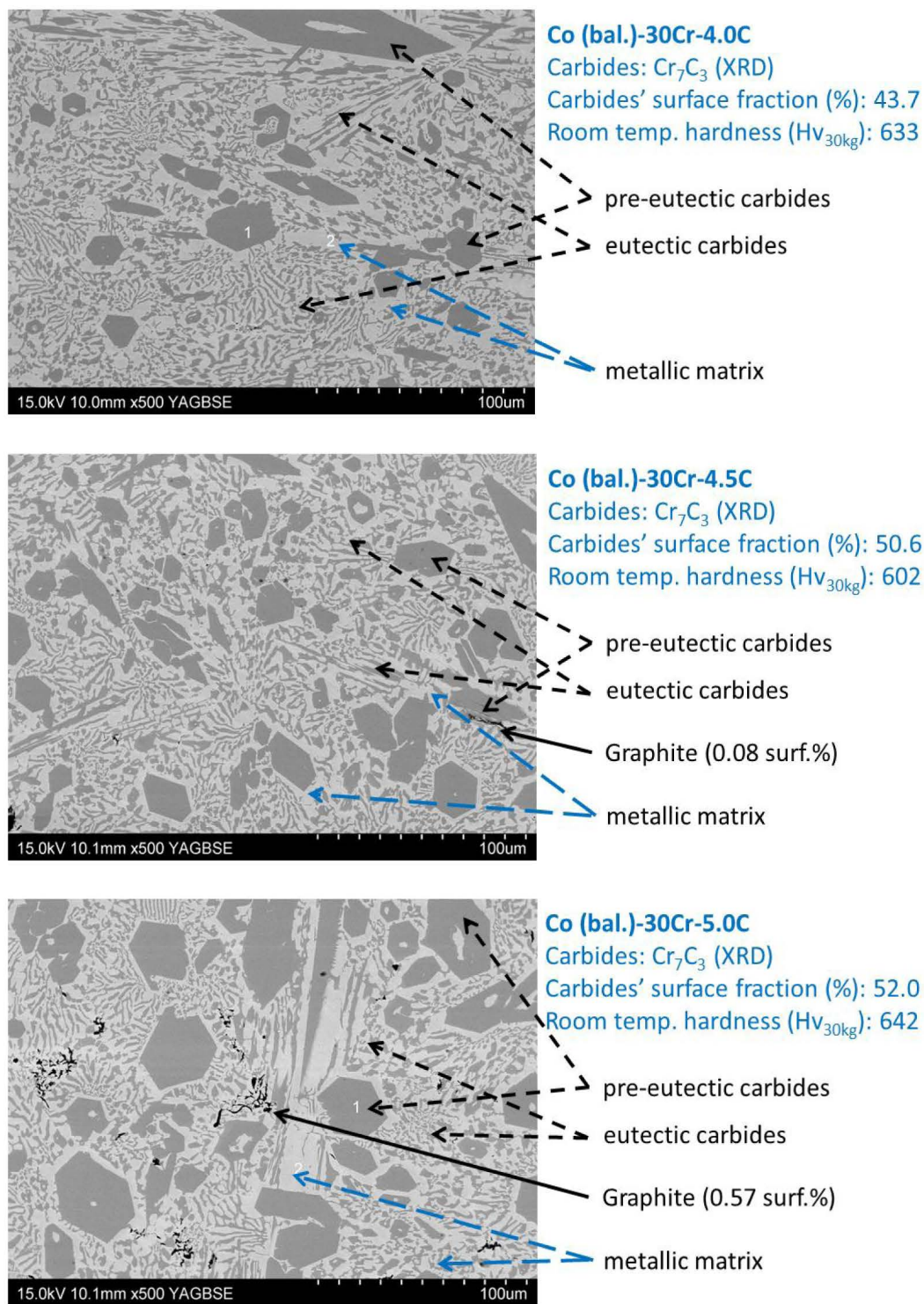


Figure 2. Results concerning the Co(bal.)-30Cr-xC alloys for x = 4, 4.5 and 5.0wt% C.

becomes to appear when the carbon content reaches 4.5 wt% C: graphite. These graphite particles are extremely rare for 4.5 wt% C but they are more visible for 5 wt% C. They begin to look like flake graphite as in lamellar graphite cast irons. The Vickers hardness of the alloys increases progressively from about 590 to about 640 Hv_{30kg} when the carbon content increases from 2.5 to 5 wt%.

3.2. Nickel-Based Alloys

The results concerning the nickel-based alloys are presented in **Figure 3** for the three carbon-lowest ones and in **Figure 4** for the three carbon-richest ones.

The microstructure of the first nickel alloy (the one containing 2.5 wt% C) seems being eutectic, with an

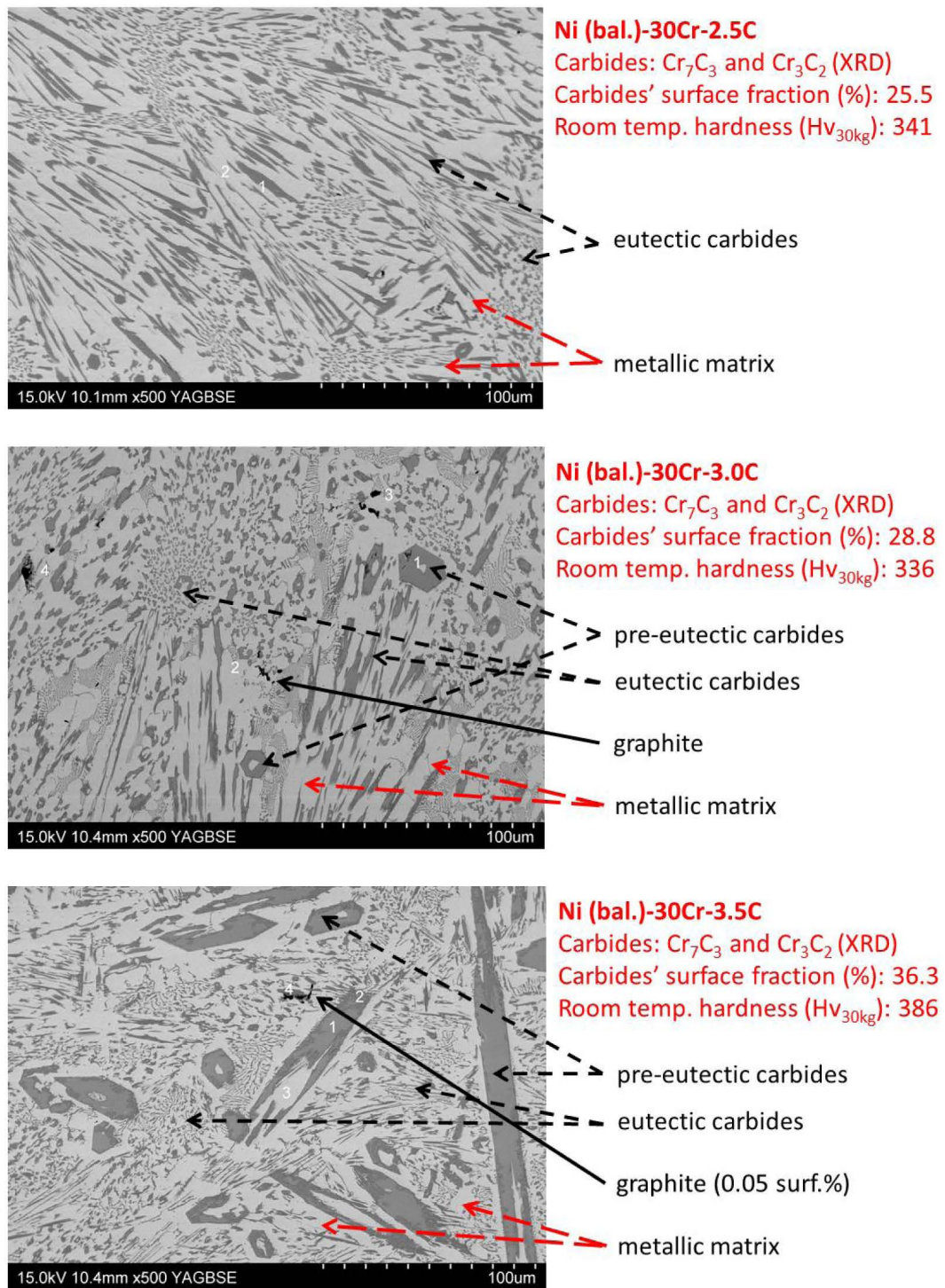


Figure 3. Results concerning the Ni(bal.)-30Cr-xC alloys for x = 2.5, 3.0 and 3.5wt% C.

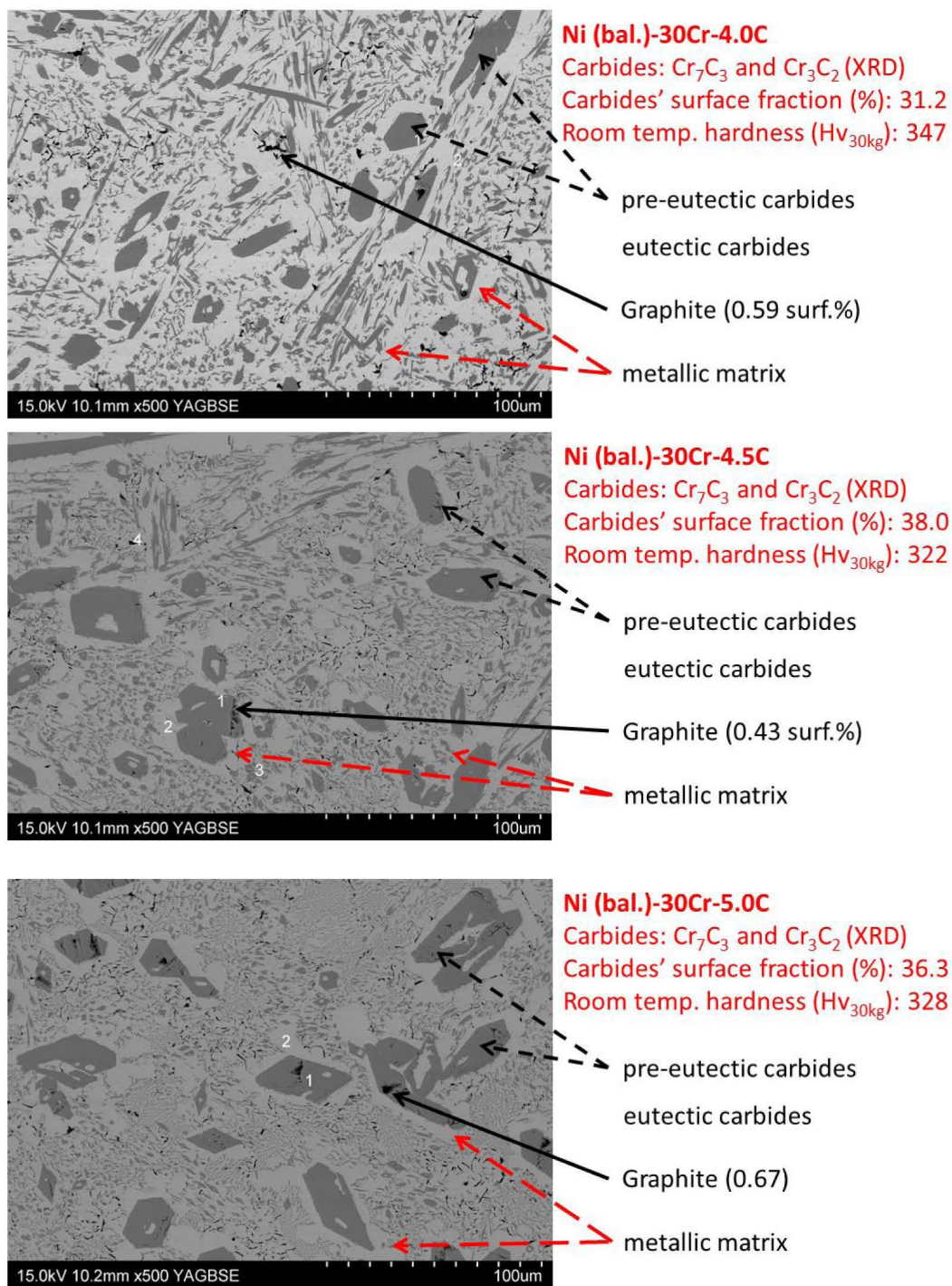


Figure 4. Results concerning the Ni(bal.)-30Cr-xC alloys for x = 4, 4.5 and 5.0 wt% C.

homogeneous presence of acicular chromium carbides totally mixed with the matrix. The second alloy (3 wt% C) is globally of the same structure but first angular blocky compact chromium carbides. When the carbon content goes on increasing the alloys become more and more hyper-eutectic, with pre-eutectic carbides which become coarser and coarser and represent a greater surface fraction. The graphite phase appears in this system too but for lower carbon contents. Indeed traces of graphite can be detected in the 3.5 wt% C-containing alloy and flake graphite develops when the carbon contents increases. It may represent about 0.7 surf.% in the 5 wt% C-con-

taining alloy in which it is not so clearly flake-shaped as in the corresponding cobalt-based alloy but it is here more homogeneously present in the microstructure in the Ni-30Cr-5C alloy.

The total surface fraction of eutectic and pre-eutectic carbides increases from about 26% to about 38% when the carbon content increases from 2.5 to 4.5 wt% C. For the two C-richest nickel alloys the increase in carbides fraction with carbon is decelerated and even inverted (about 36 surf.% in the Ni-30Cr-5C alloy) since the precipitation of graphite consumes a significant part of carbon which is therefore not available to form carbides. These carbides are composed of both Cr_7C_3 and Cr_3C_2 , as revealed by XRD. This double nature is illustrated in **Figure 5**.

The Vickers hardness of the alloys increases progressively from about 340 to about 390 $\text{Hv}_{30\text{kg}}$ when the carbon content increases from 2.5 to 3.5 wt%. Thereafter the presence of graphite seems lowering hardness.

3.3. Iron-Based Alloys

The results concerning the iron-based alloys are presented in **Figure 6**.

The microstructure of the first one (with 2.5 wt% C) is typically hypo-eutectic, as for the cobalt alloy with the same carbon content. Dendrites of the iron solid solution can be clearly seen while the eutectic compound made of matrix and carbides occupies the main part. With 1 wt% C more (Fe-30Cr-3.5C) the character is changed in hyper-eutectic, with the disappearance of the matrix dendrites and the presence of pre-eutectic phase angular blocky compact chromium carbides. The volume fraction and the average size of the latter become higher for 1 wt% C more again (Fe-30Cr-4.5C). The total surface fraction of eutectic (and pre-eutectic if any) carbides increases from about 17% to about 46% when the carbon content increases from 2.5 to 4.5 wt% C. According to XRD these carbides are all Cr_7C_3 in each of the three alloys. Rare very small graphite particles seem having precipitated too but their surface fraction is negligible.

The measured Vickers hardness increases with the carbon content from about 600 (2.5 wt% C) to about 760 $\text{Hv}_{30\text{kg}}$ (4.5 wt%).

4. Conclusion

It is thus possible to elaborate by classical foundry (however under inert atmosphere) highly refractory and very hard alloys composed of a metallic matrix (based on Co, Ni or Fe) and of chromium carbides. Their hardness may be simply rated by the carbon content in presence of chromium in excess, however with some limitations to avoid the presence of softening graphite. In parallel high contents in chromium also allows high resistance against high temperature corrosion, as in some superalloys. Such simple ternary alloys may be used as bulk

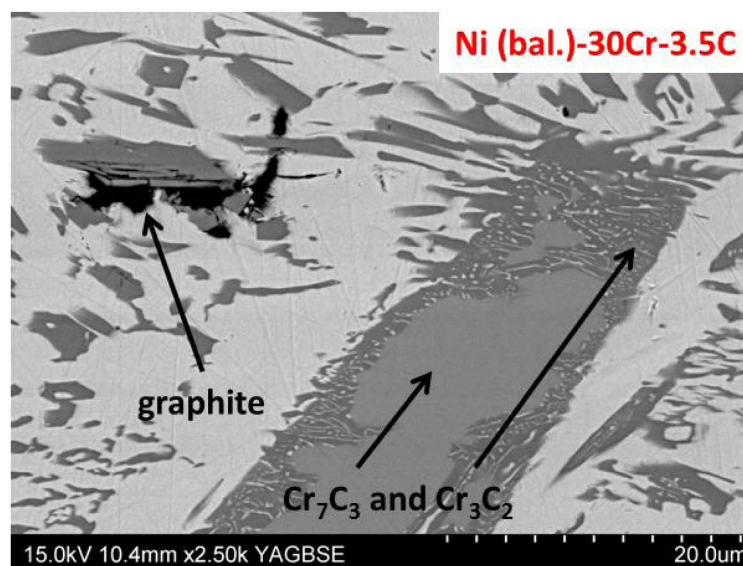


Figure 5. Enlarged view of the Ni(bal.)-30Cr-3.5C alloy showing the double nature of the chromium carbides as well as some graphite particles.

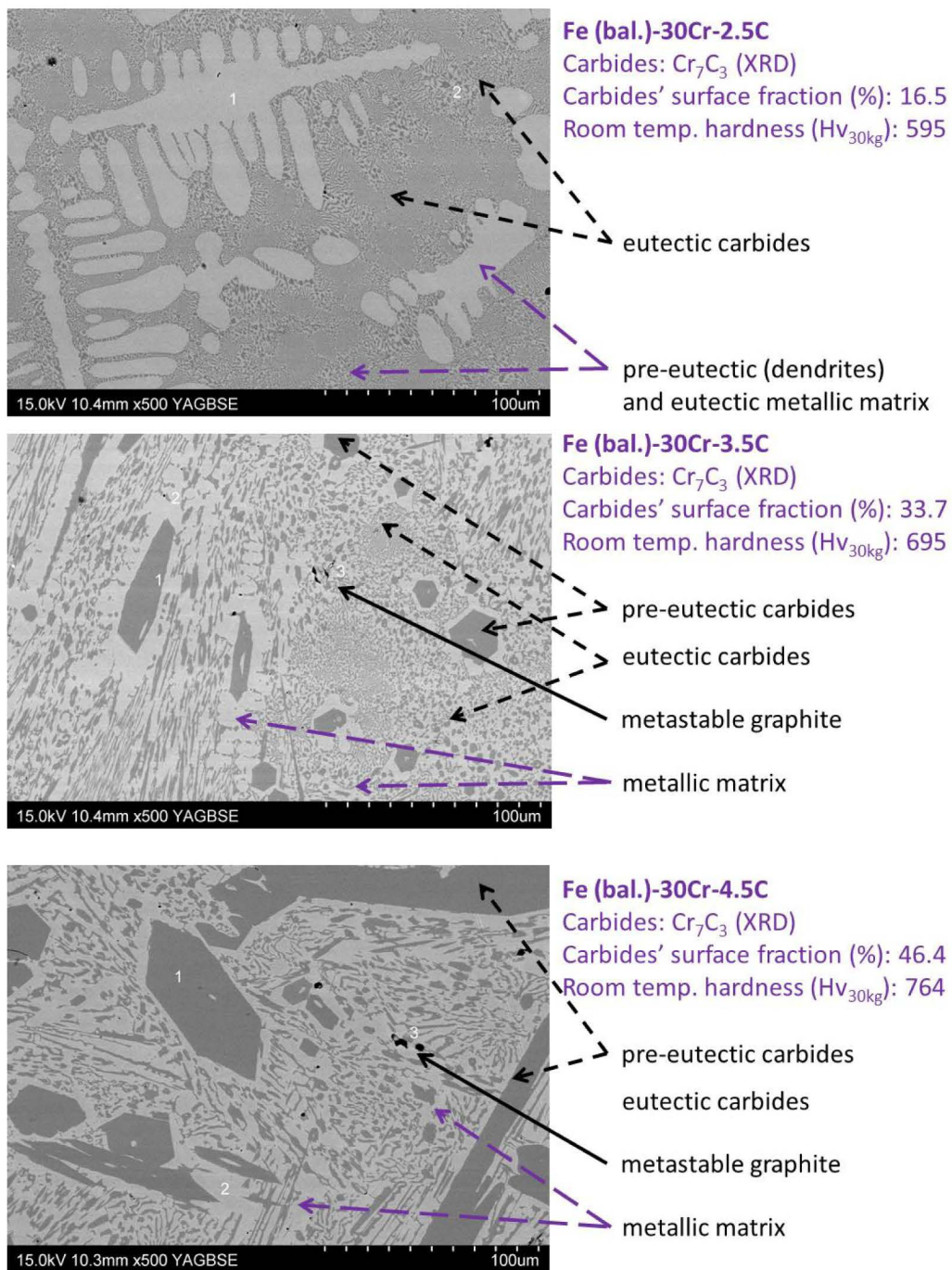


Figure 6. Results concerning the Fe(bal.)-30Cr-xC alloys for x = 2.5, 3.5 and 4.5wt% C.

materials for applications requiring both mechanical (wear notably but also stiffness) and chemical (hot oxidation) resistances, as well as a minimal fracture toughness.

References

- [1] Shaffer, P.T.B. (1964) High Temperature Materials. N°1: Materials Index. Plenum Press Handbooks, New York.
- [2] Samsonov, G.V. (1964) High Temperature Materials. N°2: Properties Index. Plenum Press Handbooks, New York.
- [3] Bradley, E. (1988) Superalloys: A Technical Guide. ASM International, Metals Park.

- [4] Sims, C.T. and Hagel, W.C. (1972) *The Superalloys*. John Wiley & Sons, New York.
- [5] Donachie, M.J. and Donachie, S.J. (2002) *Superalloys: A Technical Guide*. 2nd Edition, ASM International, Materials Park.
- [6] Masumoto, Y. and Imasato, S. (1985) Extremely Hard Sintered Cobalt Base Alloy. *Nippon Tungsten Review*, **18**, 23.
- [7] Miranda, J.C. and Ramalho, A. (2001) Abrasion Resistance of Thermal Sprayed Composite Coatings with a Nickel Alloy Matrix and a WC Hard Phase. Effect of Deposition Technique and Remelting. *Tribology Letters*, **11**, 37-48.
<http://dx.doi.org/10.1023/A:1016692304440>
- [8] Ando, K., Kikko, T. and Yoshida, Y. (2011) Toyota Jidosha Kabushiki Kaisha. International Patent, WO 2011101706.
- [9] Kofstad, P. (1988) *High Temperature Corrosion*. Elsevier Applied Science, London.
- [10] Young, D. (2008) *High Temperature Oxidation and Corrosion of Metals*. Elsevier Corrosion Series, Amsterdam.