Microstructure of laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites

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In order to improve the ductility of Cr_3Si metal silicide alloys, rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites were fabricated by laser melting/rapid solidification technology using Cr-Si-Ni alloy powders. Microstructure of the γ/Cr_3Si "*in situ*" composites was characterized by OM, SEM, XRD and EDS. The effect of Ni content in the alloy powder on microstructure and hardness of the γ/Cr_3Si composites was investigated. The γ/Cr_3Si metal silicide "*in situ*" composites have high hardness and rapidly solidified fine microstructure consisting of primary Cr_3Si dendrites and the interdendritic γ/Cr_3Si eutectics. The volume fraction of the Cr_3Si primary dendrites in the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites decreases with the increasing nickel content. Because of the presence of the ductile nickel-base solid solution and the rapidly solidified fine microstructure, the γ/Cr_3Si metal silicide "*in situ*" composites are expected to have adequate combination of strength and toughness. The results demonstrate that laser melting/rapid solidification for γ/Cr_3Si metal silicide "*in situ*" composites is a promising toughening method for improving the ductility of Cr_3Si metal silicide alloys.

1. Introduction

The transition metal silicide Cr_3Si is considered as one of the promising candidate high-temperature structural materials for hot-section components of advanced aerospace gas turbines in view of its outstanding balance of low density, high melting point, excellent elevated-temperature mechanical properties, excellent oxidation resistance, good corrosion resistance and wear resistance [1–4]. Unfortunately, very poor ductility and fracture toughness from room to middle temperatures hinder the practical industrial applications of the Cr_3Si metal silicide alloys as bulk structural materials. Several strategies such as incorporation of ductile second phases, grain refinement and reduction of impurities, have been utilized to improve the ductility and the fracture toughness of the Cr_3Si structural materials. Among these toughening methods, ductile second phase toughening was the primary method to improve the toughness of Cr_3Si, because it can offer efficient toughening effect to the material while maintaining the excellent high-temperature properties of Cr_3Si metal silicide. Addition of chromium solid solution as a second ductile phase showed some success in toughening Cr_3Si [5–9]. The toughness of the Cr-Cr_3Si eutectic composite is significantly superior to that of single phase Cr_3Si alloy. However, the dissolution of silicon (up to 3.92 wt%) was observed to noticeably reduce the toughness of chromium solid solution [9]. Moreover, the extreme sensitivity of the toughness and DBTT of chromium to impurities prevented the further toughness improvement for the Cr-Cr_3Si eutectic composite. Mechanical alloying with V was adopted to improve the toughness of chromium solid solution [10] and it did show that the hot-pressed V-alloyed chromium – $(Cr_{0.57}, Mo_{0.43})_3Si$ composite had significantly improved microhardness and toughness. Additions of intermetallic phase such as FeAl and Ni_3Al were also applied to increase the ductility of Cr_3Si intermetallic alloy. However, the toughness of hot-pressed Cr_3Si-25% FeAl and Cr_3Si-25% Ni_3Al composites was not significantly improved and severe cracking phenomenon was noticed during the microindentation test process for both of the composites [10]. Alloying of Cr_3Si with Mo for improving high-temperature oxidation resistance was also extensively studied [3, 4, 11]. Results indicated that the Mo-alloyed Cr_3Si had slightly better toughness and noticeably improved high-temperature properties than the stoichiometric Cr_3Si for both the arc-melted and hot-pressed materials. As toughening phases, the Pt-6%Rh, saphikon fibers and tungsten fibers were introduced into molybdenum-modified Cr_3Si/Cr_5Si_3 intermetallics in attempt to improve both the toughness and strength [12–14]. Unfortunately, due to the large mismatch in the coefficients of thermal expansion (CTE) between the fiber and the intermetallic matrix, microcracks are inevitably generated at the interface and in the matrix. Hot

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forging of Cr-Cr_3Si composites was also employed to produce a micro-fiberous or micro-laminated Cr/Cr_3Si composite, which are expected to exhibit excellent combination of strength and toughness [10]. Nickel solid solution γ is well known for its excellent combination of high-temperature strength and ductility as well as for its good compatibility with Cr_3Si (Ni has high solid solubility in Cr_3Si). A γ/Cr_3Si metal silicide composite containing some amount of γ nickel solid solution ductile phase is naturally expected to have improved ductility while maintaining the high-temperature properties of Cr_3Si metal silicide. In this paper, laser melting/rapid solidification technology was adopted to produce γ/Cr_3Si metal silicide "*in situ*" composites mainly composed of the Cr_3Si primary dendrites and the remaining ductile nickel-base solid solution. The microstructure of laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites was characterized by OM, SEM, XRD and EDS. The effect of Ni content on microstructure and hardness of laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites was investigated and discussed.

2. Experimental procedures

The commercially pure chromium, silicon and nickel elemental powders were selected as the starting precursor materials for making γ/Cr_3Si metal silicide composite materials by laser melting/rapid solidification process. The particle size of the powders ranges from −200 to +320 mesh. The nominal chemical compositions of the Cr-Si-Ni alloy powders used in this paper are listed in Table I. As schematically illustrated in Fig. 1, the Cr-Si-Ni elemental powder blends, approximately 10 mm in thickness, were preplaced on the surface of a thick nickel plate in order to increase the solidification cooling rate and were melted under the irradiation of a high-power laser beam from a 5 kW continuous-wave CO_2 laser in argon shielding atmosphere. Laser melted button-like samples in diameter of approximately 6 mm and in weight of approximately 10 g was finally produced. The laser melting parameters are: laser outpower 2.8 kW, laser beam size 17 mm × 1 mm and beam traverse speed 1.33 mm/s. Because of the rapid heat conduction of the thick nickel plate, the laser melted button-like samples have rapidly solidified microstructure.

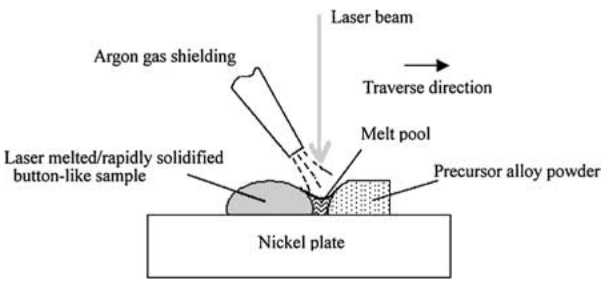

Figure 1 Schematic illustration of the laser melting for rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites.

TABLE I The nominal chemical compositions of Cr-Si-Ni alloy powders used for production of the γ/Cr_3Si composites by laser melting/rapid solidification process

Sample no.	Ni (wt%)	Si (wt%)	Cr (wt%)
M1	20	18	62
M2	30	15.75	54.25
M3	40	13.5	46.5

Metallographic cross-sections of the laser melted/rapidly solidified button-like samples were prepared using standard procedures and were etched using the etchant of HF, HNO_3 and H_2O in volume ratio of 1 : 6 : 7. Microstructure of the laser melted/rapidly solidified Cr-Si-Ni "*in situ*" composites was characterized using the optical microscope Nephot II and the scanning electron microscope KYKY-2800. Phases presented in the laser melted/rapidly solidified Cr-Si-Ni "*in situ*" composites were identified by X-ray diffraction using the Rigaku D/max 2200 pc automatic X-ray diffractometer with Cu K_α radiation and the chemical composition of the phases was analyzed by energy dispersive spectrometer Noran Ventage DSI. Microhardness of the laser melted/rapidly solidified "*in situ*" composites was measured using MH-6 semi-automatic Vickers hardness tester with a testing load of 200 g and a loading time of 15 s.

3. Results and discussions

Fig. 2 shows the XRD pattern of the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composite

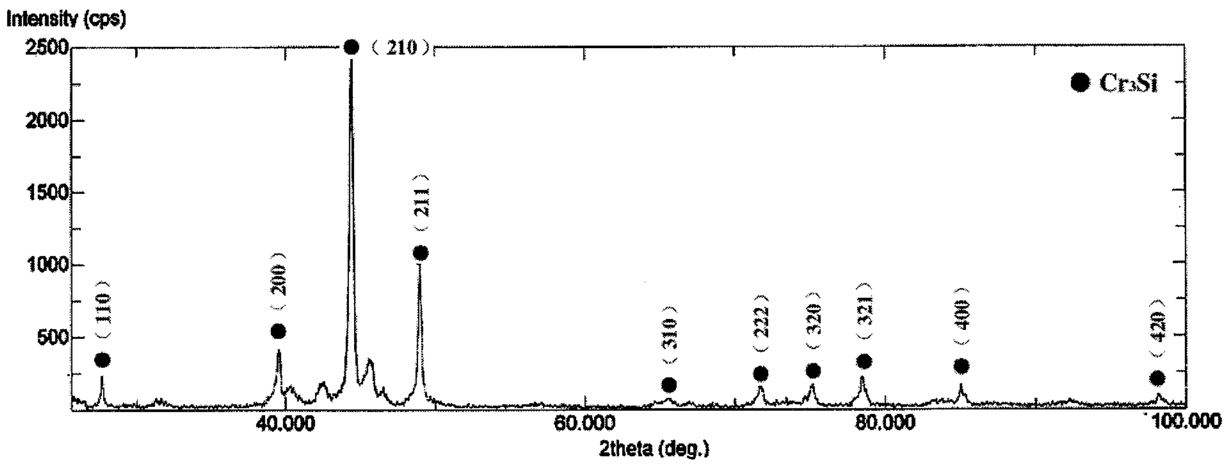

Figure 2 X-ray diffraction analysis result of the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composite (the precursor powder composition Ni20Si18Cr62).

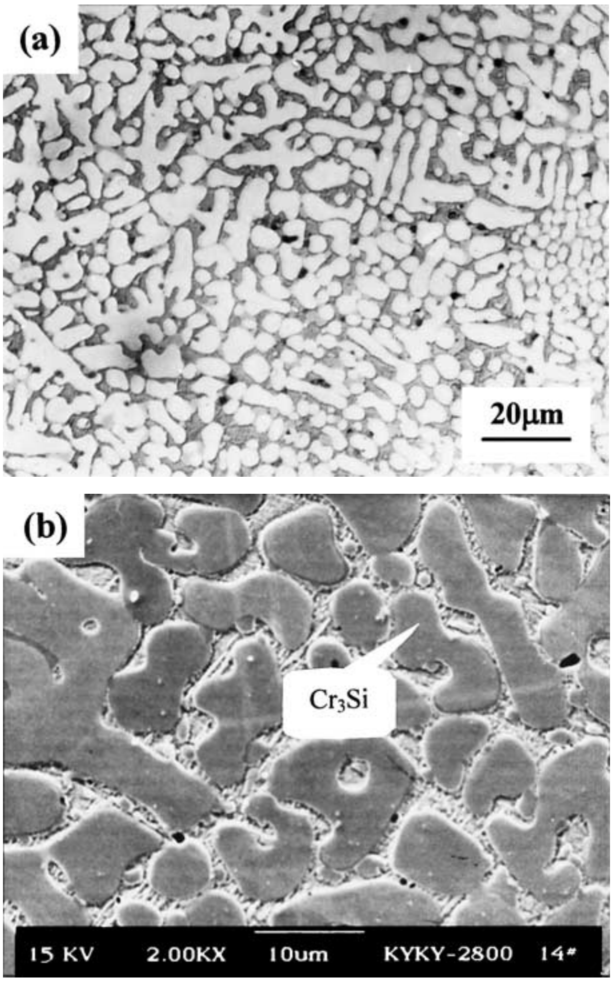

Figure 3 OM (a) and SEM (b) photographs showing the microstructure of laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composite with Ni20Si18Cr62 alloy powder.

with Ni20Si18Cr62 alloy powder and it is indicated that the predominant constitution phase is Cr_3Si metal silicide. Typical microstructure of the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composite with Ni20Si18Cr62 alloy powder is shown in Fig. 3. The composite has a rapidly solidified fine microstructure consisting of predominantly primary dendritic phase and small amount of interdendritic eutectics. EDS analysis indicates that the chemical composition (at.%) of the dendritic primary phase and the interdendritic eutectics are: 76.26Cr-21.81Si-1.93Ni and 60.99Ni-22.12Cr-16.89Si, respectively. According to both the XRD and EDS analysis results, the primary dendrites are identified as Cr_3Si metal silicide phase. The interdendritic eutectics consist of Cr_3Si and the nickel-base solid solution γ which is highly supersaturated with Cr and Si.

The content of Ni in the precursor powder material has no influence on the phase constitution of the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites. However, the volume fraction of the dendritic Cr_3Si primary phase decreases significantly with the increasing Ni content, as shown clearly in Figs 3a, 4a and 5a.

The metal silicide Cr_3Si has high melting point (2043 K) and the large negative free energy of formation in the Ni-Cr-Si system. Under laser melting/rapid

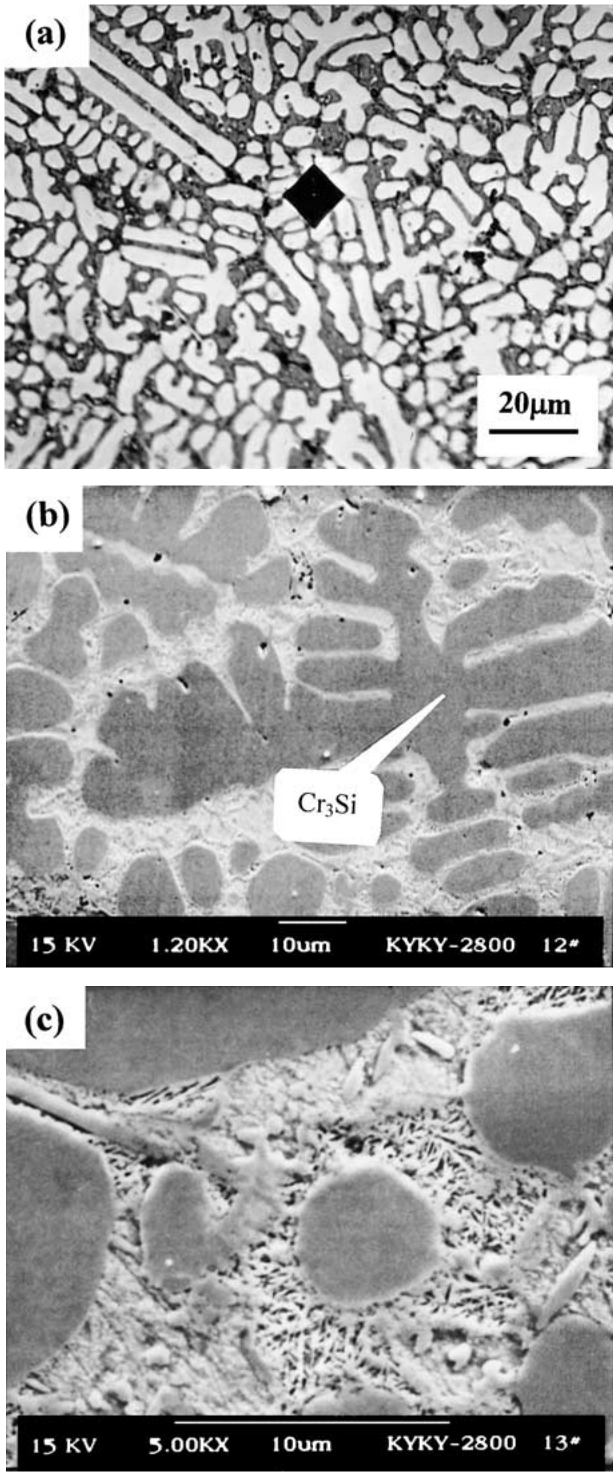

Figure 4 OM (a) and SEM (b and c) photographs showing the microstructure of laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composite with Ni30Si15.8Cr54.2 alloy powder.

solidification conditions, Cr_3Si metal silicide precipitates from the liquid as the primary phase during rapid solidification process and grows freely in the melt as well-developed primary dendrites. Accompanying the solidification of the primary Cr_3Si dendrites, the residual liquid is enriched in nickel and finally the interdendritic eutectic structure consisting of γ nickel-base solid solution and Cr_3Si is formed.

The Ni content has not only significant influence on the microstructure but also noticeable effect on the hardness of the laser melted/rapidly solidified γ/Cr_3Si "*in situ*" composites. In order to evaluate the effect of Ni

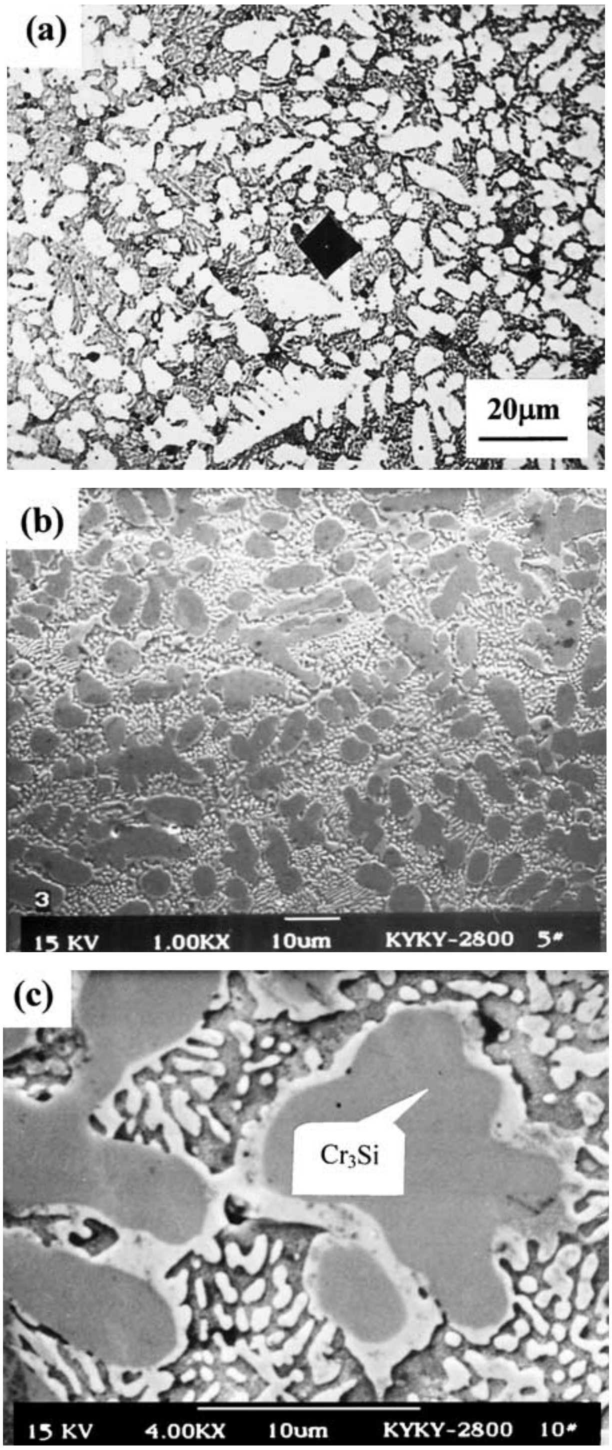

Figure 5 OM (a) and SEM (b and c) photographs showing the microstructure of laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composite with Ni40Si13.5Cr46.5 alloy powder.

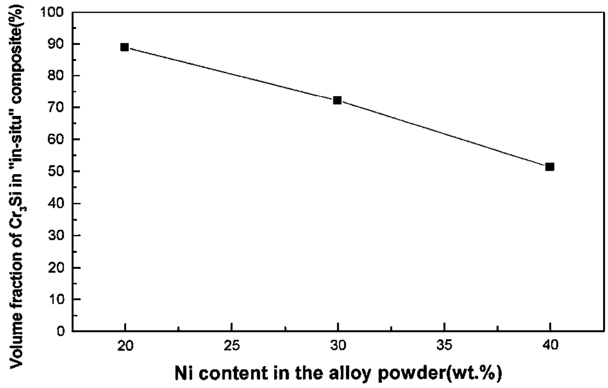

Figure 6 The volume fraction of primary Cr_3Si dendrites in the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites as a function of Ni content.

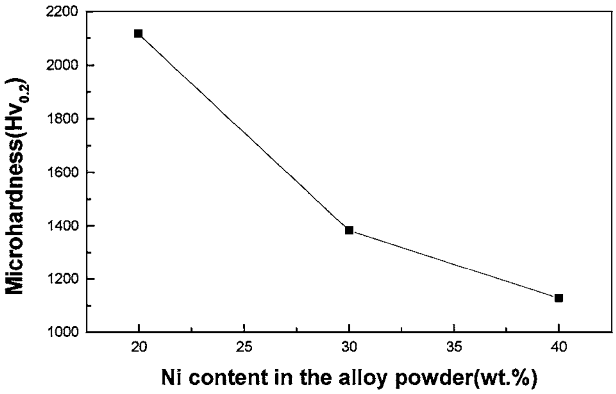

Figure 7 Microhardness of the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites as a function of Ni content.

content, a fixed weight ratio of Si: Cr (22.5 : 78.5) in the precursor powder material was designed and only the Ni content was regulated. Under identical laser melting processing conditions, the volume fraction of the primary Cr_3Si phase in the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites decreases with the increasing Ni content, as indicated in Fig. 6. The average volume fraction of primary Cr_3Si dendrites decreases from approximately 88% to 50% as Ni content increases from 20 wt% to 40 wt%, as clearly shown in Figs 3a, 4a and 5a. Fig. 7 indicates the microhardness of the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites as a function of Ni content in the alloy powder. All the three laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites have very high hardness because of the refined rapidly solidified microstructure and the presence of the high volume fraction of primary Cr_3Si dendrites uniformly distributed in the γ/Cr_3Si eutectic. However, the hardness of the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites decreases drastically with the increasing Ni content, as shown in Fig. 7. The lower the Ni content, the higher the volume fraction of Cr_3Si primary dendrites and consequently the higher the hardness of the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composite.

Due to the inherent room temperature brittleness, Cr_3Si is very brittle and cracking phenomenon is unavoidable even under the extremely soft stress conditions of microindentation process [10]. By virtue of the indentation cracking phenomenon, Cruse *et al.* proposed a method to evaluate the fracture toughness of Cr_3Si by correlating the relationship between the indentation load and the cracking length. Because of the presence of the ductile nickel-base solid solution and the rapidly solidified fine microstructure, the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites possess improved ductility. No indentation cracks are observed for the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites except that of with Ni20Si18Cr62 powder even under high load indentation test conditions. This indicates that the laser/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites have reasonable combination of strength and toughness.

4. Conclusions

Rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites were fabricated by the laser melting/rapid solidification process using Cr-Si-Ni alloy precursor powder materials. The laser melted γ/Cr_3Si metal silicide "*in situ*" composites have high hardness and rapidly solidified fine-microstructure consisting of primary Cr_3Si dendrites and the interdendritic γ/Cr_3Si eutectics. The volume fraction of the Cr_3Si primary dendrites in the laser melted/rapidly solidified γ/Cr_3Si metal silicide "*in situ*" composites decreases with the increasing nickel content. Because of the presence of the ductile nickel-base solid solution and the rapidly solidified fine microstructure, the γ/Cr_3Si metal silicide "*in situ*" composites are expected to have adequate combination of strength and toughness.

Acknowledgements

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