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Acta Metall. Sin. (Engl. Lett.) Vol.26 No. 6 pp. 687—692 December 2013

ACTA
METALLURGICA SINICA
(ENGLISH LETTERS)

Phase Stability of the Laves Phase Cr_2Nb in a Two-Phase Cr-Cr_2Nb Alloy

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[Manuscript received 11 March 2013, in revised form 14 July 2013]

The phase stability of the Laves phase Cr_2Nb in a two-phase Cr-Cr_2Nb alloy produced by arc-melting was investigated using X-ray diffraction, transmission electron microscopy and selected area electron diffraction. The experimental results indicated that the as-cast ingot was consisted of C15-Cr_2Nb and Cr phases; the intermediate C36 and high-temperature C14 modifications of Cr_2Nb, reported in literatures, were not detected in this study. These results, combined with a detailed analysis of the actual solidification conditions, revealed that the C14-Cr_2Nb was a metastable rather than a stable high-temperature modification. Moreover, a kind of extremely fine lamellar structure was found to be randomly distributed in the eutectic cells, which may be formed by decomposition of the supersaturated C15-Cr_2Nb *via* a discontinuous precipitation reaction.

KEY WORDS: Laves phase; Microstructure; Intermetallics; Phase tranformation

1. Introduction

The Laves phase Cr_2Nb has a great potential for aerospace applications due to its high melting points, relatively low densities, excellent creep behavior, reasonable oxidation resistance and attractive high temperature strength[1−3]. Meanwhile, the Cr_2Nb Laves phase exhibits a relatively wide single-phase homogeneity range and forms a Laves/bcc two-phase field with both (Cr) and (Nb) on either side of the compound in the binary system. Thus, composite structures of a C15 Laves phase and a bcc phase were designed to improve the low-temperature fracture toughness of the Cr_2Nb Laves phase and maintain adequate high-temperature properties[3−7].

In addition, the Cr_2Nb Laves phase has three polytypes: cubic C15 ($MgCu_2$-type) structure below ~1873 K, hexagonal C14 ($MgZn_2$-type) structure between this temperature and its melting point (between 2003 and 2043 K) and dihexagonal C36[1,3]. Recently, a study indicated that the mechanical properties of polycrystalline materials were largely determined by the phase transformations during the preparation process[8], and the deformability of complex Laves phases can be improved by controlling their crystalline structure in a way that phase transformation and/or mechanical twinning can be introduced during plastic deformation[9−11]. Therefore, a number of studies have been conducted on the phase stability of the Cr_2Nb Laves phase[12−16]. Unfortunately, the phase stability of the Cr_2Nb Laves phase in the two-phase alloys have not been well understood.

In this study, the phase stability of the Cr_2Nb Laves phase in a two-phase alloy containing the Cr_2Nb and Cr phases was investigated. The aim is to give a better understanding of the details of the structural transformations among the different polytypes. By achieving a better understanding of the changes in the polytypes of the Cr_2Nb Laves phase, new structural materials for applications at very high temperatures can be designed which make use of the advantageous physical properties of the Cr_2Nb Laves phase.

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DOI: 10.1007/s40195-013-0140-x

2. Experimental

The Cr-20 at.%Nb hypereutectic alloy was produced by vacuum non-consumable arc-melting (VCAM) with high purity metals (Nb: 99.99% and Cr: 99.9%, hereafter, all compositions in this paper are given in terms of at.% unless otherwise stated) under a titanium-gettered argon atmosphere. Each ingot was re-melted five times to ensure chemical homogeneity. Finally, a button-like ingot of Cr-20 at.%Nb with a weight of 150 g was obtained. The compositions of the as-cast ingot in different positions were analyzed by inductively coupled plasma mass spectrometer (ICP-MS) and the measure results demonstrated that the compositions were very close to the nominal composition with the deviations less than 0.62 at.% for Cr.

Then, the samples from different positions along the centre line correspond to the bottom, middle and top parts of the arc-melted ingot were denoted as L, M and U as described in our previous work[17]. The samples were prepared for optical and electron microscopy (SEM). The phases were identified by X-ray diffraction (XRD, D/MAX2400, CuK_α). A scanning electron microscopy (SEM, JSM-6390A) equipped with an energy dispersive spectrometer (EDS) was employed to characterize the microstructure. A transmission electron microscopy (TEM, Tecnai G^2 F30) was used to identify the phases.

3. Results and Discussion

Fig. 1 illustrates the partial X-ray diffraction patterns of the L, M and U samples together with the simulated patterns of the C14, C15 and C36 modifications of the Cr_2Nb Laves phase. It can be found that the diffraction peaks of the measured patterns match very well with the C15 modification, but not fit with the hexagonal C14 or C36. Thus, the samples taken from different positions of the as-cast ingot consist of two different phases: C15-Cr_2Nb and Cr phases. The conclusion is in agreement with the currently existing Cr-Nb phase diagram[17]. In addition, the Cr peaks were found to slightly shift to lower angles, which may cause by the dissolution of Nb atoms into the Cr lattices. It agrees with the previous results that supersaturated solution Cr had been formed by mechanical alloying[16].

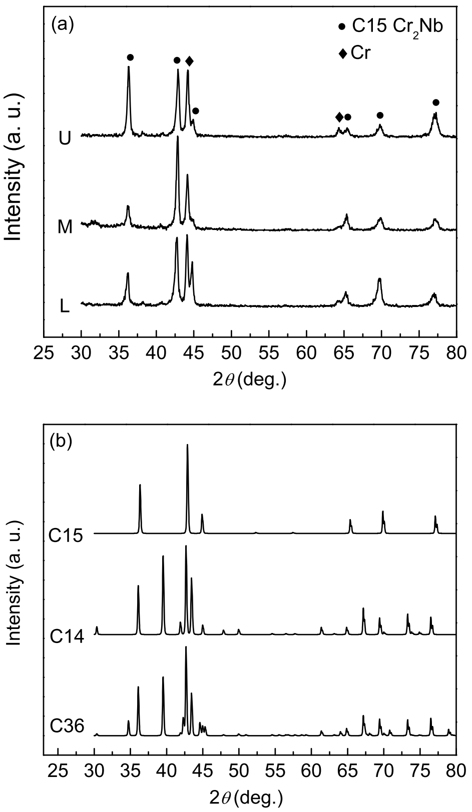

Fig. 1 (a) Partial X-ray diffraction patterns of the samples taken from different positions of the Cr-20%Nb ingot, (b) the simulated patterns of C14, C15 and C36 modifications of Cr_2Nb for Cu$K_{\alpha1}$ radiation

Based on the results shown in Fig. 1, the samples were selected for further analysis. Fig. 2 illustrates the typical microstructure solidified in different positions of the arc-melted Cr-20 at.%Nb ingot. For this composition, the first phase precipitated is clearly Cr_2Nb, as would be expected from the phase diagram, which precipitates as primary intermetallic particles from the liquid and then the remaining liquid solidifies isothermally by the simultaneous coupled growth of the α-Cr and β-Cr_2Nb phases. However, as shown in Fig. 2, the microstructure is heterogeneous as a series of microstructure morphologies along the centre line of the ingot occurred: fully coupled eutectic → petal-like Cr_2Nb primary dendrites distributing in the eutectic matrix → plate-like Cr_2Nb primary phase distributing in the eutectic matrix. The microstructure was difficult to solidify as homogeneous structure may cause by the narrow stoichiometry, the likelihood of crystal growth kinetic limitations, and sluggish diffusion associated with the Cr_2Nb Laves phase[18]. This kind of microstructural evolution can be explained by the coupled eutectic zone involving the competitive growth among α-Cr, β-Cr_2Nb and eutectic[17,19].

It is worth noting that the morphology of Cr_2Nb primary phase in the sample M is a round structure with a smooth surface. This suggests that the growth mode of Cr_2Nb primary phase is nonfaceted. The morphology of Cr_2Nb primary phase at the top surface of the arc-melted ingot becomes angular features in Fig. 2(e) and Fig. 2(f). It indicates that the growth mode becomes faceted gradually at the top surface. In general, the heat conduction ability of copper is higher than that of gas. Also, the released latent heat of solidification at the water-cooled copper hearth will reduce the cooling rate at the top surface. So the cooling rate of the sample L is higher than these of the samples M and U. Consequently, the formation of faceted morphology is due to the decrease in cooling rate.

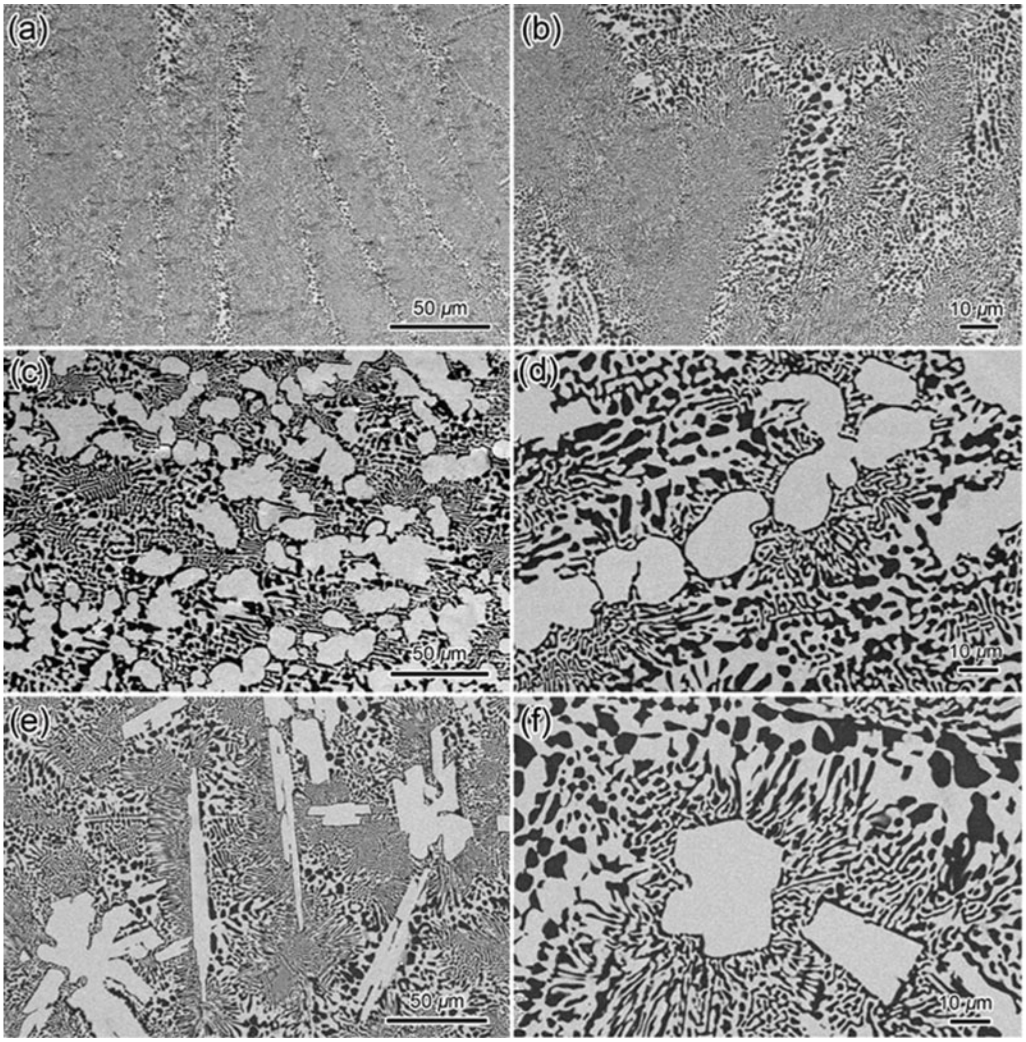

Fig. 2 Typical SEM micrographs of the arc-melted Cr-20%Nb alloy: (a, b) sample L, (c, d) sample M, (e, f) sample U

Interesting behavior was also observed when the microstructures were examined in more detail. Fig. 3 presents a kind of fine lamellar structure distributing among the eutectic cells at some distance away from the bottom of the ingot. This kind of fine structure is analogous to the Cr/Cr_2Nb eutectic, and has not been reported in the Cr-Nb alloys. Moreover, the Cr_2Nb Laves phase is known to exhibit a high temperature structure (C14) and a low temperature structure (C15). Furthermore, the C14-to-C15 transformation was reported to be a function of the cooling rate[13]. In this case, the fine structure may contain the C14 or C36 modification of Cr_2Nb. Consequently, further examination is required.

Fig. 4 shows the bright fields of TEM of different kinds of microstructures in the Cr-20 at.%Nb alloy. The structures outside and within of the eutectic cell (areas A, B and C, D) in sample L were chosen for the selected area electron diffraction analysis. Meanwhile, the Cr_2Nb primary phase and the Cr phase in the eutectic in the samples M (areas E and F) and U (areas G and H) were also identified. The phases were identified by the selected area electron diffraction (SAED) patterns of three different zone axes. For clarity, not all these SAED patterns are listed; just representative patterns are shown in Fig. 4. According to the SAED patterns (Fig. 4(b), Fig. 4(c), Fig. 4(h), Fig. 4(i), Fig. 4(k) and Fig. 4(l)), all the lamellar structures were determined as Cr and C15-Cr_2Nb phases, while high temperature modifications such as hexagonal C14 and dihexagonal C36 were not detected in this study. The results are consistent with the XRD results shown in Fig. 1 and the currently existing Cr-Nb phase diagram. In addition, the C15-Cr_2Nb phase was observed to accompany with a high density of micro twins, and a number of dislocations (see in Fig. 4).

A number of studies have been conducted on the phase stability of the Cr_2Nb Laves phase[9,12–16]. Thoma *et al.*[4,18] reported hexagonal C14 and C36 modifications occurred in arc-melted ingot of a relatively high cooling rate. Aufrecht *et al.*[13], however, observed the C14/C36 modifications appeared in the arc-melted ingot at a relatively low cooling rate. In

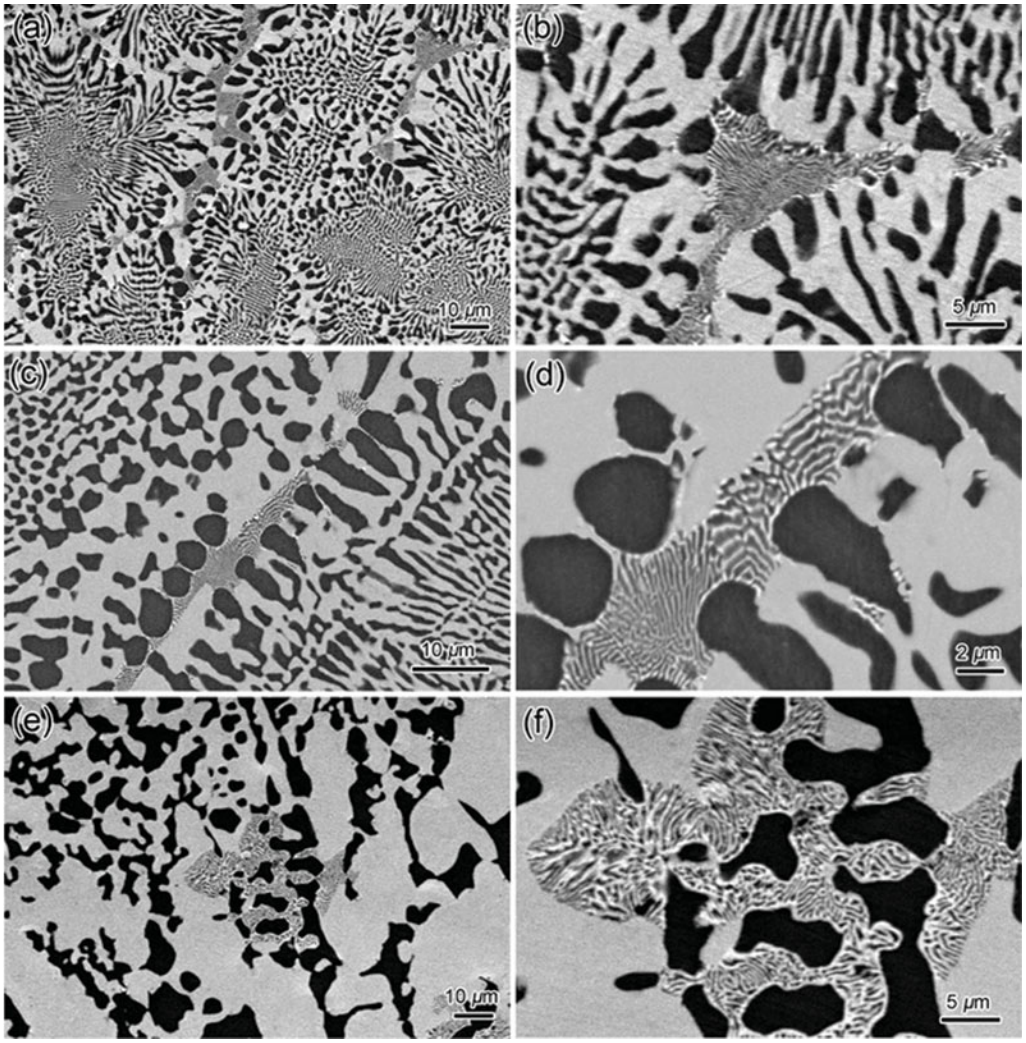

Fig. 3 SEM micrographs of the fine lamellar structure observed in different position of the arc-melted Cr-20%Nb ingot: (a) sample L, (c) sample M, (e) sample U, (b, d, f) high magnification micrographs of (a), (c) and (e), respectively

this case, this topic involves the C14 modification as a stable phase or not, which remains controversial up to the present[9,12−15]. Some researchers considered the C14 modification as a stable high-temperature phase just as the Cr-Nb phase diagram suggested[4,16,18]. However, some other researchers supposed the C14 modification as a metastable phase rather than a stable high-temperature phase[14]. In our studies, neither the C14 nor C36 modification was detected. Combined with a detailed analysis of the actual solidification conditions, the stability of the C14 modification was explained as follows.

As the Cr-20 at.%Nb alloy located in the hypereutectic composition range, so long-range diffusion is required but in the single-phase alloys, it is unexpected. The kinetics of the C14-to-C15 transformation is therefore become sluggish in the two-phase alloy. If the C14 phase is a stable high-temperature modification of Cr_2Nb, as proposed before[4], the amount of C14 modification should be greater at locations where relatively high cooling rates occurred since the C14→C15 transformation of the Laves phase is suppressed more completely. However, neither C14 nor C36 was detected in the bottom of the arc-melted ingot where experienced the highest cooling rates due to contacting with the water-cooled cooper hearth. Thus, the C14-Cr_2Nb modification must be a metastable phase precipitates at specific solidification conditions rather than a stable high-temperature modification. This result is in consistent with the Refs. [13, 14].

In this case, the formation of the fine lamellar structure showing in Fig. 3 can be explained by discontinuous precipitation. As the cooling rates of the sample L were quite high, the precipitated Cr and Cr_2Nb phases were supersaturated. During the further solidification, the supersaturated β_0-Cr_2Nb phase decomposed through β_0-$Cr_2Nb \rightarrow \beta$-Cr_2Nb + α-Cr to form a fine lamellar eutectoid structure. The residual β_0-Cr_2Nb was observed to be surrounded by the eutectoid, as shown in Fig. 3(b). Then, the discontinuous precipitation was pushed forwards by the

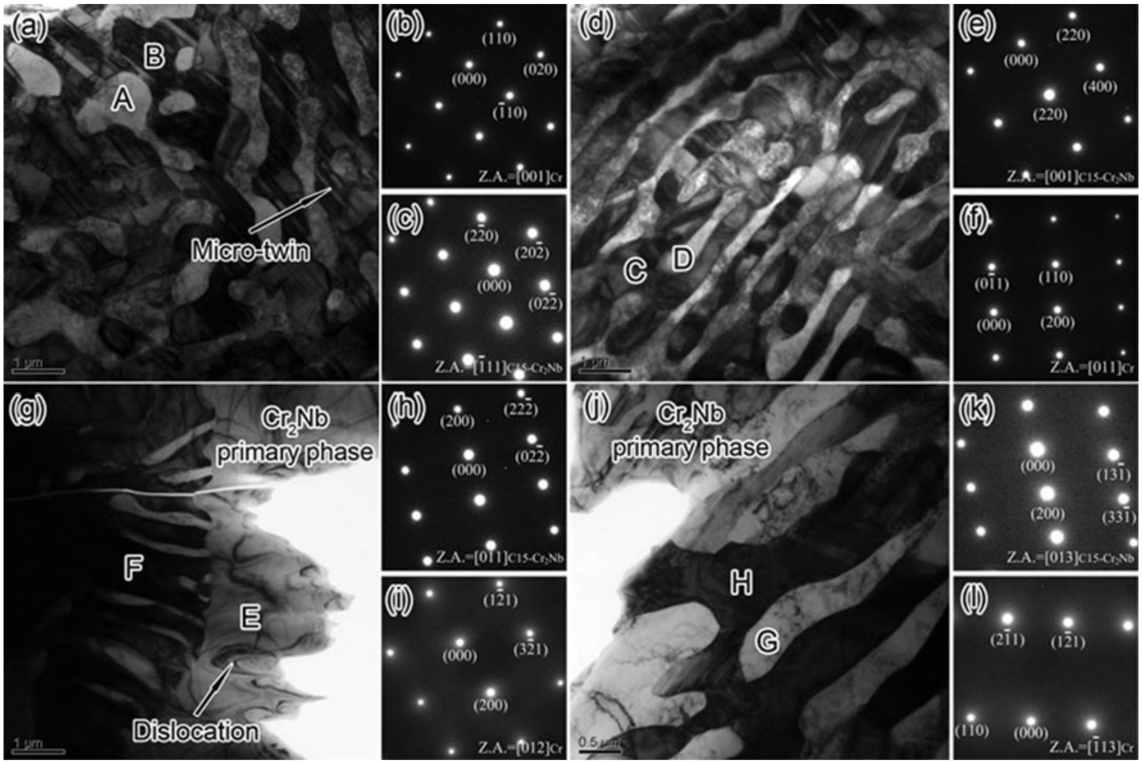

Fig. 4 (a) Bright field of eutectic outside of the eutectic cell in the sample L, (b, c) SAED patterns at the areas A and B, (d) bright field of eutectic inside of the eutectic cell in the sample L, (e, f) SAED patterns at the areas C and D, (g) bright field of the sample M, (h, i) SAED patterns at the areas E and F, (j) bright field of the sample U, (k, l) SAED patterns at the areas G and H

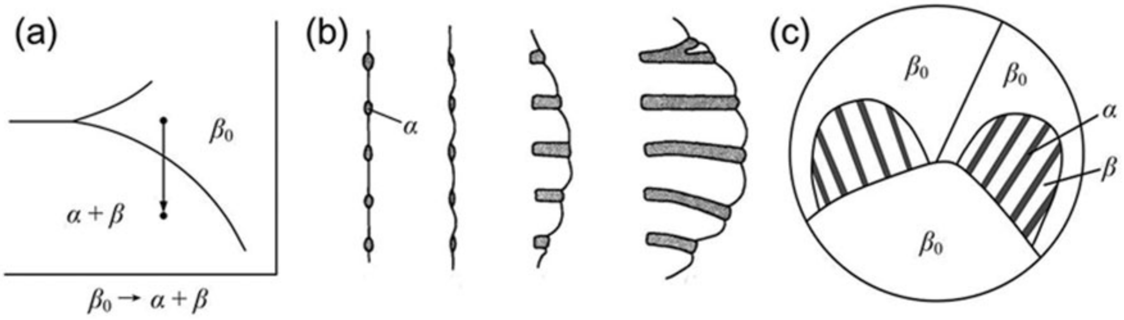

Fig. 5 (a) Composition variations during the discontinuous precipitation, (b) mechanism of the discontinuous precipitation, (c) sketch map of the cellular precipitate

developing precipitates[20,21], as shown in Fig. 5.

4. Conclusions

The phase stability of Cr_2Nb Laves phase in the Cr-Cr_2Nb two-phase alloy has been studied. It is found that the microstructure of the arc-melted ingot is heterogeneous. The microstructure of the Cr-20 at.%Nb hypereutectic alloy consists of C15-Cr_2Nb and Cr phases, the intermediate C36-Cr_2Nb and high-temperature C14-Cr_2Nb modifications, reported in literatures, were not detected in this study. The C15-Cr_2Nb phase was observed to accompany with a high density of micro twins, and a number of dislocations. By considering the effects of cooling rate and second Cr phase, the C14 modification was indicated to be a metastable phase rather than a high-temperature modification. In addition, a kind of extremely fine lamellar structure was found to be randomly distributed among the eutectic cells, which may be formed by decomposition of the supersaturated C15-Cr_2Nb *via* a discontinuous precipitation reaction.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 50971101, 51074127 and 51104120).

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